

# **The 3<sup>rd</sup> International Solvothermal & Hydrothermal Association Conference**

**ISHA 2013**

**January 13-17, 2013**

**Austin, Texas, USA**

**AT&T Executive Education and Conference Center**

# **ISHA 2013**

## **The 3<sup>rd</sup> International Solvothermal & Hydrothermal Association Conference**

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**Austin, Texas, USA**

## **Abstract & Program Book**

### **Organized By**

Brian Korgel, The University of Texas at Austin McKetta Department of Chemical Engineering

Richard Riman, Rutgers University Department of Materials Science and Engineering

Tadafumi Adschari, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University





# The 3rd International Solvothermal and Hydrothermal Association Conference

**JANUARY 13-17, 2013  
AUSTIN, TX, USA**

## Welcome From The ISHA President

On behalf of myself and the rest of the ISHA Advisory Board, welcome to the 3<sup>rd</sup> International Solvothermal & Hydrothermal Association Conference (ISHA 2013)! I would especially like to thank Brian Korgel, Rik Rimann and Tad Adschari for their efforts to organize this event here in Austin, TX, USA. They have brought together experts from around the world working in all areas of Hydrothermal and Solvothermal research to present and discuss their findings. I look forward to the next few days of active and open discussion about the cutting edge problems being worked on in our field. The work is taking place in a truly international backdrop, with speakers from over 20 different countries in attendance.

The International Solvothermal and Hydrothermal Association (ISHA) was established in 2006 when the Joint meeting of the International Solvothermal and Hydrothermal Research (ISHR-8) and International Conference on Sovothermal Research (ICSTR-7) was held in Sendai, Japan. The previous ISHR meetings were held in Japan (1982), USA (1985), Russia (1989), France (1993), USA (1997), Japan (2000) and China (2003), bringing together scientists in various aspects of high-pressure/temperature research in different solvent media including aqueous solutions. The previous ICSTR meetings were held in Japan (1994 and 1996), France (1999), Japan (2000), USA (2002) and India (2004), with a focus on the reactions in a variety of solvent media including aqueous solutions. The joint meeting of ISHR-7 and ICSTR-6 was first held in Kochi, Japan (2000), which seeded the formation of ISHA six years later.

Since the founding of ISHA, it has actively advanced solvothermal and hydrothermal research. The first ISHA International Conference was held in 2008 at the University of Nottingham, UK. The second conference was held in Beijing, China in 2010. It is our great pleasure to hold ISHA 2013 in Austin, TX, USA. We hope that the Conference offers experts working on Hydrothermal and Solvothermal research from all over the world the opportunity to exchange information and ideas. ISHA is also striving to promote the application of Hydrothermal and Solvothermal Technology for processing advanced materials and solving the many challenging problems related to the environment.

Thank you again for your attendance of ISHA 2013 and please enjoy your time here in the United States.

Sridhar Komarneni, Ph.D., FRSC

Penn State University  
President, International Solvothermal & Hydrothermal Association  
Distinguished Professor of Clay Mineralogy Adjunct Professor of Civil and Environmental  
Engineering





# The 3rd International Solvothermal and Hydrothermal Association Conference

**JANUARY 13-17, 2013  
AUSTIN, TX, USA**

## Welcome To Austin for ISHA 2013

On behalf of myself and Conference Organizers, Rik Rimann of Rutgers University and Tad Adschari of Tohoku University: welcome to Austin, TX, for the 3<sup>rd</sup> International Solvothermal & Hydrothermal Association Conference (ISHA 2013)! The ISHA conference is held every two years, rotating locations between Asia, Europe and North America, and we are proud to host it this year at The University of Texas. Austin is a welcoming and fun place to visit, so please take some time to see some local sites, as well as meeting with many colleagues and friends working on Solvothermal and Hydrothermal research.

The program is very exciting this year and covers a diverse range of topics. Hydrothermal and Solvothermal research continues to thrive, addressing new energy technologies, materials and nanomaterials with unique and useful properties, and solving some of the most pressing global challenges, especially in the area of sustainability. Please enjoy hearing about the latest and greatest work from your colleagues in these many areas of research.

The organization of ISHA 2013 required the hard work of many people, and I would like to thank all of those who helped make it happen. Thanks to the ISHA Council, International Advisory Board and International Scientific Committee. I am especially thankful for the input of Byron Byrappa, Shouhua Feng, Sridhar Komarneni, Ed Lester, Juan Carlos Rendón-Ángeles, Richard Walton, Dan Wang, Jim Watkins and Masahiro Yoshimura, who offered many great suggestions and were always available to offer advice and insight about how to ensure a great conference. A huge thanks to Jon Peck for all of his hard work organizing the meeting and serving as Secretariat—a challenging and sometimes thankless job, so if you see him around let him know how much you appreciate his efforts to make everything run smoothly. And finally, thanks to all of the speakers and attendees of ISHA 2013 for their commitment to take the time and make the effort to come to Austin to present their work and participate in the conference. Your participation is fundamental to continued progress and success in the field.

Our goal for ISHA 2013 is to provide a venue for Hydrothermal and Solvothermal researchers to “compare notes” and learn from each other. Take some time to talk to researchers working just outside your specific area. From these conversations, collaborations and new research ideas emerge, and sometimes new directions for the field. In my own case, it was a brief conversation in the hall in 1998 with Keith Johnston that led me into Hydrothermal and Solvothermal research in the first place. That dialogue seeded nearly a decade of collaboration with Keith and about 24 co-authored papers. He was also the one who first introduced me to the ISHA community by helping arrange an invited talk for me at the 2000 joint ISHR/ICSTR meeting in Kochi, Japan—the meeting that seeded the creation of ISHA six years later. Now, here I am organizing ISHA 2013! So please, take the time to see old friends and colleagues and make new ones. Enjoy the meeting and thanks again for coming to Austin for ISHA 2013.

Brian A. Korgel  
The University of Texas at Austin  
Cockrell School of Engineering Temple Professor #1  
& Matthew Van Winkle Regents Professor of Chemical Engineering





# The 3rd International Solvothermal and Hydrothermal Association Conference

**JANUARY 13-17, 2013  
AUSTIN, TX, USA**

## Committees

### International Advisory Board

- A. Cheetham (Cambridge Univ., UK)  
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E. Lester (Univ. of Nottingham, UK)  
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Richard Walton (Univ. of Warwick, UK)  
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### International Scientific Committee (cont'd)

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### ISHA Council

- Patrons: Prof. Shigeyuki Somiya, Japan  
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Prof. Gerard Demazeau, France  
Prof. Richard E. Riman, USA



# The 3rd International Solvothermal and Hydrothermal Association Conference

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## ISHA 2013 Award Winners

### **ISHA-Sawyer Lifetime Achievement Award:** Prof. Masahiro Yoshimura, Japan

Prof. Yoshimura will accept his award on January 16<sup>th</sup> at 8:00 AM and give an award lecture entitled “Feature and Future of Hydrothermal/Solvothermal Reactions for Synthesis/Preparation of Nano-Materials with Desired Shapes, Sizes and Structures.”

### **Roy-Somiya Medal:** Prof. Edward Lester, UK

Prof. Lester will accept his award on January 15<sup>th</sup> at 8:00 AM and give a speech entitled “From Lab to Factory Floor.”

### **Best Ph.D. Thesis Award:** Dr. Christina Mossaad, USA for her Thesis: “Thermodynamic design, characterization, and evaluation of a nanocrystalline hydroxyapatite collagen allograft composite.”

## Previous Winners

### ISHA-2010 Beijing, PRC

#### **ISHA-Sawyer Lifetime Achievement Award**

Prof. Shigeyuki Somiya, Japan

#### **Roy-Somiya Medal**

Prof. Shu-Hong Yu, PRC

#### **Best Ph.D. Thesis Award**

Takaaki Taniguchi, Japan

### ISHA-2008 Nottingham, UK

#### **ISHA-Sawyer Lifetime Achievement Award**

Prof. Rustum Roy, USA

#### **Roy-Somiya Medal**

Prof. Brian A. Korgel, USA



# The 3rd International Solvothermal and Hydrothermal Association Conference

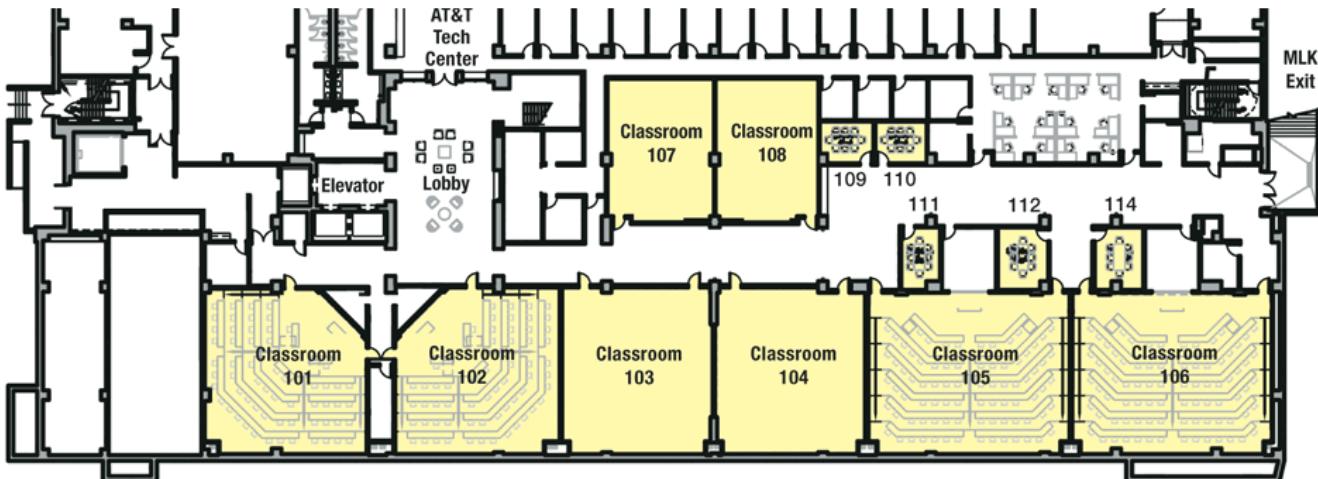
**JANUARY 13-17, 2013  
AUSTIN, TX, USA**

## AT&T Executive Education and Conference Center Maps

The meeting will primarily utilize Room 204 (Amphitheatre) and Classrooms 101 and 102. Breakfast and Lunch will be served in the Tejas Dining Room that is located on the 2<sup>nd</sup> Floor. Please refer to the detailed schedule for information on the specific location for the breakout sessions you are interested in attending.

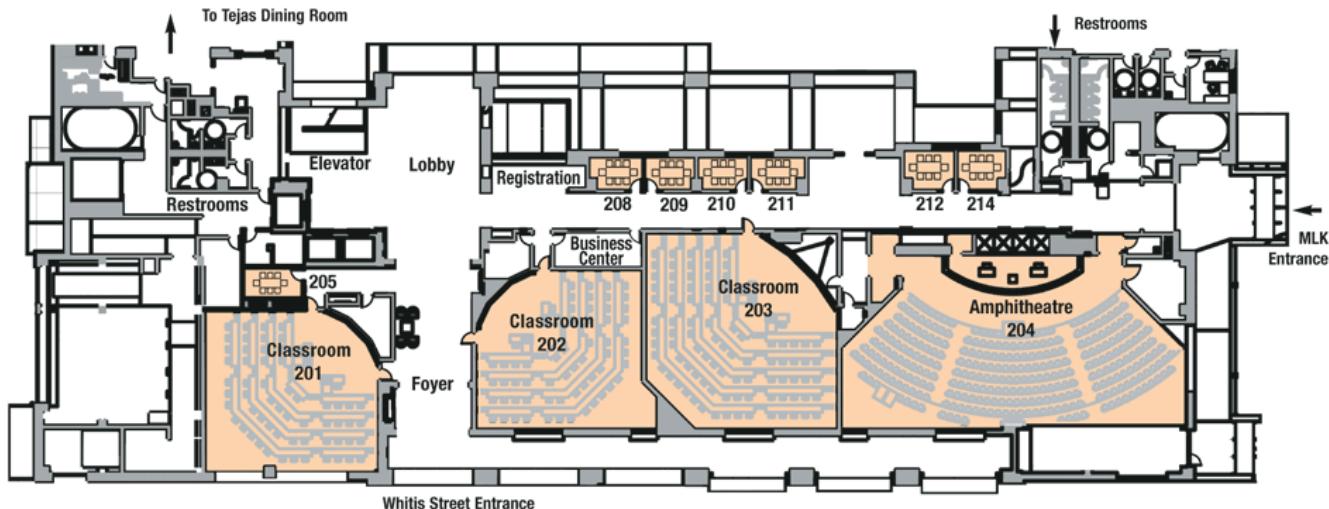
### AT&T CONFERENCE CENTER

### MEETING LEVEL ONE



### AT&T CONFERENCE CENTER

### MEETING LEVEL TWO Whitis Street Entrance



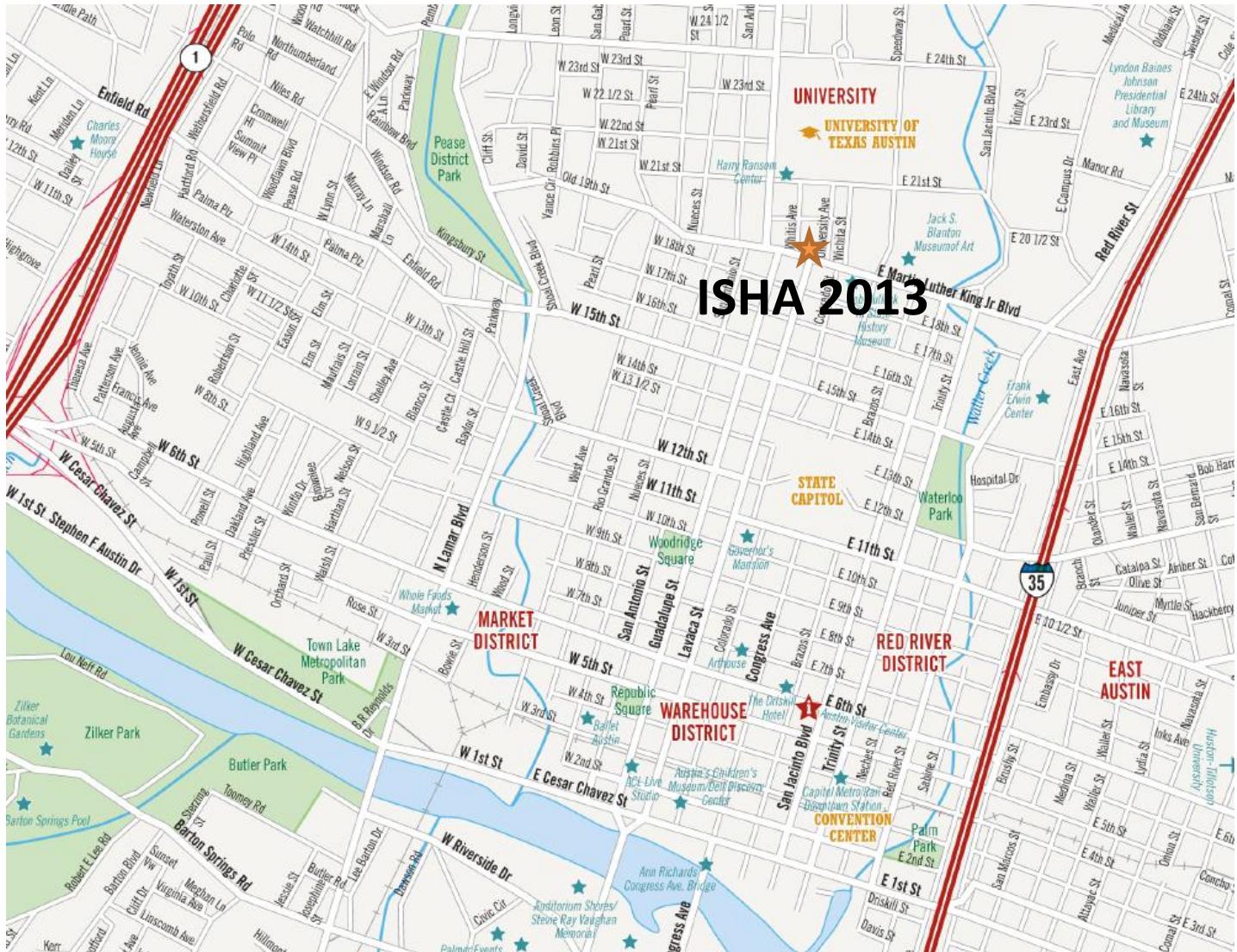


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## Map of Downtown Austin and Surrounding Area

Please find the map below that will provide an overview of the area around the location of ISHA 2013. The conference center is located along the edge of the University of Texas at Austin's campus, just north of downtown and the Texas State Capitol. For a larger and more comprehensive version of this map and others, please visit: <http://www.austintexas.org/visit/plan-your-trip/maps/>.





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and Hydrothermal Association  
Conference

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## Sunday, January 13<sup>th</sup> (Afternoon)

Location: Outside Room 204 (Amphitheatre)

| Time                      | Title                                     | Speaker | Affiliation |
|---------------------------|---|---------|-------------|
| <b>Early Registration</b> |   |         |             |
| 4:00 - 6:00 pm            | Register and Collect Conference Documents |         |             |

## Monday, January 14<sup>th</sup> (Morning)

Location: Outside Room 204 (Amphitheatre) & Tejas Dining Room

| Time                | Title                                     | Speaker | Affiliation |
|---------------------|---|---------|-------------|
| <b>Registration</b> |   |         |             |
| 7:00 - 8:00 am      | Register and Collect Conference Documents |         |             |
| 7:00 - 8:00 am      | Breakfast (Tejas Dining Room)             |         |             |

Location: Room 204 (Amphitheatre)

| Time                    | Title   | Speaker                   | Affiliation                                       |
|-------------------------|---|---------------------------|---|
| <b>Opening Ceremony</b> |   |                           |   |
| 8:00 - 8:15 am          | ISHA 2013 Introduction and Welcome Remarks                                    | Brian Korgel / K. Byrappa | University of Texas at Austin / Mysore University |
| 8:15 - 9:00 am          | <b>Plenary:</b> Multi-energy Solvothermal Processing: Retrospect and Prospect | Sridhar Komarneni         | Penn State University                             |
| 9:00 - 9:30 am          | Break   |                           |   |

Location: Room 204 (Amphitheatre)

| Time  | Title  | Speaker            | Affiliation                   |
|---|--|--------------------|-------------------------------|
| <b>Session 1 – Materials: Lithium Ion Battery Synthesis</b> (Chair: Justin Holmes, University College Cork) |  |                    |                               |
| 9:30 - 10:00 am   | <b>1-1:</b> Microwave-assisted Solvothermal Synthesis of Nanostructured Materials for Lithium-ion Batteries              | Arumugam Manthiram | University of Texas at Austin |
| 10:00 - 10:30 am  | <b>1-2:</b> Architectural Control of Nanostructured TiO <sub>2</sub> (B) and Morphological Dependent Lithiation Behavior | Keith Stevenson    | University of Texas at Austin |
| 10:30 - 11:00 am  | <b>1-3:</b> Supercritical solvothermal synthesis of oxide nanostructures in water/alcohol mixtures                       | Cyril Aymonier     | University of Bordeaux        |
| 11:00 - 11:15 am  | <b>1-4:</b> Solution-Grown Si and Ge Nanowires as High Capacity Anodes for Lithium-Ion Batteries                         | Timothy Bogart     | University of Texas at Austin |

|                  |  |                   |                    |
|------------------|--|-------------------|--------------------|
| 11:15 - 11:30 am | <b>1-5:</b> Direct growth of silicon and germanium nanowires on metal foils: opportunities and challenges for high-throughput processing | Benjamin Richards | Cornell University |
| 11:30 – noon     | <b>1-6:</b> Tailor-Made Ceramic Nanocrystals by Organic-Ligand-Assisted Hydrothermal Synthesis   | Satoshi Ohara     | Osaka University   |

Location: Room 101

| Time  | Title  | Speaker            | Affiliation                                    |
|---|--|--------------------|--|
| <b>Session 2 – Materials: Nanomaterials (Chair: Jim Watkins, University of Massachusetts)</b> |  |                    |  |
| 9:30 - 10:00 am   | <b>2-1:</b> Fabrication and Application of Inorganic Nanoparticle Superstructures  | Zhiyong Tang       | National Center for Nanoscience and Technology |
| 10:00 - 10:30 am  | <b>2-2:</b> Solvothermal Synthesis of Monodisperse Nanocrystals and their Surface  | Xun Wang           | Tsinghua University                            |
| 10:30 - 11:00 am  | <b>2-3:</b> Hydrothermal Formation and Application of advanced Ca/Mg-bearing Whiskers  | Lan Xiang          | Tsinghua University                            |
| 11:00 - 11:30 am  | <b>2-4:</b> Feature and Future of Hydrothermal-Electrochemical Processing for Inorganic Materials                              | Masahiro Yoshimura | National Cheng Kung University                 |
| 11:30 - noon  | <b>2-5:</b> Multiplex Templating Hydrothermal Synthesis of Functional Nanowires, Macroscopic Assemblies and Their Applications | Shu-Hong Yu        | Hefei National Laboratory                      |

Location: Room 102

| Time   | Title   | Speaker        | Affiliation                        |
|--|---|----------------|------------------------------------|
| <b>Session 3 – Sustainability (Chair: Richard Riman, Rutgers University)</b> |   |                |                                    |
| 9:30 - 10:00 am  | <b>3-1:</b> Hydrothermal Conversion of Algal Biomass to Fuels and Chemicals   | Phillip Savage | University of Michigan             |
| 10:00 - 10:30 am   | <b>3-2:</b> Supercritical Water Oxidation: The Next Generation of Processes for Hazardous Waste Treatment   | Bushra Al-Duri | University of Birmingham           |
| 10:30 - 10:45 am   | <b>3-3:</b> Sub-critical Water Technology as a Green and Sustainable Tool for Oil Extraction  | Wael Abdelmoez | Minia University                   |
| 10:45 - 11:15 am   | <b>3-4:</b> Carbon Dioxide Capture in Metal-Organic Frameworks  | Jeffrey Long   | University of California, Berkeley |
| 11:15 - 11:30 am   | <b>3-5:</b> Greener Synthesis of Metal Organic Frameworks in High Temperature Water   | Peter Bayliss  | University of Nottingham           |
| 11:30 - noon   | <b>3-6:</b> Microporous Metal Organic Frameworks: Solvothermal-Hydrothermal Synthesis, Structure-Pore Functionalization, and Potential Applications | Jing Li        | Rutgers University                 |

Location: Tejas Dining Room

| Time           | Title |
|----------------|-------|
| Noon - 1:30 pm | Lunch |

## Monday, January 14<sup>th</sup> (Afternoon)

Location: Room 204 (Amphitheatre)

| Time  | Title  | Speaker        | Affiliation                       |
|---|--|----------------|-----------------------------------|
| <b>Session 4 – Materials: Catalysis and Nanomaterials</b> (Chair: Tadafumi Adschiri, Tohoku University) |  |                |                                   |
| 1:30 - 2:00 pm  | <b>4-1:</b> New Oxide Materials for Catalysis from Hydrothermal Chemistry  | Richard Walton | University of Warwick             |
| 2:00 - 2:30 pm  | <b>4-2:</b> Hydrothermal-galvanic couple synthesis of perovskite oxide thin films                                    | Fu-Hsing Lu    | National Chung-Hsing University   |
| 2:30 - 3:00 pm  | <b>4-3:</b> Shape-selective Growth of Noble Metal Nanocrystals   | Xianmao Lu     | National University of Singapore  |
| 3:00 - 3:30 pm  | <b>Break</b>   |                |                                   |
| 3:30 - 4:00 pm  | <b>4-4:</b> Synthesis and Applications of Nanoparticles  | Richard Tilley | Victoria University of Wellington |
| 4:00 - 4:30 pm  | <b>4-5:</b> Generalized Syntheses of Nanocrystal–Graphene Hybrids in Hot Solvents                                    | Hsing-Yu Tuan  | National Tsing Hua University     |
| 4:30 - 5:00 pm  | <b>4-6:</b> Nanoparticle Assembly Using Polymer Templates and Printing Technologies for Hybrid Materials and Devices | Jim Watkins    | University of Massachusetts       |

Location: Room 101

| Time  | Title   | Speaker              | Affiliation                           |
|---|---|----------------------|---------------------------------------|
| <b>Session 5 – X-Rays, Microreactors and In situ studies</b> (Chair: Edward Lester, University of Nottingham) |   |                      |                                       |
| 1:30 - 2:00 pm  | <b>5-1:</b> Hydrothermal synthesis of VO <sub>2</sub> nanocrystals and applications   | Yanfeng Gao          | SIC                                   |
| 2:00 - 2:30 pm  | <b>5-2:</b> Neutron Radiography on Mixing Behavior of Supercritical Water and Room-Temperature Water in Tubular Flow Reactor for Hydrothermal Synthesis | Seiichi Takami       | Tohoku University                     |
| 2:30 - 3:00 pm  | <b>5-3:</b> Hydrothermal Media on Chip: Supercritical Microreactors for Studying Water / CO <sub>2</sub> Systems  | Samuel Marre         | University of Bordeaux                |
| 3:00 - 3:30 pm  | <b>Break</b>  |                      |                                       |
| 3:30 - 4:00 pm  | <b>5-4:</b> Design Methodology of Microreactor and its Application for Supercritical Nanoparticle Synthesis   | Nobuaki Aoki         | Tohoku University                     |
| 4:00 - 4:30 pm  | <b>5-5:</b> The In Situ Supercritical Suite at Pacific Northwest National Laboratory  | Todd Schaefer        | Pacific Northwest National Laboratory |
| 4:30 - 4:45 pm  | <b>5-6:</b> Watching chemistry happen: In situ studies of nanoparticle formation and growth in sub- and supercritical fluids                            | Kirsten M. Ø. Jensen | Aarhus University                     |
| 4:45 - 5:00 pm  | <b>5-7:</b> Liquid Crystals of Zirconium Phosphate disks with Various Aspect Ratios Controlled through Hydrothermal Method                              | Min Shuai            | Texas A&M University                  |

Location: Room 102

| Time  | Title  | Speaker               | Affiliation                   |
|---|--|-----------------------|-------------------------------|
| <b>Session 6 – Materials (Chair: Byron Byrappa, University of Mysore)</b> |  |                       |                               |
| 1:30 - 1:45 pm  | <b>6-1:</b> Low temperature sol gel processing of pure and Al doped ZnO films  | Sampyady Dharmaprkash | Mangalore University          |
| 1:45 - 2:00 pm  | <b>6-2:</b> Preparation of transparent zeolite film on glass substrate without using structure directing agents  | Takamasa Onoki        | Osaka University              |
| 2:00 - 2:30 pm  | <b>6-3:</b> Hydrothermal Synthesis of New Functional Polar Inorganic Materials   | P. Shiv Halasyamani   | University of Houston         |
| 2:30 - 2:45 pm  | <b>6-4:</b> Direct Synthesis of Oxides from Solvothermal Oxidation of Metallic Gallium   | Helen Playford        | University of Warwick         |
| 2:45 - 3:00 pm  | <b>6-5:</b> Characterisation of Doped Perovskites Prepared by Hydrothermal Synthesis   | Hilni Harunsani       | University of Warwick         |
| 3:00 - 3:30 pm  | <b>Break</b>   |                       |                               |
| 3:30 - 3:45 pm  | <b>6-6:</b> New Metastable Ternary Metal Ruthenium Oxides from Low Temperature Hydrothermal Synthesis  | Craig Hiley           | University of Warwick         |
| 3:45 - 4:00 pm  | <b>6-7:</b> Synthesis of Nanocomposites of ZnO/ZrO <sub>2</sub> , Ag-RuO <sub>2</sub> and Ru-ZnS by Electrochemical method in aqueous medium for photocatalytic degradation kinetics reaction for dyes and for antibacterial study | Sannaiah Ananda       | University Of Mysore          |
| 4:00 - 4:15 pm  | <b>6-8:</b> A strategy for Design of Concave Pt-Ni Alloy with Controllable Chemical Etching  | Yuen Wu               | Jilin University              |
| 4:15 - 4:30 pm  | <b>6-9:</b> Synthesis of a Novel Implant for Bone Grafting Using Sub-critical Water Technology   | Hiroyuki Yoshida      | Osaka University              |
| 4:30 - 4:45 pm  | <b>6-10:</b> The use of continuous hydrothermal synthesis in the formulation and functionalization of flame retardant polymers   | Sherif Elbasuney      | University of Nottingham      |
| 4:45 - 5:00 pm  | <b>6-11:</b> Bifunctional, Non-precious Metal Perovskite Electrocatalysts with High Mass Activities for Water Oxidation and Oxygen Reduction   | William Hardin        | University of Texas at Austin |

## Monday, January 14<sup>th</sup> (Evening)

Location: Interior Courtyard

| Time           | Title  |
|----------------|--|
| 5:30 - 7:30 pm | <b>Reception:</b> Poster Session & ISHA Graduate Student Poster Competition<br>(Detailed Listing of Participants at End of Program Schedule) |

## Tuesday, January 15<sup>th</sup> (Morning)

Location: Tejas Dining Room

| Time           | Title            |
|----------------|------------------|
| 7:00 - 8:00 am | <b>Breakfast</b> |

Location: Room 204 (Amphitheatre)

| Time                    | Title   | Speaker       | Affiliation              |
|-------------------------|---|---------------|--------------------------|
| <b>Morning Ceremony</b> |   |               |                          |
| 8:00 - 8:45 am          | Roy-Somiya Award: "From Lab to Factory Floor" | Edward Lester | University of Nottingham |
| 8:45- 9:00 am           | Break   |               |                          |

Location: Room 204 (Amphitheatre)

| Time   | Title   | Speaker         | Affiliation                   |
|--|---|-----------------|-------------------------------|
| <b>Session 7 – Materials: Nanowires (Chair: Richard Tilley, Victoria University of Wellington)</b> |   |                 |                               |
| 9:00 - 9:30 am   | <b>7-1:</b> Metal-Assisted Silicon and Germanium Nanowire Growth: Novel Methods for High-Throughput Production        | Tobias Hanrath  | Cornell University            |
| 9:30 - 10:00 am  | <b>7-2:</b> Tailoring the Growth and Morphology of Germanium Nanowires in Supercritical fluids                        | Justin Holmes   | University College Cork       |
| 10:00 - 10:30 am   | <b>7-3:</b> Colloidal Synthesis of Silicon Nanowires and Nanorods   | Andrew Heitsch  | Dow Chemical                  |
| 10:30 - 11:00 am   | Break   |                 |                               |
| 11:00 - 11:15 am   | <b>7-4:</b> Monophenyl Silane Catalyzed Growth of Germanium Nanowires with Gold and Nickel Seeds                      | Xiaotang Lu     | University of Texas at Austin |
| 11:15 - 11:30 am   | <b>7-5:</b> Self-Seeded Growth of Germanium Nanowires in Supercritical Fluids   | Olan Lotty      | University College Cork       |
| 11:30 - 11:45 am   | <b>7-6:</b> The structure and properties of W <sub>18</sub> O <sub>49</sub> ultrathin nanowire bundles                | Guangsheng Pang | Jilin University              |
| 11:45 – noon   | <b>7-7:</b> Visible Light Driven Photoelectrochemical Water Oxidation on Nitrogen-Modified TiO <sub>2</sub> Nanowires | Son Hoang       | University of Texas at Austin |

Location: Room 101

| Time   | Title   | Speaker              | Affiliation                         |
|--|---|----------------------|-------------------------------------|
| <b>Session 8 – Materials: Crystallization/Processing (Chair: Dan Wang, Institute of Process Engineering)</b> |   |                      |                                     |
| 9:00 - 9:30 am   | <b>8-1:</b> High Quality, Low Cost Ammonothermal Bulk GaN Substrates  | Dirk Ehrentraut      | Soraa, Inc.                         |
| 9:30 - 10:00 am  | <b>8-2:</b> Densification Behavior and Interfaces of Tantalum Carbide Nanopowders Prepared by a Solvothermal Process and Consolidated by Spark Plasma Sintering | Olivia Graeve        | University of California, San Diego |
| 10:00 - 10:30 am   | <b>8-3:</b> Ultrasonic-assisted hydrothermal method for the piezoelectric materials   | Takeshi Morita       | University of Tokyo                 |
| 10:30 - 11:00 am   | <b>8-4:</b> Hydrothermal growth of perovskites: a strategy for processing advanced ferroic structures   | Paula Vilarinho      | University of Aveiro                |
| 11:00 - 11:30 am   | <b>8-5:</b> Hydrothermal Growth of Calcite Crystals by Slow Cooling Method  | Kazumichi Yanagisawa | Kochi University                    |
| 11:30 – noon   | <b>8-6:</b> Hydrothermal Production and Surface Characterization of Novel Alpha Alumina – based Nanomaterials   | Wojciech Suchanek    | Sawyer Technical Materials, LLC     |

Location: Tejas Dining Room

| Time              | Title |
|-------------------|-------|
| noon -<br>1:30 pm | Lunch |

## Tuesday, January 15<sup>th</sup> (Afternoon)

Location: Room 204 (Amphitheatre)

| Time   | Title   | Speaker              | Affiliation  |
|--|---|----------------------|--|
| <b>Session 9 – Materials: Particle production/Continuous reactors</b> (Chair: Richard Walton, University of Warwick) |   |                      |  |
| 1:30 -<br>2:00 pm  | <b>9-1:</b> Supercritical Hydrothermal Synthesis of Organic Modified Nanoparticles for the Fabrication of Hybrid Polymers                           | Tadafumi Adschari    | Tohoku University  |
| 2:00 -<br>2:30 pm  | <b>9-2:</b> Hydrothermal Synthesis of Layered $\alpha$ -Zirconium Phosphate Disks: Control of Aspect Ratio and Polydispersity for Nano-architecture | Zhengdong Cheng      | Texas A&M University   |
| 2:30 -<br>3:00 pm  | <b>9-3:</b> SHYMAN – Sustainable Hydrothermal Manufacturing of Nanomaterials  | Edward Lester        | University of Nottingham   |
| 3:00 -<br>3:30 pm  | <b>Break</b>  |                      |  |
| 3:30 -<br>4:00 pm  | <b>9-4:</b> Hydrothermal Synthesis of Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> Spinel in a Continuous Flow Reactor                           | Karl Thomas Fehr     | LMU Munich   |
| 4:00 -<br>4:30 pm  | <b>9-5:</b> Numerical Simulation of Supercritical Water Flows in Continuous Hydrothermal Synthesis Reactors   | Takashi Furusawa     | Tohoku University  |
| 4:30 -<br>5:00 pm  | <b>9-6:</b> Fluid mixing engineering on continuous supercritical hydrothermal synthesis   | Shin-ichiro Kawasaki | National Institute of Advanced Industrial Science and Technology |
| 5:00 -<br>5:30 pm  | <b>9-7:</b> Rearrangement of Organic-inorganic hybrid Cerium Oxide Nanocrystals during Tetrahydrofuran Annealing                                    | Daisuke Hojo         | Tohoku University  |

Location: Room 101

| Time   | Title  | Speaker        | Affiliation                    |
|--|--|----------------|--------------------------------|
| <b>Session 10 – Materials: Nanomaterials</b> (Chair: Shouhua Feng, Jilin University) |  |                |                                |
| 1:30 -<br>2:00 pm  | <b>10-1:</b> Hydrothermal Soft Chemical Synthesis of {010}-Faceted Anatase TiO <sub>2</sub> Nanocrystals for High Performance Dye-Sensitized Solar Cells | Qi Feng        | Kagawa University              |
| 2:00 -<br>2:30 pm  | <b>10-2:</b> Solubility and Supersaturation in Hydrothermal Crystal Growth of ZnO  | Maria Gelabert | Winthrop University            |
| 2:30 -<br>3:00 pm  | <b>10-3:</b> Synthesis of TiO <sub>2</sub> mesoporous beads and its use in all-plastic dye-sensitized solar cell   | Jyh-Ming Ting  | National Cheng Kung University |
| 3:00 -<br>3:30 pm  | <b>Break</b>   |                |                                |
| 3:30 -<br>4:00 pm  | <b>10-4:</b> Novel Optical Properties from Solution-Derived Nanoparticles  | Luiz Jacobsohn | Clemson University             |
| 4:00 -<br>4:30 pm  | <b>10-5:</b> Fabrication of Artificial Photosynthesis Devices Using Hydrothermal Synthesis of Photocatalysts   | Young Soo Kang | Sogang University              |

|                   |   |          |                                     |
|-------------------|---|----------|-------------------------------------|
| 4:30 -<br>5:00 pm | <b>10-6:</b> Hydrothermal Preparation of High Efficient TiO <sub>2</sub> -Graphdiyne<br>Photocatalyst | Dan Wang | Institute of Process<br>Engineering |
|-------------------|---|----------|-------------------------------------|

Location: Room 102

| Time   | Title  | Speaker                  | Affiliation                      |
|--|--|--------------------------|----------------------------------|
| <b>Session 11 – Materials (Chair: Juan Carlos Rendón-Angeles, Cinvestav)</b> |  |                          |                                  |
| 1:30 -<br>2:00 pm  | <b>11-1:</b> Understanding the mechanism of formation of nanoporous materials under hydrothermal conditions by in situ X-ray techniques    | Gopinathan Sankar        | University College London        |
| 2:00 -<br>2:30 pm  | <b>11-2:</b> Solvothermal Reactions For Novel Chemical Syntheses: From Graphene To MOFs  | John Stride              | University of New South Wales    |
| 2:30 -<br>3:00 pm  | <b>11-3:</b> Microbial-Mineralization-Inspired Syntheses of Nanostructured Iron Oxides and Manganese Oxides with Controlled Crystal Phases | Hiroaki Imai             | Keio University                  |
| 3:00 -<br>3:30 pm  | <b>Break</b>   |                          |                                  |
| 3:30 -<br>3:45 pm  | <b>11-4:</b> Spark Plasma Solvothermal Technique for the Formation of Graphitic Pattern - A Soft Solution Process (SSP)                    | Jaganathan Senthilnathan | National Cheng Kung University   |
| 3:45 -<br>4:00 pm  | <b>11-5:</b> Solvothermal Synthesis of Acmite Conversion Coatings on Steel   | Terence Whalen           | Rutgers University               |
| 4:00 -<br>4:15 pm  | <b>11-6:</b> Continuous hydrothermal synthesis of functional nanomaterials for high-performance textiles                                   | Miquel Gimeno-Fabra      | University of Nottingham         |
| 4:15 -<br>4:30 pm  | <b>11-7:</b> Continuous Hydrothermal Synthesis of Stabilised Zinc Sulphide Nanoparticles with Fluorescent Properties                       | Miquel Gimeno-Fabra      | University of Nottingham         |
| 4:30 -<br>5:00 pm  | <b>11-8:</b> Vapor Phase Hydrothermal Synthesis: A New Approach for Fabrication of Nanomaterials   | Huijun Zhao              | Griffith University              |
| 5:00 -<br>5:30 pm  | <b>11-9:</b> Synthesis of Semiconducting Chalcogenide Nanocrystals for Solar Cell Application  | Ningzhong Bao            | Nanjing University of Technology |

## Tuesday, January 15<sup>th</sup> (Evening)

Location: Interior Courtyard

| Time              | Title  |
|-------------------|--|
| 5:30 -<br>7:30 pm | <b>Reception:</b> Networking / ISHA Gold & Silver Winners Announcement |

## Wednesday, January 16<sup>th</sup> (Morning)

Location: Tejas Dining Room

| Time              | Title            |
|-------------------|------------------|
| 7:00 -<br>8:00 am | <b>Breakfast</b> |

Location: Room 204 (Amphitheatre)

| Time                    | Title   | Speaker            | Affiliation                    |
|-------------------------|---|--------------------|--------------------------------|
| <b>Morning Ceremony</b> |   |                    |                                |
| 8:00 - 8:45 am          | <b>ISHA Lifetime Achievement Award:</b> Feature and Future of Hydrothermal/Solvothermal Reactions for Synthesis/Preparation of Nano-Materials with Desired Shapes, Sizes and Structures | Masahiro Yoshimura | National Cheng Kung University |
| 8:45 - 9:00 am          | <b>Break</b>  |                    |                                |

Location: Room 204 (Amphitheatre)

| Time  | Title   | Speaker                 | Affiliation             |
|---|---|-------------------------|-------------------------|
| <b>Session 12 – Materials (Chair: Motonobu Goto, Nagoya University)</b> |   |                         |                         |
| 9:00 - 9:30 am  | <b>12-1:</b> Hydrothermal Synthesis of Noncentrosymmetric Mixed Metal Oxide-Fluorides   | Kenneth R. Poeppelmeier | Northwestern University |
| 9:30 - 10:00 am   | <b>12-2:</b> Hydrothermal access to oxide catalysts and sensors: From MARS methods to environmental applications  | Greta Patzke            | University of Zurich    |
| 10:00 - 10:30 am  | <b>Break</b>  |                         |                         |
| 10:30 - 11:00 am  | <b>12-3:</b> Construction of a Series of Coordination Polymers Based on Tetracarboxylate Ligand: Synthesis, Structure, Gas Adsorption and Magnetic Properties | Yunling Liu             | Jilin University        |
| 11:00 - 11:30 am  | <b>12-4:</b> Novel Solution Processing and In situ Surface Modification of Metal Oxide Nanomaterials  | Byron Byrappa           | University Of Mysore    |
| 11:30 - noon  | <b>12-5:</b> Hydrothermal Growth of Multifunctional YAG Single Crystals for Laser Applications: Teaching an Old Dog New Tricks                                | Joseph Kolis            | Clemson University      |

Location: Room 101

| Time  | Title   | Speaker             | Affiliation                                    |
|---|---|---------------------|--|
| <b>Session 13 – Materials (Chair: Shu-Hong Yu, Hefei National Laboratory)</b> |   |                     |  |
| 9:00 - 9:30 am  | <b>13-1:</b> Hierarchical PbTiO <sub>3</sub> Nanostructures Grown by Self-Assembly of Nanocrystals during Hydrothermal Synthesis                        | Mari-Ann Einarsrud  | Norwegian University of Science and Technology |
| 9:30 - 10:00 am   | <b>13-2:</b> Atomic-Scale p-n Junctions of Manganese Perovskite Oxides from Hydrothermal Systems  | Shouhua Feng        | Jilin University                               |
| 10:00 - 10:30 am  | <b>Break</b>  |                     |  |
| 10:30 - 10:45 am  | <b>13-3:</b> Facile Synthesis of Au@TiO <sub>2</sub> Core-shell Hollow Spheres for Dye-sensitized Solar Cells   | Jiang Du            | University of Texas at Austin                  |
| 10:45 - 11:00 am  | <b>13-4:</b> Recycling of carbon fibre composites in supercritical hydrothermal conditions  | Cyril Aymonier      | University of Bordeaux                         |
| 11:00 - 11:15 am  | <b>13-5:</b> Single-step Transformation of SrMoO <sub>4</sub> Particles from SrSO <sub>4</sub> Ore Under Alkaline Hydrothermal Conditions               | Joaquin Diaz Algara | Autonomous University of Baja California       |
| 11:15 - 11:30 am  | <b>13-6:</b> Hydrothermal Synthesis and Characterisation of New Rare-Earth Orthochromite Perovskites La <sub>1-x</sub> Sm <sub>x</sub> CrO <sub>3</sub> | Luke Daniels        | University of Warwick                          |
| 11:30 - 11:45 am  | <b>13-7:</b> New Applications of Hydrothermal Reactions in Creating Abnormal Materials Properties   | Guangshe Li         | Fujian Institute of Research                   |

|              |   |                      |                    |
|--------------|---|----------------------|--------------------|
| 11:45 - noon | <b>13-8:</b> Synthesis and Development of Li-Cd nano Ferrites by Citrate Precursor Gel Method for Multilayers Chip Inductors Applications | Dacheppalli Ravinder | Osmania University |
|--------------|---|----------------------|--------------------|

Location: Room 102

| Time  | Title   | Speaker             | Affiliation                                  |
|---|---|---------------------|--|
| <b>Session 14 – Materials</b> (Chair: Sridhar Komarneni, Penn State University) |   |                     |  |
| 9:00 - 9:30 am  | <b>14-1:</b> Hydrothermal Synthesis of CeO <sub>2</sub> with Hollow Architecture  | Ranbo Yu            | University of Science and Technology Beijing |
| 9:30 - 10:00 am   | <b>14-2:</b> Application of Hydro- and Solvo-Thermally Processed Ceramic Nanoparticles for OTN-NIR Biomedical Imaging   | Kohei Soga          | Tokyo University of Science                  |
| 10:00 - 10:30 am  | <b>Break</b>  |                     |  |
| 10:30 - 11:00 am  | <b>14-3:</b> Exploration of New Inorganic SHG Materials based on Metal Iodates  | Jiang-Gao Mao       | Fujian Institute of Research                 |
| 11:00 - 11:15 am  | <b>14-4:</b> Organics Assisted Selectively Doped and Codoped ZnO Nanoparticles by Hydrothermal and Solvothermal Processes for Enhancing Biological Activities | Namratha KeerthiRaj | University Of Mysore                         |
| 11:15 - 11:30 am  | <b>14-5:</b> Controllable Synthesis and Zn <sub>2+</sub> Adsorption of γ-MnO <sub>2</sub> Nanostructures  | Chengxiang Liu      | Tsinghua University                          |
| 11:30 - 11:45 am  | <b>14-6:</b> Synthesis of ZnO nano-whiskers in the presence of SDNS   | Chengxiang Liu      | Tsinghua University                          |

Location: Tejas Dining Room

| Time           | Title |
|----------------|-------|
| Noon - 1:30 pm | Lunch |

## Wednesday, January 16<sup>th</sup> (Afternoon)

Location: Room 204 (Amphitheatre)

| Time   | Title  | Speaker                    | Affiliation                |
|--|--|----------------------------|----------------------------|
| <b>Session 15 – Sustainability</b> (Chair: Bushra Al-Duri, University of Birmingham) |  |                            |                            |
| 1:30 - 2:00 pm   | <b>15-1:</b> Novel Structural Materials developed by CO <sub>2</sub> Sequestration of Mineral Silicates                | Surojit Gupta              | University of North Dakota |
| 2:00 - 2:30 pm   | <b>15-2:</b> Carbonate Concrete: A Hydrothermal Technology for CO <sub>2</sub> Utilization and Construction            | Richard (Rik) Riman        | Rutgers University         |
| 2:30 - 3:00 pm   | <b>15-3:</b> Hydrothermal Technology for Ore Treatment and Metal Recovery  | Fathi Habashi              | Université Laval           |
| 3:00 - 3:30 pm   | <b>Break</b>   |                            |                            |
| 3:30 - 4:00 pm   | <b>15-4:</b> Hydrothermal Recovery of Zn and Pb from MSWI Bottom Ashes and APC Residues                                | Amanda Günther             | LMU Munich                 |
| 4:00 - 4:30 pm   | <b>15-5:</b> Single Step Transformation of Raw Minerals for Inorganic Compound Synthesis Under Hydrothermal Conditions | Juan Carlos Rendón-Angeles | Cinvestav                  |

|                   |  |                         |                 |
|-------------------|--|-------------------------|-----------------|
| 4:30 -<br>5:00 pm | <b>15-6:</b> Hydrothermal Conversion of Brominated Compounds to Alcohols in Aqueous Amphiphilic Solution without Catalysts | Toshitaka<br>Funazukuri | Chuo University |
|-------------------|--|-------------------------|-----------------|

Location: Room 101

| Time  | Title  | Speaker           | Affiliation                   |
|---|--|-------------------|-------------------------------|
| <b>Session 16 – Supercritical CO<sub>2</sub> (Chair: Brian Korgel, University of Texas at Austin)</b> |  |                   |                               |
| 1:30 -<br>2:00 pm   | <b>16-1:</b> Understanding supercritical CO <sub>2</sub> : from fundamental to industrial applications   | Lourdes Vega      | MATGAS                        |
| 2:00 -<br>2:30 pm   | <b>16-2:</b> CO <sub>2</sub> -expanded solvents: unique media for the synthesis of micro- and nano-particulate molecular materials with high structural homogeneity          | Nora Ventosa      | ICMAB-CSIC                    |
| 2:30 -<br>3:00 pm   | <b>16-3:</b> Fabrication of PVP Micro-Hollow Fiber by Electrospinning Process in Near-Critical CO <sub>2</sub>   | Motonobu Goto     | Nagoya University             |
| 3:00 -<br>3:30 pm   | <b>Break</b>   |                   |                               |
| 3:30 -<br>4:00 pm   | <b>16-4:</b> Metal Deposition on Porous Supports Using Supercritical CO <sub>2</sub>   | Albertina Cabañas | The Complutense University    |
| 4:00 -<br>4:15 pm   | <b>16-5:</b> Extraction Kinetics for Dioxins-Contaminated Soil by Supercritical Carbon Dioxide with Methanol   | Ming-Tsai Liang   | I-Shou University             |
| 4:15 -<br>4:30 pm   | <b>16-6:</b> Lycopene/Cyclodextrin Nanoparticle Formation Using Solution Enhanced Dispersion by Supercritical Fluid Process  | Hazuki Nerome     | Nagoya University             |
| 4:30 -<br>4:45 pm   | <b>16-8:</b> Supercritical Carbon Dioxide-in-Water Foams Stabilized with Nanoparticle and Surfactant Amphiphiles   | Andrew Worthen    | University of Texas at Austin |
| 4:45 -<br>5:00 pm   | <b>16-9:</b> Switchable Ethoxylated Nonionic to Cationic Amine Surfactants for CO <sub>2</sub> Enhanced Oil Recovery in High Temperature, High Salinity Carbonate Reservoirs | Yunshen Chen      | University of Texas at Austin |

## Wednesday, January 16<sup>th</sup> (Evening)

Location: Interior Courtyard

| Time              | Title                                  |
|-------------------|--|
| 5:30 -<br>7:00 pm | <b>Reception:</b> Networking / Wrap-Up |

## Monday, January 14<sup>th</sup> (Evening)

Location: Interior Courtyard

| Time  | Title   | Speaker                        | Affiliation                                  |
|---|---|--------------------------------|--|
| <b>Reception:</b> Poster Session and ISHA Graduate Student Poster Competition |   |                                |  |
|   | <b>P-1:</b> Silanization of Silica SBA-15 using Supercritical Carbon Dioxide  | Albertina Cabañas              | The Complutense University                   |
|   | <b>P-2:</b> Synthesis of Carbonated Doped Hydroxyapatite Powders by Urea Decomposition Under by Hydrothermal Method   | José Ricardo Escalona-González | Cinvestav                                    |
|   | <b>P-3:</b> Hydrothermal Conversion of 1-Bromododecane to 1-Dodecanol in Aqueous 2-Butanone Solution without Catalysts  | Yuki Goto                      | Chuo University                              |
|   | <b>P-4:</b> Influence Of Hydrothermal Alkaline Activation on the Co-Cr-Mo Biodur CCmplus 799 Alloy Compacts   | Zully Matamoros Veloza         | Technological Institute of Saltillo          |
|   | <b>P-5:</b> Effect of Phosphate Precursor on the Crystallization of Ca10-xMgx(PO4)6(OH)2 Solid Solutions Under Hydrothermal Conditions  | Karla Montoya                  | Cinvestav                                    |
|   | <b>P-6:</b> Hydrothermal Conversion of Celluloses to Glucose and Celooligosaccharides in Dilute Aqueous Formic Acid Solution  | Shingo Ozawa                   | Chuo University                              |
|   | <b>P-7:</b> Phase Transformation and Photoluminescence of CePO4 Nano-wires  | Pengfei Xu                     | University of Science and Technology Beijing |
|   | <b>P-8:</b> Superparamagnetic Iron Oxide Nanoparticles Grafted with Sulfonated Copolymers are Stable in Concentrated Brine at Elevated Temperatures and Weakly Adsorb on Silica | Zheng Xue                      | University of Texas at Austin                |
| <b>ISHA Gold/Silver Participants</b>  |   |                                |  |
| 5:30 - 7:30 pm  | <b>3-5:</b> Greener Synthesis of Metal Organic Frameworks in High Temperature Water   | Peter Bayliss                  | University of Nottingham                     |
|   | <b>1-4:</b> Solution-Grown Si and Ge Nanowires as High Capacity Anodes for Lithium-Ion Batteries  | Timothy Bogart                 | University of Texas at Austin                |
|   | <b>16-9:</b> Switchable Ethoxylated Nonionic to Cationic Amine Surfactants for CO2 Enhanced Oil Recovery in High Temperature, High Salinity Carbonate Reservoirs                | Yunshen Chen                   | University of Texas at Austin                |
|   | <b>13-6:</b> Hydrothermal Synthesis and Characterisation of New Rare-Earth Orthochromite Perovskites La1-xSmxCrO3   | Luke Daniels                   | University of Warwick                        |
|   | <b>13-5:</b> Single-step Transformation of SrMoO4 Particles from SrSO4 Ore Under Alkaline Hydrothermal Conditions   | Joaquin Diaz Algara            | Autonomous University of Baja California     |
|   | <b>13-3:</b> Facile Synthesis of Au@TiO2 Core-shell Hollow Spheres for Dye-sensitized Solar Cells   | Jiang Du                       | University of Texas at Austin                |
|   | <b>6-10:</b> The use of continuous hydrothermal synthesis in the formulation and functionalization of flame retardant polymers  | Sherif Elbasuney               | University of Nottingham                     |
|   | <b>11-6:</b> Continuous hydrothermal synthesis of functional nanomaterials for high-performance textiles  | Miquel Gimeno-Fabra            | University of Nottingham                     |
|   | <b>6-11:</b> Bifunctional, Non-precious Metal Perovskite Electrocatalysts with High Mass Activities for Water Oxidation and Oxygen Reduction                                    | William Hardin                 | University of Texas at Austin                |
|   | <b>6-5:</b> Characterisation of Doped Perovskites Prepared by Hydrothermal Synthesis  | Hilni Harunsani                | University of Warwick                        |
|   | <b>6-6:</b> New Metastable Ternary Metal Ruthenium Oxides from Low Temperature Hydrothermal Synthesis   | Craig Hiley                    | University of Warwick                        |
|   | <b>7-7:</b> Visible Light Driven Photoelectrochemical Water Oxidation on Nitrogen-Modified TiO2 Nanowires   | Son Hoang                      | University of Texas at Austin                |
|   | <b>5-6:</b> Watching chemistry happen: In situ studies of nanoparticle formation and growth in sub- and supercritical fluids  | Kirsten M. Ø. Jensen           | Aarhus University                            |

|   |                          |                                |
|---|--------------------------|--------------------------------|
| <b>14-4:</b> Organics Assisted Selectively Doped and Codoped ZnO Nanoparticles by Hydrothermal and Solvothermal Processes for Enhancing Biological Activities | Namratha KeerthiRaj      | University Of Mysore           |
| <b>14-6:</b> Synthesis of ZnO nano-whiskers in the presence of SDNS   | Chengxiang Liu           | Tsinghua University            |
| <b>7-5:</b> Self-Seeded Growth of Germanium Nanowires: Coalescence and Ostwald ripening   | Olan Lotty               | University College Cork        |
| <b>7-4:</b> Monophenyl Silane Catalyzed Growth of Germanium Nanowires with Gold and Nickel Seeds  | Xiaotang Lu              | University of Texas at Austin  |
| <b>16-6:</b> Lycopene/Cyclodextrin Nanoparticle Formation Using Solution Enhanced Dispersion by Supercritical Fluid Process                                   | Hazuki Nerome            | Nagoya University              |
| <b>6-4:</b> Direct Synthesis of Oxides from Solvothermal Oxidation of Metallic Gallium  | Helen Playford           | University of Warwick          |
| <b>13-8:</b> Synthesis and Development of Li-Cd nano Ferrites by Citrate Precursor Gel Method for Multilayers Chip Inductors Applications                     | Dachepalli Ravinder      | Osmania University             |
| <b>1-5:</b> Direct growth of silicon and germanium nanowires on metal foils: opportunities and challenges for high-throughput processing                      | Benjamin Richards        | Cornell University             |
| <b>11-4:</b> Spark Plasma Solvothermal Technique for the Formation of Graphitic Pattern - A Soft Solution Process (SSP)                                       | Jaganathan Senthilnathan | National Cheng Kung University |
| <b>5-7:</b> Liquid Crystals of Zirconium Phosphate disks with Various Aspect Ratios Controlled through Hydrothermal Method                                    | Min Shuai                | Texas A&M University           |
| <b>11-5:</b> Solvothermal Synthesis of Acmite Conversion Coatings on Steel  | Terence Whalen           | Rutgers University             |
| <b>16-8:</b> Supercritical Carbon Dioxide-in-Water Foams Stabilized with Nanoparticle and Surfactant Amphiphiles  | Andrew Worthen           | University of Texas at Austin  |

# ISHA 2013 Abstracts

## Plenary Talk: Multi-energy Solvothermal Processing: Retrospect and Prospect

Sridhar Komarneni

Materials Research Institute, 205 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

Multi-energy solvothermal (including hydrothermal) processing appears to have started with the application of electric field under hydrothermal conditions starting about 1948 [1] for the electrolytic synthesis of clays. Magnesium anode was used to make antigorite-like mineral while Al anode was used to make kaolinite. Hawkins and Roy [2] claimed the synthesis of kaolinite on the anode at about 350°C while in the absence of an electric field no kaolinite was formed under conventional conditions at the same *p-t-x* conditions. Yoshimura's group coined the term "Hydrothermal-Electrochemical (H-E) Method" in 1989 [3] and prepared fine powders and thin films of BaTiO<sub>3</sub>. The H-E synthesis apparently has the advantage in that high thickness of BaTiO<sub>3</sub> films can be achieved in a short reaction time.

The application of microwaves in liquid state began in 1985 for the fast synthesis of titania gel spheres [4] and Komarneni's group coined the term "Microwave-Hydrothermal (M-H) process" in 1992 [5] and reported that the M-H process has several advantages over the conventional hydrothermal process such as (a) the kinetics of reaction are increased by one to two orders of magnitude, (b) novel phases are formed, (c) metastable phases are eliminated in some chemical systems and (d) the initial heating is rapid which can lead to energy savings. The use of microwave-solvothermal process is now practiced the world over.

A novel concurrent hydrothermal and ultrasonic treatment was also reported by us in 2003 [6] for the synthesis of nanosized, mesoporous Co<sub>3</sub>O<sub>4</sub> powder and I believe this is the beginning of ultrasonic-hydrothermal process. Morita's group has been focusing on the crystallization of electroceramic powders using ultrasonic-hydrothermal process by designing new equipment for the last several years and found that the crystallization kinetics are faster by about 4 times [7].

Another innovation in using the combination of microwave and ultrasonic hydrothermal treatment was recently reported using newly designed equipment [8] and this technique perhaps leads to well dispersed powders.

This talk will summarize the achievements and drawbacks of multi-energy solvothermal processing to date. Future directions such as potential combining of magnetic, laser and gamma radiation with solvothermal methods will also be discussed.

- [1] S. Caillere, and S. Henin, Verre Silicates Ind., **13**, 63 (1948).
- [2] D. B. Hawkins, and R. Roy, J. Amer. Ceram. Soc., **45**, 507 (1962).
- [3] M. Yoshimura, S-E. Yoo, M. Hayashi, and N. Ishizawa, Japanese J. Appl. Phys., **28**, L 2007 (1989).
- [4] S. Komarneni, and R. Roy, Mat. Lett., **3**, 165 (1985).
- [5] S. Komarneni, R. Roy, and Q. H. Li, Mat. Res. Bull., **27**, 1393 (1992).
- [6] P. E. Meskin, A. E. Baranchikov, V. K. Ivanov, E. V. Kisterev, A. A. Burukhin, B. R. Churagulov, N. N. Oleinikov, S. Komarneni, and Yu. D. Tret'yakov, Doklady Chemistry, **389**, 62 (2003).
- [7] M. Ishikawa, Y. Kadota, N. Takiguchi, H. Hosaka, and T. Morita, Japanese J. Appl. Phys., **47**, 7673 (2008).
- [8] H. Li, E-T Liu, Frankie Y.F. Chan, Z. Lu, R. Chen, Mat. Lett., **65**, 3440 (2011).

## **1-1: Microwave-assisted Solvothermal Synthesis of Nanostructured Materials for Lithium-ion Batteries**

Arumugam Manthiram

Materials Science and Engineering Program & Texas Materials Institute  
University of Texas at Austin  
Austin, TX 78712, USA

Lithium-ion batteries have revolutionized the portable electronics market, and they are being intensively pursued for electric vehicles and stationary storage of electricity produced by renewable energies like solar and wind. Cost, safety, cycle life, and energy and power densities are the critical parameters for these applications. With this perspective, there is immense interest to develop new cathode and anode materials and to develop novel synthesis and processing approaches. We present here novel microwave-assisted solvothermal (MW-ST) and hydrothermal (MW-HT) approaches to obtain high-performance, nanostructured phosphate and silicate cathodes as well as graphene nanosheet, iron oxide nanowire, and anatase thin film anodes. These microwave-assisted processes give highly crystalline materials with unique nanomorphologies within a short reaction time at much lower temperatures compared to the conventional synthesis approaches, offering cost-effective manufacturing.

For example, single crystalline olivine  $\text{LiMPO}_4$  ( $\text{M} = \text{Mn, Fe, Co, Ni, and VO}$ ) and their solid solutions with a nanorod morphology have been obtained by a MW-ST process within 5 minutes at  $< 300^\circ\text{C}$  in a polyol medium without requiring any reducing gas atmosphere [1]. The  $\text{LiMPO}_4$  nanorods thus produced have the easy lithium-diffusion direction (*b* axis) perpendicular to the length of the nanorod, offering unique advantages to enhance the rate capability. Similarly, carbon-coated  $\text{Li}_2\text{MSiO}_4$  ( $\text{M} = \text{Fe and Mn}$ ) silicates exhibiting the reversible extraction of more than one lithium have been obtained by a MW-ST process followed by firing at  $650^\circ\text{C}$  in an inert atmosphere [2]. Graphene nanosheets have been produced by a MW-ST reduction of graphite oxide with polyol within 15 minutes at  $< 300^\circ\text{C}$  without requiring the conventional toxic reducing agent, hydrazine [3]. Carbon-decorated, single-crystalline  $\text{Fe}_3\text{O}_4$  nanowires offering high capacities of  $> 800 \text{ mAh/g}$  have been produced by a two-step MW-HT process [4]. Finally, highly crystalline anatase  $\text{TiO}_2$  thin films have been obtained by a MW-ST process on conductive substrates such as indium tin oxide (ITO) at temperatures as low as  $150^\circ\text{C}$ . In addition to being battery anodes, the ability to achieve high-quality nanocrystalline  $\text{TiO}_2$  thin films at low-temperatures could enable processing with plastics.

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## **1-2: Architectural Control of Nanostructured TiO<sub>2</sub>(B) and Morphological Dependent Lithiation Behavior**

Anthony G. Dylla, Penghao Xiao, Graeme Henkelman and Keith J. Stevenson\*

Department of Chemistry and Biochemistry, The University of Texas at Austin,  
1 University Station, Austin, Texas, 78712, USA

The lithium insertion behavior of nanoparticle (3-D) and nanosheet (2-D) architectures of TiO<sub>2</sub>(B) is quite different, as observed by differential capacity plots derived from galvanostatic charging/discharge experiments along with DFT+U calculations. The ability to nanostructure this unique polymorph of titania into several distinct architectures provides opportunities to systematically study the key lithiation mechanisms. Though surface energy typically controls the growth process of bulk crystals and their resultant architecture, shape-controlled synthesis of nanocrystals is possible through solvo- and hydrothermal reactions involving adsorbates that kinetically control growth rates along specific crystallographic orientations. For 2-D nanosheets a solvothermal synthesis promotes (010) facet exposure due to specific binding of ethylene glycol. In the case of 3-D nanoparticles, a titanium glycolate complex intermediate used in a hydrothermal synthesis is responsible for size control of the resultant TiO<sub>2</sub>(B) nanoarchitecture.

\*Corresponding author: stevenson@mail.cm.utexas.edu

## **1-3: Supercritical solvothermal synthesis of oxide nanostructures in water/alcohol mixtures**

C. Aymonier, S. Marre,  
H. Reveron, C. Bousquet, M. Théodet, D. Mesguich, Y. Roig and C. Słostowski

*CNRS, Université de Bordeaux, ICMCB 87 av. du Dr. A. Schweitzer, 33608 Pessac, France*  
*aymonier@icmcb-bordeaux.cnrs.fr*

Supercritical fluids offer continuous, scalable, fast and facile routes towards well-crystallized tailor-made oxide nanoparticles [1, 2]. This method has already been used to synthesize various inorganic materials (metals, semiconductors, nitrides, oxides, etc.) with controlled size, complex shapes and compositions. In the last 20 years the use of sc-water as solvent was extended to other fluids to synthesize nanostructures, mainly scCO<sub>2</sub>/alcohols (ethanol, isopropanol...), sc-MeOH, sc-iPrOH, water/alcohols (ethanol, isopropanol...), scNH<sub>3</sub> or sc-alkanes (hexane,...). This variety of solvents opens avenue towards the use of numerous precursors for the investigation of a very rich chemistry.

This lecture will make a focus on the chemistry and nucleation & growth of nanostructures (Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (0≤x≤1) - BST, Nd<sub>2</sub>NiO<sub>4+δ</sub>, NiMoO<sub>4</sub>, ZnO or still CeO<sub>2</sub>) in supercritical water/alcohols mixtures (methanol, ethanol and isopropanol) but also in 7 different alcohols – MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH. Firstly, our pioneer works in supercritical water/ethanol mixtures for the formation of BST nanoparticles [3] have shown the possibility to obtain well-crystallized material at relatively low temperature (<400°C) what was recently confirmed with the synthesis of exciton luminescent ZnO nanocrystals [4]. The second important result which will be discussed is the possibility to change the reaction pathway, and so the material characteristics, just modifying the composition of the water / ethanol mixture [5]. Beyond the water / ethanol composition, we demonstrated that the nature of the alcohol is playing also a great role on the nucleation & growth process with a direct impact on the specific surface area of NiMoO<sub>4</sub> nanopowders: 79 m<sup>2</sup>.g<sup>-1</sup> for a synthesis in a water/methanol mixture (50/50 molar) up to 179 m<sup>2</sup>.g<sup>-1</sup> in a water/isopropanol mixture (50/50 molar) [6]. Finally, these studies in water/alcohol mixtures brought us to alcohol (MeOH, EtOH, PrOH, iPrOH, ButOH, PentOH and HexOH) for the synthesis of CeO<sub>2</sub> nanocrystals. The crystallite size of the CeO<sub>2</sub> nanocrystals can be tuned in the range 3-7 nm depending on the considered alcohol, and their surface has been modified by these solvents without the use of surfactants [7].

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## 1-4: Solution-Grown Si and Ge Nanowires as High Capacity Anodes for Lithium-Ion Batteries

Timothy D. Bogart<sup>1</sup>, Aaron M. Chockla<sup>1</sup>, Kyle C. Klavetter<sup>1</sup>, Colin M. Hessel<sup>1</sup>, C. Buddie Mullins<sup>1</sup>, and Brian A. Korgel.<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-1062

Silicon (Si) and germanium (Ge) nanowires were synthesized via a supercritical fluid-liquid-solid (SFLS) growth and evaluated as high capacity anode materials for lithium-ion batteries.[1,2] Free-floating nanowires were produced at a rate of milligrams per minute using either tin or gold seeds, which can be removed via chemical etching prior to battery assembly. Figure 1 shows representative SEM and TEM images of Ge nanowires and a cross sectional view of the anode architecture. When cycled against lithium metal the Ge nanowire batteries showed reversible capacities as high as 1248 mAh/g for over 100 galvanostatic cycles, a 235% increase compared to carbon 372 mAh/g.[3] Si nanowires were studied similarly and exhibited reversible capacities over 2000 mAh/g for 100 cycles, an astounding 438% capacity increase with respect to current carbon anode materials.[4,5] The enhanced lithium storage capacities of Ge and Si nanowire anodes relative to graphite clearly demonstrate their potential for smaller, lighter lithium-ion batteries with greater energy density.

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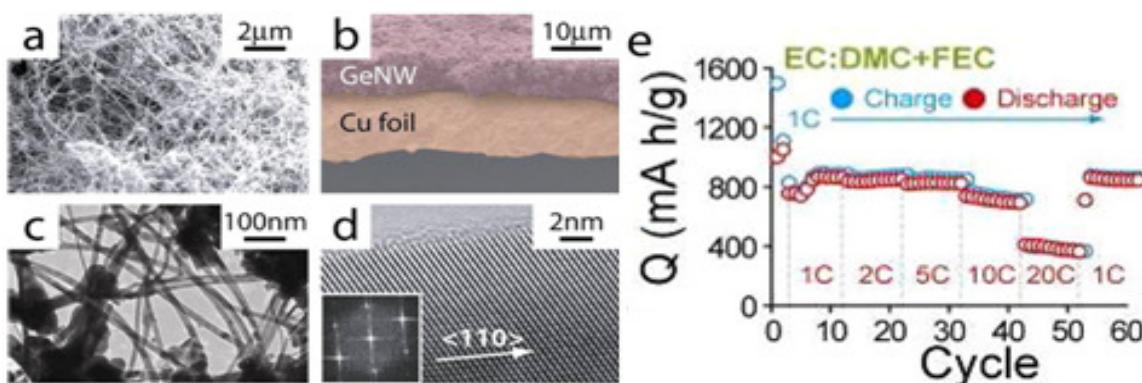


Fig. 1. (a) SEM image of SLS-grown Ge nanowires. (b) SEM image of a cross-sectioned Ge nanowire anode. (c, d) TEM images of Ge nanowires. (e) Charge and discharge capacity Q, for a Ge nanowire anode at various cycle rates.[3]

## **1-5: Direct growth of silicon and germanium nanowires on metal foils: opportunities and challenges for high-throughput processing**

Benjamin Richards<sup>1</sup>, Bernard Gaskey<sup>2</sup>, Tobias Hanrath<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering, Cornell University

<sup>2</sup>Department of Chemical and Biomolecular Engineering, Cornell University

Silicon and Germanium nanowires have immense potential as a material platform for many energy applications; most prominently as anodes in next generation high capacity Li-ion batteries. The charge capacity of silicon exceeds that of currently used graphite anodes by more than tenfold. Transforming this much-heralded potential to technological fruition is ultimately contingent on innovative approaches to outstanding challenges concerning the high-throughput fabrication of nanowires and integration into functional device structures. To sustain progress in the field, we need to advance beyond the preparation of microscopic quantities in the lab and develop novel solvothermal routes to create nanowires and nanowire-enabled devices. Ordinary nanowire synthesis methods rely on noble metal seed particles (most commonly gold) to nucleate wire growth. Clearly, this is not practical at commercial scales. To address this challenge, we investigated alternative processes that allow nanowires to be grown from bulk metal substrates. This introduces exciting opportunities for novel roll-to-roll and spool-to-spool fabrication methods. Moreover, the bulk metal surfaces provide convenient external macroscopic contact for this nanoscale material. We discuss scientific and engineering challenges and opportunities to the fabrication of nanowire-based hierarchical structures and their application in prototype electrochemical devices.

## **1-6: Tailor-Made Ceramic Nanocrystals by Organic-Ligand-Assisted Hydrothermal Synthesis**

Satoshi Ohara<sup>1\*</sup>, Kazuhiro Yamamoto<sup>1</sup>, Zhenquan Tan<sup>1</sup>, Nan Qiu<sup>1</sup> and Takeshi Hashishin<sup>1</sup>

<sup>1</sup>Joining and Welding Research Institute, Osaka University,  
11-1 Mihogaoka, Ibaraki 567-0047, Japan

To fine-tune the properties of ceramics, they can now be processed into uniform-size nanocrystals with spherical, wire, rod, tadpole shapes. Another trend in research aims at arranging individual nanocrystals into superlattices and investigating their unique properties. Despite these recent advances, controlling the shape, crystal structure, and surface characteristics of ceramic nanocrystals is still a difficult task. Here, we report an approach to tailor-made ceramic nanocrystals by means of organic ligand-assisted hydrothermal synthesis. We succeeded in the synthesis of rare earth doped CeO<sub>2</sub> nanocrystals with cubic facets. Also important, the use of water, instead of an organic solvent, provides an environmentally benign “green” chemistry route to nano building blocks for advanced materials and devices. Here, we also report an integration of rare earth doped CeO<sub>2</sub> nanocrystals by aerosol route in order to fabricate solid oxide fuel cell device with high performance.

## **2-1: Fabrication and Application of Inorganic Nanoparticle Superstructures**

Yunsheng Xia,<sup>a</sup> Jianxiao Gong,<sup>a</sup> Zhengtao Li,<sup>a</sup> Zhiyong Tang<sup>a,\*</sup>

<sup>a</sup>National Center for Nanoscience and Technology, Beijing 100190, China

E-mail: zytang@nanoctr.cn

Fabrication of inorganic nanoparticle superstructures is one of the most important ways to realize the practical applications of nanomaterials in many fields, e.g., photonics, electronics and sensors. In this talk, I will introduce the recent progress in our group on this research topic, which include: (1) Fabrication of large-scale and hierarchy superstructures via manipulation of the physical interactions between inorganic nanoparticle building blocks [1]; (2) Preparation of dynamic and reversible superstructures by design of Janus-type inorganic nanoparticles [2]; and (3) Application of inorganic nanoparticle superstructures in the field of photonic devices including optical signal storage and Raman scattering enhancement [3]. At the end of the talk, I will briefly discuss current challenge in our work.

**Keywords:** Inorganic nanoparticle, self-assembly, optical property.

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## 2-2: Solvothermal Synthesis of Monodisperse Nanocrystals and their Surface Activities

Xun Wang\*

Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

Over the past decade monodisperse nanocrystals, which exhibit many interesting shape- and size- dependent phenomena and properties, have been extensively investigated for both their scientific and technological applications. Monodisperse nanocrystals are usually obtained through hot-injection synthesis or heat-up synthesis under normal pressure conditions. Solvothermal/hydrothermal processes could take place above the boiling point of the solvent, extending the synthetic condition. However, the product of a solvothermal synthesis usually suffered from wide size distribution and severe aggregation. In the recent years, with the development of the standard-pressure wet-chemical routes and the further understanding of the growth mechanism involved, solvothermal synthesis could provide nanocrystals with the quality as high as the products via the normal pressure routes. We will discuss some nearest development in the solvothermal synthesis of nanocrystals.

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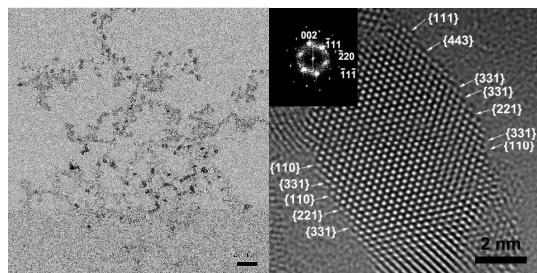


Fig. 1 left, TEM image of as-synthesized Pd cluster nanowires;  
Right, Aberration-corrected HRTEM images of Pd cluster nanowires  
oriented along the  $\langle 110 \rangle$  zone axis

## **2-3: Hydrothermal Formation and Application of advanced Ca/Mg-bearing Whiskers<sup>#</sup>**

L.Xiang

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Based on the effective utilization of the rich mineral resources and the recycling of the industrial by-products in China, we have done some work on the hydrothermal formation of Ca/Mg-bearing whiskers, such as  $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mg}_2\text{B}_2\text{O}_5$  and  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ , etc, focusing mainly on the development of the hydrothermal growth technologies and the revealing of the corresponding one-dimensional growth mechanisms. Our work showed that the morphology and structures of the Ca/Mg-bearing whiskers can be adjusted based on the anisotropic crystal structures, the selective adsorption of capping agents and the varying of the solution environment (super-saturation, composition, etc). The relationships among the growth of the crystals, the variation of the solution composition and the selective surface adsorption were discussed. Proper flux-assisted sintering of the intermediate whiskers formed at hydrothermal condition can prevent the occurrence of the porous structure, producing whiskers with little pores. The possibility of the utilization of the Ca/Mg-bearing whiskers to fabricate the inorganic papers was also investigated.

**Key words:** Ca/Mg-bearing whiskers, hydrothermal technology, morphology control

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## **2-4: Feature and Future of Hydrothermal-Electrochemical Processing for Inorganic Materials**

Masahiro YOSHIMURA

Promotion Center for Global Materials Research, Dept. Mater.Sci. & Eng.,National.Cheng Kung University.,Tainan,Taiwan: yoshimur@mail.ncku.edu.tw  
Professor Emeritus of Tokyo Institute of Technology, Japan:  
[yoshimura@msl.titech.ac.jp](mailto:yoshimura@msl.titech.ac.jp)

“Hydrothermal Processing” is an expanded area of “Solution Processing” using aqueous solutions and/or H<sub>2</sub>O containing solvents. Even though in “Solvothermal Processing” using non-aqueous solutions, the action of aqueous components, which have been added or even existed as one of impurities, would have the major roles for the overall reactions. Those reactions would be called reasonably as “diluted or controlled Hydrothermal Processing”. Electrochemistry is really powerful method for material processing because electrochemical driving force is counted to huge thermal driving force: i.e. 1 eV corresponds to 11,604 K in temperature via E = kT. Therefore Hydrothermal-Electrochemical(HE) processing should be important in material Science and technology.

We used them to fabricate ceramic films of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> in 1989[1],then applied to other materials like KTaO<sub>3</sub>,BaWO<sub>4</sub>,CaWO<sub>4</sub>,etc.[2,3] Moreover they developed to fabricate nanostructure-controled films like porous, dense, layered and/or integrated.[4]

More recently, we have applied those HE processing to a novel concept and technique: Growing Integration Layer[ GIL] strategy[5,6] where Compositonally ,structurally and functionally graded layers can be fabricated on a substrate in a solution. It can be used for coating, joining/bonding between ceramic and metallic materials.

Bioactive titanate porous layers could be formed on Ti-Based Bulk Metallic Glasses with only 1 mA/cm<sup>2</sup> electric current at 90 C for 1 h. Those soft(mild) conditions can be applied easily to practical(even industrial) materials fabrication processes because they have no need to use highly energetic sources like plasma, high vacuum, high temperature, high pressure nor particular containers. They are therefore important for future materials science and engineering as typical Soft(Green) Processing.

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## 2-5: Multiplex Templating Hydrothermal Synthesis of Functional Nanowires, Macroscopic Assemblies and Their Applications

Hai-Wei Liang, Jian-Wei Liu, Kai Wang, Shu-Hong Yu\*

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, China, 230026. Email: [shyu@ustc.edu.cn](mailto:shyu@ustc.edu.cn)

The physical properties, as well as the unique transport feature along the longitudinal direction and the large surface-to-volume ratio make 1D nanostructures attract extensive attention in both fundamental research and engineering applications. From a synthetic point of view, it is highly desirable to develop a simple route for fabricating 1D nanostructures in large-scale at low cost. On the other hand, in order to transfer the intrinsic features of individual 1D nanostructures into macroscopic scale and realize practical applications, we need to explore highly efficient and scalable assembling methods to integrate 1D nanostructures into functional macroscopic architectures.

The template-directed synthetic method has some obvious advantages, e.g., easy fabrication, low cost, high throughput, and various compositions of materials [1]. On the other hand, although the properties of nanomaterials are frequently superior to those of their bulk counterparts, translating the unique characteristics of individual nanoscale components into macroscopic functional devices still remains a challenge.

We independently developed a facile hydrothermal method for synthesizing ultrathin Te nanowires (TeNWs) by using conventional chemicals. Through systematical study in past several years, we have demonstrated that the ultrathin TeNWs can be employed as a versatile templating material for fabricating a series of high-quality 1D nanostructures by taking the unique advantages of TeNWs, *i.e.*, large-scale synthesis, high processability and high reactivity [1,2]. Importantly, the obtained 1D products inherit the dimensional (high aspect ratio) and mechanical (high flexibility) features of original TeNWs templates, thus allowing for constructing macroscopic architectures by using them as nanoscale building blocks [3].

A family of 1D nanostructures that covers a wide range of materials, including noble metals, metal oxides, semiconductors, carbon, polymers, their binary and multiple hybrids can be prepared through this multiplex templating hydrothermal process starting from TeNWs. A series of macroscopic assemblies of 1D nanostructures based on these well-defined nanowires/nanocables, including free-standing membranes, films, hydrogels, and aerogels, can be fabricated, showing enormous application potential in diverse fields, such as liquid filtration and separation, continuous-flow catalysis, electrocatalysis, electronic devices, super adsorbent, elastomeric conductors, and polymer-based nanocomposites [1-6].

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### 3-1: Hydrothermal Conversion of Algal Biomass to Fuels and Chemicals

Phillip. E. Savage

University of Michigan, Chemical Engineering Department, Ann Arbor, MI 48109

There is much interest in using renewable biomass resources to meet the growing energy demands. Algal biomass is an attractive source for renewable fuels because it requires less land area and has a higher energy density than terrestrial biomass and it does not involve a food vs. fuel competition as does corn ethanol or soy biodiesel. Microalgae grow to biomass densities of around 1 g/L in nature, so a tremendous amount of water accompanies the biomass feedstock. Conventional algal bioenergy processes (e.g., lipid extraction for biodiesel production) first remove the water and then process the dried biomass. These dewatering and drying steps are costly and energy intensive. Thus, there is a need for algal biomass conversion processes that operate in the aqueous phase. We are helping to develop the science and technology bases for hydrothermal and solvothermal processes that can convert wet algal biomass directly (no drying) and thereby reduce process energy demands for biofuel production. These processes mimic nature in that they take advantage of the combined action of heat, water, and pressure to depolymerize the biomacromolecules in the biomass. This presentation will describe recent progress in our lab on algae gasification (catalytic and non-catalytic) in supercritical water [1] to produce CH<sub>4</sub> and H<sub>2</sub>, algae carbonization followed by in situ, supercritical transesterification to produce biodiesel [2] or by hydrothermal catalytic deoxygenation [3] to produce green diesel, microalgae liquefaction in near-critical water to produce a crude bio-oil [4], and catalytic upgrading of the crude bio-oil in supercritical water [5]. The figure below illustrates these different pathways from wet algal biomass to fuels. Our focus is on the reaction pathways, kinetics, and mechanisms, and these are elucidated from experiments and modeling with both algal biomass and fractions thereof and simple model compounds [6,7].

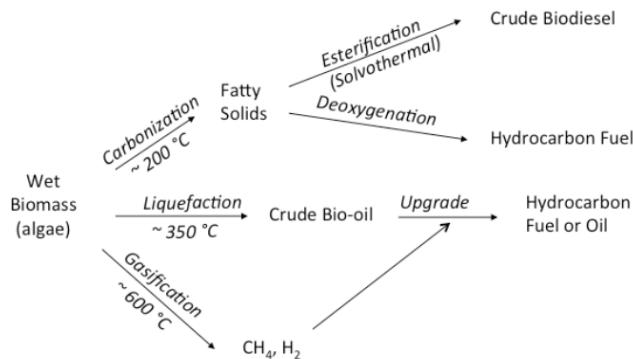


Figure 1: Some Hydrothermal Routes from Wet Algae to Fuels

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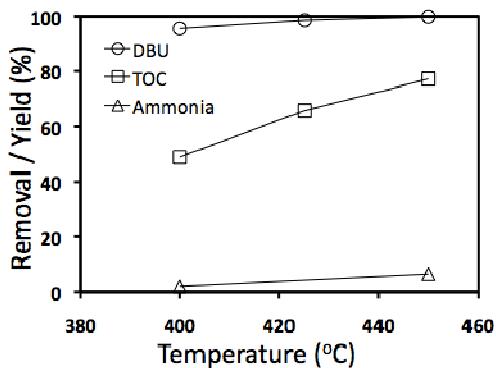
### **3-2: Supercritical Water Oxidation: The Next Generation of Processes for Hazardous Waste Treatment**

B. Al-Duri\*, O. Osibo\* and Y. Oshima\*\*

\* School of Chemical Engineering, University of Birmingham, B15 2TT, United Kingdom

\*\* Department of Environment Systems, Graduate School of Frontier Sciences, University of Tokyo, Japan

This work presents supercritical water oxidation (SCWO) as the next generation of advanced processes for the treatment of chemically stable, hazardous Nitrogen-containing hydrocarbons. This paper explains the chemistry of water and its relation to SCW behaviour and the applications of SCW technology in waste minimisation and energy production. Furthermore, this work presents the supercritical water oxidation of: 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (a bicyclic compound with two nitrogen atoms found in pharmaceutical wastewaters); in a continuous tubular reactor. The effect of operating variables, namely temperature and initial oxygen concentration were investigated to optimize DBU removal. The results show > 99% DBU removal converting it into carbon dioxide, water and ammonia; 83 % TOC removal was achieved at 450°C and 25 MPa after 7seconds residence time.



**Figure 1** Effect of operating temperature on the removal of DBU, TOC and the yield of Ammonia at 25 MPa and 7s residence time.

DBU and TOC removal increased with temperature to 100% and 77% respectively, at 450°C. The yield of ammonia increased from 2% to 7% as the temperature increased, indicating the scission of the C-N bond in DBU is facilitated at higher temperatures. This in agreement with Cocero's work on aniline (Cocero et al., 2000). Previous work with quinoline showed that ammonia yield increased with temperature till 550°C and then began to decrease (Pinto et al., 2006).

This paper also highlights how SCWO offers advantages over such techniques.

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### **3-3: Sub-critical Water Technology as a Green and Sustainable Tool for Oil Extraction**

Wael Abdelmoez<sup>1</sup>, and Hiroyuki Yoshida<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Elminia University, 61519 Elminia, Egypt

<sup>2</sup>Research Organization for the 21st Century, Osaka Prefecture University 1-2, Gakuen-Cho, Naka-Ku, Sakai, Osaka 599-8570, Japan

This study presents the extraction of oil using subcritical water technology from different oil containing procurers. The effect of extraction parameters including temperature, water to feed ratio, extraction time and mean particle sizes were studied for different procurers. Cotton seeds, jojoba seeds and edible oil bleaching powder were presented and compared to explore the efficiency as well as the diversity of the subcritical water technology in oil extraction as a green solvent. Moreover, the kinetic as well as the thermodynamic of the extraction process were investigated.

The obtained results revealed that the increase in both temperature and the time of extraction while a decrease in particle size generally improved the yield of extraction up to certain limits. It was also found that in the case of oil extraction using subcritical water, the reaction kinetics could be correlated well with an irreversible consecutive unimolecular-type first order.

### 3-4: Carbon Dioxide Capture in Metal-Organic Frameworks

Thomas M. McDonald, Zoey R. Herm, Eric D. Bloch, Jarad A. Mason, Kenji Sumida, Brian M. Wiers, Wendy L. Queen, Leslie J. Murray, and Jeffrey R. Long\*

Department of Chemistry, University of California, Berkeley and  
Materials Sciences Division, Lawrence Berkeley National Laboratory

Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications. In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for use as solid adsorbents in postcombustion and precombustion CO<sub>2</sub> capture, and for the separation of O<sub>2</sub> from air, as required for oxyfuel combustion.<sup>1</sup> In particular, MOFs with open metal cation sites or alkylamine-functionalized surfaces are demonstrated to provide high selectivities and working capacities for the adsorption of CO<sub>2</sub> over N<sub>2</sub> under dry flue gas conditions. Breakthrough measurements further show compounds of the latter type to be effective in the presence of water, while calorimetry data reveal a low regeneration energy compared to aqueous amine solutions.<sup>2</sup> MOFs with open metal cation sites, such as Mg<sub>2</sub>(dobdc) (dobdc<sup>4-</sup> = 2,5-dioxido-1,4-benzenedicarboxylate), are highly effective in the removal of CO<sub>2</sub> under conditions relevant to H<sub>2</sub> production, including in the presence of CH<sub>4</sub> impurities.<sup>3</sup> Redox-active Fe<sub>2+</sub> sites in the isostructural compound Fe2(dobdc) allow the selective adsorption of O<sub>2</sub> over N<sub>2</sub> via an electron transfer mechanism (see Fig. 1).<sup>4</sup> The same material is demonstrated to be effective at 45 °C for the fractionation of mixtures of C1 and C2 hydrocarbons, and for the high-purity separation of ethylene/ethane and propylene/ propane mixtures.<sup>5</sup>

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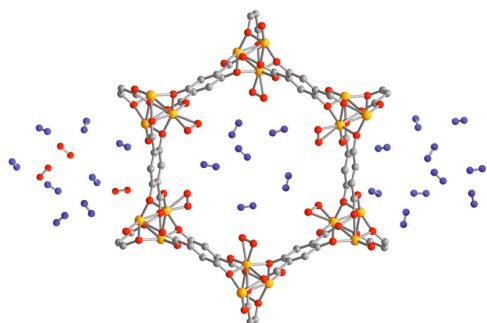


Fig. 1. Selective adsorption of O<sub>2</sub> over N<sub>2</sub> at the open Fe sites within Fe2(dobdc).

### 3-5: Greener Synthesis of Metal Organic Frameworks in High Temperature Water

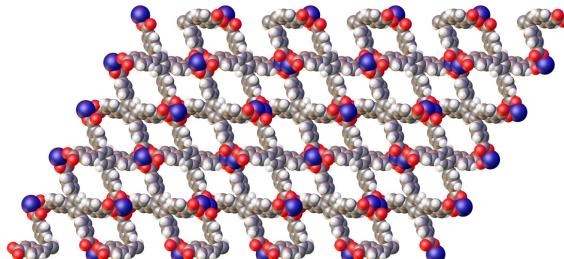
Peter A. Bayliss<sup>1\*</sup>, Eduardo Perez, Ilich A. Ibarra, Martyn Poliakoff, and Martin Schröder.

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.  
pcxpab1@nottingham.ac.uk

There is a need for greener alternatives and routes to the synthesis of metal-organic framework (MOF) materials because current methods often use environmentally hazardous solvents such as N,N-dimethylformamide (DMF) with long reaction times, typically 2-3 days. MOFs are crystalline materials which often exhibit porosity and high surface areas and consist of metal centres coordinated by bridging organic ligands to form an infinitely extended network. It is important to develop alternative synthetic methods that are fast, scalable and green to meet the increasing demand so that MOFs can fulfill a large number of potential applications. Many of these applications are consistent with green chemistry and include hydrogen and methane storage, carbon dioxide capture, and gas separations and catalysis; these provide potential for new energy supplies with lower carbon dioxide emissions.

We have successfully demonstrated that high temperature water (HTW) can be used for the synthesis of both new MOFs such as NOTT-402<sup>1</sup> and known MOFs such as MIL-53 (Al)<sup>2</sup> and scandium terephthalate  $[\text{Sc}_2(\text{C}_6\text{H}_4(\text{CO}_2)_2)_3]_\infty$ <sup>3</sup>.

NOTT-402 is a zinc(II) and tetracarboxylate ligand based framework. The material is porous with reasonable stability, one dimensional channel pores of *ca.* 4.3 Å in diameter and with a high isosteric heat of adsorption of hydrogen of 11 kJ mol<sup>-1</sup>.



**Figure 1.** View of structure of NOTT-402  $\{[\text{Zn}_2(\text{L}) \cdot (\text{H}_2\text{O})_3]_\infty$  ( $\text{H}_4\text{L}$  = 1,2,4,5-tetrakis(4-carboxyphenyl)benzene) along the  $a$  axis.

The use of HTW has advantages over toxic solvents such as DMF since it is non-toxic, abundant, renewable and inexpensive. HTW is able to solubilise and deprotonate commonly used MOF linkers such as terephthalic acid and therefore the synthesis of MOF materials becomes possible via systems using only the metal salt, ligand and water.

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## **3-6: Microporous Metal Organic Frameworks: Solvothermal-Hydrothermal Synthesis, Structure-Pore Functionalization, and Potential Applications**

Jing Li

Department of Chemistry and Chemical Biology  
Rutgers, The State University of New Jersey  
Piscataway, NJ 08854

Metal organic framework (MOF) materials (also referred to as coordination polymers) are crystalline solids built on metals (or metal clusters) and organic ligands via coordinate bonds. They form one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) network structures and a sub-group of this material family has sustainable pores with pore diameters in the micropore region (less than 2 nm). Current research and development on these materials have revealed many interesting and unique features and porosity-related functionality, making them promising for possible utility in a number of areas. This presentation will focus on our recent progress in solvothermal synthesis and crystal growth of microporous MOFs, and in systematic tailoring of their crystal structures (e.g. dimensionality, connectivity, and topology), chemical composition (e.g. type and form of metals and ligands) and pore characteristics (e.g., pore size and shape, pore volume and the chemical functionality of the pore walls) to enhance targeted properties and achieve improved performance for several important applications.<sup>[1-6]</sup>

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## 4-1: New Oxide Materials for Catalysis from Hydrothermal Chemistry

Richard I. Walton

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK  
r.i.walton@warwick.ac.uk

In this presentation I will describe our recent results in an investigation of the scope of the hydrothermal method in the synthesis of complex oxide systems, where the control of the metal oxidation state is important in dictating their properties, in particular for redox catalysis applications. The aqueous solutions used in synthesis provide a convenient means for the inclusion of oxidising or reducing agents to permit the control of metal oxidation state in the final product. Some new examples of this approach to synthesis will be described.

In the case of cerium(IV) oxides, doped  $\text{CeO}_2$  can be prepared in a nanocrystalline form from aqueous, basic solutions of  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  heated above 100 °C and the addition of oxidising agents tends to form nanocrystalline samples with well-defined particle size. The choice of oxidant may lead to novel doped materials. With  $\text{NaBiO}_3 \cdot 2\text{H}_2\text{O}$  we have thus prepared the materials  $\text{Ce}^{\text{IV}}_{1-x}\text{Bi}^{\text{III}}_x\text{O}_{2-x/2}$  ( $x < 0.6$ ).[1] If additional metals with a preference for six-coordination are added to the hydrothermal reactions and  $\text{H}_2\text{O}_2$  used as oxidant, then a pyrochlore family is produced:  $(\text{Na}_{0.33}\text{Ce}^{\text{IV}}_{0.67})_2(\text{Ir},\text{Ru})_2\text{O}_7$  (where  $\text{M}^{4+} = \text{Ti}, \text{Sn}, \text{Ge}$  etc.). Applications as redox supports in the water-gas shift (WGS) reaction have been investigated for the conversion of water and carbon monoxide to hydrogen and carbon dioxide, a reaction of relevance for the purification of hydrogen for fuel cell applications. The pyrochlores show excellent low temperature reducibility that is reversible over several cycles: these materials we have gone on and used as gold supports for WGS, the results of which we here present.[2]

We have extended this approach more recently to precious-metal oxides containing ruthenium and iridium for use as electrochemical oxygen evolution (OER) catalysis. Control of the initial Ru and Ir oxidation state, between +4 and +5, in pyrochlore materials such as  $\text{Bi}_2\text{Ir}_2\text{O}_7$  and  $(\text{Na}_{0.33}\text{Ce}^{\text{IV}}_{0.67})_2(\text{Ir},\text{Ru})_2\text{O}_7$  by hydrothermal synthesis conditions, coupled with the nano-scale powders produced from solution reactions produces highly active materials for OER under aqueous acid conditions. We have performed Ru K-edge and Ir L<sub>III</sub>-edge XANES studies under operating conditions using a specially designed reaction cell and this allows us to understand their mechanism of catalysis in comparison for existing materials used for this important application.

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## 4-2: Hydrothermal-galvanic couple synthesis of perovskite oxide thin films

Fu-Hsing Lu, Chia-Jong Yang, Chia-Chun Lin, Di-You Tsai

Department of Materials Science and Engineering, National Chung Hsing University  
250 Kuo Kuang Road, Taichung 402, Taiwan

Perovskite oxide thin films exhibiting excellent ferroelectric and dielectric properties have many industrial applications. Hydrothermal and electrochemical methods have often been used to make these types of oxides. In this hydrothermal technique –galvanic couple technique, both working and counter electrodes were directly connected without applying any external electrical currents or voltages. Barium titanate thin films were selected as a model system for the synthesis. The growth rate of the films synthesized by such a technique is much faster than that made by a sole hydrothermal method. The galvanic-couple setup could considerably enhance the growth of the oxide films. Moreover, using the conductive nitride-coated substrates with strong preferred orientations could facilitate the directionally-oriented growth of the films. The effect of the galvanic couple was verified by examining the current flow during the synthesis although no external power sources were applied. The directional growth and the growth kinetics of the oxide films were also analyzed.

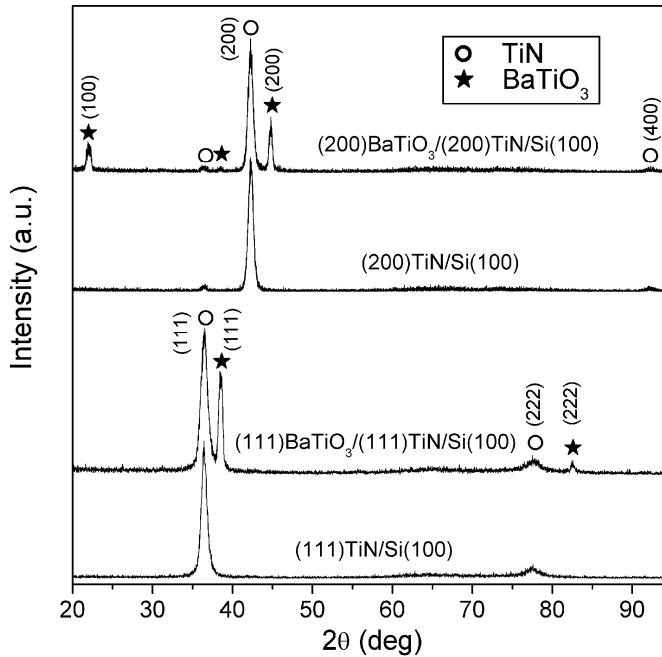


Fig. 1. Eptaxial growth of barium titanate thin films over TiN/Si substrates by a hydrothermal-galvanic couple technique.

### 4-3: Shape-selective Growth of Noble Metal Nanocrystals

Xianmao Lu\*

<sup>1</sup>Department of Chemical & Biomolecular Engineering, National University of Singapore,  
Singapore 117576

Shape-selective synthesis of noble metal nanocrystals has attracted much attention in recent years owing to their shape-dependent properties and wide variety of applications. Among various approaches to tune the geometry of metal nanocrystals, the use of foreign ions has shown drastic morphology-selection effect. This strategy has been most successfully demonstrated in the gold-silver system where the presence of Ag(I) ions in trace amount induces the formation of Au nanocrystals with various shapes. Here, we present our recent study on using foreign ions (e.g., Pd<sup>2+</sup>, Ag<sup>+</sup>) as shape-selective agents for noble metal nanostructures with exotic shapes.[1] With the assistance of Pd<sup>2+</sup>/Ag<sup>+</sup> ions, Au polyhedra with high-index facets including ditetragonal prisms enclosed by {310} facets, truncated octahedra with both {111} and {310} facets, and bipyramids bounded by {117} facets can be prepared in high yields. In addition, we also show that novel bimetallic Pt-Ag nanostructures, including dimeric and popcorn-shaped hollow particles, can be synthesized via the reactions between Ag nanotemplates and Pt precursor.[2] It is found that by tailoring the reaction kinetics and controlling the number of pitting sites, the diffusion of Ag and the deposition of Pt on Ag nanotemplates can be tuned, leading to the formation of nanoboxes attached with different number of hollow particles. The resultant novel nanostructures exhibit higher electrocatalytic activity than commercial Pt/C catalyst.

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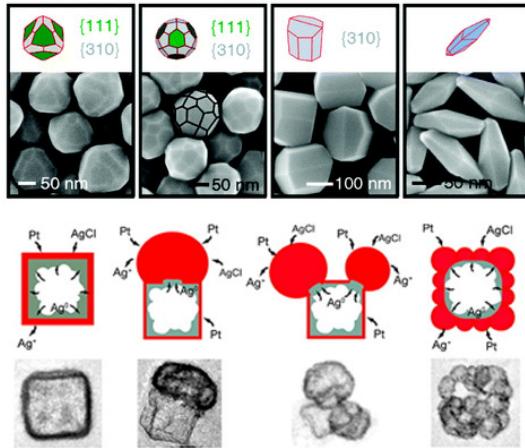


Fig. 1. Au nanocrystals with high-index facets (top) and Au-Pt bimetallic hollow nanostructures (bottom).

## 4-4: Synthesis and Applications of Nanoparticles

R D. Tilley

School of Chemical and Physical Sciences and MacDiarmid Institute, Victoria University of Wellington, New Zealand.

Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such as gold core palladium shell nanoparticles, below and magnetic nanoparticles and silicon and germanium quantum dots. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Biomedical and catalytic applications will be discussed.

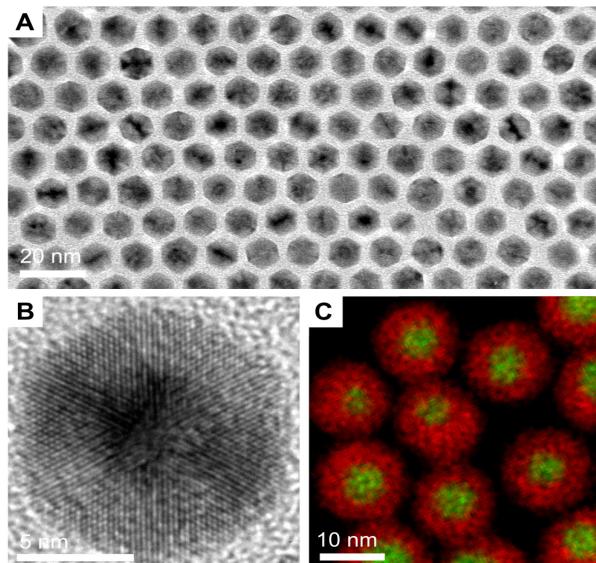


Fig. 1. Faceted Au-Pd core-shell nanocrystals. (A) Bright field TEM image of an ordered array of highly faceted Au-Pd core-shell nanocrystals with an average size of 11.4 nm. (B) High-resolution TEM image of a single Au-Pd core-shell nanocrystal, with contrast difference between the dark core (gold) and lighter shell (palladium). Lattice fringes correspond to an icosahedral structure oriented along  $<111>$ . (C) STEM-EDX map shown as an overlay of gold and palladium signal, confirming the core-shell structure of the Au-Pd nanocrystals.

## 4-5: Generalized Syntheses of Nanocrystal–Graphene Hybrids in Hot Solvents

Danny Wei-Ping Pang, Fang-Wei Yuan, Hong-Jie Yang, and Hsing-Yu Tuan\*

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, 30013,  
Republic of China

Graphene has the theoretical largest surface area ( $2630\text{ m}^2\text{g}^{-1}$ ) among allotropes of carbon, and therefore has been considered as a promising immobile platform for nanocrystals (NCs) support. The NC–graphene hybrids inherit outstanding mechanical, electronic and thermal properties of graphene synergized with novel properties of inorganic entities to form an exciting class of materials for a wide range of application areas including catalysts, electronics, sensors, biomedicine, and energy storage, and more. Although a variety of methods have been developed for graphene hybrid synthesis, a facile and general synthetic approach is still highly required. High-temperature colloidal synthesis method, so called hot solvent synthesis, is the most common and probably the most successful method to obtain high-quality inorganic nanocrystals. Organometallic precursors are decomposed at high temperature reactions and NCs are nucleated and grown in a size- and shape-controllable manner. We will report general syntheses of nanocrystal-graphene hybrids in high-boiling-point organic solvents. A rich library of nanocrystals, with types including noble metal, metal oxide, magnetic material and semiconductor were nucleated and grown heterogeneously on chemically converted graphene (CCG) sheets (simultaneously reduced from GO during the synthesis). In high-temperature environments, sufficient thermal energy is offered to assure highly crystalline NCs and obviates the post-annealing process. For example, figure 1 shows a HRTEM image of CdSe nanocrystals on a graphene sheet, revealing their single crystalline nature. In controlled experiments, i.e., in a reaction without addition of graphene oxide sheets, severe aggregates of NCs were observed, showing graphene oxide serving as nuclei anchorage media. The properties of as-obtained graphene hybrids were also characterized. This synthetic protocol may bring one step closer to achieve "unity in diversity" on the preparation of nanocrystal-graphene hybrids.

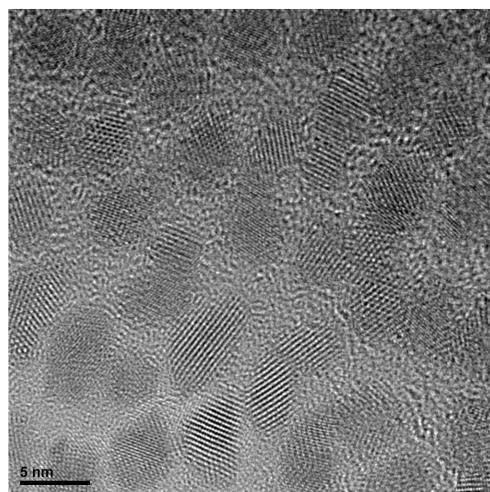


Figure 1. CdSe nanocrystals on a graphene sheet as CdSe/graphene hybrid

## 4-6: Nanoparticle Assembly Using Polymer Templates and Printing Technologies for Hybrid Materials and Devices

Jim Watkins

Polymer Science and Engineering Department  
and NSF Center for Hierachal Manufacturing  
University of Massachusetts Amherst  
Amherst, MA 01003

Well defined nanoparticles are at the heart of the active layer of many emerging devices for application in fields ranging from energy generation and storage, to flexible electronics to optoelectronics. In some cases, stable hybrid nanoparticle/polymer films containing high loadings of well dispersed nanoparticles provide the necessary performance attributes. Examples include solution coat-able high dielectric constant films for flexible electronics and hybrid films of tuned refractive index for applications in optical devices. In other cases, periodic arrangement of the NPs on well-ordered lattices offers unique properties that can be exploited in devices or in new approaches for metamaterial design. In this talk we describe how controlling the interactions between nanoparticles, which can be prepared using hydrothermal or solvothermal routes, and at least one segment of a polymer or block copolymer host can be used to control the structure and properties of hybrid nanoparticle/polymer composites to meet these challenges. Specific examples in flexible electronics, energy, and memory devices are provided. We also discuss how these materials, and devices based on these materials, can be prepared at scale using roll-to-roll processing technologies.

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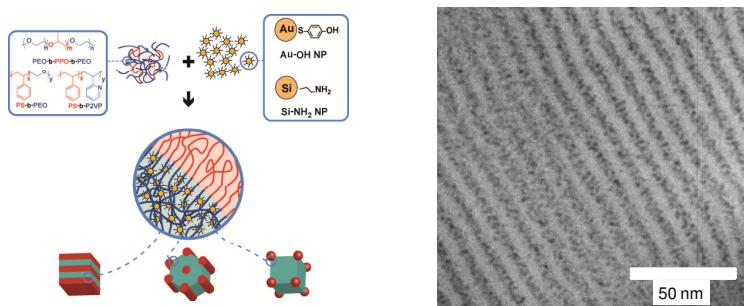


Fig. 1. Additive-driven assembly of nanoparticle/polymer hybrids

## **5-1: Hydrothermal synthesis of VO<sub>2</sub> nanocrystals and applications**

Yanfeng Gao, Hongjie Luo, Minoru Kanehira

School of Materials Science and Engineering, Shanghai University, 99 Shangda Rd.,  
Shanghai 200444, China  
Email: yfgao@mail.sic.ac.cn

Quasi-spherical VO<sub>2</sub> nanoparticles with uniform size and high crystallinity are ideal functional materials for applications in field-effect transistors, smart window coatings and switches. However, the synthesis of these VO<sub>2</sub> nanoparticles has long been a challenge. This article presents a novel doping strategy for the simultaneous control of the size, morphology and polymorphology of VO<sub>2</sub> nanoparticles. Doping is able to induce the crystal structure change and exhibits a significant promoting effect on the formation of doped monoclinic VO<sub>2</sub> (VO<sub>2</sub>(M)). Specifically, by antimony (Sb<sup>3+</sup>) doping, hexagonal-shaped, well crystalline monoclinic VO<sub>2</sub> nanoparticles with tunable sizes (8 - 30 nm) and controllable polymorphs were synthesized via one-pot, hydrothermal method. Sb<sup>3+</sup> dopant, which is larger in radius and lower in valence than a V<sup>4+</sup> ion, can introduce extra oxygen vacancies during the nucleation and growth of VO<sub>2</sub> nanoparticles. These positively charged nuclei may suppress the adsorption of VO<sup>2+</sup> aqua ions, and therefore inhibit the growth of the VO<sub>2</sub>(M) nanoparticles. Comparably, Sb<sup>5+</sup> dopants that possess higher valence counts than V<sup>4+</sup> ions can induce the growth of VO<sub>2</sub>(M) particles to 200 - 300 nm in width and above 500 nm in length. The Sb<sup>3+</sup>-doped VO<sub>2</sub>(M) nanoparticles exhibit excellent properties in metal-semiconductor transformation at transition temperatures ranging from 55 - 68 °C. Films obtained by casting these nanoparticles show excellent optical properties (both visible transmittance and infrared regulation), comparing with those prepared from gas phases, such as sputtering. This synthetic strategy that involves the doping of an element with a different valence count than the matrix cation, may be useful for controlling the solution growth of some technologically significant nanomaterials. In addition, the formation mechanism of solid and crystalline transformation was also studied by designing a specific reaction autoclave.

## 5-2: Neutron Radiography on Mixing Behavior of Supercritical Water and Room-Temperature Water in Tubular Flow Reactor for Hydrothermal Synthesis

Seiichi Takami<sup>1\*</sup>

<sup>1</sup>Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
2-1-1 Katahira, Sendai 980-8577, Japan

Supercritical water is used in various chemical reaction processes including hydrothermal synthesis of metal oxide nanoparticles, oxidation, and chemical conversion of biomass and plastics. Because continuous flow reactors are applied for these processes by mixing several streams of reactants and water at supercritical conditions, rapid and uniform mixing of the streams is important to minimize the fluctuation of the products. In order to visualize and understand the mixing of streams under supercritical conditions, various experimental and computational studies have been performed. Although these methods provide various types of valuable information, there remain several problems, including difficulties in reproducing the real reactor shape and in modeling the complicated behavior of water near the critical point and/or in the turbulent flow regime.

In order to study the mixing of streams under supercritical conditions, we used neutron radiography. Neutrons can penetrate materials with heavier elements and are mostly scattered by hydrogen atoms. Therefore, neutron radiography, that is, imaging of the internal structure of an object by measuring the scattered neutron intensity, is suitable for visualizing the density of water inside a tube or container composed of stainless steel or other alloys. Using neutron radiography, Peterson et al. have studied salt precipitation processes in supercritical water [1]. In this study, we attempted to investigate the mixing of room-temperature water and supercritical water in a tubular flow reactor.

Experiments were performed using a thermal neutron beam emitted from the B4 port of the Kyoto University Reactor at the Research Reactor Institute, Kyoto University. Experimental setup is shown in Fig. 1. The obtained images clearly showed the differences in the density of water in the tubes near the mixing point (Fig. 2). The partitioned flow in the side tube was also visualized while feeding room-temperature water [2]. This result demonstrated that neutron radiography can be used to study the mixing behavior of supercritical water with cool water.

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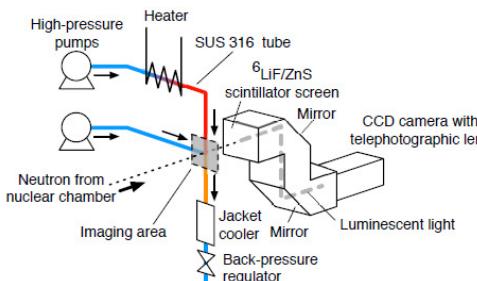


Fig. 1. Experimental setup for neutron radiography on a tubular flow reactor.

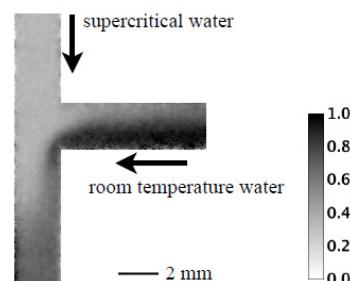


Fig. 2. Water density at the T-junction of a tubular flow reactor.

## **5-3: Hydrothermal Media on Chip: Supercritical Microreactors for Studying Water / CO<sub>2</sub> Systems**

Samuel Marre, Na Liu, Carole Lecoutre, Yves Garrabos, Cyril Aymonier

CNRS, Université de Bordeaux, ICMCB,  
87 avenue du Dr. A. Schweitzer, 33608 Pessac Cedex, France  
marre@icmcb-bordeaux.cnrs.fr

The last few years have seen the development of a new field of investigation, so called “Supercritical Microfluidics” [1] with the basic idea to combine the advantages of size reduction provided by microsystems – advanced control of operating parameters, reproducibility, *in situ* and online characterization, rapid screening, fast mass and heat transfer and low reagent consumption – to the unique properties of supercritical fluids - “hybrids” thermophysical properties, intermediate between liquids and gases, continuously adjustable with small variations of pressure and temperature, gas-like viscosities and diffusivities, liquid-like densities. The design of microreactors capable of handling working conditions compatible with high pressure fluids [2] opens new ways for characterizing and studying hydrothermal and supercritical fluids processes, generally limited to the use of “blind” stainless steel devices.

This talk will first highlights the main interests of combining supercritical fluids to Microfluidic systems (Supercritical Microfluidics). We will later detail briefly the strategy for designing high pressure microchips. Some applications of supercritical microreactors coupled to optical visualization and spectroscopy analysis for studying of water / CO<sub>2</sub> systems at high pressure will eventually be presented. In particular, we will focus on the transition from dripping to jetting in coflowing supercritical CO<sub>2</sub> / water [3] and on CO<sub>2</sub> solubility measurements in water and brine [4].

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## 5-4: Design Methodology of Microreactor and its Application for Supercritical Nanoparticle Synthesis

Nobuaki Aoki

WPI-Advanced Institute for Materials Research (WPI-AIMR), Tohoku University,  
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Microreactor is a reactor that includes small scale of the order of micrometer. Such a small scale provides rapid heat and mass transfer, instantaneous mixing, and short residence time. These characteristics enable precise operations to control highly rapid and exothermic reactions [1]. For the versatile use of microreactors, a design method of reactor from the information for production such as reaction mechanism, kinetics, product quality, desired throughput is required. In this talk, a design methodology of microreactors based on mixing using fluid segments will be discussed. Fluid segments are split reactant fluids to reduce the diffusion length between reactants [2]. In a miniaturized space, the flow regime tends to be laminar, and the mixing is driven mainly by molecular diffusion. To enhance the mixing rate, the convection arises by channel confluence and bend is useful without decreasing channel size, which leads to a high pressure drop and the ease of clogging. The channel geometry, the fluid segment size that represents the convective mixing rate, and the reaction rate are quantitatively correlated to establish a design methodology of microreactor as summarized in Fig. 1 [3].

As an application of microreactor, supercritical hydrothermal synthesis of nanoparticles will be illustrated. Under the high temperature of supercritical regime, reaction rates of particle formation tend to be extremely high. The effect of mixing performance is a key to the particle formation with a small particle size and narrow size distribution.

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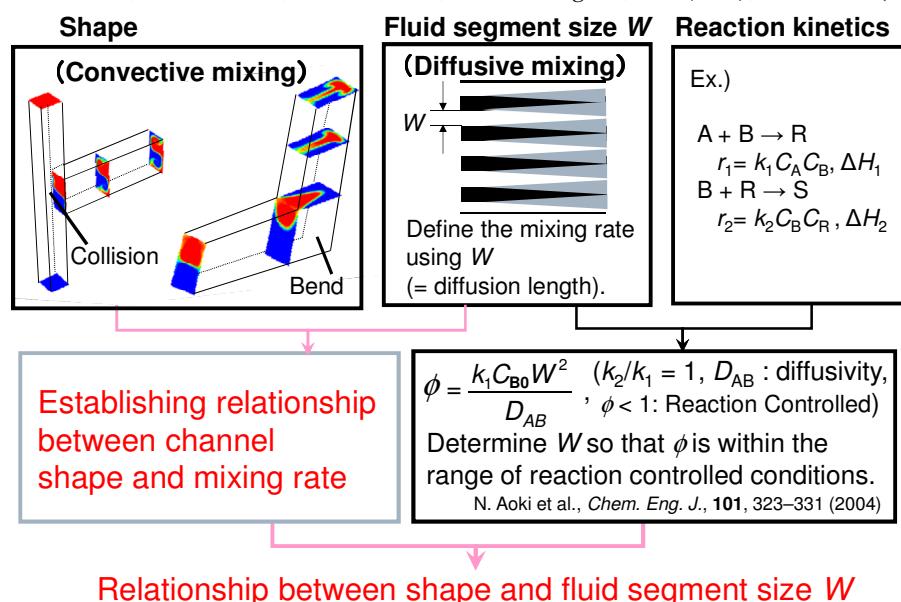


Fig. 1. Flow for the Establishment of Microreactor Design Based on Fluid Segments

## **5-5: The In Situ Supercritical Suite at Pacific Northwest National Laboratory**

H.T. Schaef, J. Loring, C.J. Thompson, and K.M. Rosso  
Pacific Northwest National Laboratory, Richland Washington, 99352

Laboratory investigations of carbonation routes in supercritical carbon dioxide ( $\text{scCO}_2$ ) dominated fluids are experimentally challenging and often lack *in situ* monitoring techniques. Intermediate transitional phases and solid structural changes occurring in the presence  $\text{scCO}_2$  are difficult to observe without real time measurements collected at pressure and temperature. Compounding the problem further is the corrosive nature of water bearing  $\text{scCO}_2$  and impacting the safety and longevity of a pressurized system. In this paper we present experimental results derived from a powerful suite of laboratory instrumentation specifically designed to provide real time chemical and structural data occurring in supercritical fluids. These techniques, solid-state nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and atomic force microscopy (AFM), are designed to operate at modest pressures and temperatures examining *in situ* chemistry spanning from the pore-scale to the molecular-level. Studies emphasizing model minerals in contact with water bearing  $\text{scCO}_2$  fluids show a wide range of carbonation reactivities depending on the mineralogy. Reactions between water bearing  $\text{scCO}_2$  and olivines produce intermediate hydrated carbonates that become dehydrated depending on water content and temperature. Examples that elucidate the role of water and demonstrate water concentration thresholds for catalyzing mineralization will be discussed.

In addition to mineral carbonation,  $\text{scCO}_2$  is also capable of redistributing structurally bound water in phyllosilicates, an important subset of minerals to environmental and industrial applications. Through a combination of *in situ* techniques (NRM, FTIR, and HXRD) the stability of clay minerals when exposed to  $\text{scCO}_2$  has been evaluated. Overall, illite, montmorillonite, and chlorite are robust and show little in the way of carbonation. However, our studies indicate montmorillonites are susceptible to dehydration processes associated with anhydrous  $\text{scCO}_2$ . Water partitioning studies with *in situ* FTIR show concentrations of interlayer water are altered through exposure to  $\text{scCO}_2$ . Testing with a Na saturated montmorillonite indicated dehydration occurs and is directly related to the overall water concentration.

These *in situ* capabilities provide a means for developing a comprehensive understanding of chemical reactions relevant to both solvothermal and hydrothermal processes. They are intended for both programmatic and industrial research and are available to the external scientific community through competitive user proposal access. They form a unique tool suite that can provide valuable insight into chemical reaction progress at every stage, supply the data needed to improve relevant thermodynamics and kinetics databases, and ultimately help assess and assure prospective  $\text{scCO}_2$  reservoir permanence.

## 5-6: Watching chemistry happen: *In situ* studies of nanoparticle formation and growth in sub- and supercritical fluids.

Kirsten M. Ø. Jensen; Christoffer Tyrsted, Mogens Christensen, Martin Bremholm, Espen D. Bøjesen, Nina Lock, Bo B. Iversen

Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, DK-8000 Aarhus C, Denmark

To fully understand the mechanisms determining particle characteristics in sub- and supercritical synthesis and thereby obtain the knowledge needed to produce tailor-made nanoparticles, *in situ* studies are required to probe reactions as they occur [1]. During recent years, we have developed X-ray *in situ* reactors specifically designed for studies of reactions in sub- and supercritical fluids [2]. By means of Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS), we have obtained knowledge of the formation and growth of several inorganic nanoparticle systems, for example iron oxide [3] and  $\gamma\text{-Al}_2\text{O}_3$  [4].

Most recently, we have used *in situ* X-ray Total Scattering (TS) with pair distribution function (PDF) analysis. TS allows us to study the *local structure* and to extract the atomic structure of both amorphous and crystalline compounds. The whole reaction mechanism from molecular complexes over amorphous intermediates to crystalline nanoparticles can thus be followed. Here, some of our most recent results regarding the formation of  $\text{SnO}_2$  [5],  $\text{CeO}_2$  [6] and  $\gamma\text{-Fe}_2\text{O}_3$  will be presented. In the case of  $\text{SnO}_2$ , we have shown that when dissolving the  $\text{SnCl}_4$  precursor, complexes of the form  $[\text{SnCl}_x(\text{H}_2\text{O})_{6-x}]^{4-x}$  ( $x=0\text{-}6$ ) form. However, under hydrothermal treatment,  $\text{SnO}_2$  nanoparticles form uniquely from the complexes with  $x=0$ , as illustrated in Fig. 1. For  $\text{CeO}_2$  we have shown that the nanoparticles form from previously unknown dimeric Ce-complexes. In both cases, the studies reveal the changes in material characteristics (atomic structure, particle size/shape/distributions, crystallinity) throughout the synthesis to give a comprehensive description, which can be used to tailor syntheses on a larger scale.

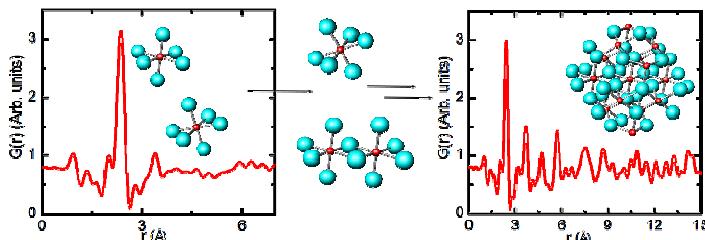


Fig 1: The formation of  $\text{SnO}_2$  from  $[\text{Sn}(\text{H}_2\text{O})_6]^{4+}$  can be followed by PDF analysis

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## 5-7: Liquid Crystals of Zirconium Phosphate disks with Various Aspect Ratios Controlled through Hydrothermal Method

Min Shuai<sup>1,2</sup>, Andres Mejia<sup>1</sup>, and Zhengdong Cheng<sup>1,2,3,4\*</sup>

<sup>1</sup>McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843, Fax: +1 979 8456446; Tel: +1 979 8453413; E-mail: zcheng@tamu.edu

<sup>2</sup>Materials Science and Engineering Program, Texas A&M University, College Station, Texas, 77843, USA.

<sup>3</sup>The Professional Program in Biotechnology (PPiB), Texas A&M University, College Station, Texas, 77843, USA.

<sup>4</sup>Soft Matter Research Center, School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, China

Nanoparticles with quasi two-dimensional shapes serve as building blocks for discotic colloidal liquid crystals<sup>1</sup>, which has applications involving the self-assembly of nanoparticles in liquid or solid solutions. However, due to difficulty of synthesis and especially shape-tuning of disk-shaped nanoparticles, good model systems for the study of discotic colloidal liquid crystals are hard to found.  $\alpha$ -zirconium phosphate (ZrP) crystals synthesized through hydrothermal treatment has regular disk shapes and controllable size, thickness, as well as size polydispersity. We experimentally illustrate that aqueous suspensions of these ZrP disks form stable liquid crystal phase easily. By choosing the thickness of the disks, an iridescent liquid crystal phase has been achieved, as shown in Fig. 1. The critical concentration of the phase transition was found to be dependent on the aspect ratio of the disks.

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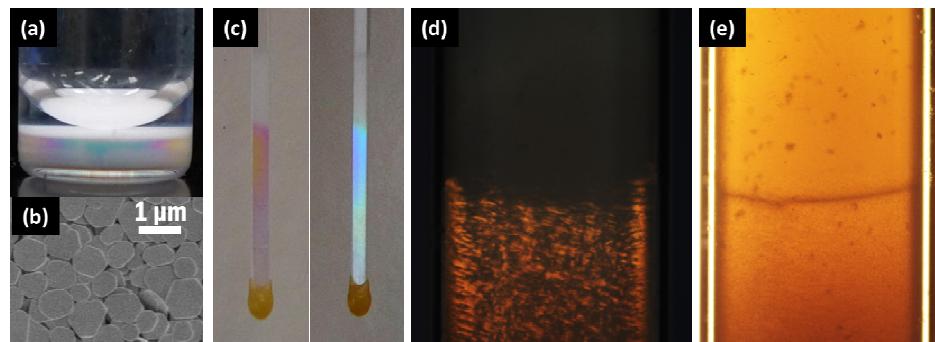


Fig. 1. Liquid crystals of aqueous ZrP disk suspensions: (a) A photograph showing the iridescent color of the liquid crystal; (b) A SEM image of the ZrP disks; (c) The sample loaded into 100  $\mu\text{m}$ -thin flat capillary tubes viewing from different angle; (d) A microscopic image of the sample in capillary under cross-polarized light; and (e) image (d) under white light.

## **6-1: Low temperature sol gel processing of pure and Al doped ZnO films.**

S M Dharmaprakash<sup>1</sup> and K Byrappa<sup>2</sup>

<sup>1</sup>Department of Physics, Mangalore University, Mangalagangotri 574199

<sup>2</sup>Department of Earth Sciences, University of Mysore, Manasagangotri Mysore 570006

Thin films of undoped and doped ZnO films are used for a wide variety of electronic and optoelectronic applications. An attempt has been made to develop undoped and Al doped zinc oxide films by sol gel spin coating technique using a novel precursor combination. The methods obtaining films have been optimised to produce quality films. It is observed that properties of metal oxide films are strongly influenced by degree of non stoichiometry, dopant and its concentration, type of the substrate and post deposition annealing. The characterization techniques like XRD, SEM, AFM, optical absorption/transmission and electrical resistivity measurements were used to determine the properties of the films. The deposited films were polycrystalline, homogeneous, smooth and highly oriented densely packed grains. The films developed were more than 80% transparent and showed decreased transparency at higher doping concentrations.

## **6-2: Preparation of transparent zeolite film on glass substrate without using structure directing agents**

Takamasa Onoki<sup>1\*</sup>

<sup>1</sup> Department of Materials Science, Osaka Prefecture University  
onoki@mtr.osakafu-u.ac.jp

The preparation of molecular sieve films has attracted considerable interest due to their potentials uses as membranes, membrane-reactors, components of optical and electrical devices, and selective sensors [1]. Despite considerable advances in synthetic procedures, the challenge of preparing continuous, highly oriented, sub-micrometer thickness molecular sieve films remains to be met. A simple and general processing scheme particularly promising to meet this goal consists of using suspensions of small size zeolite crystals to prepare precursor particle layers, followed by solidification of these particles to a continuous film. In this study, new techniques for preparing transparent zeolite thin films have been reported.

Zeolite Y powder (HSZ-320NAA, TOSOH, Japan) was selected for a deposited material in this research. The zeolite powder was crashed by beads milling. And then the crashed powder was immersed to some alkaline solutions in order to remove amorphous phase. The nano-sized zeolite powder was added to 2 mol/L sodium hydroxide solutions at 10-30 mass % and homogenized in a mortar. This mixed slurry was dropped on the glass substrate. The slurry mounted glass substrates were encapsulated into double layered plastic films. The capsules were located into the middle of the autoclave. Simple and easy pressing and heating method, which was named double layered capsule hydrothermal hot-pressing (DC-HHP) [2], was employed for depositing zeolite on the glass substrates in this research.

Slurry of Zeolite powder was pressed with a glass plate at following conditions; 40 MPa, 403 K and 1h. An SEM micrograph around the interface between zeolite and glass in a cross sectional view has been shown in Fig.1. It is demonstrated that simple hot-pressing treatment is useful for a new method for zeolite Y deposition on glass substrate.

This work was partly supported by a "Grant-in Aid for Young Scientists (B), 23760702" from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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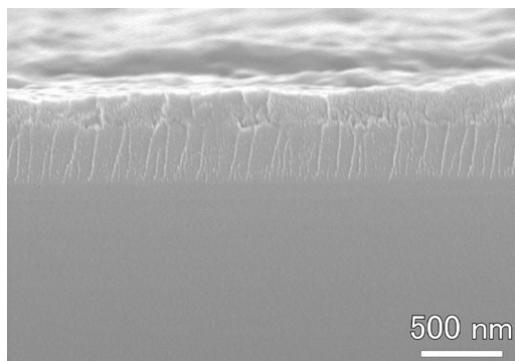


Fig. 1. SEM micrograph of zeolite coating on glass substrate in a cross sectional view.

## 6-3: Hydrothermal Synthesis of New Functional Polar Inorganic Materials

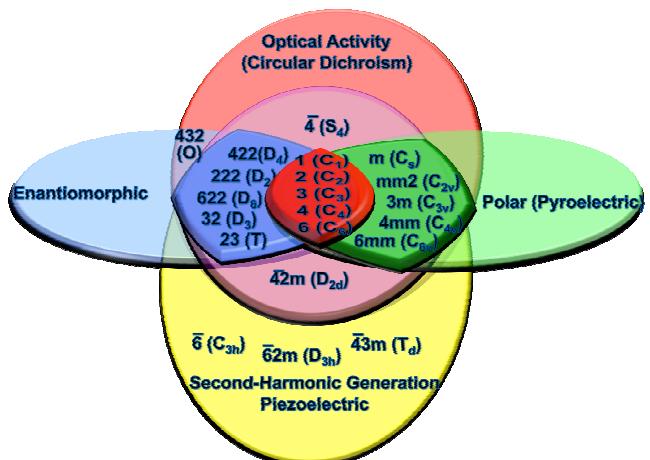
P. Shiv Halasyamani<sup>1\*</sup>, Sau Doan Nguyen<sup>1</sup> and Weiguo Zhang<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Houston, 136 Fleming Building, Houston, TX 77204-5003

Polar oxide materials – those with a macroscopic dipole moment – represent a vast, varied, and technologically relevant class of materials, and are ubiquitous in advanced technologies, i.e. computer memories, sensors, etc.[1,2] The design and synthesis of new polar oxides, however, remains an ongoing challenge. Macroscopic polarity implies microscopic polarity, in other words some of the coordination polyhedra must be polar. As is often the case, the local dipole moment in the coordination polyhedra is directed in opposite directions resulting in a non-polar material. In this presentation we will discuss strategies toward designing new polar oxide materials, as well as the characterization of their functional properties. Specifically we will demonstrate that by using cations susceptible to second-order Jahn-Teller (SOJT) effects we can substantially increase the incidence of macroscopic polarity in any new material. We will describe the hydrothermal synthesis of characterization of several new polar materials. Functional properties such as piezoelectricity and ferroelectricity are presented, and structure-property relationships will be discussed and explored.

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## 6-4: Direct Synthesis of Oxides from Solvothermal Oxidation of Metallic Gallium

Helen Y. Playford<sup>1\*</sup>, Richard I. Walton<sup>1</sup>, Alex C. Hannon<sup>2</sup> and Emma R. Barney<sup>2,3</sup>

<sup>1</sup>Department of Chemistry, University of Warwick, Coventry, UK.

<sup>2</sup>ISIS Facility, Rutherford Appleton Laboratory, Didcot, UK.

<sup>3</sup>Faculty of Engineering, University of Nottingham, Nottingham, UK.

The solvothermal reaction of metallic gallium in oxidising aminoalcohol solvents provides a simple synthetic route to the metastable  $\gamma\text{-Ga}_2\text{O}_3$  polymorph. Control of particle size can be achieved through choice of solvent and reaction time. The structure of the  $\gamma\text{-Ga}_2\text{O}_3$  polymorph is somewhat analogous to that of  $\gamma\text{-Al}_2\text{O}_3$  [1], and is best described as a significantly disordered defect spinel in space group  $Fd\bar{3}m$  with four partially occupied gallium sites. Here we present a detailed investigation of its structure using total neutron scattering, a technique which allows the structure to be examined on multiple length scales and reveals distortion in the octahedral gallium coordination environments.

In addition, we report the extension of the synthesis to mixed metal oxides via addition of a  $M^{2+}$  salt to the reaction mixture. In this manner, spinel oxides of general formula  $M_x\text{Ga}_{3-x}\text{O}_{4-y}$ , for a range of different metals, including  $M = \text{Zn}$ ,  $\text{Ni}$ ,  $\text{Co}$  and  $\text{Fe}$ , have been synthesised. The potential for further extending the synthesis into quaternary oxides, such as the promising photocatalyst  $(\text{Co}, \text{Mn})_x\text{Ga}_{3-x}\text{O}_4$ , [2] is great.

The structure of the solvothermally produced mixed-metal oxide where  $M = \text{Co}$  and Ga:Co ratio 2:1, is a defect spinel containing mixed valent cobalt and a small proportion of oxygen vacancies. This is, to the best of our knowledge, a novel cobalt gallate structure. Local deviations from the average crystal structure are observed in this material and attributed to the preference of both  $\text{Ga}^{3+}$  and  $\text{Co}^{2+}$  for distorted octahedral environments. Previous reports of cobalt gallate spinels have indicated that they display interesting magnetic properties including ferrimagnetism and spin-glass behavior [3], [4]. Therefore an examination of the magnetic behavior of the solvothermal cobalt gallate, using SQUID magnetometry, is also presented.

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## 6-5: Characterisation of Doped Perovskites Prepared by Hydrothermal Synthesis

Mohammad H. Harunsani<sup>1</sup> and Richard I. Walton<sup>1</sup>

<sup>1</sup>University of Warwick, Department of Chemistry, Gibbet Hill, Coventry, CV4 7AL

Lead-based materials such as PZT are widely used in electronics due to their impressive piezoelectric properties.<sup>1</sup> However, the use of lead-based materials may be prohibited in the near future due to the toxicity of lead. Hence, there is a need to replace these materials with lead-free alternatives.  $\text{NaBi}_{0.5}\text{Ti}_{0.5}\text{O}_3$  based solid solutions have been found to yield excellent properties making it a possible replacement for PZT.<sup>2</sup> In this work, Zr doped  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$  and its La analogue has been prepared by hydrothermal synthesis. The series  $\text{NaBi}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  ( $0 \leq x \leq 0.5$ ) and  $\text{NaLa}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  ( $0 \leq x \leq 0.1$ ) can be formed directly in a single step reaction at  $240^\circ\text{C}$  to give highly crystalline products. These materials are usually prepared by conventional solid state synthesis where high temperatures above  $1000^\circ\text{C}$  are used. However, by using hydrothermal synthesis, not only does it allow milder conditions to be used, it also gives greater control on the particle size of these materials

The samples were then characterised using powder X-ray diffraction (XRD) and neutron diffraction.  $\text{NaBi}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  is refined with the space group  $R\bar{3}c$ , while  $\text{NaLa}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  using  $R\bar{3}c$ . In both materials, the unit cell volume increases as more Zr is added, indicating that the Zr has been introduced into the structure. By preparing these materials hydrothermally, their morphology can be changed by modifying the mineralizer concentration and the solvent used. By using scanning electron microscopy (SEM), the shape of the particles were found to be cubic and “flower-like” for  $\text{NaBi}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  and  $\text{NaLa}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  respectively. The elemental composition was determined by energy dispersive X-ray analysis (EDXA) and found to be in agreement with the expected values. The ferroelectric and piezoelectric properties of  $\text{NaBi}(\text{Ti}_{1-x}\text{Zr}_x)_2\text{O}_6$  were also studied and the Zr doped samples was found to exhibit a reduction in both the  $d_{33}$  value and the remnant polarization.

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## 6-6: New Metastable Ternary Metal Ruthenium Oxides from Low Temperature Hydrothermal Synthesis

Craig I. Hiley<sup>1\*</sup>, Richard I. Walton<sup>1</sup>, Janet Fisher<sup>2</sup> and David Thompsett<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

<sup>2</sup>Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK.

A large number of mixed metal ruthenium oxides have already been successfully prepared using solid state synthesis, particularly those containing Ca, Sr and Ba. Of these, several have been found to exhibit interesting magnetic properties, such as superconductivity in  $\text{SrRu}_2\text{O}_4$  [1] and paramagnetism in  $\text{CaRuO}_3$  [2]. However, the high temperatures (typically in excess of 1000 °C) inevitably involved in solid state synthesis mean that only the most stable oxides can be isolated. Recently the high temperature hydrothermal synthesis of the pyrochlore  $\text{Ca}_2\text{Ru}_2\text{O}_7$ , which contained Ru<sup>5+</sup> and displayed spin glass type ordering was reported [3].

Low temperature hydrothermal reactions of  $\text{KRuO}_4$  and a metal peroxide,  $\text{MO}_2$  (where M = Ca, Sr or Ba) yield a diverse range of previously unreported ternary metal oxides. The reaction of  $\text{KRuO}_4$  and  $\text{CaO}_2$  yields the A-site deficient pyrochlore  $\text{Ca}_{1.45}\text{Ru}_2\text{O}_7$ ; whilst  $\text{KRuO}_4$  and  $\text{SrO}_2$  under the same conditions give  $\text{SrRu}_2\text{O}_6$ , which adopts the unusual layered  $\text{PbSb}_2\text{O}_6$ -type structure ( $P31m$ ,  $a = 5.20557(6)$  Å,  $c = 5.2344(1)$  Å).  $\text{Ca}_{1.45}\text{Ru}_2\text{O}_7$  was found to have a spin glass transition at 27 K, whilst  $\text{SrRu}_2\text{O}_6$  displayed magnetic ordering up to extraordinarily high temperatures. The hydrothermal reaction of  $\text{BaO}_2$  and  $\text{KRuO}_4$  in a 2:3 ratio gives the previously unreported  $\text{Ba}_2\text{Ru}_3\text{O}_9$  with orthorhombic space group  $P222$  ( $a = 12.194122(11)$  Å,  $b = 9.878306(9)$  Å and  $c = 7.058250(6)$  Å).

A wide array of techniques have been employed to characterise these ruthenates, including: synchrotron X-ray and neutron powder diffraction; thermodiffractometry, Ru K-edge XANES; ICP-MS; SEM; TGA and magnetometry.

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**6-7: Synthesis of Nanocomposites of ZnO/ZrO<sub>2</sub>, Ag-RuO<sub>2</sub> and Ru-ZnS by Electrochemical method in aqueous medium for photocatalytic degradation kinetics reaction for dyes and for antibacterial study.**

S. Ananda\*, G. Chaitanya Lakshmi, K. R. Raksha, R. Somashekhar, C. Ranganathaiah and K. Byrappa.

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, India.

Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore, India.

Department of Studies in Earth Science, University of Mysore, Manasagangotri, Mysore, India.

ZnO/ZrO<sub>2</sub>, Ag-RuO<sub>2</sub> and Ru-ZnS have been synthesized by electrochemical method in aqueous medium. This were characterized by UV-Visible spectroscopy, IR spectroscopy, SEM, XRD, PALS. The UV-Visible spectroscopy results reveals the band gap energy of nanocomposites. The XRD results show the crystallite size to be from 10 nm to 30 nm, calculated by Williamson-Hall plot. The PALS measurements gives defects concentration of nanocomposites. An improvement of photocatalytic degradation and reaction kinetics for dyes in comparison to commercial pure ZnO was observed. The photo degradation efficiency were found to be 85% to 90%. The nanocomposites prepared were used for antibacterial study, which shows very good inhibition towards the rate of growth of bacteria. Suitable mechanisms were proposed for synthetic reactions. The enhancement in photocatalytic activity of nanocomposites were used for degradation of industrial effluents.

## 6-8: A strategy for Design of Concave Pt-Ni Alloy with Controllable Chemical Etching

Yuen Wu, Dingsheng Wang, and Yadong Li\*

Department of Chemistry, Tsinghua University, Beijing 100084 (China)

Through selectively etching the less noble metal and rearranging the remaining metal atoms, the chemical etching has been proved to be one effective and classical “top-down” method to simultaneously control shape, size, and composition of bimetallic nanostructures. However, chemical etching suffers from some minor intrinsic drawbacks, including the surface atoms of alloy are usually etched in random sites which results in nanoporous structure and the etching process is usually too drastic to control. Till now, how to improve the technique of chemical etching and make it a moderate and controllable way still poses great challenges.

Herein, we converted the starting octahedral Ni-rich Pt-Ni alloys [1] to concave Pt<sub>3</sub>Ni structures by a coordination-assisted chemical etching process. A deterministic priority mechanism that Ni could be preferably etched from the Ni-rich alloy was proposed to decipher these rational and controllable processes. [2] Parallel to the original octahedron, the concave Pt-Ni exhibited higher density of low-coordinated atoms in steps and kinks, and thereby underpinned great potentiality as a new-type material in fuel cell, organic catalysis and so on.

[1] Y. Wu, S. Cai, D. Wang, W. He, Y. Li. J Am Chem Soc. **134**, 8975 (2012).

[2] Y. Wu, D. Wang, Z. Niu, P. Chen, G. Zhou, Y. Li. submitted

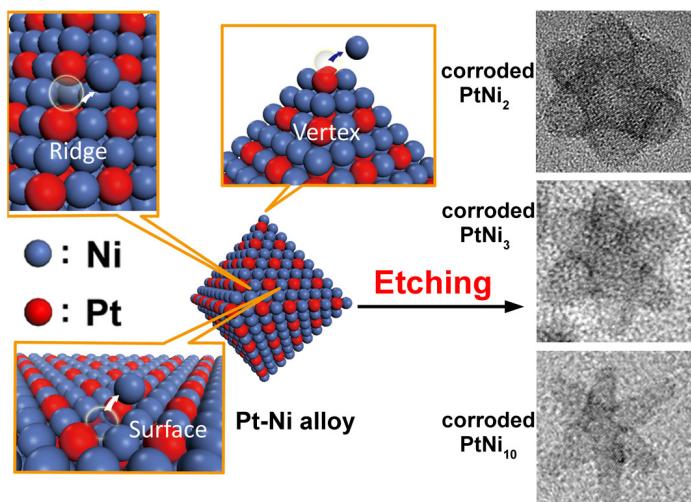


Fig. 1. Schematic view of the chemical etching process

## **6-9: Synthesis of a Novel Implant for Bone Grafting Using Sub-critical Water Technology**

Wael Abdelmoez<sup>1</sup>, and Hiroyuki Yoshida<sup>2</sup>

<sup>1</sup>Department of Chemical Engineering, Elminia University, 61519 Elminia, Egypt

<sup>2</sup>Research Organization for the 21stCentury, Osaka Prefecture University 1-2, Gakuen-Cho,  
Naka-Ku, Sakai, Osaka 599-8570, Japan

In the present work, we are introducing a novel protein-based implant in the field of bone grafting. Our novel biomaterial synthesized from bovine serum albumin using our newly developed technology (sub-critical water technology). The biomaterial showed a variety of mechanical properties and biodegradability that might allow for its application in the biomedical field and in particular as an alloplastic bone substitute.

The results revealed satisfactory results when used as a bone grafting material in surgically created bone defects in the rabbit models. The obtained results showed that these novel materials are having many unique properties, specifically, biocompatibility, nontoxic and nonirritant, act as a haemostatic agent and maintained the blood clot inside the defect, osteoconductive property, biodegradability property, easily manipulated and handled.

## **6-10: The use of continuous hydrothermal synthesis in the formulation and functionalization of flame retardant polymers**

Sherif Elbasuney, Derek Irvine, Edward Lester

School of Chemical, Environmental and Mining Engineering, The University of Nottingham,  
University Park, Nottingham NG7 2RD.

The incorporation of low concentrations of nanometer-sized fillers is a potential method to improve and diversify polymeric materials. Nanoparticles can improve flame resistance as well as the mechanical and rheological properties that reduces the heat release rate and minimizes the dripping of molten polymer. The successful achievement of flame retardant (FR) nanocomposites requires a combination of nano filler and FR agent. However it might be possible to develop nanoparticles have an inherent flame retardant action through the release of effective flame inhibitors, or by absorbing heat with the release of H<sub>2</sub>O and CO<sub>2</sub>, or by preventing the access of oxygen to the burning material.

The University of Nottingham has devised a system for the manufacture of bespoke nanoparticles using continuous hydrothermal synthesis (CHS). CHS technique was used to manufacture bespoke nanomaterials including ATH, MDH, AlOOH, TiO<sub>2</sub> and hydroxyapatite. Hydroxyapatite (HA), is an interesting bio ceramic material since it has a phosphorous content of about 20 wt % which is much higher than most commercially available phosphorous based FR additives. All materials were formulated and surface modified using different organic ligands and polymeric surfactants, post reaction but prior to collection. The dispersion of the materials in epoxy resin was investigated, with and without organic modification, was investigated and quantified using SEM and EDAX analysis.

The impact of different proportions of these nanomaterials on the mechanical and flame retardant properties was then investigated. Image analysis techniques were developed to quantify the performance of the epoxy under flame conditions including aspects such as initial ignition, flame size and shape, flammable dripping and the ability to self-extinguish.

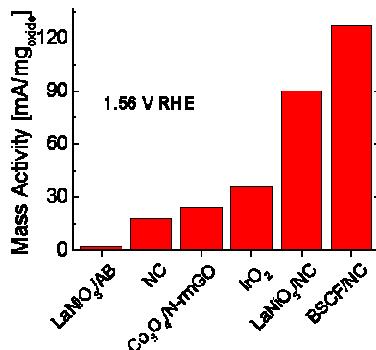
## 6-11: Bifunctional, Non-precious Metal Perovskite Electrocatalysts with High Mass Activities for Water Oxidation and Oxygen Reduction

William G. Hardin,<sup>a</sup> Daniel A. Slanac,<sup>b</sup> Tyler Mefford,<sup>c</sup> Xiqing Wang,<sup>d</sup> Sheng Dai,<sup>d</sup> Keith P. Johnston,<sup>b,a</sup> and Keith J. Stevenson<sup>c,a,\*</sup>

<sup>a</sup>Texas Materials Institute, <sup>b</sup>Department of Chemical Engineering, <sup>c</sup>Department of Chemistry and Biochemistry, The University of Texas at Austin,  
1 University Station, Austin, Texas, 78712

<sup>d</sup>Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Nanocrystal perovskite catalysts with high phase purity are of great interest as replacements for precious metals and oxides used in the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Perovskite electrocatalysts have been shown to have greater specific activities than precious metals and their oxides, but high mass activities have not yet been realized due to inadequate synthesis techniques which often result in unwanted phase impurities and micron-scale materials. Herein, we demonstrated precise control over the synthesis of essentially phase pure perovskite nanocrystals with mass activities exceeding that of  $\text{IrO}_2$  and possessing comparable or greater bifunctional character than leading precious metals. In this presentation we discuss the robust aqueous synthesis of  $\text{ABO}_3$  perovskites such as  $\text{LaNiO}_3$  and  $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3+\delta}$ . We present the resulting electrocatalytic activities of these materials, while also examining them in the current context of proposed perovskite activity descriptors. Catalytic activity is determined using electroanalytical techniques such as rotating disk electrochemistry and cyclic voltammetry in conjunction with materials characterization enabled by dynamic light scattering, electron microscopy, nitrogen sorption, X-ray photoelectron spectroscopy and X-ray diffraction. It is demonstrated that these highly active perovskite catalysts are an emerging replacement for the precious metals used not just for the OER and ORR, but also for the chlor-alkali and oxygen depolarized cathode industries as well.



[1] Hardin, W. G.; Slanac, D. A.; Wang, X.; Dai, S.; Johnston, K. P.; Stevenson , K. J. *JPCL*  
under review

\* Corresponding author: Keith J. Stevenson (stevenson@cm.utexas.edu) (T) +1-512- 232-9160;  
(F) +1-512-471-8696

## **7-1: Metal-Assisted Silicon and Germanium Nanowire Growth: Novel Methods for High-Throughput Production**

Benjamin Richards, Bernard Gaskey, Tobias Hanrath

Chemical Engineering, Cornell University, Ithaca, NY

Advances in the solvothermal synthesis of nanostructured materials have created exciting opportunities to create novel materials with properties by design. Semiconductor nanowires constitute one of the principal building blocks of emerging nanotechnologies. Silicon and germanium nanowires, in particular, have garnered immense interest from the fundamental and applied research communities due to their intriguing size-dependent properties and their broad potential in technologies including sensors, nanoelectronics, thermoelectric, and next-generation solar cells. Solvothermal synthesis of nanowires requires high temperatures to crystallize the nanowire; these conditions can be realized in supercritical fluids. Ordinary nanowire synthesis methods rely on the use of noble metal seed particles, most prominently gold; this is obviously not practical at commercial scales. To address this challenge, several groups have investigated alternate process that allows nanowires to be grown from bulk metal substrates. This introduces exciting opportunities for novel roll-to-roll and spool-to-spool fabrication methods. To better understand the fundamental growth mechanism, we investigated a select set of metals including copper, aluminium, and platinum with various geometries--wires, foils, and thin-films. This synthesis method facilitates scalable fabrication of nanowires and the direct integration into prototype test structures.

## 7-2: Tailoring the Growth and Morphology of Germanium Nanowires in Supercritical fluids

Subhajit Biswas<sup>1,2</sup>, Sven Barth<sup>3</sup>, Justin D. Holmes<sup>1,2\*</sup>

<sup>1</sup>Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland

<sup>2</sup>Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland

<sup>3</sup>Institute for Materials Chemistry, Vienna University of Technology, A-1060 Vienna, Austria

Germanium nanowires have been successfully synthesized from a variety of supercritical fluid (SCF) methods, including supercritical fluid-liquid-solid (SFLS) [1] and supercritical fluid-solid-solid (SFSS) [2, 3] approaches. The use of bi-metallic alloy seeds for growing one-dimensional nanostructures has recently gained momentum amongst researchers. The compositional flexibility of alloys provides the opportunity to manipulate the chemical environment, reaction kinetics and thermodynamic behavior of nanowire growth, in both the eutectic and sub-eutectic regimes. This presentation highlights the role of  $\text{Au}_x\text{Ag}_{1-x}$  alloy nanoparticles in defining the growth characteristics and crystal quality of solid-seeded Ge nanowires, via SCF growth processes [4]. The enhanced diffusivity of Ge in the alloy seeds, compared to pure Ag seeds, and slow interparticle diffusion of the alloy nanoparticles, allows realization of high-aspect ratio nanowires with diameters below 10 nm, via a seeded bottom-up approach (fig 1a). Solid seeded techniques, using Ag and Ag rich alloy seeds also facilitated growth of diameter-controlled nanowires in the sub-10 nm growth regime (fig. 1(b)). Furthermore, the alloyed solid seeds enabled control over the crystallinity of the Ge nanowires produced, through an epitaxial defect transfer process from the seeds to the nanowires [4].

- [1] J. D. Holmes, K. P. Johnston, C. Doty and B. A. Korgel, *Science*, **287**, 1471 (2000).
- [2] S. Barth, M. Kolešnik, K. Donegan, V. Krstić, J. D. Holmes, *Chem. Mater.* **23**, 3335 (2011).
- [3] S. Barth, S., J. Boland, J. D. Holmes, *Nano Lett.* **11**, 1550 (2011).
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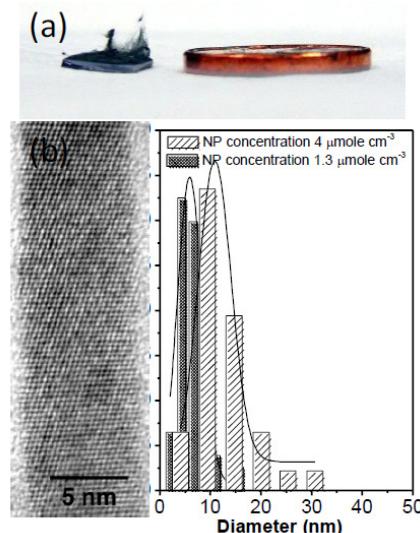


Fig. 1. (a) Realization of millimeter long nanowires with Au-rich alloy seed. (b) TEM image of a sub-10 nm nanowire and diameter distribution of these nanowires grown with

## 7-3: Colloidal Synthesis of Silicon Nanowires and Nanorods

Andrew Heitsch,<sup>1,2\*</sup> and Brian Korgel<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712-1062, United States

<sup>2</sup>Current affiliation with Dow Core R&D-Inorganic Materials and Heterogenous Catalysis, The Dow Chemical Company, Midland, Michigan 48674, United States

Over the past decade, many advancements have been made in the design and development of solution chemistry to synthesize crystalline one-dimensional (1D) silicon (Si) nanomaterials. The first demonstration relied on solvothermal reaction conditions in supercritical organic solvents to grow Si nanowires using monophenyl- or diphenylsilane (MPS or DPS) as a reactant and Au nanocrystal seeds[1]. This approach was optimized and yielded reasonable quantities of material at laboratory-scale production rates of ~50 mg/hr; however it was observed that MPS decomposition led to the undesirable deposition of a polyphenylsilane shell on the nanowire surface[2]. This shell influences the nanowire properties and prevents access to the Si surface, as needed for surface contacting or doping, important in applications like transistors, solar cells, sensors, and batteries, etc.

This talk will focus on recent advancements of solution methods to produce 1D Si materials, including silicon nanowires and nanorods, using similar supercritical-fluid-liquid-solid (SFLS) or solution-liquid-solid (SLS) growth techniques with trisilane as a reactant (Figure 1)[3, 4, 5]. The importance of precursor selection, precursor decomposition pathways, seed choice, ligand chemistry, reaction conditions, and reactor design on the 1D Si nanomaterials' growth rate, morphology, yield, and crystalline quality will be discussed. Additionally, a method to quickly cool the reaction allowing for post processing removal of Au seeds from the 1D Si nanomaterials will be presented[6]. Time permitting, *in situ* surface passivation of clean silicon nanowire surfaces via amination and potential high concentration doping routes may also be discussed.

- [1] J. Holmes, K. Johnston, C. Doty, and B. Korgel, *Science* **287**, 1471 (2000).
- [2] H. Tuan and B. Korgel, *Chemistry of Materials* **20**, 1239 (2008).
- [3] A. Heitsch, C. Hessel, V. Akhavan, and B. Korgel, *Nanoletters* **9**, 3042 (2009)
- [4] A. Heitsch, H. Tuan, D. Fanfair, and B. Korgel, *J. of Am. Chem. Soc.* **130**, 5436 (2008).
- [5] A. Heitsch, V. Akhavan, and B. Korgel, *Chemistry of Materials* **23**, 2697 (2010).
- [6] C. Hessel, A. Heitsch, and B. Korgel, *Nanoletters* **10**, 176, (2010)

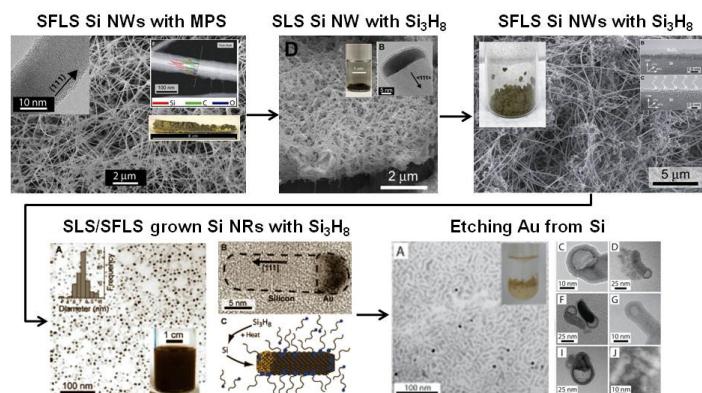


Fig. 1. SFLS and SLS grown of one dimensional silicon.

## 7-4: Monophenyl Silane Catalyzed Growth of Germanium Nanowires with Gold and Nickel Seeds

Xiaotang Lu<sup>1</sup>, Justin T. Harris<sup>1</sup>, Julián E. Villarreal<sup>1</sup>, Brian A. Korgel<sup>1\*</sup>

<sup>1</sup>Department of Chemical Engineering, Texas Materials Institute, Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712, USA

Germanium nanowires can be synthesized by thermal decomposition of diphenyl germane (DPG) in supercritical solvent with either Au or Ni seeds. In this reaction, DPG undergoes a phenyl redistribution reaction before pyrolyzing into germanium. Au-seeded growth occurs by a supercritical fluid-liquid-solid (SFLS) mechanism, while Ni-seeded growth by a supercritical fluid-solid-solid (SFSS) mechanism. In a typical supercritical reaction, Au nanocrystals work better than Ni nanocrystals in seeding the nanowire growth and yield the Ge nanowires of much higher quality. In our study, we found that it is the rate of the phenyl redistribution of DPG that significantly influence the nanowire growth. Slower reaction kinetics yield poorer nanowires. It turns out that Au can catalyze DPG decomposition, whereas Ni does not.

We also found that addition of monophenyl silane (MPS) dramatically improves the nanowire yield and quality. MPS creates a phenyl sink in the redistribution reaction and speeds up DPG decomposition. The elevated kinetics promoted by MPS leads to a much higher yield and higher quality Ge nanowires. The conversion from DPG to Ge was nearly 100% when MPS was added, using either Au or Ni seeds, which is well beyond the theoretical yield of 50% without it.

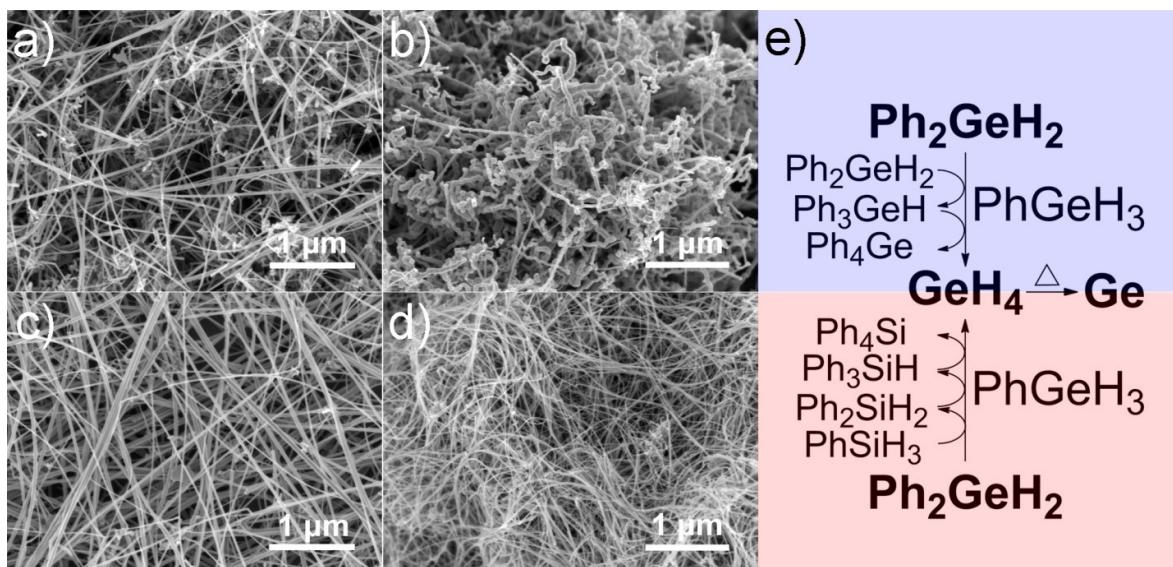


Fig. 1. SEM images of Ge nanowires formed by (a) Au nanocrystal seeds; (b) Ni nanocrystal seeds; (c) Au nanocrystal seeds with addition of MPS; (d) Ni nanocrystal seeds with addition of MPS. (e) Mechanism of phenyl redistribution reactions with/without MPS.

## 7-5: Self-Seeded Growth of Germanium Nanowires in Supercritical Fluids

Olan Lotty<sup>1\*</sup>, Richard Hobbs<sup>1</sup>, Johann Hlina<sup>2</sup>, Christoph Marschner<sup>2</sup>, Colm O'Dwyer<sup>1</sup>, Nikolay Petkov<sup>1</sup> and Justin D. Holmes<sup>1\*</sup>

<sup>1</sup>Department of Chemistry and the Tyndall National Institute, University College Cork, Cork, Ireland

<sup>2</sup>Institut für Anorganische Chemie der Technischen Universität Graz, Stremayrgasse 16, A-8010 Graz, Austria.

Germanium (Ge) nanowires have been successfully synthesized from a variety of supercritical fluid (SCF) approaches, including supercritical fluid-liquid-solid [1] and supercritical fluid-solid-solid [2] growth mechanisms. The self-seeded, SCF growth of Ge nanowires in the absence of conventional metal seed catalysts will be discussed in this presentation [3]. This approach differs from the conventional seeding of nanowires by a (noble) metal catalyst, but still relies on the decomposition of a synthetic metalorganic precursor to allow growth to proceed. While excellent levels of control and scalability have been demonstrated using metal seeds, the catalysts can often act as contaminants in the nanowires. For example, solid seeding of Ge nanowires in SCFs using Ni catalyst seeds results in inadvertent doping of the Ge nanowires by Ni atoms [4]. To overcome this contamination problem, we have grown Ge nanowires in the absence of conventional metal seeds, using various mixtures of Ge and Si containing precursor compounds, in a SCF environment. Analysis of the diameter distributions of the nanowires grown in each of these experiments revealed several trends in growth behavior, which can be directly linked to the precursor used and the temperature employed. Analysis of the diameter distributions of the Ge nanowires formed, in addition to extensive morphological characterization by electron microscopy, leads to some inference of the mechanism of nanowire growth in SCFs (fig. 1). This presentation also highlights the possibility of achieving Ge nanowire diameter control in SCFs through the engineering of various Ge precursor molecules.

- [1] J. D. Holmes, K. P. Johnston, C. Doty and B. A. Korgel, *Science*, **287**, 1471 (2000).
- [2] S. Barth, S., J. Boland, J. D. Holmes, *Nano Lett.* **11**, 1550 (2011).
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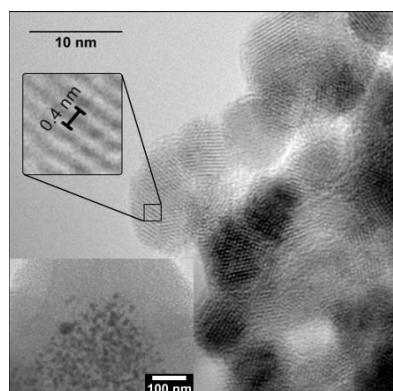


Fig. 1. TEM micrograph of aggregated Ge nanoparticles observed at the surface of Si rich microparticles. Inset bottom left, a lower magnification TEM image of similar nanoparticles showing the surrounding Si based matrix, scale bar 100 nm.

## **7-6: The structure and properties of W<sub>18</sub>O<sub>49</sub> ultrathin nanowire bundles**

Guangsheng Pang<sup>\*</sup>, Dong Wang, Jing Li, Xuan Cao, and Shouhua Feng  
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry,  
Jilin University, Changchun 130012, P. R. China.

The non-stoichiometry tungsten oxides have offered many interesting physical and chemical properties, which can be used in gas sensing, field emitting, and electrochemical nanodevices. Among them, W<sub>18</sub>O<sub>49</sub> have attracted more interest due to its unique structure and the oxygen defects within its structures. We prepared ultra-thin W<sub>18</sub>O<sub>49</sub> nanowire bundles by using a solvothermal method without any template. The morphologies and microstructures of W<sub>18</sub>O<sub>49</sub> nanowire bundles have been characterized by using X-ray diffraction, scanning electron microscope, transmission electron microscope, and FTIR spectrum. The selected area electron diffraction analysis of the W<sub>18</sub>O<sub>49</sub> nanowire bundles demonstrates that the nanowires are highly ordered and regular hexagonal mesocrystals are observed. The building blocks of the mesocrystals are ultra-thin W<sub>18</sub>O<sub>49</sub> nanowires with diameter of 2-3 nm. The oriented attachment of nanowires has generated the regular hexagonal mesocrystals. Electrochemical behavior of the mesocrystals has been evaluated by cyclic voltammogram. The mesocrystals have fast electron-proton transfer rate and the large pseudocapacitance because of their high surface to volume ratio and small grain size of the highly ordered ultra-thin nanowires. The tungsten oxide mesocrystals with more oxygen vacancies exhibit high sensitivity and selectivity at low temperature to NO<sub>2</sub> of low gas concentration. The room temperature photoluminescence and EPR spectra demonstrate that there are more oxygen active sites in the structure of mesocrystals comparing with single nanowires.

## 7-7: Visible Light Driven Photoelectrochemical Water Oxidation on Nitrogen-Modified TiO<sub>2</sub> Nanowires

Son Hoang,<sup>1</sup> Sean P. Berglund,<sup>1</sup> Siwei Guo,<sup>1</sup> Nathan T. Hahn,<sup>1</sup> Allen J. Bard,<sup>2</sup> and C. Buddie Mullins <sup>\*1,2</sup>

<sup>1</sup>Department of Chemical Engineering, <sup>2</sup>Department of Chemistry and Biochemistry, Center for Electrochemistry, Texas Materials Institute, Center for Nano and Molecular Science, University of Texas at Austin, 1 University Station C0400 Austin, Texas 78712-0231, United States

Sunlight energy can be captured and stored in the form of a renewable and clean fuel H<sub>2</sub> via photoelectrochemical (PEC) water splitting using semiconductor materials [1, 2]. Titanium dioxide (TiO<sub>2</sub>) is well-known as a candidate semiconductor for PEC water splitting as it is abundant, stable in aqueous solution under irradiation, and has strong photocatalytic activity. However, TiO<sub>2</sub> has a large band gap (3.0 eV for rutile and 3.2 eV for anatase), thus setting its theoretical maximum solar energy (AM 1.5 G conditions) conversion efficiency at 2.2 %. Numerous efforts have focused on improving the solar energy conversion efficiency of TiO<sub>2</sub> materials via either (1) reducing the band gap of TiO<sub>2</sub> to absorb visible light or (2) fabricating nanostructures of TiO<sub>2</sub> to improve charge transport properties [1-4].

We report here a solvothermal synthesis of TiO<sub>2</sub> nanowire arrays with small feature sizes of 5 nm and lengths up to 4.4 μm on fluorine-doped tin oxide (FTO) substrates. A substantial amount of nitrogen can be incorporated into the TiO<sub>2</sub> lattice via annealing the TiO<sub>2</sub> nanowires in NH<sub>3</sub> to shift the active spectrum of the nanowires to 520 nm (~2.4 eV). In addition, we demonstrated that co-treatment of the TiO<sub>2</sub> nanowires with NH<sub>3</sub> and H<sub>2</sub> can shift the active spectrum to the longer wavelength of 570 nm due to the interactions of bulk Ti<sup>3+</sup> and N dopant. We also report a simple solvothermal synthesis of Ta-incorporated TiO<sub>2</sub> nanowire arrays with Ta concentrations ranging from 0.11 up to 3.47 atomic %. Co-incorporation of N and Ta into TiO<sub>2</sub> nanowires via annealing Ta-incorporated TiO<sub>2</sub> nanowires in NH<sub>3</sub> showed better PEC performance than monoincorporation of N or Ta. We believe that the enhancement shown by the N, Ta-coincorporated TiO<sub>2</sub> sample is due to less recombination centers from charge compensation effects and suppression of the formation of an amorphous layer on the nanowires during the nitridation process.

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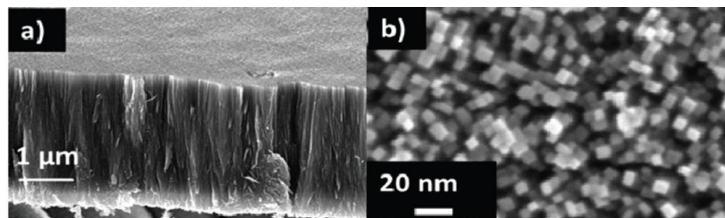


Figure 1. Vertically aligned single crystalline TiO<sub>2</sub> rutile nanowire arrays on FTO glass: (a) cross-sectional and (b) top view SEM images

## 8-1: High Quality, Low Cost Ammonothermal Bulk GaN Substrates

Dirk Ehrentraut,\* Rajeev T. Pakalapati, Derrick S. Kamber, Wenkan Jiang, Bradley C. Downey, Melvin McLaurin and Mark P. D'Evelyn

Soraa, Inc., Goleta, California 93117, USA

\*E-mail: dehrentraut@soraa.com

The vast majority of semiconductor device technologies are based on native substrates, and gallium nitride (GaN) is no exception with true bulk GaN generally regarded as the ideal substrate for GaN-based devices, including LEDs, lasers, and electronics. However, although HVPE GaN substrates have been available commercially for about a decade, bulk-GaN-based devices have largely remained in the realm of research, with the exception of laser diodes. Obstacles to commercial bulk-GaN-based devices include high cost, limited diameter, and complex microstructure [1].

Soraa has developed a novel ammonothermal approach for growth of high quality, true bulk GaN crystals at a greatly reduced cost. Soraa's patented approach, known as SCoRA (Scalable Compact Rapid Ammonothermal) utilizes internal heating to circumvent the material-property limitations of conventional ammonothermal reactors. The SCoRA reactor has capability for temperatures and pressures as high as 750 °C and 600 MPa, respectively, enabling higher growth rates than conventional ammonothermal techniques, but is less expensive and more scalable than conventional autoclaves fabricated from nickel-based superalloys.

SCoRA GaN growth has been performed on *c*-plane, *m*-plane, and semipolar seed crystals with diameters up to two inch to thicknesses of 0.5-3 mm. The highest growth rate observed to date is 50  $\mu\text{m h}^{-1}$ , and we routinely observe rates in the 10-30  $\mu\text{m h}^{-1}$  range for all orientations. These values are 5-100 times larger than those achieved by conventional ammonothermal GaN growth and are easily sufficient for a very cost-effective manufacturing process. The crystals have been characterized by x-ray diffraction rocking-curve (XRC) analysis, optical and scanning electron microscopy, cathodoluminescence (CL), electron channeling contrast imaging (ECCI), electron beam-induced current (EBIC), optical spectroscopy, and capacitance-voltage measurements. The XRC scans are single-peaked, indicating that the GaN grown via the SCoRA process possess very high structural quality and are composed predominantly of a single grain. The FWHM values of the grown crystals are similar to or, in some cases, narrower than those of the seed crystals, about 60-100 arcsec. Dislocation densities are typically in the range of  $1 \times 10^5 - 5 \times 10^6 \text{ cm}^{-2}$  in vertically-grown SCoRA GaN. Crystals are typically n-type and transparent but yellowish, due to unintentional impurities. Epitaxial quantum well structures have been successfully grown on SCoRA wafers.

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Fig. 1. Image of a SCoRA-grown two inch large bulk GaN crystal.

## **8-2: Densification Behavior and Interfaces of Tantalum Carbide Nanopowders Prepared by a Solvothermal Process and Consolidated by Spark Plasma Sintering**

Olivia A. Graeve<sup>1\*</sup> and James P. Kelly<sup>1</sup>

<sup>1</sup>Alfred University, Kazuo Inamori School of Engineering, 2 Pine St., Alfred, NY 14802

We present a fundamental study of the sintering behavior of tantalum carbide powders produced by a solvothermal synthesis method and characterized using dynamic light scattering, X-ray diffraction, and microscopy. The sintering of tantalum carbide is a challenge due to its covalent bonding and high vapor pressure. Grain growth is often cited as a primary obstacle to obtaining fully dense tantalum carbide. It is typically favorable to use a smaller particle size to improve densification, but smaller tantalum carbide particle sizes result in higher oxygen contents that can facilitate grain growth.

The goal of this research was to investigate the grain growth of reactive sintered tantalum carbide nanopowders produced by a hybrid solvothermal/combustion synthesis technique [1-3]. Details of ignition, process control, post-synthesis, and sintering will be discussed. We will show that grain growth can be directly correlated to strain introduced into the tantalum carbide lattice. Strain can be introduced by loss of carbon from the tantalum carbide crystal structure or by forming solid solutions with other compounds. The additions of WC, HfC, and ZrC can introduce tensile or compressive strains on the tantalum carbide lattice, having a marked effect on the grain growth during sintering. We estimate that the lattice can be strained approximately 2-3%.

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### 8-3: Ultrasonic-assisted hydrothermal method for the piezoelectric materials

Takeshi MORITA<sup>1\*</sup>, Gaku ISOBE<sup>1</sup>, Kanako OHTA<sup>1</sup>, Ryo KUDOH<sup>1</sup>, Takafumi MAEDA<sup>1</sup>, Peter BORNMANN<sup>2</sup> and Tobias HEMSEL<sup>2</sup>

<sup>1</sup>Graduate School of Frontier Sciences, The University of Tokyo,  
5-1-5 Kashiwanoha, Kashiwa, 277-8563 Japan

<sup>2</sup>Mechatronics and Dynamics, The University of Paderborn,  
47-49 Pohlweg, Paderborn, Nordrhein-Westfalen, 33098 Germany

In order to accelerate the hydrothermal reactions, we developed an ultrasonic-assisted hydrothermal method using a special container<sup>[1]</sup> as shown in Fig. 1. From the ultrasonic transducer, high-power ultrasound can be irradiated into the hydrothermal solutions directly. The transducer was excited in first longitudinal mode whose resonant frequency was around 30 kHz. In this study, we applied the ultrasonic-assist hydrothermal method to synthesize KNbO<sub>3</sub> and NaNbO<sub>3</sub> powders as the source materials for (K, Na)NbO<sub>3</sub> ceramics. This ceramics is a promising lead-free piezoelectric material. In the conventional solid solution, it is difficult to synthesize pure KNbO<sub>3</sub> powders due to unstable K<sub>2</sub>CO<sub>3</sub> property as a potassium source. On the other hand, the hydrothermal method enables high quality KNbO<sub>3</sub> powders without any secondary phase<sup>[2]</sup>. The KNbO<sub>3</sub> and the NaNbO<sub>3</sub> powders were synthesized for 12 hours and 6 hours by the ultrasonic assisted hydrothermal method. Synthesized particle size was reduced and the particle size distribution became uniform owing to the ultrasonic irradiation. It is thought that the nucleation process of the hydrothermal synthesis was accelerated. Using these powders, (K, Na)NbO<sub>3</sub> ceramics was sintered. Compared to the ceramics from the powders without the ultrasonic assist, the grain size of the ceramics became smaller as shown in Fig. 2. The piezoelectric performances were almost equal; however, the dielectric loss, tanδ was reduced to 1.04% from 4.00% and mechanical quality factor was improved to 138 from 72.

When we utilized the ultrasonic assisted hydrothermal method for piezoelectric thin films, thicker film was obtained. In case of PZT polycrystalline films, thicker and dens film is required for the actuator applications. Usually, the thickness of PZT is saturated at around 2 μm with 24 hours reaction. By applying the ultrasonic irradiation, the thickness was increased to 10μm. At the same time, the particle size containing the film was reduced and the film flatness became smooth.

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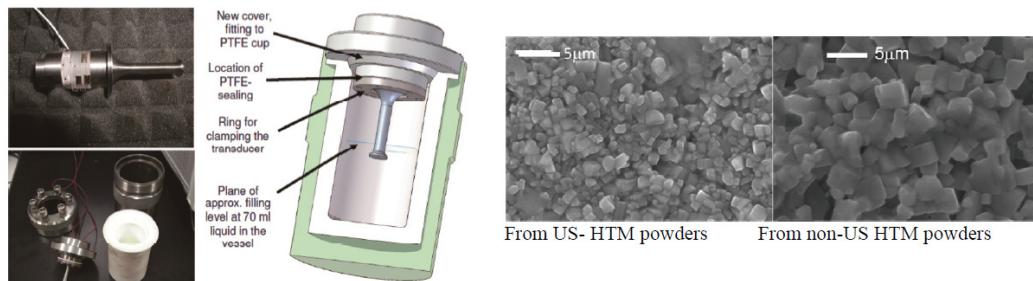


Fig. 1 US-assisted hydrothermal container

Fig. 2Ultrasonic effect for (K,Na)NbO<sub>3</sub> ceramics

## **8-4: Hydrothermal growth of perovskites: a strategy for processing advanced ferroic structures**

Paula Maria Vilarinho

Department of Materials & Ceramic Engineering, Centre for Research in Ceramics and Composite Materials, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal  
paula.vilarinho@ua.pt; <http://electroceramicsgroup.web.ua.pt>

It is a fact that the number of devices using a microchip is expanding. Indeed low cost electronic devices that can connect wirelessly to the internet are proliferating. By 2013 1 trillion of objects will be communicating. Additionally these devices do not require more power instead they require higher levels of functionality. As reported [1] one of the progress lines of microelectronics, known as More than Moore, incorporates new devices, new materials and new techniques. Besides the micro and nano-systems (MEMs and NEMs) already in development, sensors and actuators should permit a wide and varied interaction with different media and non electronic properties (pressure, temperature, optical, chemical, biochemical, among others). Functional materials, in particular ferroics and multiferroics may be potential important candidates for some of these applications.

This talk is about the low temperature processing of functional perovskite oxides by hydrothermal synthesis and its exploitation for processing advanced ferroic structures. The talk covers a few concepts that should be of interest to the solvothermal and hydrothermal community, as well as to the microelectronics one.

The talk revises the fundamental aspects of hydrothermal synthesis of perovskites. Emphasis will be given to the synthesis of some ferroic oxides ( $\text{BaTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ) and nanoscale structures. The feasibility and importance of the hydrothermal process towards the low temperature synthesis of ferroic nanostructures will be discussed via a set of case studies.

Using 1D shaped precursors (titanate layered and carbon nanotubes (CNTs)) aspects of the kinetics of the crystallization of  $\text{BaTiO}_3$  will be presented and discussed. Using titanate layered nanotubes the anisotropic growth of  $\text{BaTiO}_3$  crystals can be controlled by manipulating synthesis parameters (as temperature / time), and additives used [2, 3]. A kinetic study revealed that at the early stages of crystallization pseudocubic  $\text{BaTiO}_3$  nucleates on the surfaces of the tubes. Growth subsequently proceeds by a phase-boundary mechanism. As the reaction proceeds beyond 70% completion, the nanotubes fully dissolve, and nucleation and growth of tetragonal rather than pseudocubic  $\text{BaTiO}_3$  takes place [4]. Aiming at preparing CNTs/ $\text{BaTiO}_3$  composites, CNTs were coated with Ti and by an hydrothermal reaction with barium precursors, crystalline  $\text{BaTiO}_3$  coated CNTs were prepared at temperatures lower than 200°C. The stability of CNTs under the hydrothermal conditions is discussed.

The fabrication of ferroelectric thin films on flexible metal foils or polymeric substrates is of particular interest for embedded circuitry and towards the expansion of flexible electronics. The growth of  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  thin films via a polymer- compatible hydrothermal process on commercial flexible Kapton films will be described. Electrical characterization showed high capacitance densities and acceptable dielectric loss for the films after post-annealing in oxygen. Existence of polar domains in the hydrothermally synthesized  $\text{BaTiO}_3$  thin films was proved by piezo- response force microscopy (PFM) [5]. These results are a good demonstration of the applicability of this route to the synthesis of ferroic nanostructures on polymeric flexible substrates opening avenues for possible new generations of electronic packaging.

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## 8-5: Hydrothermal Growth of Calcite Crystals by Slow Cooling Method

Kazumichi Yanagisawa<sup>1\*</sup>, Tomomi Gotouda<sup>1</sup>, Ayumu Onda<sup>1</sup>,  
Arito Sakaguchi<sup>2</sup>, Hide Sakaguchi<sup>2</sup>

<sup>1</sup>Research Laboratory of Hydrothermal Chemistry, Kochi University, Kochi 780-8520 Japan

<sup>2</sup>Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, Yokohama 236-0001, Japan.

Calcite crystals record plastic strain as stress-dependent intracrystalline deformation by mechanical twinning. Sakaguchi et al. [1] found that the statistically averaged calcite twin density can be regarded as a good stress indicator in real sandstones, and suggested that if a population of calcite grains with well characterized twin densities is included in a concrete structure, safety evaluations of the building may be possible after stress - related damage [2]. For this purpose, concrete structures should be prepared by the addition of calcite crystals without twins. The size of calcite crystals must be large enough for twin observation, but not too large to decrease the mechanical strength of the concrete structures. Thus, we have to develop a technique to prepare a large amount of submillimeter calcite crystals without twins for the application of calcite crystals to a stress indicator.

Hydrothermal method is one of the most promising techniques to obtain calcite crystals, because natural calcite crystals are believed to grow under hydrothermal conditions. Furthermore, the hydrothermal method has the advantage of suppressing the dissociation of CO<sub>2</sub> and yielding high quality crystals without thermal strain. Hydrothermal growth of calcite single crystals was carried out in many kinds of mineralizers such as NaCl, LiCl, CaCl<sub>2</sub>, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and CH<sub>3</sub>COOH, but all researches focused on growing large single crystals. In order to prepare a large amount of small single crystals of calcite, we used the slow cooling method. In this technique, the nutrient of calcite is completely dissolved in a solution at high temperatures, and then the crystal nuclei formed by spontaneous nucleation grow larger by slow cooling of the solution from high temperatures.

Autoclaves made of stainless steel equipped with a Teflon beaker (inner volume of 90 mL) were used for the experiments. The nutrient was a commercially available reagent of CaCO<sub>3</sub>, and the mineralizer used was 45 mL of 5M NH<sub>4</sub>NO<sub>3</sub> solution. The autoclaves were heated in an air oven and were rotated in the oven for agitation. The obtained crystals were sieved by size, >1000 µm, 1000-710 µm, 710-500 µm, 500-350 µm, 350-250 µm, 250-150 µm, and <150 µm. The weight of the crystals with each size was measured and the median value was determined.

In the typical experiment, 0.675g of CaCO<sub>3</sub> powder (15g/L) was added to the mineralizer after adjusting the pH value to 7.5. The autoclaves were heated to 200 °C for 2 hours and then cooled down to room temperature with a cooling rate of 2.5 °C/min. The rotation speed of the autoclaves was 18 rpm. After the hydrothermal growth run, calcite crystals of about 0.5g were harvested at the bottom of the Teflon beaker, but not on the wall of the beaker. The crystals were rounded as shown in Fig. 1 and the median value was 325 µm.

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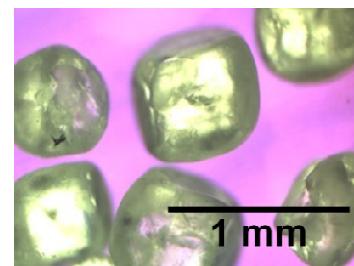


Fig. 1 Calcite crystals in the range of 500-710 µm.

## 8-6: Hydrothermal Production and Surface Characterization of Novel Alpha Alumina – based Nanomaterials

Wojciech L. Suchanek<sup>1\*</sup>

<sup>1</sup>Sawyer Technical Materials, LLC, 35400 Lakeland Boulevard, Eastlake, OH 44095, USA

Hydrothermal synthesis allows crystallization of anhydrous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> directly in aqueous environment at  $\sim$ 400°C under moderate pressures and therefore is a low-temperature alternative to high-temperature methods that require at least 1000°C to form  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [1]. The hydrothermal method enables  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particle control in very wide range of sizes ( $10^{-2}$  –  $10^2$   $\mu\text{m}$ ) and morphologies (equiaxed, elongated, platelets, etc.). Morphology of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles can have tremendous impact on microstructure, mechanical performance, and catalytic selectivity. In addition, dopants can easily be introduced to modify acid/base properties, surface energy, electric charge, thermal stability, and sinterability of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

Novel  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets, nano-needles, whiskers, platelets, and equiaxed powders with controlled chemical compositions were synthesized at 380–450°C under  $\sim$ 10 MPa pressure by the hydrothermal treatment of aluminum hydroxides in the presence of soluble salts of metal dopants,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> seeds, and morphology modifiers. Metal dopants from nearly every group of the Periodic Table were used. The hydrothermal synthesis was performed on industrial scale in large production autoclaves. The materials were characterized by XRD, SEM, HRTEM, XPS, TPD, BET, chemical analysis, etc. Selected powders were extruded and subsequently sintered to obtain porous ceramic bodies with controlled microstructures.

Although a variety of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles were synthesized, emphasis is given to the nano-sheets, which exhibited unique properties. The as-synthesized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets were typically phase-pure  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals with (001) faceting, thicknesses of 10–50 nm, aspect ratios up to a few hundred (Fig. 1a), and specific surface areas in excess of 40  $\text{m}^2/\text{g}$  [2]. Metal dopants from nearly every group of the Periodic Table were present in these  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets in concentrations up to  $\sim$ 0.5 atom % either as solid solutions (Fig. 1b) or as nanosized inclusions (Fig. 1c) [3]. Thorough surface analysis revealed a very wide range of control of the surface charge, surface purity, and acid-base properties of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets by selection of different dopants and controlling their distribution within the nanosheets. The BET surface area of the hydrothermally-synthesized nanosheets was stable up to 1200°C [2,3]. Large volumes of various types of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders were synthesized in commercial batch autoclaves with very high reproducibility.

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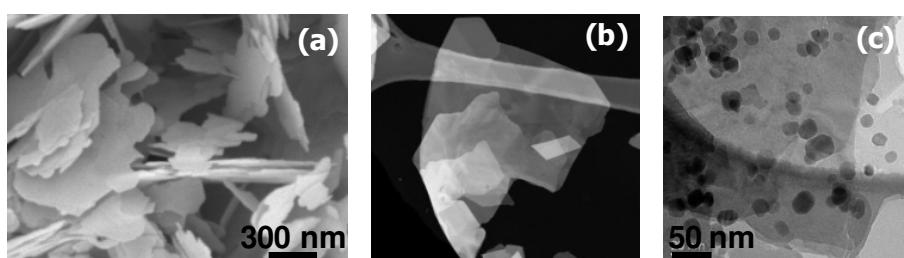


Fig. 1. (a) SEM image revealing morphology of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets [2], (b) STEM image of a typical doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheet showing uniform dopant concentration [3], (c) HRTEM image of Zr-doped  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanosheets [3].

## 9-1: Supercritical Hydrothermal Synthesis of Organic Modified Nanoparticles for the Fabrication of Hybrid Polymers

Tadafumi Adschiri

WPI-AIMR, Tohoku University, 2-1-1 Katahira, Aoba-ku Sendai 980-8577, Japan

Variety of composite materials has been developed so far, but in many cases trade-off of the functions are of important issues: fabrication becomes difficult due to the significant increase of viscosity, and transparency of the polymer is sacrificed. To overcome the trade off, control of the nano-interface is the key. Organic functionalization of inorganic nanoparticles is required to have higher affinity between NPs and polymers. For fabricating multi-functional materials, we proposed a new method to synthesize organic modified nanoparticles (NPs) in supercritical water. Since the organic molecules and metal salt aqueous solutions are miscible under the supercritical state, and water molecule works as an acid/base catalyst for the reactions, organic-inorganic conjugate nanoparticles can be synthesized in one-pot under the condition. The hybrid NPs show high affinity with the organic solvent or the polymer matrix, which leads to fabricate the organic inorganic hybrid nanomaterials with the compatible (trade-off) functions.

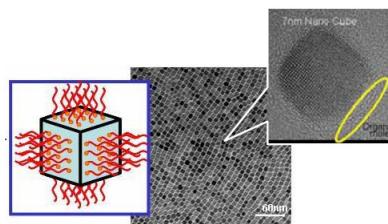


Fig. 1. Organic-inorganic hybrid nanoparticles

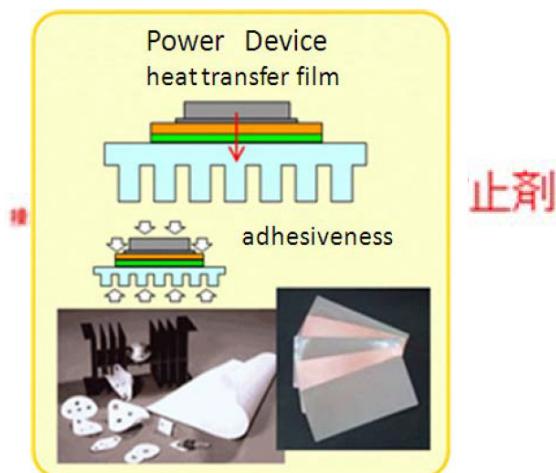


Fig. 2. Flexible heat transfer sheet:  
package Thermal conductivity: 40W/m/K

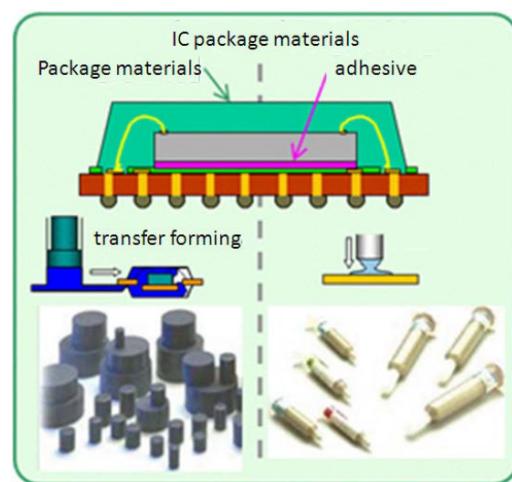


Fig. 3. High heat transfer viscosity  
materials

## 9-2: Hydrothermal Synthesis of Layered $\alpha$ -Zirconium Phosphate Disks: Control of Aspect Ratio and Polydispersity for Nano-architecture

Zhengdong Cheng<sup>1,2,3,4\*</sup>, Min Shuai<sup>1</sup>, Andres Mejia<sup>1</sup> and Ya-wen Chang<sup>1</sup>

<sup>1</sup> McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843, Fax: +1 979 8456446; Tel: +1 979 8453413; E-mail: zcheng@tamu.edu

<sup>2</sup> Materials Science and Engineering Program, Texas A&M University, College Station, Texas, 77843, USA.

<sup>3</sup> The Professional Program in Biotechnology (PPiB), Texas A&M University, College Station, Texas, 77843, USA.

<sup>4</sup> Soft Matter Research Center, School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, China

The crystals of layered compounds are normally of the shape of disks or plates. Systematic experiments revealed that regular-shaped  $\alpha$ -zirconium phosphate crystalline disks with a size-to-thickness ratio from 1 to 50 and size polydispersity as low as 0.2 can be obtained through hydrothermal treatment in 3 M to 15 M phosphoric acid solutions. TEM and SEM revealed that the growth of the disks is mediated by oriented attachment [1], which happened continuously throughout the hydrothermal treatment between various sized disks. Ostwald ripening is effective in improving the regularity and uniformity of the shape of the disks, especially under prolonged hydrothermal treatment.

Disk-like nanoparticles are widely used as building blocks for nanostructures in colloidal self-assembly approach. They have found various applications in polymer nanocomposites, biomimetic materials, functional membranes, Pickering emulsions, and discotic liquid crystal studies. The shape, size, and size polydispersity of these nanoparticles are key factors in their applications.

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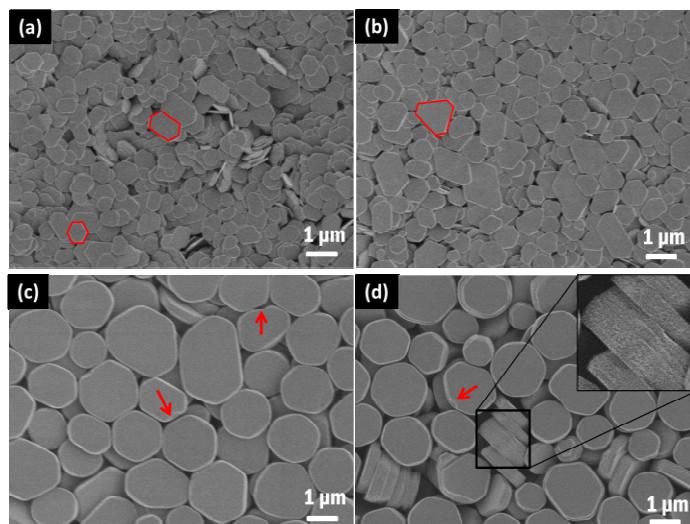


Fig. 1. SEM images of  $\alpha$ -ZrP disks synthesized in different phosphoric acid concentrations: (a) 3M, (b) 6M, (c) 12M, and (d) 15M. The hydrothermal treatment time for all these samples was 24 h. The red lines outline some of the disks with variation on shapes. The red arrows indicate the imperfections in the shapes.

## **9-3: SHYMAN – Sustainable Hydrothermal Manufacturing of Nanomaterials**

Ed Lester

Process and Environmental Research Division, Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK  
*Email: edward.lester@nottingham.ac.uk*

SHYMAN is a €10 million EU funded project with 17 partners focused on the scale up and development of hydrothermal synthesis. Some partners are interested in the scale up of the reactor and process design. Other partners are working on the sustainability of the process as a whole and the life cycle analysis of the nanomaterials that are produced. The final aspect of the project is the use of the nanomaterials in products. There are 8 case studies using the nanomaterials in areas as diverse as artificial bone to photovoltaics.

The full scale plant itself will be capable of production of over 100tn/annum of formulated nanomaterials including metals, metal oxides, sulphides, hydroxides, phosphates and carbonates.

The development of the nozzle reactor which is at the core of the project came out of pseudo-fluid and CFD modelling work that has been underway at Nottingham over the last 10 years. This system uses a counter-current pipe in pipe reactor that flows cold metal salt upwards into a downflow (through an inner pipe) of superheated fluid.

The author is coordinating this project and the paper will detail this project and how this work was carried out with reference to mixing phenomena and modeling (along with detailed analysis of other designs that were considered) and how the impact of the significance of momentum and buoyancy changes (through Grashof and Reynolds numbers) with each design as flow rates and geometries change.



## 9-4: Hydrothermal Synthesis of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> Spinel in a Continuous Flow Reactor

Karl Thomas Fehr<sup>1\*</sup>, Andreas Laumann<sup>2</sup>, Martin Bremholm<sup>3</sup>, Peter Hald<sup>4</sup> and Bo Brummerstedt Iversen<sup>4</sup>

<sup>1</sup> Department of Earth and Environmental Sciences, Section Mineralogy,  
Ludwig-Maximilians

Universität München, Theresienstr. 41, 80333 Munich, Germany

<sup>2</sup> Battery Material, Clariant Produkte, Ostenrieder Str. 41, 85368 Moosburg, Germany

<sup>3</sup> Department of Chemistry, Princeton University, Princeton, NJ 08544 (USA)

<sup>4</sup> Centre for Materials Crystallography, Department of Chemistry and iNANO, Aarhus  
University

Langelandsgade 140, DK-8000 Aarhus C (Denmark)

Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel is a new anode material in Li-rechargeable batteries and it is one of the most promising alternative materials to replace graphite as the anode. The safety, the excellent lithium ion mobility, the long cycle life, and the low volume change which Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> undergoes during the charge and discharge process are the main advantages of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> in comparison with graphite, especially for large-scale applications like electric vehicles (EV) and batteries for stationary power plants. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is a so-called “zero-strain material” due to the minute structural changes during electrochemical insertion of 3 Li<sup>+</sup> and the formation of Li<sub>7</sub>Ti<sub>5</sub>O<sub>12</sub>. Various methods to synthesize Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> have been reported, and the most common are solid-state reactions, sol-gel, and spray drying or spray pyrolysis techniques. These methods either use high synthesis temperatures or require post-annealing.

During the course of this study Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was crystallized directly via a novel continuous flow hydrothermal method using lithium ethoxide and titanium isopropoxide as reactants. Crystalline nanoparticles are obtained in a single step and in less than one minute, by mixing the reactants with superheated water in a continuous flow reactor at near- and supercritical conditions (T = 350 °C, P = 250 bar). The Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> nanoparticles have an average crystallite size of 4.5 nm with a specific surface area of  $\geq 230 \text{ m}^2/\text{g}$ . *In-situ* synchrotron powder X-ray diffraction measurements upon annealing of the hydrothermally produced nanocrystalline Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> were performed in order to investigate the structural and microstructural changes from room temperature to 727 °C. The crystalline nanoparticles show severe crystallographic strain and the smaller unit cell parameter of the nanoparticulate Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> might be because protons have entered the crystal structure during the synthesis. A diminishing unit cell due to protons entering a crystal structure was reported e.g. on cubic Li<sub>2</sub>TiO<sub>3</sub><sup>[2]</sup>. The induced crystallographic strain is found to relax upon annealing above 500 °C. The heat treatment results in a significant improvement of the performance in terms of the specific capacity and the rate capability.

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## **9-5: Numerical Simulation of Supercritical Water Flows in Continuous Hydrothermal Synthesis Reactors**

Takashi Furusawa<sup>1\*</sup>, Satoru Yamamoto<sup>1</sup>, Tadafumi Adschiri<sup>2</sup> and Edward Lester<sup>3</sup>

<sup>1</sup>Department of Computer and Mathematical Sciences, Tohoku University, 6-6-01 Aramaki Aza Aoba, Aoba-ku, 980-8579, Sendai, JAPAN

<sup>2</sup>Advanced Institute for Material Research(WPI-AIMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, 980-8577, Sendai, Japan

<sup>3</sup>Department of chemical and Environmental Engineering, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK

In recent years, supercritical fluids have been used in various chemical reaction processes as an eco-friendly method. A continuous supercritical hydrothermal synthesis was proposed for producing metal oxide nanoparticles[1]. In this process, the aqueous solution of metal salt is heated up by mixing with pre-heated supercritical water. Understanding the mixing flow of the solution and the supercritical water and prediction of the chemical reaction and the particle formation are crucial important for producing fine nanoparticles. However, the experimental observation in supercritical state is difficult because of the high pressure and temperature.

Our research group has developed a numerical method[2] for simulating supercritical-fluid flows: Supercritical-fluids Simulator (SFS). In this method, the compressible Navier-Stokes equations modified by the preconditioning method are coupled with a program package for thermophysical properties of fluids (PROPATH)[3]. In PROPATH, mathematical models based on a polynomial equation approximating thermo-physical properties are defined in wide range of temperature and pressure. This program package covers supercritical fluid, gas and liquid states for 48 substances. It is known that the thermophysial properties such as density, thermal conductivity and speed of sound change drastically near the critical point.

In this study, we investigate supercritical water flows in continuous supercritical hydrothermal synthesis reactor using SFS. The results indicate that accurate thermophysical properties such as density, isobaric specific heat and viscosity are absolutely necessary for simulating the mixing flows of supercritical water. In addition, we simulate the mixing flows with chemical reactions and particle formations with those mathematical models. Finally the characteristics of chemical reactions and particle formations in continuous hydrothermal synthesis are numerically investigated.

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## 9-6: Fluid mixing engineering on continuous supercritical hydrothermal synthesis

Shin-ichiro KAWASAKI<sup>1\*</sup>, Hiromichi HAYASHI<sup>1</sup> and Akira SUZUKI<sup>1</sup>

<sup>1</sup> Research center for compact chemical system,  
National institute of Advanced Industrial Science and Technology, AIST,  
Nigatake 4-2-1, Miyagino-ku, Sendai, JAPAN  
E-mail: shin-ichiro-kawasaki@aist.go.jp

Micromixers have been developed for the improvement of fluid mixing; however, it was applied almost under room temperature and atmospheric pressure conditions. We have studied to produce high temperature and high pressure micromixer; applicable to the continuous supercritical fluid processes. Although, supercritical fluids have high diffusion efficiency, the improvement of mixing performance will contribute to reduce the unexpected results from side reactions, especially for fast and sensitive reactions such as hydrothermal synthesis for nanoparticle production.

In case of continuous synthesis of metal oxide nanoparticles at supercritical conditions, sometimes, the formation of large particles cause blockage in the mixer or reactor. To inhibit blockage, many researchers have increased the size of reactor. We have considered that the large articles would be synthesized at the mixing point having a gradual temperature changing area. If temperature changes rapidly, the large supersaturation degree is instantly provided resulting synthesis of small particles. In this presentation, T-shaped macromixer and micromixer are compared by CFD simulation and NiO synthesis reaction. We will discuss on the relationship between the heating rate and particle size. The original swirl mixer and swirl micromixer under condition of high temperature and high pressure are developed. The effect of swirling flow will be also discussed.

Recently, Dr. Hayashi et al. have developed the Cu nanoparticle in-situ modification by organic compound for the printed electronics circuit. The modified nanoparticles can dissolve in the organic solvent completely under high concentration, and the Cu nano-ink could be produced.

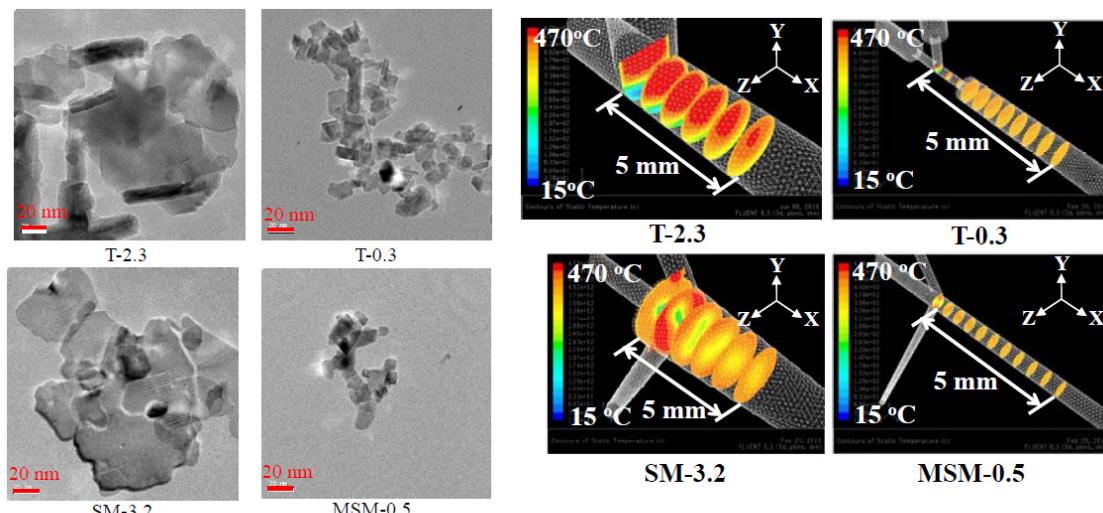


Fig.1 NiO nanoparticle TEM images by mixer configurations

Fig.2 Temperature contour diagram (CFD simulation) by mixer configurations

## 9-7: Rearrangement of Organic-inorganic hybrid Cerium Oxide Nanocrystals during Tetrahydrofuran Annealing

Daisuke Hojo<sup>1\*</sup>, Takanari Togashi<sup>2</sup>, and Tadafumi Adschiri<sup>1</sup>

<sup>1</sup> Advanced Institute for Materials Research, Tohoku University

2-1-1 Katahira Aoba, Sendai 980-8577, Japan

<sup>2</sup> Department of Material and Biological Chemistry, Yamagata University  
1-4-12 Shirokawacho, Yamagata 990-8560, Japan

Realizing the printed electronics where metal oxide nanocrystals (NCs) are incorporated has attracted considerable attention recently. Generally, high crystalline metal oxide films are only obtained through high temperature treatments. If the high crystalline metal oxide NCs are formed elsewhere at high temperature in advance and those are aligned densely on the surface at room temperature, high crystalline film layer can be fabricated even on a heat-sensitive substrate. In order to apply metal oxide NCs to the surfaces, three things have to be considered at least. 1) Disperse the NCs in a solvent. 2) Self-assemble the NCs on the substrate with drying the solvent. 3) Fix the NCs on the substrate. Among these processes, necessary interaction between the metal oxide cores, modifiers, solvent, and the substrate is totally different. This could then lead to a difficulty to apply NCs to the surface.

In this talk, dispersion of cerium oxide NCs in solvent will be a first topic to be mentioned. In order to disperse NCs, those were modified with fatty acid during synthesis of NCs at supercritical water condition to produce organic-inorganic hybrid NCs. In supercritical water medium, high-density of self-assembled monolayer of fatty acid was formed on the surfaces of metal oxide core. This results in making high-concentrated fluids dissolving NCs, over 50 wt% of NCs. Then, rearrangement of NCs during solvent annealing is discussed after self-assembly of NCs on the substrate. Atomic force microscope observation revealed that after the solvent anneal in tetrahydrofuran (THF) at 40–80°C for 5–15h, hybrid NCs adsorbed on the substrate were rearranged to be more highly-ordered structures. Due to low mobility of NCs in a solvent, arrangement of NCs had occurred insufficiently during self-assembly with drying at room temperature. This rearrangement of NCs to obtain high-ordered structures of NCs will be a key technology for precisely controlled colloidal superlattice structures. However, when THF annealing applied to the NCs after fixing on the substrate, where the chemical bonds were established between NCs and the substrate by using local ligand exchange, no rearrangement occurred during annealing. Interaction between NCs and the substrate is too strong to rearrange those NCs. To arrange NCs on such a “sticky” surface, pre-aligned NCs in the solvent should be placed on the surface before random deposition.

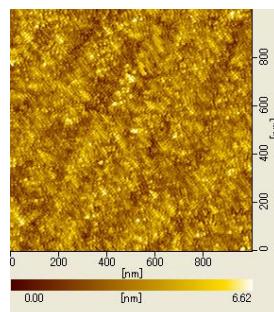


Figure 1. An AFM image of the sample after THF annealed at 40°C.

## 10-1: Hydrothermal Soft Chemical Synthesis of {010}-Faceted Anatase TiO<sub>2</sub> Nanocrystals for High Performance Dye-Sensitized Solar Cells

Qi Feng, Puhong Wen, Changdong Chen, Shunsuke Nakanishi

Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu 761-0396, JAPAN

The TiO<sub>2</sub> electrode is the most significant part of dye-sensitized solar cells (DSCs), and its performances strongly depend on the properties of the TiO<sub>2</sub> nanocrystals used. For this reason, a large number of studies have been reported on the preparation of TiO<sub>2</sub> nanocrystals. However, most of these studies focused on the controls of particle size and crystallinity of TiO<sub>2</sub> nanocrystals. Since the sensitizer-dye molecules are absorbed on the TiO<sub>2</sub> nanocrystal surface, it is expected that crystal facets exposed on TiO<sub>2</sub> nanocrystal surface will strongly affect the dye adsorption behavior. However, no any research has been reported on the facet effect of TiO<sub>2</sub> nanocrystals on DSCs performance, because the TiO<sub>2</sub> nanocrystals with a specific facet on the surface are difficult to be synthesized until our recent research. Therefore, the control the facets exposed on TiO<sub>2</sub> nanocrystal surface is a new challenge for the high performance DSCs. In the present study, we describe synthesis of {010}-faceted (or {100}-faceted) anatase TiO<sub>2</sub> nanocrystals from layered titanate nanosheets by hydrothermal soft chemical process, sensitizer-dye adsorption behavior on the anatase TiO<sub>2</sub> nanocrystals, and the relationships between the dye adsorption parameters and the DSCs cell performance parameters.

We synthesized {010}-faceted anatase TiO<sub>2</sub> nanocrystals by hydrothermal treatment of a lepidocrocite-like layered titanate (H<sub>1.07</sub>Ti<sub>1.73</sub>O<sub>4</sub>) nanosheet solution. Four kinds of TiO<sub>2</sub> nanocrystals with quadrate (AN<sub>Q</sub>), leaf-like (AN<sub>L</sub>), comb-like (AN<sub>C</sub>), and rod-like (AN<sub>R</sub>) morphologies, respectively were obtained by the hydrothermal reaction (Fig. 1). These nanocrystal samples expose the {010} facet on their particles surface, due to the transformation reaction from the layered titanate structure to the anatase structure is a topotactic structural transformation reaction. If a tetra-titanate (H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>) nanosheet solution was used in the hydrothermal reaction, anatase nanocrystals with a facet vertical to [11-1] direction on the surface were obtained, suggesting that the facet on the crystal surface can be controlled using different kinds of layered titanates nanosheets as precursor in the hydrothermal soft chemical process.

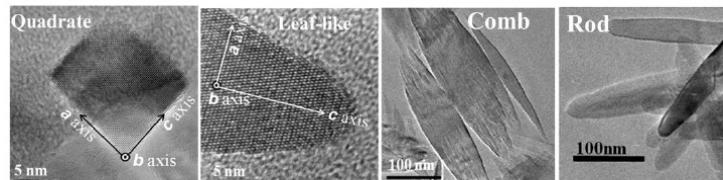


Fig. 1. Anatase nanocrystal with {010}-facet on the surface

We studied the adsorption reaction of a sensitizer dye (N719) used in DSCs on the seven kinds of anatase nanocrystal samples, including AN<sub>Q</sub>, AN<sub>L</sub>, AN<sub>C</sub>, AN<sub>R</sub> and three kinds of typical commercial samples, ST01, ST111, P25, and also their DSCs performances. We discovered a logarithmic relationship between short-circuit photocurrent density ( $J_{sc}$ ) and dye-adsorption constant  $K_{ad}$  (Fig. 2), and a linear relationship between open-circuit potential ( $V_{oc}$ ) and dye-adsorption amount for DSCs. These relationships give a simple method for forecasting DSCs performance from the dye-adsorption parameters. We also found that the {010}-faceted anatase TiO<sub>2</sub> nanocrystals shows highest  $J_{sc}$  value and is a promising high performance TiO<sub>2</sub> nanocrystal for DSCs.

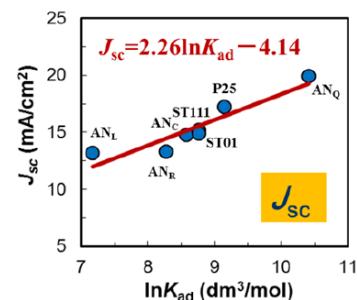


Fig. 2. Relationship between  $J_{sc}$  of DSC and dye-adsorption constant  $K_{ad}$

## 10-2: Solubility and Supersaturation in Hydrothermal Crystal Growth of ZnO

Maria C. Gelabert<sup>1</sup>

<sup>1</sup>Department of Chemistry, Physics and Geology, Winthrop University, 701 Oakland Avenue, Rock Hill, SC 29733

For subcritical hydrothermal synthesis, crystal habit is sensitive to aqueous chemistry, pH and temperature; thus, it is possible to obtain many different crystal shapes in these conditions. Current methods for obtaining a particular habit remain largely empirical, however, and in this research, the overall goal is to establish relationships between aqueous conditions and crystal habit, enabling some degree of predictability for solid state technologies relying on particular crystal habits. ZnO is being studied, in part for the ability of Zn<sup>2+</sup> to bind to many ligands; EDDA, EDTA, DTPA, dien, trien, tetren, penten, and zinc acetate, chloride and sulfate salts have been used over several years; for 200 °C growth, crystals of 20 microns to millimeters have been characterized primarily by optical microscopy [1]. Aqueous speciation software (OLI Analyzer Studio) has been used to determine supersaturations for several zinc ions believed to participate in crystal growth. Besides synthesis, microscopy and supersaturation, this talk will present the complexities of precise solubility of ZnO and the importance of its reliability for supersaturation calculations. OLI calculations of ZnO solubility have been compared with experimental data [2], and theoretical supersaturation of specific ions as a function of pH have been determined. For EDTA and counterions acetate and chloride, peak supersaturation levels are in the pH 9-10 region, respectively, with Zn<sup>2+</sup> and tetrahydroxide [Zn(OH)<sub>4</sub>]<sup>2-</sup> ions having the highest levels across the pH range; how these compare to experimental results will be presented and highlighted as critical to understanding growth of specific crystal habits from hydrothermal solutions.

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### **10-3: Synthesis of TiO<sub>2</sub> mesoporous beads and its use in all-plastic dye-sensitized solar cell**

Jyh-Ming Ting

Department of Materials Science and Engineering  
National Cheng Kung University  
Tainan, Taiwan

In this study, we report the synthesis of mesoporous anatase TiO<sub>2</sub> beads with various sizes and characteristics via a simple two-step method involving a sol-gel and hydrothermal processes. In particular, the use of hexamine as the steric agent during the sol-gel process assists the formation of beads with controllable sizes. We present the effect of hexamine in controlling the size and surface morphology of bead precursors and suggest a mechanism for the bead formation. Furthermore, hexamine has a high water solubility and is easily removable by water, thus eliminating the organic residue effect during the follow-up steps and in the final product. Moreover, we also show an obvious efficiency enhancement in plastic substrate flexible DSC (FDSC) due to the use of the resulting beads in the photoanodes, demonstrating that the obtained mesoporous anatase TiO<sub>2</sub> beads with well-defined morphology would be an excellent candidate for energy and environment applications.

## 10-4: Novel Optical Properties from Solution-Derived Nanoparticles

John Ballato<sup>1\*</sup>, Courtney Kucera<sup>1</sup> and Luiz Jacobsohn<sup>1</sup>

<sup>1</sup>Center for Optical Materials Science and Engineering Technologies (COMSET) and the School of Materials Science and Engineering, Clemson University, Clemson, SC 29634

This paper reviews the synthesis, structure and applications of solution-derived metal fluoride nanoparticles, with a particular focus on those doped with light-emitting rare earth (RE) ions. Specifically, we will discuss doped  $\text{LaF}_3$  and alkaline earth metal fluoride core/(multi-)shell nanoparticles and these nanoparticles dispersed in plastics, glasses, and coatings. The ability to controllably synthesize doped cores and shells permits unique insights into the nature of energy transfer between dopants at very local levels [1,2] and provides great practical utility for spectral engineering. This latter point enables novel white light phosphors [3], optical fiber amplifiers and light sources [4,5], and scintillators [6]. These applications, and others, also will be discussed.

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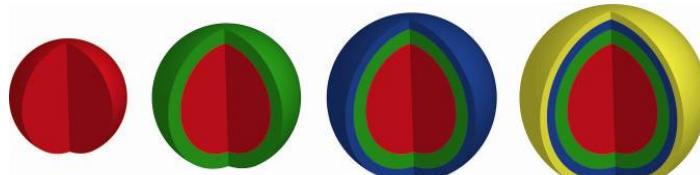


Fig. 1. Schematic representation of multiply-shelled nanoparticles; each shell to emit a different color

## 10-5: Fabrication of Artificial Photosynthesis Devices Using Hydrothermal Synthesis of Photocatalysts

Young Soo Kang\*, Chang Woo Kim and Hyun Gil Cha

<sup>1</sup>Korea Center for Artificial Photosynthesis and Department of Chemistry, Sogang University,  
Seoul 121-742, Korea

In this talk, the basic concept and fabrication technology for the nanodevices for artificial photosynthesis was introduced. Based on the solvothermal and hydrothermal synthesis and alignment of the photocatalytic nanocrystals and its assembled nano-sized monolayers of photocatalytic materials, vectorial electron transport from the higher conduction band energy to lower conduction band energy could be accelerated by suppressing the defect and optimizing the electron transport distance and diffusion capacity. The fabrication of the photocatalysts was done to get the largest exposed surface area of the most photoactive facets for nanocrystals of TiO<sub>2</sub>, Cu<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub> and ZnO. Especially,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocrystal assembled monolayer fabrication for the visible light sensitive layer on FTO and the measurement of the photocurrent density are the basic approach for the artificial photosynthesis through water splitting and CO<sub>2</sub> reduction. For the efficient electron transport through the TiO<sub>2</sub> nanotubes, SrTiO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cu<sub>2</sub>O were doped into the pores of the TiO<sub>2</sub> nanotubes and photocurrent was measured.

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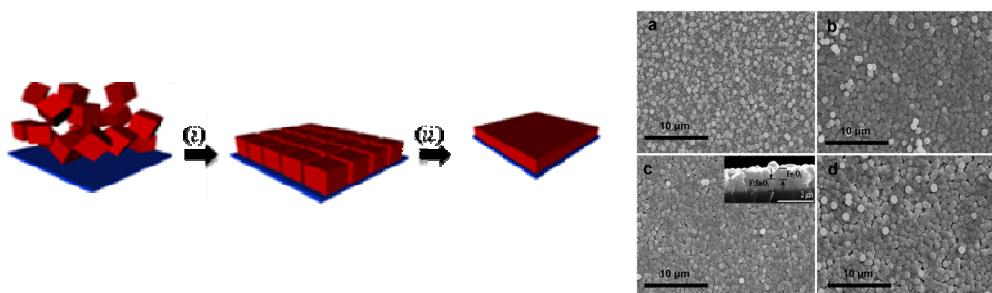


Figure 1. Fabrication process of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocrystal assembled monolayer on FTO glass surface

## 10-6: Hydrothermal Preparation of High Efficient TiO<sub>2</sub>-Graphdiyne Photocatalyst

Nailiang Yang<sup>†</sup>, Yuanyuan Liu<sup>†</sup>, Hao Wen and Dan Wang\*

State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering,  
Chinese Academy of Sciences, Beijing 100190, P. R. China

<sup>†</sup>Equivalent contribution; \*Corresponding author: danwang@mail.ipe.ac.cn

Since graphene (GR) isolated in 2004, it had captured the attention of scientists due to the novel transport properties of its carriers behaving as massless Dirac fermions. In recent years, scientists have been actively using graphene and its hybrids in supercapacitors, fuel cells, batteries, catalysis, photovoltaics, chemical and biosensors, photonics, and optoelectronics.

Recently, Graphdiyne (GD), another 2D carbon allotrope which contains both sp and sp<sup>2</sup> carbon atoms was first predicted by Baughman. Li and co-workers synthesized large area graphdiyne films with 3.61 cm<sup>2</sup> on the surface of copper via a cross-coupling reaction using hexaethynylbenzene in 2010.[1] It showed semiconducting property with conductivity of  $2.516 \times 10^{-4}$  S/m, and was predicted to be the most stable of the various diacetylenic nonnatural carbon allotropes because of the dialkyne between the benzene rings. Also Malko predicted that some GD allotrope which did not have hexagonal symmetry and featured two self-doped nonequivalent distorted Dirac cones suggesting electronic properties even more amazing than that of graphene. However, these reports were just based on the theory and lack of experimental proof.

Density functional theory (DFT) calculations predicted that graphdiyne was a narrow direct band gap material. Remarkably, the calculated intrinsic charge mobility of graphdiyne sheet was up to 105 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at room temperature, which was similar to the value of graphene. As mentioned above, we can induce that GD also has excellent electron mobility which may improve the photocatalytic performance of TiO<sub>2</sub>.

In this paper, we synthesized the P25-GD composite by hydrothermal method, it given a good catalysis performance then P25-GR composite.[2]

For understanding the reasons; first-principles calculations were used based on the density-functional theory (DFT) to clarify the electronic performance and charge transfer action between GD or GR and TiO<sub>2</sub> with different facets ((100), (001), (010)). The supercells of 6 composites had been built and geometry optimized. Corresponding a series composites of nanosheets with graphdiyne (TiO<sub>2</sub>-GD) or graphene (TiO<sub>2</sub>-GR) were obtained by a simple hydrothermal treatment of the 2D-TiO<sub>2</sub> and 2D-GD or 2D-GR in a mixture of ethanol and water, and we investigated the photocatalytic activity of the composites by testing the degradation of methylene blue (MB) in aqueous solution. The results of calculation and experiment show that, the TiO<sub>2</sub>(001)-GD possess the most effective charge separation capacity, the most abundant impurity levels and the highest oxidation ability, which bring 1.6 times higher rate constant than TiO<sub>2</sub>(001), and 1.3 times higher than the TiO<sub>2</sub>(001)-GR in the following photodegradation experiment.[3]

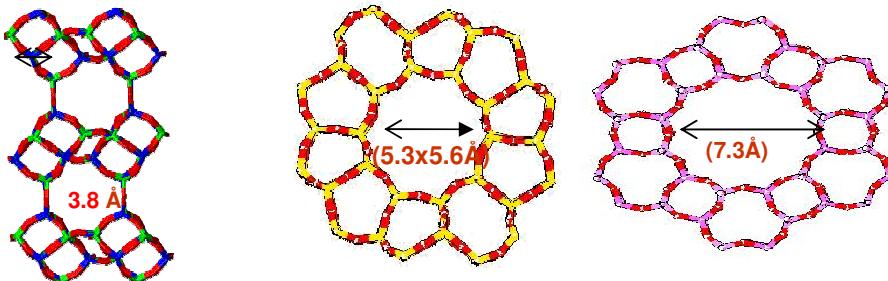
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## 11-1: Understanding the mechanism of formation of nanoporous materials under hydrothermal conditions by *in situ* X-ray techniques

Gopinathan Sankar

Department of Chemistry, University College London, 20 Gordon Street,  
London WC1H 0AJ, UK

Catalysis is the back-bone of chemical industries and they will continue to be essential in numerous applications that are indispensable to enhance quality of our life and society. Several types of heterogeneous catalysts, for example, supported catalysts, bulk oxides and nanoporous materials, are widely used for a variety of catalytic reactions. Within the family of heterogeneous catalytic systems, nanoporous materials (see figure 1) are highly effective for performing shape selective reactions and hence studied widely for a variety of catalytic applications. A variety of transition metal ions containing microporous materials have been synthesized and used as catalysts for the oxidation of organic compounds.



**Figure 1. Typical structures of nanoporous materials consisting of different pore dimensions**

To produce these nanoporous materials it is inevitable to use hydrothermal methods. Although, preparation of both the open and dense framework solids require considerable amount of effort to optimise the conditions, recent developments in the *in situ* methods, in particular X-ray diffraction and X-ray absorption spectroscopic techniques, offer considerable advantage to determine accurately the conditions required to produce phase pure materials and further more understand the mechanism of formation of these solids under operating conditions. Recent advances in these techniques allow us to collect high-quality time-resolved data to obtain the kinetics of crystallisation of solids prepared from amorphous gel mixtures. Here we will discuss the processes that take place during the crystallisation of open framework structures under hydrothermal conditions by taking examples in the synthesis of microporous aluminophosphate and aluminosilicate materials.

## 11-2: Solvothermal Reactions For Novel Chemical Syntheses: From Graphene To MOFs

John A. Stride<sup>1\*</sup>

<sup>1</sup>School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

Synthetic processes that occur beyond the limited parameters of traditional wet chemical environments offer great scope to develop novel materials and new chemistries. Within the expanded parameter space of this new regime, hydro- and solvo-thermal syntheses are particularly interesting as they extend traditional reaction conditions into higher temperature and pressure environments, whilst avoiding highly specialized reactor vessels and widely different conditions to traditional chemistry. As such they may yield highly novel or synthetic analogues of naturally occurring materials with relatively simple and low-cost synthetic protocols. It is therefore no surprise that solvothermal techniques now make up an established tool in modern chemistry laboratories and feature widely in reports of new materials.[1] The sub-critical solvent regime can lead to differences in reagent solubility, mass transport and reaction pathways or mechanisms with respect to bench-top conditions, often leading to novel products but also making prescriptive syntheses less obvious.

We have made use of solvothermal conditions to synthesize materials as diverse as precursors to nanostructured carbons (including graphene),[2] nanoparticles such as TiO<sub>2</sub> [3] and CdSe quantum dots and metal organic frameworks (MOFs).[4] We believe that in each case, the reaction conditions provide unique reaction pathways unavailable at near-atmospheric pressure and temperatures well below the solvent boiling point, although little effort has been made to this point to fully optimize reaction conditions such as absolute temperatures, pressures and times.

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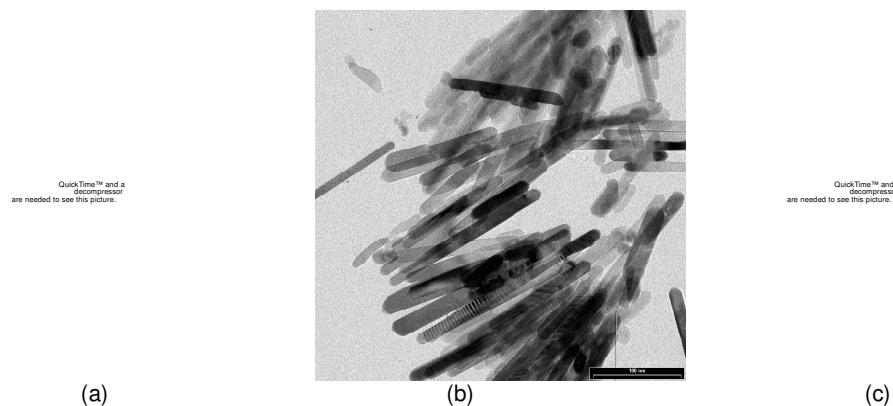


Fig. 1. Novel materials obtained from solvothermal reactions (a) graphene; (b) TiO<sub>2</sub> (rutile) nanorods and (c) a Cu-based MOF displaying size selectivity of gas uptake.[5]

### **11-3: Microbial-Mineralization-Inspired Syntheses of Nanostructured Iron Oxides and Manganese Oxides with Controlled Crystal Phases**

Hiroaki Imai<sup>1\*</sup>, Naoki Yagmita<sup>1</sup>, Manabu Oba<sup>1</sup> and Yuya Oaki<sup>1</sup>

<sup>1</sup>Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Metal-oxidizing bacteria produce iron oxides and manganese oxides with the controlled crystal phases outside of their cells. Here we show novel syntheses of iron and manganese oxides with the controlled oxidation states and the crystal phases through a microbial-mineralization-inspired approach in an aqueous solution at low temperature. Neither hydrothermal treatment nor special equipment is needed for this process.

Trivalent iron oxides, such as lepidocrocite, ferrihydrite, goethite, and hematite, are selectively obtained from an aqueous solution containing divalent iron ions below 90°C [1]. The presence of a chelating agent, such as EDTA, facilitates the control of the oxidation states because the precipitation of the divalent iron species is inhibited by the complexation between divalent iron ion and the chelating agent. The control of the crystal phases is achieved by the tuning of the synthetic conditions, such as the initial pH, the concentration of the chelating agent, and the reaction temperature. Furthermore, the resultant iron oxides have the hierarchically organized structures consisting of the nanoscale objects.

Manganese oxide nanostructures are also synthesized by the route inspired by microbial mineralization [2]. The synthesis of manganese oxide nanosheets and their oriented thin films are obtained in aqueous solution under ambient conditions. The addition of the chelating agent led to the generation of trivalent/tetravalent sodium manganese oxide (birnessite) nanosheets less than 10 nm in thickness. The synthesis and morphogenesis were controlled concurrently by the chelating agent. Moreover, the combination of antioxidant and chelating agents facilitates the parallel control of oxidation states and morphologies in an aqueous solution at room temperature [3]. Divalent manganese hydroxide ( $\text{Mn}(\text{OH})_2$ ) is selectively obtained as a stable dried powder by using ascorbic acid as an antioxidant agent. The topotactic oxidation of the resultant  $\text{Mn}(\text{OH})_2$  leads to the selective formation of trivalent manganese oxyhydroxide ( $\beta\text{-MnOOH}$ ) and birnessite.

The microbial-mineralization-inspired approach by using organic molecules has potentials for parallel control over oxidation states and morphologies of iron oxides and manganese oxides and further application to aqueous solution syntheses of various transition metal oxides.

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## 11-4: Spark Plasma Solvothermal Technique for the Formation of Graphitic Pattern - A Soft Solution Process (SSP)

J. Senthilnathan<sup>(1)</sup>, C.C. Weng<sup>(1)</sup>, J.D. Liao<sup>(1)</sup>, Y. Gogotsi<sup>(2)</sup> M. Yoshimura<sup>(1)</sup>

<sup>1</sup> Promotion Centre for Global Materials Research (PCGMR)

Department of Material Science and Engineering, National Cheng Kung University, Taiwan

<sup>2</sup> Department of Material Science and Engineering and A. J. Drexel Nanotechnology Institute,  
Drexel University, Philadelphia, PA 19104, USA

Most of the various forms of carbon based materials like nanotube, carbon nitride, diamond like carbon etc. are prepared from gaseous precursors by CVD, PVD and ion-assisted sputtering techniques [1]. SSP allows one to fabricate the advanced material in aqueous/organic solutions in an eco-friendly process without using excess energy for firing, sintering, melting and expensive equipment [2]. In this study, simultaneous deposition and patterning (1000 pulse/sec) of carbon on Si (100) substrates in ethanol solution has been demonstrated using W needle (edge 0.65μm) which was controlled by computer program (repetition rate 10kHz; pulse delay 500μs; pulse width 500μs).

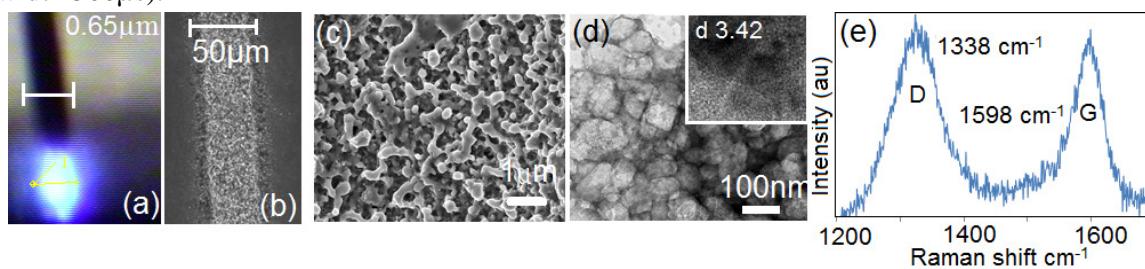


Fig.1. (a) Formation of plasma in liquid solution (b) Thickness of the carbon pattern (c, d) SEM and TEM images of patterned carbon (e) Raman spectrum of patterned carbon.

Due to the small separation in between pen and Si substrate, intense plasma developed and creates fine pattern on the Si substrate (Fig.1a). Fig.1b shows the thickness of the pattern ~ 50μm. Controlled pattern might be possible by this method [3]. The Raman spectrum shows D band at 1338 and G band at 1598 cm<sup>-1</sup>. TEM images shows discontinuous graphitic structure at the surface and d space value of 3.42 was observed. In this study, we observed the coexistence of graphitic as well amorphous carbon at the surface of patterned Si. Development of graphitic carbon pattered Si by SSP is potential candidate for the various fields of application and we believe that the findings of this study would help in the possibility of patterning new forms of carbon by SSP.

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## 11-5: Solvothermal Synthesis of Acmite Conversion Coatings on Steel

Terence Whalen, Bryan VanSaders, Cekdar Vakifahmetoglu, Asad Mughal, Eugene Zlotnikov, Seung-Beom Cho and Richard Riman

Rutgers University, 607 Taylor Rd. Piscataway NJ, 08854

Acmite ( $\text{NaFe}(\text{Si}_2\text{O}_6)$ ) is a rock forming mineral of the pyroxene group[1]. It has excellent temperature (~850°C) and corrosive environment stability, along with multiferroic properties[2,3]. These characteristics could render acmite useful as a passivation coating on steel or a functional coating that utilizes its electronic and magnetic properties. In spite of these potential applications, no mention of a controlled process for growing acmite films on steel is found in peer-reviewed literature beyond prior work at Rutgers[4].

Acmite was formed on a steel coupon via reaction of an aqueous system containing, silica, sodium hydroxide, and 1,4 butanediol(tetramethylene glycol,  $\text{C}_4\text{H}_{10}\text{O}_2$ ) in an autoclave under autogenous pressure. Control of grain morphology was demonstrated by altering concentrations of reactants, reaction time, and temperature. See Figure 1 below, demonstrating morphology manipulation by control of silica concentration. Homogenous coatings comprised of pinacoidal acmite grains with an average grain size of ~33  $\mu\text{m}$  were produced on the steel coupons from the reactants of 0.498 molal  $\text{SiO}_2$ , 1.97 molal  $\text{NaOH}$ , and 0.169 mol 1,4 butanediol upon synthesis for 72 h at 240°C. The mechanism of coating formation was also discussed, wherein magnetite forms first at the steel surface, followed by acmite on the magnetite surface some time later. Figure 2 shows experimentally and schematically the location of the two phases.

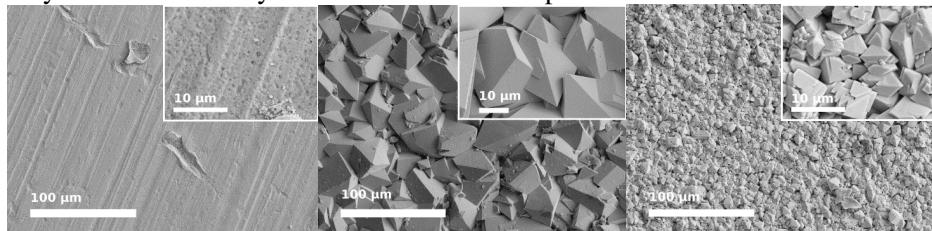


Figure 1. SEM images of varied  $\text{SiO}_2$  precursor concentration,  
a) (Acm1) 0.249 molal, b) (Acm0) 0.498 molal, and c)(Acm2) 0.995 molal.

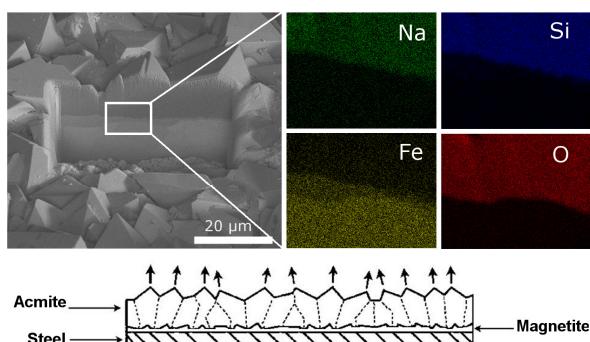


Figure 2. SEM image of FIB dug trench, followed by EDX analysis of the layer interfaces. Note the region of overlap of FE and O that excludes Na and Si. Schematic pictorially describes the interface.

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## **11-6: Continuous hydrothermal synthesis of functional nanomaterials for high-performance textiles**

M Gimeno-Fabra, E H Lester and D Grant

High-performance textiles such as Kevlar are used in many fields for protection including body armour, medical gloves, aerospace and automotive structures. While these materials are light and offer excellent protection against high velocity impacts, they fail to perform when faced with low energy, highly localised impacts due to separation of their constituent fibres.

To improve stab resistance, Kevlar has been coated with highly concentrated suspensions of different materials in poly(ethylene glycol) (PEG). PEG, however, degrades Kevlar overtime and increases slip between fibres if the solids content is not high enough (silica content > 60 %wt.) which compromises the overall weight of the fabric.

In this paper the penetration behaviour of Kevlar samples coated with different functionalised nanomaterials is presented. Hydroxyapatite plates, silica spheres and titania nanoparticles have been successfully generated using a continuous hydrothermal supercritical reactor developed at the University of Nottingham. The versatility of this reactor allowed for the introduction of different surfactants such as Dodecyl Succinic Anhydride and poly(ethylene-co-acrylic acid), coating the particles giving the specific functionality needed to bind to Kevlar. This process has also been proven easy to scale up. These materials were characterised using SEM, EDAX, TEM, TGA, FTIR-ATR, DSC and XRD.

The fabric testing includes yarn pull-out, quasi-static spike puncture and dynamic impact testing as well as TGA, SEM and optical microscopy. The results of the modified Kevlar samples were compared with a ‘baseline’ of neat Kevlar as well as fabric with polymer only coating.

Our results show that friction, stress transfer and physical entrainment of the functional particles into the fibres contribute to the improvement of the treated fabrics, performing better than the PEG samples while weighing less in a homogeneous coating but without compromising the chemical stability of Kevlar.

## **11-7: Continuous Hydrothermal Synthesis of Stabilised Zinc Sulphide Nanoparticles with Fluorescent Properties**

Selina Tang<sup>1</sup>, Andrei Khlobystov<sup>2</sup>, Stephen Briddon<sup>3</sup>, Edward Lester<sup>1</sup>

<sup>1</sup>*Department of Chemical and Environmental Engineering, <sup>2</sup>School of Chemistry, <sup>3</sup>The School of Biomedical Sciences, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

Fluorescent particles are used in a variety of industries, ranging from biological cell imaging and tracking; for targeted drug delivery; or as markers for tagging materials for the purposes of security or safety. Commonly used fluorescent nanoparticles such as quantum dots typically contain a cadmium-based core surrounded by a zinc sulphide (ZnS) shell. As well as increasing quantum yield, this shell protects the core from oxidation and prevents the Cd leaching out.

In this study, a continuous hydrothermal reactor is used, which utilises super- and sub-critical water as a medium for the synthesis of ZnS nanoparticles. These particles are cadmium-free and so do not include the same toxicity issues. Data obtained from transmission electron microscopy (TEM) indicates the size of particles to be below 30 nm, while the crystal structure was shown to be cubic from X-ray diffraction (XRD). Upon UV excitation at 350 nm, the ZnS particles exhibited emission between 470 and 680 nm.

To improve the stability and biocompatibility of these particles, organic surfactants have been incorporated into the synthesis method, either at the point of reaction or further downstream, to generate particles with a polymer coating. Analysis has shown that addition of organic material does not compromise the fluorescent properties of the ZnS particles.

The continuous reactor used in this study is currently used commercially, and scaling up from lab (g/day) to pilot (tonnes/annum) has been performed, with reproducible results for a range of materials. Hence, this study has the potential for commercial application.

## **11-8: Vapor Phase Hydrothermal Synthesis: A New Approach for Fabrication of Nanomaterials**

Huijun Zhao\*, Porun Liu, Haimin Zhang and Yun Wang

Centre for Clean Environment and Energy  
Gold Coast Campus, Griffith University, Queensland 4222, Australia  
[h.zhao@griffith.edu.au](mailto:h.zhao@griffith.edu.au)

Controllable growth of metal oxide crystals with high reactive crystal facets has attracted great interest due to their superior properties and potential applications in catalysis, photocatalysis, gas sensor, photovoltaic and lithium ion batteries. To date, titanium dioxide has been the dominant semiconductor photocatalyst owing to its excellent photocatalytic activity, low cost, abundant supply, non-toxic nature and high photocorrosion resistance. It has been well accepted that anatase TiO<sub>2</sub> possesses higher photocatalytic activity amongst other crystal phase of titanium dioxides. Recent studies reveal that the performance of anatase TiO<sub>2</sub> nanocrystals depends not only on their dimensional, morphological and structural properties, but also on their crystal facets. This sparks an upsurge research activity to fabricate anatase TiO<sub>2</sub> nanocrystals with high reactive facets. Although the anatase TiO<sub>2</sub> with highly reactive crystal facets is desirable for photocatalysis-based applications, they are often diminished during the crystal growth process due to higher surface energies. Control growth of highly reactive crystal facets is therefore a scientific challenging and practical important issue. A number of strategies have been developed to control the morphology and crystal facet growth. Among them, the surface fluorination under liquid hydrothermal conditions is the most successful one, especially for the control growth of {001} faceted anatase. Despite the success, the reported liquid hydrothermal methods have a number of drawbacks, especially for large-scale production. This presentation is therefore to introduce a newly developed vapour phase hydrothermal method [1-2] and TiO<sub>2</sub> will be used as a typical example to demonstrate control growth of nanostructures, high energy crystal facets, and related growth mechanisms.

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## **11-9: Synthesis of Semiconducting Chalcogenide Nanocrystals for Solar Cell Application**

Ningzhong Bao\*, Xiaoyan Zhang, Liming Shen, Arunava Gupta

State Key Laboratory of Materials-Oriented Chemical Engineering  
Nanjing University of Technology, Nanjing, China  
The MINT Center, The University of Alabama, Tuscaloosa, UAS  
Phone & Fax: +86-025-8317-2244 (o); Email : nzhbao@njut.edu.cn

Thin film solar cells based on semiconductor nanocrystals are promising approach to decreasing the fabrication cost of solar cells. Besides CdTe/CdSe, Cu<sub>(In<sub>x</sub>Ga<sub>1-x</sub>)Se<sub>2</sub></sub>(CIGS), etc., Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) have been studied as inexpensive, non-toxic, earth-abundant photovoltaic materials. Related to CZTS (kesterite), the naturally occurring mineral stannite, Cu<sub>2</sub>FeSnS<sub>4</sub> (CFTS) can be a viable alternative provided it exhibits the requisite optical and transport characteristics. We have been working on the synthesis of both CuInS<sub>2</sub> (CIS) and emerging materials such as CFTS. A simple solution-based route has been developed for the facile synthesis of anisotropic nanocrystals of CIS with tunable shape, size, crystal structure, and optical properties. The process involves the thermal decomposition of mixed metal oleate complexes and their reaction with a sulfur source in high-boiling solvent mixtures of OLA, OA, and ODE. Independent of the process conditions, all intermediate and final products exhibit uniform composition and structure indicating homogenous nucleation and growth of single-phase monodisperse nanocrystals. Particularly, a new wurtzite phase of CFTS was synthesized at relatively low temperature (~210 °C) using a solution-based method. The more stable zinc blende phase is formed at higher reaction temperatures (> 300 °C). Phase-pure CFTS nanocrystals of both structure-types are obtained with appropriate control of the reaction temperature, choice of solvents and capping agents. The wurtzite and zinc blende phase nanocrystals, in the shape of oblate spheroids and triangular plates, have sizes of 20 ± 2 nm and 38 ± 5 nm, respectively. The corresponding band gaps are determined to be 1.54 and 1.46 eV. Based on the results, narrow-band-gap CFTS composed of low-toxicity, earth-abundant elements appears attractive as a low-cost substitute for use in thin film solar cells.

**ISHA-Sawyer Lifetime Achievement Award:  
Feature and Future of Hydrothermal/Solvothermal Reactions for  
Synthesis/Preparation of Nano-Materials with Desired Shapes, Sizes and  
Structures**

Masahiro YOSHIMURA

Promotion Center for Global Materials Research, Dept. Mater.Sci. & Eng., National.Cheng Kung University.,Tainan,Taiwan: [yoshimur@mail.ncku.edu.tw](mailto:yoshimur@mail.ncku.edu.tw)  
Professor Emeritus of Tokyo Institute of Technology, Japan: [yoshimura@msl.titech.ac.jp](mailto:yoshimura@msl.titech.ac.jp)

Hydrothermal reactions have widely been recognized in natural and artificial systems on the earth<sup>1,2)</sup>. Particularly, the formation, production, alteration, decomposition of all substances and materials in natural systems are always related with the action of water (aqueous solutions) at higher temperatures under pressures. The origin and development of life might be influenced by the action of aqueous solutions most probably around the hydrothermal vents in deep sea<sup>2)</sup>. Not only the bio-systems but also artificial materials systems can be related to the actions of water.

Solvothermal reactions using non-aqueous solvents have also been considered to be useful for various materials and chemical processing. Often Non-aqueous solvent may contain impurity water and/or byproduct water during the processing. Similarly Hydrothermal reactions may include non aqueous components during their processing. Therefore, Hydrothermal and Solvothermal are overlapping in many cases. Moreover, Hydrothermal/Solvothermal reactions can contain almost all species of liquids, gases and solids, therefore, they have following features: [1] Wide variety of liquid media , [2] Additional gases and solids,[3] Wide variety of temperature and pressure,[4] Static and Dynamic, flowing and circulating, systems, [5] Those liquids acting as (a) Surface Adsorption/Desorption agents,(b) Reactants(Coordination/Chelating agents),(c) Solvents, etc. Thus,[6] Variety of applications like chemical, physical, biological, medical, mechanical, electrical, electronic, optical, photonic, magnetic, materials, environmental, etc. I believe that Future of Hydrothermal and Solvothermal processing should be quite wide and successful.

In the present lecture, I will summarize Hydrothermal reactions on various natural and artificial materials. [1]Hydrothermal Syntheses of Nano-particles<sup>3)</sup>,ZrO<sub>2</sub>,CeO<sub>2</sub>, (Zr,Ce)O<sub>2</sub>,HAp, Fe<sub>3</sub>O<sub>4</sub>,TiO<sub>2</sub>,BaTiO<sub>3</sub>,etc. [2]Nanostructured Films<sup>2,4)</sup> of BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, LiCoO<sub>2</sub> , BaWO<sub>4</sub> CaWO<sub>4</sub>, HAp etc .,and [3] Nanostructured Patterns<sup>5)</sup> of BaTiO<sub>3</sub>,Carbon,etc. established in our group will be reviewed. In the formation of films,

additional activation(s) with thermal one are very useful. Particularly electrochemistry is very attractive to prepare oxide films and patterns. Recent proposal: Growing Integration Layer[GIL] method<sup>6)</sup> is also using electrochemistry to make integrated oxide layer(s) on metallic material(s) to improve adhesion, anti-oxidation, bioactivity and/or other functionalities. Combination of Polymer Complex Method and Hydrothermal reactions have been developed<sup>7)</sup>.

Eu-doped CaAlSiN<sub>3</sub> phosphors and LaTaON<sub>2</sub> have been synthesized under pressured ammonia atmosphere<sup>8)</sup>.

Acknowledgements:

I would like to thank to my senior and younger colleagues including students during my research on hydrothermal/solvothermal and soft (solution) processing.

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## **12-1: Hydrothermal Synthesis of Noncentrosymmetric Mixed Metal Oxide-Fluorides**

Kenneth Poeppelmeier <sup>1\*</sup>, Martin Donakowski <sup>1</sup>, Kelvin Chang <sup>1</sup> and Romain Gautier <sup>1</sup>

<sup>1</sup>Northwestern University, Department of Chemistry, Evanston, Illinois, 60201

This talk will discuss the chemical rationale we have employed to make new mixed metal oxyfluoride compounds and their relationship with well-known noncentrosymmetric materials such as lithium niobate and potassium titanyl phosphate. Synthesis of noncentrosymmetric materials – materials that lack an inversion center – has been a long-standing and difficult goal of inorganic chemistry. Noncentrosymmetric crystals are used for their piezoelectric, ferroelectric, and second-harmonic generation (SHG) properties. Recently, nanolithography has sought UV lasers to create increasingly small lithographic features. To pursue UV lasers, scientists have sought new SHG active crystals to double the frequency of laser light to higher energies. One such material is the oxyfluoride KBe<sub>2</sub>BO<sub>3</sub>F<sub>2</sub>; we seek to develop similar materials for use as SHG-active crystals. Efficient SHG-active crystals often have anions with aligned polar moments in the solid state. Therefore, to synthesize highly-efficient SHG crystals, a promising strategy is to utilize anions that inherently contain polar moments to establish principles and guidelines to target syntheses of SHG-active materials.

## 12-2: Hydrothermal access to oxide catalysts and sensors: From MARS methods to environmental applications

Greta R. Patzke<sup>1\*</sup>, Hongfei Liu<sup>1</sup>, Roman Kontic<sup>1</sup>, Ying Zhou<sup>2</sup> and Min Sheng<sup>1</sup>

<sup>1</sup>Institute of Inorganic Chemistry, University of Zurich, CH-8057 Zurich, Switzerland.

<sup>2</sup>School of Materials Science and Engineering, Southwest Petroleum University,  
Chengdu, 610500, China

Oxide nanomaterials are emerging as powerful tools to ensure our access to clean environmental and energy resources. We focus on the straightforward conventional hydrothermal (HT) and microwave-hydrothermal (MW-HT) synthesis of functional oxides with special emphasis on visible-light-driven photocatalysts for wastewater treatment and water oxidation catalysts (WOCs).

**HT methodology:** As the underlying reaction mechanisms of HT processes still leave plenty of room for exploration, we have systematically monitored the formation processes of Bi-, W- and Mo-containing oxide materials with complementary *in situ* methods. New morphology-mechanism relations for Bi/W/Mo oxide wastewater treatment catalysts were, for example, elucidated with *in situ* X-ray absorption spectroscopy and energy dispersive X-ray diffraction methods [1].

**HT-approaches to sensor materials:** We furthermore applied the above expertise on the exploration of new Bi-containing humidity sensors via HT preparation of bismuth phosphates. In parallel, hexagonal W/Mo-oxides are hydrothermally tuned for gas sensor applications.

**MW-HT strategies:** Defect spinel-type  $\gamma\text{-Ga}_2\text{O}_3$  is a promising matrix material for catalytic metal centers, but implementation of copper into nanostructured  $\gamma\text{-Ga}_2\text{O}_3$  remains challenging. We thus developed flexible MW-HT approaches to nanoscale spinel-type  $\gamma\text{-Ga}_2\text{O}_3\text{:Cu}^{2+}$  (Fig. 1, left) and to  $\text{ZnGa}_2\text{O}_4\text{:Cu}^{2+}$  materials. The latter were compared to MW-HT synthesized Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts for methanol synthesis in order to investigate the role of matrix effects in the catalytic performance [2].

**HT parameters in WOC development:** The above MW-HT strategy furthermore permits exclusive access to new spinel-type Co/Mn/Ga-WOCs (Fig. 1, right) with particle sizes in the 15 - 40 nm range and BET surface areas around 70 m<sup>2</sup> g<sup>-1</sup> [3]. Their visible-light-driven photocatalytic performance points to an interaction of Co and Mn centers within the gallium spinel host lattice which was investigated with a wide variety of analytical methods. Moreover, the influence of HT methodology and parameters on the performance optimization of Co/Mn-oxide catalysts is discussed in detail.

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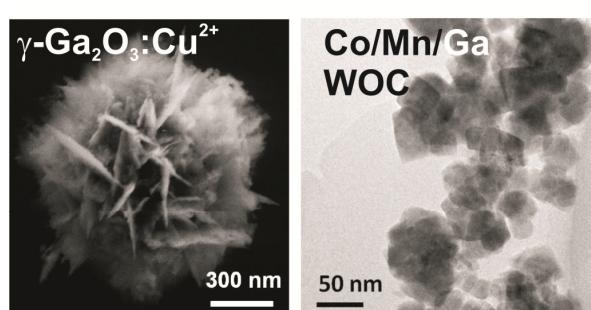


Fig. 1. MW-HT synthesized gallium oxide spinel materials.

## 12-3: Construction of a Series of Coordination Polymers Based on Tetracarboxylate Ligand: Synthesis, Structure, Gas Adsorption and Magnetic Properties

Bing Zheng<sup>1</sup>, Jiahuan Luo<sup>1</sup>, Qisheng Huo<sup>1</sup> and Yunling Liu<sup>1\*</sup>

<sup>1</sup>State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012

In recent years, the design and construction of coordination polymers have attracted increasing attention, and numerable coordination polymers have been reported not only because of their intriguing variety of architectures and topologies, but also for their properties of highly porosity and enormous internal surface areas. These properties have potential applications in clean energy, such as storage media for methane, hydrogen, and acetylene, or as absorbents or membrane fillers in separation and purifications of various chemicals. Besides the mentioned above, the coordination polymers can be also used in catalysis, magnetism, luminosity, and chemical sensors [1]. To date, impressive progress has been made on the theoretical forecasts and practical approaches of controlled syntheses of coordination polymers.

Our group have been focusing on exploring alkyne functioned tetracarboxylate acid ligands and using them to build new coordination polymers [2]. H<sub>4</sub>EBDC, as a tetracarboxylate acid having alkyne functionality, has also been used by other groups to constructed coordination polymers. Though there have been several 3D coordination polymers reported, most of them present **nbo** networks based on [Cu<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub>] or [Zn<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub>] paddle wheel units. To speed up the discovery of coordination polymers based on the tetracarboxylate ligand with other different inorganic building units, and enrich examples of H<sub>4</sub>EBDC ligand for the design of novel networks, we reported a series of new coordination compounds with intriguing structures based on H<sub>4</sub>EBDC (Fig. 1). Single crystal analyses reveal that their structures are constructed by different inorganic SBUs, containing single metal ion, binuclear, trinuclear and metal chains. Interestingly, the H<sub>4</sub>EBDC ligand in some compounds is distorted and forms 4- or 3- tetrahedral connected node, these are different from previously reported linkers which served as square-planar 4-connected nodes. Network topologies of these coordination polymers are examined. In addition, the gas adsorption, separation, and magnetic properties of the coordination polymers have also been investigated in the solid state.

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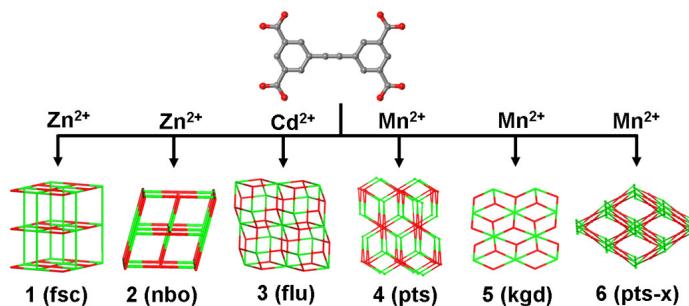


Fig. 1. Structural representations of coordination polymers based on tetracarboxylate ligand.

## **12-4: Novel Solution Processing and *In situ* Surface Modification of Metal Oxide Nanomaterials**

K. Namratha and K. Byrappa\*

Center for Materials Science, University of Mysore, P.B. No. 21,

NCHS Bldg., Manasagangotri, Mysore – 570006, India

\*Corresponding author Email: kbyrappa@gmail.com

Metal oxides like  $\text{TiO}_2$  and  $\text{ZnO}$  have captured the attention of researchers in the past one decade owing to their multi-functional application potential in the modern technology. Major breakthrough occurred during 1970s when Fujishima and Honda (1972) reported electrochemical photolysis of water at semiconductor electrode ( $\text{TiO}_2$ ).  $\text{TiO}_2$  has several other specific applications and the common ones are as photocatalyst, dye sensitized solar cells, ceramic glazes, sun screen and UV absorbers, also as electronic data storage, and so on. Similarly, zinc oxide is well-known as *n*-type wide band gap semiconductor ( $\Delta E = 3.37 \text{ eV}$  at 300 K) with a large exciton energy of 60 meV and thermal energy of 27 meV. Due to bright UV-luminescence,  $\text{ZnO}$  is a perspective material for the manufacture of UV-light emitting diodes, UV lasers operating at room temperature and display devices. Moreover,  $\text{ZnO}$  quantum dots with very low toxicity, high photostability, biofriendly and biodegradable have been demonstrated.

*In situ* surface modification of  $\text{TiO}_2$  and  $\text{ZnO}$  metal oxide particles has been carried out under hydrothermal and solvothermal conditions within a wide range of temperature and pressure ( $T = 150$  to  $400^\circ\text{C}$ ;  $P = \text{up to } 20 \text{ MPa}$ ). The influence of the surfactant and selective doping with active metal ions on the crystal size, morphology, and photocatalytic activity of  $\text{TiO}_2$  and  $\text{ZnO}$  particles has been carried out. A “good” synthesis protocol has to provide control over the crystal size, morphology, and size distribution. Further requirements are the control over the surface properties, because these parameters are important with respect to the use of nanoparticles as building blocks for the assembly into larger nanostructures, high crystallinity and phase purity, high yield and general applicability of the synthesis methodology. Novel solution routes covering Hydrothermal, Solvothermal and Supercritical fluids are gaining popularity in the recent years because of several advantages related to the control over the diffusion kinetics, high quality of the products and phase purity. The recent trends in hydrothermal and solvothermal syntheses have shown much lower experimental pressure and temperature requirements even for high temperature and high melting ceramics compounds. Capping agents nowadays play a very important role in novel advanced materials for altering the surface chemistry in order to enhance the reaction kinetics and in turn modify the size and shape of nanocrystals or bulk crystals. The selective doping of the metal oxides also has a great influence on the morphology, size and properties of the materials. In this paper, the authors discuss the role of surface modifiers, and selective doping on the control of size, morphology and bandgap of the metal oxides in general with some specific examples. A systematic characterization of the product has been carried out using powder XRD, FTIR, TGA, SEM/TEM, UV-Vis spectroscopy and Positron annihilation lifetime spectroscopy. Similarly the photocatalytic activity in these metal oxides has been studied. Tuning of the bandgap and the nanoporosity has been discussed with respect to the size, shape, dopant metals and the bandgap.

## **12-5: Hydrothermal Growth of Multifunctional YAG Single Crystals for Laser Applications: Teaching an Old Dog New Tricks**

Joseph W. Kolis<sup>1,2\*</sup>, Colin D. McMillen<sup>1,2</sup> Cheryl Moore<sup>1</sup>

<sup>1</sup>Department of Chemistry Clemson University Clemson SC 29634

<sup>2</sup>Center for Optical Materials Science and Engineering Technology, Clemson University Clemson SC 29634

The hydrothermal method is an excellent route to high quality single crystals. In particular, the use of aqueous solutions at temperatures between 400-650°C and 1-3 kbar pressure with appropriate mineralizers (e.g. OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, F) provides an excellent pathway to large single crystals of refractory metal oxides. [1] Since these oxides often have melting points in excess of several thousand degrees, classical melt based crystal growth methods such as Czochralski pulling is often problematic. Thus the hydrothermal growth method provides a very attractive alternative. One important application for high quality crystal growth of oxides is in the field of lasers and optics. As new compositions and configurations of single crystals are required for laser applications, alternative growth options are required for such new materials. Thus, the hydrothermal growth of YAG was reexamined after nearly 40 years of inactivity and met with promising new results. While the hydrothermal growth of YAG at 500 °C was previously met with slow growth rates or poor crystal quality, we found that growth at 600-630 °C yields good quality single crystals at rates of about 0.5 mm/side/week on (100) seeds.

In the current study, high quality transition metal and rare earth doped YAG have been grown. A particularly useful new result is the ability to grow high quality epitaxial layers of heterodoped materials on a YAG. The layers can range in thickness from 50 microns to many millimeters. We can grow multiple layers of YAG doped with a variety of different ions, where each layer has a specific optical functionality. Therefore single crystals can be grown with five or more optical functions all within the same laser crystal. We demonstrate some proof of concept designed growth experiments for various specific laser applications, including the growth of co-doped Ca<sup>2+</sup>,Cr<sup>4+</sup>,Nd:YAG for self Q-switching pulsed lasers, and the growth of Sm:YAG around Nd:YAG to potentially suppress amplified spontaneous emission in the laser cavity. [2] The interface quality of the substrate and the new growth was investigated and application of a very narrow thermal gradient at the early stages of growth has proven to greatly reduce optical scattering at the interface. The morphology of hydrothermally-grown YAG crystals is also discussed and several intermediate forms are occasionally observed. The growth, spectroscopy and potential applications of several of these multifunctional single crystals in laser devices is discussed.

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## 13-1: Hierarchical PbTiO<sub>3</sub> Nanostructures Grown by Self-Assembly of Nanocrystals during Hydrothermal Synthesis

Mari-Ann Einarsrud<sup>1\*</sup>, Per Martin Rørvik<sup>1</sup>, Guozhong Wang<sup>1</sup> and Tor Grande<sup>1</sup>

<sup>1</sup>Department of Materials Science and Engineering, Norwegian University of Science and Technology, NTNU, 7431 Trondheim, Norway

Nanorods and nanostructures of ferroelectric perovskites have recently been studied with increasing intensity due to their potential use in non-volatile ferroelectric random access memory, nano-electromechanical systems, energy-harvesting devices and advanced sensors [1]. This presentation describes hydrothermal synthesis of different hierarchical nanostructures of PbTiO<sub>3</sub> and discusses mechanisms for the particular growth of the nanostructures.

An amorphous lead titanate precursor mixed with sodium dodecylbenzenesulfonate surfactant was used during the hydrothermal synthesis. Novel bur-like hierarchical nanostructures of PbTiO<sub>3</sub> were formed without the use of substrates [2]. The bur-like nanostructures exhibit a microsphere core with an outer shell of nanorods. The nanorods were between 50 nm and 100 nm in diameter and from several hundreds nm up to 2 μm in length. The growth of the bur-like nanostructures is proposed to be a two-step process with agglomeration of PbTiO<sub>3</sub> nanoparticles in the first step, followed by the nanorod mesocrystal growth.

In the presence of SrTiO<sub>3</sub> substrates, hierarchical arrays of ferroelectric lead titanate (PbTiO<sub>3</sub>) nanorods were grown on the substrates [3], see Fig. 1. Changing the crystallographic orientation of the substrate resulted in a systematic change in the orientation of the nanorods. The nanorods had a square cross-section of 35–400 nm and were up to 5 μm long. The nanorods were shown to grow in the [001] direction by self-assembly of cube-shaped or faceted nanocrystals into anisometric mesocrystals, which ripen into nanorods. The domain structure of the nanorods was studied by TEM and the polarization of the heat-treated nanorods could be successively switched in the direction perpendicular to the nanorod axis by piezoresponse force spectroscopy. This control of the polarization in PbTiO<sub>3</sub> nanorods opens up possibilities of tailoring the ferroelectric properties and is therefore highly relevant for the use of ferroelectric nanorods in devices.

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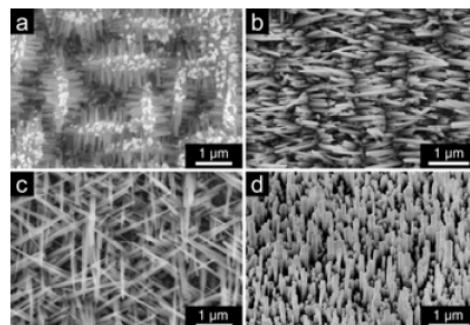


Fig. 1. SEM images of PbTiO<sub>3</sub> nanorods grown hydrothermally on single-crystalline SrTiO<sub>3</sub> substrates with different crystallographic directions. (a) (100)-orientation (b) (110)-orientation (c) (111)-orientation and (d) (100)-oriented SrTiO<sub>3</sub> substrate inserted after 6 h synthesis.

## 13-2: Atomic-Scale p-n Junctions of Manganese Perovskite Oxides from Hydrothermal Systems

Shouhua Feng

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry,  
Jilin University, Changchun 130012, P. R. China

\*Email: [shfeng@mail.jlu.edu.cn](mailto:shfeng@mail.jlu.edu.cn)

Perovskite oxides have exhibited high-temperature superconducting in copper oxides and colossal magnetoresistance (CMR) in manganites, basically originating from the mixed valence states of the transition-metals and particularly linked oxygen lattices through electron-electron and electron-lattice interactions. The perovskite oxides,  $\text{La}_{1-x-y}\text{Ca}_x\text{K}_y\text{MnO}_3$  with triplet mixed valence of  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$ - $\text{Mn}^{5+}$  may provide new models for microscopic electrical devices. Here we show the fast photovoltaic conversion and the rectification characteristic of p-n junctions in the perovskite oxides. The concept of the atomic-scale p-n junctions is therefore proposed based on the basic structural linkages of  $[\text{Mn}^{3+}\text{-O-Mn}^{4+}\text{-O-Mn}^{5+}]$ , where  $\text{Mn}^{3+}$  ( $t_{2g}^3 e_g^1$ ) and  $\text{Mn}^{5+}$  ( $t_{2g}^2 e_g^0$ ) in octahedral symmetry serve as a donor and an acceptor, respectively corresponding to the localized  $\text{Mn}^{4+}$  ( $t_{2g}^3 e_g^0$ ). The semiconducting perovskite oxides are compositionally tuneable from n-type to p-type semiconductors. This study reveals the extraordinary phenomena and features of the atomic-scale p-n junctions of the triplet mixed valence oxides on macroscopic scale. Important applications start to happen only when a single semiconductor crystal contains both n-type and p-type regions, consisting of a macroscopic p-n junction. The atomic-scale p-n junction, beyond the nano-scale, may give rise to entirely new atomic devices of semiconductors for potential applications to the atomic-effective processes on the photoelectric conversion and room temperature superconductivity as well.

### 13-3: Facile Synthesis of Au@TiO<sub>2</sub> Core-shell Hollow Spheres for Dye-sensitized Solar Cells

Jiang Du<sup>3</sup>, Jian Qi<sup>2</sup>, Dan Wang<sup>1\*</sup>, Zhiyong Tang<sup>2\*</sup>

<sup>1</sup>State Key Laboratory of Multi-phase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, P. R. China

<sup>2</sup>Laboratory for Nanomaterials, National Center for Nanoscience and Technology, Beijing, 100190, P. R. China.

<sup>3</sup>Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States

Herein we report facile synthesis of Au@TiO<sub>2</sub> hollow submicrospheres with well-defined hollow structures by controllably hydrolyzing TiF<sub>4</sub> in an Au nanoparticle solution under hydrothermal conditions (Fig. 1). The Au@TiO<sub>2</sub> hollow submicrospheres were synthesized using a modification of the novel synthetic work done by Zeng's group[1]. An important improvement is the use of a water-ethanol system rather than pure water as the reaction medium. In our system, the well-defined hollow submicrospheres are easily obtained in the presence of ethanol. Ethanol is believed to accelerate both the formation process of amorphous Au@TiO<sub>2</sub> solid microspheres as well as the subsequent Ostwald ripening process. Meanwhile, both the size and the shell thickness of Au@TiO<sub>2</sub> were easily adjusted by changing the amount of TiF<sub>4</sub> in reaction mixture.

Notably, when these Au@TiO<sub>2</sub> hollow submicrospheres are used as the working electrodes for DSSCs, an obvious improvement in conversion efficiency is achieved compared to those solar cells based on TiO<sub>2</sub> hollow spheres or TiO<sub>2</sub> nanoparticles. In our system, Au@TiO<sub>2</sub> hollow submicrospheres achieve a remarkably higher efficiency of 8.13%.

For Au@TiO<sub>2</sub> hollow submicrospheres, the significant difference in both current density-voltage characteristics and the conversion efficiency are likely attributed to the following factors: (1) The open-circuit voltage is in proportion to the difference between the Fermi level and the Nernst potential of the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox pair;[2] (2) a Schottky barrier is formed at the Au-TiO<sub>2</sub> metal-semiconductor interface;[3] (3) Au cores in the submicrospheres further increase the light absorption due to strong surface plasmon resonances (SPR);[4] and (4) the Au in the submicrospheres improves the conductivity of the electrolyte.

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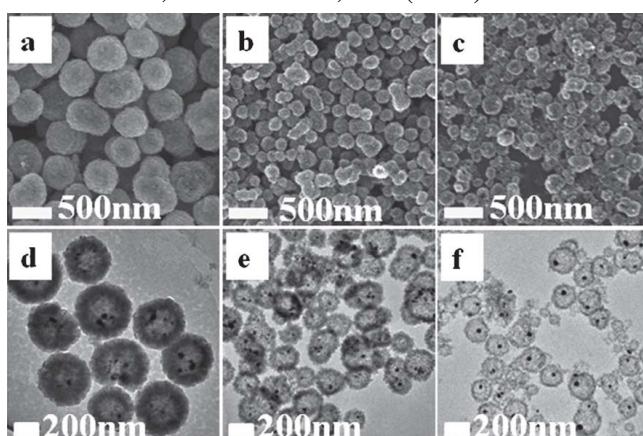


Fig. 1. SEM of Au@TiO<sub>2</sub> hollow submicrospheres with (a) thick shell, (b) medium-thickness shell, and (c) thin shell. (d), (e) and (f) are corresponding TEM images of (a), (b) and (c).

## **13-4: Recycling of carbon fibre composites in supercritical hydrothermal conditions**

C. Aymonier, A. Loppinet-Serani, M. Antal, A. Debeauvais, C. Morin

CNRS, Université de Bordeaux, ICMCB 87 av. du Dr. A. Schweitzer, 33608 Pessac, France  
aymonier@icmcb-bordeaux.cnrs.fr

Manufacturers are increasingly using carbon fibre composites instead of metal alloys to build their new products, for example aircraft manufacturers, because it is lighter and stronger.

Up to now, disposal of carbon fibre composites can be achieved through land filling, incineration (possible recovery of energy) or still grinding (recycling for compounding for example). Studies on carbon fibre recycling have been mainly carried out using thermal processes to recover the polymer resin as pyrolysis techniques. As an alternative, we are investigating a cleaner and more efficient way of recycling the carbon fibres in dissolving the polymer resin by solvolysis in supercritical fluids.

In this communication, we propose to present, first, the interest in using supercritical fluids and the principle of the recycling of carbon fibres by solvolysis of the polymer resin in these reaction media. We will discuss the results obtained on different kinds of carbon fibre composites in terms of polymer resin conversion but also of mechanical properties of the recycled fibres as a function of the process operating parameters [1]. A brief overview of the on-going French project will highlight the perspectives of development of this promising technology associated to the works focused on the process of carbon fibre recycling to form new products.

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### **13-5: Single-step Transformation of SrMoO<sub>4</sub> Particles from SrSO<sub>4</sub> Ore Under Alkaline Hydrothermal Conditions.**

J. Diaz-Algara<sup>1</sup>, J. C. Rendón-Angeles<sup>2</sup>, Z. Matamoros-Veloz<sup>3</sup>, K. Yanagisawa<sup>4</sup>, J. L. Rodriguez-Galicia<sup>2</sup> and J. M. Cobo-Rivera<sup>1</sup>.

<sup>1</sup>Institute of Engineering, Autonomous University of Baja California, Mexicali, Baja California 21280, México. joaquin.diaz.algara@uabc.edu.mx

<sup>2</sup>Research Institute of Advanced Studies of the National Polytechnic Institute, Saltillo Campus, Ramos Arizpe, 25900, Coahuila México.

<sup>3</sup>Technological Institute of Saltillo, Faculty of Metal-Mechanics, Saltillo 25280, México.

<sup>4</sup>Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Kochi 780-8073.

The transformation of SrSO<sub>4</sub> mineral powder with three different sizes (38 - 180 µm) into Scheelite structure SrMoO<sub>4</sub> powders was investigated by conventional hydrothermal treatments, under static and stirring conditions (50 rpm), at temperatures in the range of 150 – 250 °C for several reaction intervals (0.5 - 48 h). The complete transformation of SrSO<sub>4</sub> into SrMoO<sub>4</sub> was found to proceed at lower temperatures below 200 °C for 48 h in a 5 M NaOH solution without stirring, but this process was further accelerated when the autoclave was shacked during the treatment at a speed of 50 rpm. This lead to produce Scheelite structure SrMoO<sub>4</sub> powders without byproducts at 200 °C for a short reaction interval as 6 h. The produced SrMoO<sub>4</sub> particles had a particular morphology resembling octahedral by-pyramidal shape (Figure 1) and small particles size between 1 and 5 µm, these particles exhibited a marked agglomeration which proceeded at intermediate and final stage of the reaction, but the autoclave stirring markedly reduced the growth of bulky agglomerated SrMoO<sub>4</sub> particles. A coupled process that achieved the crystallization of SrMoO<sub>4</sub> particles involves the bulk dissolution of the SrSO<sub>4</sub> powder and the precipitation of SrMoO<sub>4</sub> in an alkaline solution (5 M NaOH) saturated with MoO<sub>4</sub><sup>2-</sup> ions. Kinetic analyses depicted that the activation energy required for the formation of the SrMoO<sub>4</sub> octahedral shaped particles was of 26.70 kJmol<sup>-1</sup> maintaining the system without agitation. In contrast, the activation energy was further decreased (9.80 kJmol<sup>-1</sup>) when the transformation was conducted under stirring conditions. These differences are discussed on terms of the convection conditions that are promoted during the hydrothermal treatment.

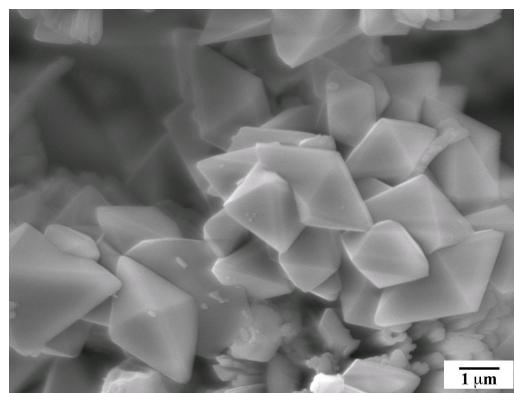


Figure 1 FE-SEM micrograph of SrMoO<sub>4</sub> powders particles prepared by the transformation of SrSO<sub>4</sub> powders under hydrothermal conditions at 200 °C for 6 h in NaOH 5 M with a Mo/Sr molar ratio of 1.5.

## 13-6: Hydrothermal Synthesis and Characterisation of New Rare-Earth Orthochromite Perovskites $\text{La}_{1-x}\text{Sm}_x\text{CrO}_3$

Luke M. Daniels<sup>1\*</sup>, Richard I. Walton<sup>1</sup>, Martin R. Lees<sup>2</sup>, Reza J. Kashtiban<sup>2</sup>, Jeremy Sloan<sup>2</sup>, Jens Kreisel<sup>3</sup> and Mads Weber<sup>2,3</sup>

<sup>1</sup>Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK;

<sup>2</sup>Department of Physics, University of Warwick, Coventry, CV4 7AL, UK;

<sup>3</sup>Materials Science, CRP Gabriel Lippmann, 41, Rue du Brill, 4422 Belvaux, Luxembourg

Rare-earth orthochromite perovskites  $RCrO_3$  are receiving renewed interest due to their potential for a multitude of applications. The materials are p-type semi-conductors and some of them are multiferroic; properties useful for electronic and sensor applications. Their high electrical conductivity and stability under reducing conditions makes them ideal for solid oxide fuel cell interconnect materials, whilst some do Albertinped chromites display catalytic properties suitable for the oxidation of hydrocarbons [1-3].

Previously, lanthanum chromite has been synthesised through conventional solid state routes, involving numerous cycles of heating to temperatures well above 1000 °C and grinding to ensure homogeneity of the product. Single-step hydrothermal synthesis of an entire range of rare-earth chromites was not reported until recently [4]. A new mixed rare-earth orthochromite series,  $\text{La}_{1-x}\text{Sm}_x\text{CrO}_3$ , is reported here along with structural and property investigation.

A one step high-pressure hydrothermal treatment of amorphous mixed-metal hydroxide has yielded polycrystalline solid solutions of  $\text{La}_{1-x}\text{Sm}_x\text{CrO}_3$  ( $x = 0, 0.125, 0.25, 0.375, 0.5, 0.75$  and 1.0) never before reported in the literature. Successful formation of the materials requires heating in solution at temperatures above 370 °C under pressures of 200 bar for 48 h. Such syntheses were performed using hydrothermal vessels constructed from Inconnel.

Structural studies were undertaken using high-resolution powder X-ray diffraction and low-temperature Raman scattering. The distorted perovskite structures were resolved and are described by the orthorhombic space group *Pnma*. The structure was found to depend greatly upon composition and average ionic radius of the rare-earths. Unit cell volumes along with Cr—O—Cr bond angles decrease monotonically across the series with increasing samarium content, consistent with the presence of the smaller lanthanide ion. Transmission electron microscopy reveals the formation of highly crystalline particles with dendritic-type morphologies, unlike those of previously hydrothermally synthesised rare-earth chromites [4]. Raman spectroscopy confirms the formation of solid solutions and was used to evidence the degree of structural distortion. Phonon modes identified as octahedra tilt ( $A_g$ ) modes were observed to soften as structural distortion and samarium content decreased. Magnetometry as a function of temperature reveals the onset of low temperature antiferromagnetic behaviour with Néel temperatures that scale linearly with unit cell volume and structural distortion.

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## 13-7: New Applications of Hydrothermal Reactions in Creating Abnormal Materials Properties

Guangshe Li\* and Liping Li

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou  
350002, P. R. China

Hydrothermal synthesis of oxide materials to create new properties represents a forefront approach to enrich the technological uses of nanomaterials. Using this approach, one is able to easily control the chemical compositions, structures, morphologies, and even the defects of oxide nano-materials to create novel performance. This work will address the recent progress of our group in this area, according to five catalogues: (i) preparation of oxide nanoparticles that converts the conventional red phosphors to the white ones; (ii) creation of ferromagnetism from non-magnetic materials; (iii) stabilization of meta-stable phases with a giant-dielectric constant, (iv) assembly of simple oxide nanoparticles of superior catalytic performance, and [v] exposure of some specific facets that tunes the inert materials (e.g., brookite  $\text{TiO}_2$ ) from inert to highly active. All these achievements are based on the understandings of the unique hydrothermal reactions, as demonstrated by highlights of a variety of relevant synthetic strategies and examples in preparing new nanosized-oxides never accessible by traditional preparation methods.

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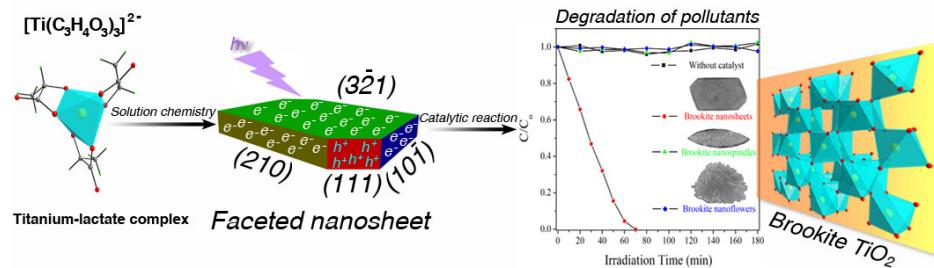


Fig. 1. An example that shows the applications of hydrothermal reactions to tune the inert brookite to highly active.

## **13-8: Synthesis and Development of Li-Cd nano Ferrites by Citrate Precursor Gel Method for Multilayers Chip Inductors Applications**

D. Ravinder<sup>1</sup>, K. Rama Krishna<sup>2</sup>, C. Ravindarnathgupta<sup>3</sup>

<sup>1</sup>Department of Physics, Nizam College, Osmania University,  
Hyderabad – 500 004.A.P. India

<sup>2</sup>Department of Physics, Malla Reddy College of Engineering & Technology,  
Secunderabad – 500 014. A.P. India.

<sup>3</sup>Department of Physics, Govt. Polytechnic, Nizamabad-503 002. A.P. India

A novel gel auto-combustion method was used to synthesize Li-Cd ferrite powders with compositions of  $\text{Li}_{0.5-X}/2\text{CdXFe}_{2.5-X}/2\text{O}_4$  (where  $x=0, 0.2, 0.4, 0.6, 0.8\&1$ ). X-ray diffraction results showed that the dried gels, synthesized from metal nitrates and citric acid, transformed directly into nano-sized ferrite particles of particle size in the range of 40 nm after an autocombustion process in air. The synthesized powders exhibited high-sintering activity, and can be sintered at temperature 600 °C. The low-temperature sintered Li-Cd ferrites prepared possess good electromagnetic properties, as well as fine-grained microstructures, making them become good materials for multilayer chip inductors with high-performance and low-cost.

## 14-1: Hydrothermal Synthesis of CeO<sub>2</sub> with Hollow Architecture

Ranbo Yu<sup>\*</sup>, Pengfei Xu, Xiaodan Yang, Lingbo Zong, Jiali Wang

Department of Physical Chemistry, University of Science and Technology Beijing, Beijing  
100083, China

CeO<sub>2</sub> has earned intensive interest in the past decade due to its vital role in emerging technologies for environmental and energy-related applications. With the fluorite-type structure and cycling easily between reduced and oxidized states (Ce<sup>3+</sup> and Ce<sup>4+</sup>) it shows superior chemical and physical stability, high oxygen mobility, and high oxygen vacancy concentrations has been probed for many different applications in a variety of fields, such as active component of three-way catalysts (TWC) [1], oxygen ion conductors in solid oxide fuel cells [2], polishing agents for chemical mechanical planarization (CMP) process [3], and ultraviolet (UV) blocking materials in UV shielding [4]. Recently, nanostructural CeO<sub>2</sub> or CeO<sub>2</sub>-based compounds with hollow architectures have attracted special attention due to the improvements in the stable self-supported microstructure, specific surface area to volume ratio, redox properties, and transport properties with respect to condensed bulk materials [5-7]. Although various nano-sized CeO<sub>2</sub> have been obtained, to synthesize CeO<sub>2</sub> with stable large specific surface area is still a big challenge.

In the present work, pure and cation-doped CeO<sub>2</sub> with hollow architectures including single/multi-shelled microspheres have been hydrothermally synthesized. By using small organic species as the template, hollow microspheres of pure and cation-doped CeO<sub>2</sub> were obtained in a low-temperature hydrothermal process as well as a subsequent calcination. BET measurement indicated that the as-synthesized microspheres possessed pretty high specific surface areas and multiple pore systems. Although the doping content of the cations was pretty low, it made these porous microspheres showing much improved oxygen storage capacity (OSC). The CeO<sub>2</sub> microsphere might be a promising catalyst for selective CO oxidation.

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## 14-2: Application of Hydro- and Solvo-Thermally Processed Ceramic Nanoparticles for OTN-NIR Biomedical Imaging

Kohei SOGA<sup>1, 2\*</sup>

<sup>1</sup>Department of Materials Science and Technology, Tokyo University of Science,  
2641 Yamazaki, Noda, Chiba 278-8510, Japan

<sup>2</sup>Center for Technologies against Cancer, Tokyo University of Science,  
2669 Yamazaki, Noda, Chiba 278-0022, Japan  
(mail@ksoga.com)

Over-1000-nm (OTN) near infrared (NIR) wavelength range in 1000-1700 nm has been known to be a "biological window," where the both tails of scattering and infrared absorption decrease to form a valley in optical loss spectra of biological objects. However, most of the currently used wavelengths for fluorescence bioimaging (FBI) are limited up to 1000 nm due to the use of Si-CCD, while InGaAs CCD has become popular in the past several years to image in the 1000-1700 nm wavelength range. Rare-earth doped ceramic are known to emit efficient luminescence in the OTN-NIR range. For example, Nd<sup>3+</sup> doped in yttrium aluminum garnet (YAG) for Nd:YAG laser can emit efficient 1064-nm OTN-NIR fluorescence under 800-nm excitation. Er<sup>3+</sup> doped in silicate glass can emit efficient 1550-nm OTN-NIR emission under 980-nm excitation for the signal amplification in optical fiber communication. By making those ceramics as nanoparticles, rare-earth doped ceramic nanophosphors (RED-CNP), such as Y<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, YPO<sub>4</sub>, YVO<sub>4</sub>, NaYF<sub>4</sub> or LaOCl nanoparticles doped with Er, Ho, Nd or Tm, can be good candidates of the luminescent agents for the OTN-NIR FBI.

The characteristics of the RED-CNP to fulfill the requirements as a bioimaging probe are controlled size, dispersion stability in ionic solutions and avoided non-specific interaction with non-targeting substances. The size must be between 10-500 nm with homogeneity. If the size is less than 10 nm, one cannot control the optical property by selecting a ceramic host. The doped rare-earth ions are too strongly affected by the electric fields from surrounding ions or molecules in the solution to quench the NIR emission. If the size is more than 500 nm, the particles settle down in a solution with any surface modification. The homogeneity of the size is important to guarantee the same luminescence intensity to each particle. Normally, ceramic particles with a size between 10 and 500 nm can be mono-dispersed in pure water by the electrostatic repulsion due to their surface charge. However, biological or physiological conditions are always ionic solutions. Ionic strength of physiological saline is 0.15 mol/L. Under such ionic condition, because of the attraction of the ions in the solution, the particles lose their surface charge and form agglomerates with several hundred nm size to decrease the surface energy. For keeping the particles mono-dispersed in ionic solution, surface modification by a hydrophilic polymer is effective. The motion of the polymers give rise steric repulsions among the nanoparticles in ionic solutions. The polymer of course must be a biocompatible one.

For fabricating such size-controlled and surface modified ceramic nanoparticles, hydro- or solvo-thermal processes are useful. In the present paper, the author will discuss the application of the hydro- and solvo-thermal processes for fabricating the RED-CNP as OTN-NIR FBI probes by comparing them with other processes for fabricating RED-CNP, such as homogeneous precipitation or a core-shell process. The paper will also cover the device development and some demonstrative works for achieving the OTN-NIR FBI [1,2].

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### 14-3: Exploration of New Inorganic SHG Materials based on Metal Iodates

Jiang-Gao Mao\*, Chuan-Fu Sun, Bing-Ping Yang and Ting Hu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China (mjj@fjirsm.ac.cn)

The search of new second-order nonlinear optical (NLO) materials (or SHG materials) is of current interest and great importance owing to their applications in photonic technologies [1]. It is reported that systems contain a lone pair cation such as I(V) are apt to form non-centrosymmetric structures (NCS) with good second-order NLO properties [2]. In recent year, we have been exploring new NLO materials based on metal iodates by the combination of two types of NLO active building units such as lone pair cation, octahedrally coordinated cation with  $d^0$  electronic configuration, and etc [3-4].

By the combination of octahedrally coordinated cation with  $d^0$  electronic configuration such as  $\text{Nb}^{5+}$  or  $\text{V}^{5+}$  and lone pair containing iodate anion, three new SHG materials, namely,  $\text{BaNbO}(\text{IO}_3)_5$ ,  $\text{NaVO}_2(\text{IO}_3)_2(\text{H}_2\text{O})_2$ , and  $\text{K}(\text{VO})_2\text{O}_2(\text{IO}_3)_3$ , were prepared. Their anionic structures feature 0D  $[\text{NbO}(\text{IO}_3)_5]^-$ , 1D helical chain of  $[(\text{VO}_2)(\text{IO}_3)_2]^-$ , and 1D chain of  $[(\text{VO})_2\text{O}_2(\text{IO}_3)_3]^-$ , respectively. Their SHG responses are measured to be  $14 \times \text{KDP}$  ( $\text{KH}_2\text{PO}_4$ ),  $20 \times \text{KDP}$  and  $3.6 \times \text{KTP}$  ( $\text{KTiO}(\text{PO}_4)$ ), respectively. These three polar materials are phase-matchable and also have relatively high thermal stability.

A serial of noncentrosymmetric (NCS) mixed metal iodates, namely,  $\text{Ln}_3\text{Pb}_3(\text{IO}_3)_{13}(\mu\text{-O})$  ( $\text{Ln} = \text{La, Ce, Pr, Nd}$ ), have been synthesized. They exhibit a three-dimensional network that consists of  $\text{LnO}_9$  polyhedra that are connected by asymmetric  $\text{IO}_3$  group with the  $\text{Pb}^{2+}$  inserted into the voids of the thus formed network. La, Pr and Nd compounds display SHG responses of  $2 \times$ ,  $1 \times$  and  $0.8 \times \text{KDP}$ , respectively. By a similar method,  $\text{PbPt}(\text{IO}_3)_6(\text{H}_2\text{O})$  with a large SHG response of  $8 \times \text{KDP}$  has also also prepared.

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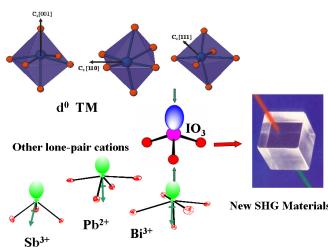


Fig. 1. Two synthetic routes for new SHG materials based on metal iodates.

## **14-4: Organics Assisted Selectively Doped and Codoped ZnO Nanoparticles by Hydrothermal and Solvothermal Processes for Enhancing Biological Activities**

**K. Namratha and K. Byrappa\***

Center for Materials Science, University with Potential for Excellence Building  
University of Mysore, P.B. No. 21, Manasagangothri, Mysore – 570006, India

\*Corresponding author: kbyrappa@gmail.com

ZnO is a versatile semiconductor having excellent applications towards modern technology owing to their unique properties. ZnO having a wide band gap of 3.37 eV and large exciton energy 60meV. ZnO is considered as a green material for their non-toxic, biodegradable, bio-safe and biocompatible nature leading to several biomedical and environmental applications. Over the past one decade the interest in the synthesis of ZnO nanocrystals has multiplied exponentially. Several synthesis methods are being employed. However, hydrothermal and solvothermal methods are very popular owing to a controlled diffusion, and high quality of the products. The authors have carried out the synthesis of ZnO nanocrystals under mild hydrothermal and solvothermal conditions. A variety of both aqueous and nonaqueous solvents were used as solvents, and *in situ* surface modification under these hydrothermal and solvothermal conditions was carried out using surface modifiers. The *in situ* surface modification has resulted in obtaining desired surface chemistry to the particles, and controls the size, shape and dispersion of the particles in various solvents. Several dopants and co-dopants were used selectively to alter the physico-chemical characteristics of these nanoparticles. The experiments were carried out in the temperature range 150 – 240°C and pressure was autogenous. The experimental products were freeze-dried. A systematic characterization using powder XRD, FTIR, UV-VIS, SEM, BET surface area, particle size distribution was carried out, and the results were correlated with the experimental conditions, and the raw materials. The bandgap was calculated using the UV-Vis spectroscopic technique.

The cytotoxic and genotoxic impacts of nanoparticles on the root tip cells of *Allium cepa*, and antioxidant property of these ZnO nanoparticles have been investigated. Similarly, the free radical scavenging capacity was investigated by using DPPH assay. DPPH (1,1diphenyl -2-picryl-hydrazyl) is a stable free radical and is frequently used to evaluate the effectiveness of antioxidants. The hydroxyl radical (·OH) scavenging activity of ZnO nanoparticles was established by a simple photometric system *in-vitro*. The free radical- and hydroxyl radical scavenging activity of the ZnO nanoparticles was studied for size and dose dependency. Novel nanoparticle antioxidants having significant free-radical scavenging activity with neuroprotective, anti-inflammatory properties can find potential therapeutic applications. The results of these biological studies are compared with the bandgap, particle size, and morphology of the products.

## 14-5: Controllable Synthesis and Zn<sup>2+</sup> Adsorption of $\gamma$ -MnO<sub>2</sub> Nanostructures<sup>#</sup>

C.X. Liu and L. Xiang\*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Manganese dioxides (MnO<sub>2</sub>) were effective sorbents for cations such as Zn<sup>2+</sup>, Pb<sup>2+</sup>, Li<sup>+</sup>, etc., owing to their porous structures and rich adsorption sites. The adsorption of Zn<sup>2+</sup> by  $\gamma$ -MnO<sub>2</sub> was studied by some researchers with the aims of improving the efficiency of Zn/MnO<sub>2</sub> batteries or Zn recovering from the spent batteries. The former work showed that OH<sup>-</sup> was liable to be formed on the hydrous  $\gamma$ -MnO<sub>2</sub> surface and Zn<sup>2+</sup> was usually adsorbed by the interactions between the hydrous Zn<sup>2+</sup> and MnO<sub>6</sub> units. But most of the former work was limited in dilute solutions containing 10<sup>-4</sup>-10<sup>-3</sup> mol.L<sup>-1</sup> Zn<sup>2+</sup> and focused mainly on the influence of the process parameters (time, pH, ionic strength and temperature, etc.) on the adsorption of Zn<sup>2+</sup> by  $\gamma$ -MnO<sub>2</sub>, little work was reported on the influence of  $\gamma$ -MnO<sub>2</sub> structures on the adsorption of Zn<sup>2+</sup> in concentrated Zn<sup>2+</sup> systems. Herein, using 0.01-1mol.L<sup>-1</sup> Zn<sup>2+</sup> solutions as the raw materials, Zn<sup>2+</sup> adsorption on  $\gamma$ -MnO<sub>2</sub> nanostructures was studied.  $\gamma$ -MnO<sub>2</sub> nanostructures with varying surface properties were formed by oxidation of Mn<sup>2+</sup> with Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> at 90°C for 2.0h.  $\gamma$ -MnO<sub>2</sub> (M-1) formed in the case of initial pH 1.0-1.5 showed a gradual morphology change from the assembled plates (L: 200-300nm) to the nano-rods (L: 1-2μm, D: 30-100 nm), while the morphology of  $\gamma$ -MnO<sub>2</sub> (M-2) formed in the case of initial pH 8.5-9.0 was converted from the hexagonal micro-particles (D: 1μm) to agglomerated nano-particles (D: 20-50nm). Compared with M-2, M-1 was more liable to absorb OH<sup>-</sup> and Zn<sup>2+</sup> ions even though the specific surface areas (BET) of M-1 (14.1m<sup>2</sup>/g) was smaller than that of M-2 (39.4m<sup>2</sup>/g). The different adsorption behaviors of Zn<sup>2+</sup> on  $\gamma$ -MnO<sub>2</sub> nanostructures were considered to be connected mainly with the complexation and electrostatic interaction between the hydrated Zn<sup>2+</sup> and  $\gamma$ -MnO<sub>2</sub>.

**Key words:**  $\gamma$ -MnO<sub>2</sub> nanostructures, adsorption of Zn<sup>2+</sup>, surface

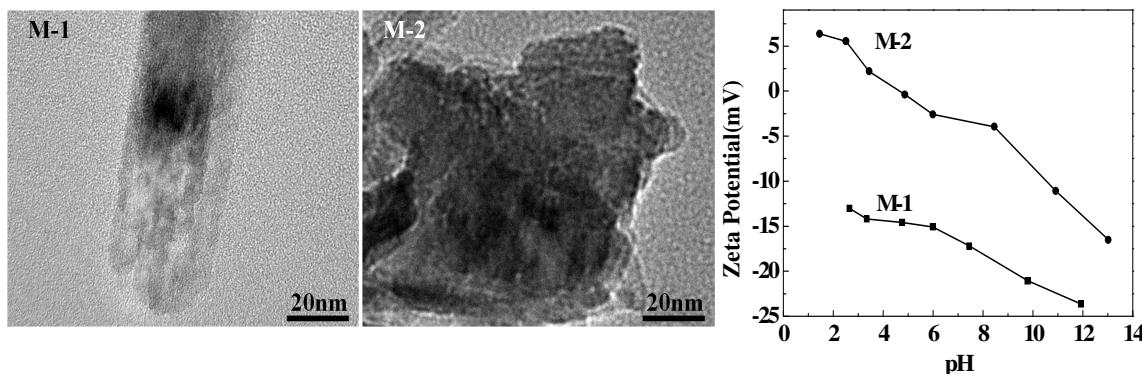


Fig.1. TEM images and zeta potential-pH curves of  $\gamma$ -MnO<sub>2</sub>

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\*Corresponding author: xianglan@mail.tsinghua.edu.cn

## 14-6: Synthesis of ZnO nano-whiskers in the presence of SDNS<sup>#</sup>

J. Wang, C.X. Liu and L. Xiang\*

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

ZnO nano-whiskers with small diameter can be used in many fields as photocatalysis, UV-lasers, field emission and solar cells owing to their one-dimensional morphologies and large specific surface areas. It was reported that ZnO nano-whiskers with a diameter of 10-300 nm and a length of 1-20  $\mu\text{m}$  can be formed by treating the mixture of 0.1-10 mmol·L<sup>-1</sup> Zn salt ( $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{Ac})_2$  or  $\text{ZnCl}_2$ ) and 0.1-10 mmol·L<sup>-1</sup> hexamethylenetetramine(HMTA) at 60-95 °C for 6-48h[1], thus the poor efficiency restricted their further application. Recently the formation of one-dimensional ZnO from  $\varepsilon\text{-Zn(OH)}_2$  precursor has attracted more and more attention owing to the simplicity and high efficiency of the process. It was reported that ZnO nanorods with a length of 1-15  $\mu\text{m}$  and a diameter of 100–1000 nm can be produced by this method[2] and the presence of sodium dodecyl sulfate (SDS) can reduce the diameter to 80-150 nm[3]. Herein, a facile SDSN-assisted solution method was developed to synthesize ZnO nano-whiskers with a smaller diameter from  $\varepsilon\text{-Zn(OH)}_2$  precursor in NaOH solution, and the effects of SDNS and temperature on the formation of ZnO nano-whiskers, especially on the diameter were investigated. It was revealed that the slow release of soluble zinc(II) from  $\varepsilon\text{-Zn(OH)}_2$  in the presence of SDSN at low temperature (60 °C) favored the anisotropic growth and inhibited the radial growth of one dimensional ZnO, leading to the formation of ZnO nano-whiskers with a diameter of 20-80 nm and a length of 0.5-5  $\mu\text{m}$ . The enhanced photocatalytic activity of the synthesized nanowhiskers compared to commercial ZnO on the photodegradation of RhB was also demonstrated.

**Key words:** ZnO nano-whiskers, diameter control,  $\varepsilon\text{-Zn(OH)}_2$ , sodium dodecyl sulfonate

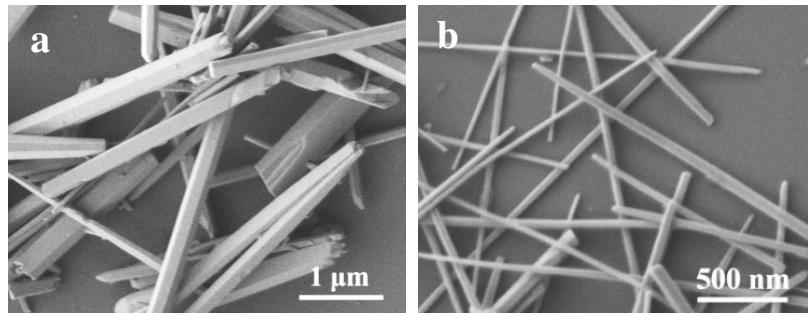


Fig.1. Morphology of ZnO nano-whiskers formed in the absence (a) and presence of SDSN (b)

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\*Corresponding author: xianglan@mail.tsinghua.edu.cn

## **15-1: Novel Structural Materials developed by CO<sub>2</sub> Sequestration of Mineral Silicates**

S. Gupta<sup>1\*</sup>, Q. Li<sup>1</sup>, L. Tang<sup>1</sup>, V. Atakan<sup>1#</sup>, and R.E. Riman<sup>1</sup>

<sup>1</sup>Dept. of Materials Science and Engineering, Rutgers University, Piscataway, NJ

\*Present Address: Dept. of Mechanical Engineering, University of North Dakota,  
Grand Forks, ND

#Present Address: Solidia Technologies, Piscataway, NJ

In this talk, we will present a detailed study about the different components of microstructure, and their correlation with mechanical properties of novel monolithics fabricated by hydrothermal processing of mineral silicates. FESEM and EDS studies showed that the microstructure of hydrothermally carbonated mineral silicates is composed of predominantly two regions: (a) SiO<sub>2</sub>-rich regions encapsulated by carbonate grains, for example CaCO<sub>3</sub>, which are formed after complete carbonation of fine mineral silicate grains (<4 µm), and (b) partially carbonated coarser acicular mineral silicate grains composed of an outer amorphous SiO<sub>2</sub>-rich first layer encapsulated by carbonate crystals. The cementitious property of these solids is due to a combination of mechanical and chemical bonds in the carbonate network. These solids have mechanical properties comparable to structural concrete and different dimension stones like limestone (sedimentary rock), marble (metamorphic rock), and granite (igneous). After a rigorous literature survey, we observed that the reported microstructure is also unique, and is not observed in, either carbonate based rocks, or conventional cementitious material like hydrated Portland Cement. Although in nature, numerous geological formations like sedimentary and metamorphic rocks are formed by carbonates [1]. These carbonate based rocks have adequate mechanical and physical properties for their usage in different applications like dimension stones, carved ornamental stones, and aggregates in concrete etc. [2]. Recently, carbonate based solids have also aroused intense attention due to their potential for CO<sub>2</sub> storage via carbonation of mineral silicates [3, 4]. Thus, there is a lot of potential for commercial usage of these novel monolithics. During the latter part of the talk, we will also demonstrate that by using the hydrothermally processed mineral silicates, it is possible to design and fabricate different types novel composites which can have similar, if not better, properties than high performance concrete. Finally, it is also speculated that novel damage resistant solids can also be designed by exploiting the presence of interfaces between different layers.

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## **15-2: Carbonate Concrete: A Hydrothermal technology for CO<sub>2</sub> Utilization and Construction**

R. E. Riman,<sup>1,\*</sup> S. Gupta,<sup>1,3</sup> Q. Li,<sup>1</sup> V. Atakan,<sup>2</sup> Ç. Vakifahmetoglu,<sup>1,4</sup> J. Azurdia,<sup>2</sup> J. Krishnan, M. A. Bitteto,<sup>1</sup> L. Tang,<sup>1</sup> J. Czerepinski,<sup>1</sup> Larry E. McCandlish,<sup>2</sup> and Nick Decristofaro<sup>2</sup>

<sup>1</sup>Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ USA

<sup>2</sup>Solidia Technologies Inc., Piscataway, NJ USA

<sup>3</sup>Presently at the University of North Dakota, Department of Mechanical Engineering, Grand Forks ND USA

<sup>4</sup>Presently at the Istanbul Kemerburgaz University, Department of Mechanical Engineering, İstanbul – Turkey

\*Corresponding author: [riman@rci.rutgers.edu](mailto:riman@rci.rutgers.edu), 848-445-4946 (v), 732-445-6264 (f)

### **Abstract**

Alternatives to Carbon Capture and Storage (CCS) are needed that can use captured CO<sub>2</sub> directly or convert it to valuable products, such as fuels, chemicals, plastics, or building materials. This paper will describe a breakthrough process invented and patented by Rutgers called gas-assisted reactive hydrothermal liquid phase densification (g-rHLPD). When CO<sub>2</sub> is incorporated into the hydrothermal liquid phase to react with synthetic and mineral silicates at temperatures below 100°C, carbonate-bound ceramics can be produced with outstanding properties. A processing paradigm and corresponding experimental results to validate the paradigm will be presented. In addition, structure-property relationships for the materials will be discussed along with third party assessments that demonstrate that both building and infrastructure materials can be manufactured that meet or exceed property specifications for a range of construction applications. At the same time, this process is green in terms of its carbon footprint and energy consumption. CO<sub>2</sub> mass balance computations suggest that use of mineral-based CaSiO<sub>3</sub> can yield a truly carbon-negative material that consumes a fraction of the energy required for cement or concrete processing. In addition, relative to Portland cement, even synthetic mineral silicates offer reduced energy and CO<sub>2</sub> emissions. Because of the outstanding commercial and environmental impact of this technology, Solidia Technologies was founded in 2007 as a Rutgers start-up to commercialize this technology. Progress towards commercialization and its potential impact on global CO<sub>2</sub> emissions and energy will be discussed. This presentation will also provide a perspective on the sustainability of carbonate concrete processing relative to that of stone, ceramic and Portland cement concrete.

## **15-3: Hydrothermal Technology for Ore Treatment and Metal Recovery**

Fathi Habashi

Department of Mining, Metallurgical, and Materials Engineering

Laval University, Quebec City, Canada

[Fathi.Habashi@arul.ulaval.ca](mailto:Fathi.Habashi@arul.ulaval.ca)

Pressure hydrometallurgy is nearly hundred and fifty years old. It is applied for leaching of ores and concentrates and for the precipitation of metals and oxides from leach solutions. The technology expanded gradually resulting in introducing new processes and new equipment. Hydrothermal oxidation of sulfide concentrates has the enormous advantage of producing elemental sulfur, hence solving the SO<sub>2</sub> and sulfuric acid problems associated with smelters. In the 1940's, the need for uranium to make an atomic bomb introduced many new technologies in extractive metallurgy among these was the hydrothermal leaching of certain Canadian uranium ores with sodium carbonate solution. In 1980 pressure hydrometallurgy replaced the pyrometallurgical process for zinc. A similar process was adopted recently for the treatment of nickel sulfide concentrates from deposits in the Canadian North. Precipitation of pure nickel and cobalt from aqueous solutions at high temperature and pressure has been successfully applied in Canada for over sixty years. An illustrated review will be given.

## **15-4: Hydrothermal Recovery of Zn and Pb from MSWI Bottom Ashes and APC Residues**

Amanda Günther, Alexander Beck and Karl Thomas Fehr

Department of Earth and Environmental Sciences, Section Mineralogy, Petrology and Geochemistry,  
Ludwig-Maximilians Universität München, Theresienstr. 41, 80333 Munich, Germany

The deposits of the future are the municipal wastes of today and will be the source of raw materials (urban mining). Therefore it is necessary to develop methods to extract all recoverable elements from the residuals that results by the incineration of solid municipal waste (MSWI). Products of incineration are bottom ashes and aerial pollution cleaning residues (APC), which contain appreciable amounts of Fe and non-iron (NE) metals as well. Pure metals like Fe, Al or Cu can be separated by physical methods but there are no attempts to extract NE metals which are incorporated in oxide or silicate mineral phases like Zn and Pb. In MSWI bottom ashes the Zn- and Pb-contents vary from 2000 ppm up to 7000 ppm and 1000 ppm up to 3500 ppm, respectively. In APC residues the Zn- and the Pb-contents are much higher covering a range from 5000 ppm up to 100000 ppm and from 2500 ppm up to 25000 ppm, respectively [1,2]. The aim of this study is to recover NE-metals like Zn and Pb by applying hydrothermal methods. The Zn- and Pb-content of the investigated MSWI ashes are 3700 ppm for Zn and 1830 ppm for Pb and of the investigated APC residues 42000 ppm for Zn and 26380 ppm for Pb as determined by X-Ray Fluorescence Analysis (XRF) [3]. The Zn- and Pb-bearing mineral phases were characterised by X-Ray Powder Diffraction (XRPD) and Electron Microprobe Analysis (EMPA). In MSWI bottom ashes Zn and Pb are mainly incorporated in silicates, e.g. Zn is incorporated in Hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ )-Melilite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) solid solution like corrosion product of refractories in a MSWI plant [4]. In APC residues this metals are built into Ca-aluminates. The leaching experiments were performed under hydrothermal conditions in the temperature range from 50°C up to 200°C, at pH 3 and 5 by using a solid-liquid ratio of 1:10 and solution kinetics were studied within a time range up to 300 min. The Zn- and Pb-concentrations of the eluates were analysed by AAS. The extraction of Zn and Pb of the MSWI bottom ashes and the APC residues strongly depends on the pH-value. The lower the pH-value the higher is the extraction rate. The kinetic studies reveal a high solution rate even at low temperatures and display a negligible influence of temperature. At these conditions 5% of total Zn and 2% of total Pb of APC residues and 3% of total Zn and 5% of total Pb of MSWI bottom ashes can be recovered.

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## **15-5: Single Step Transformation of Raw Minerals for Inorganic Compound Synthesis Under Hydrothermal Conditions.**

J. C. Rendón-Angeles<sup>1,2</sup>

<sup>1</sup>Research Institute of Advanced Studies of the National Polytechnic Institute, Saltillo Campus, Ramos Arizpe, 25900, Coahuila México. Email: jcarlos.rendon@cinvestav.edu.mx

Recently, the raw materials have attracted the attention of various research groups for preparing inorganic particles of a wide number of compounds in a more simple, economical and environmentally friendly ways. Therefore, much work has been directed towards the designing of single step reactions able for transforming mineral ores without preliminary purifying stage, which might lead to reduce energy consumption and producing a less pollutants. One route widely studied involves the mineral replacement reactions in hydrothermal environments. Much work has been conducted on this field by a great number of researches related to geochemistry, mineralogy, and chemistry areas, because this particular type of reactions take place primarily by dissolution-reprecipitation mechanism. Thus, processes such as cation exchange, chemical weathering, leaching, pseudomorphism, metasomatism and metamorphism are all linked by common features in which mineral ore or mineral assemblage is replaced by, or transformed into a more stable crystalline structural assemblage.

A different approach derived from the experimental work carried out on the pseudomorphic transformation of strontium inorganic species, namely  $\text{SrCO}_3$ ,  $\text{Sr}(\text{OH})_2$  or  $\text{SrF}_2$  from  $\text{SrSO}_4$  mineral ore under alkaline hydrothermal conditions, guide us to propose simple reaction systems for exploring the feasibility of preparing other strontium based compounds, such as  $\text{SrTiO}_3$  or  $\text{SrWO}_4$  oxides and inorganic  $\text{SrSn}(\text{OH})_6$ , with more potential industrial applications. Single step chemical reactions that achieve the transformation of mineral sulphate, either pure or impure species, are affected by several hydrothermal experimental parameters, namely the temperature and the pH of the hydrothermal media. The control of these parameters might achieve optimum conditions that decrease the mineral chemical stability, resulting in an improvement of the solubility of the mineral ore in contact with the solvent phase; in consequence, the kinetics of the crystallization process derived from the coupled dissolution-precipitation mechanism is further improved. In some of the studied cases, the morphological characteristics of the transformed product result from the disruption of the original shape and dimensions, indicating that the reaction proceeds pseudomorphically under hydrothermal conditions. The differences in the establishment of a local chemical equilibrium between the dissolution and solvent saturation in some cases yield fine powders as reaction product with different morphologies and sizes. Hence, the aspects related to the synthesis of some strontium based inorganic compounds by a single step reaction will be discussed in the present, based on the chemical stability and reactivity of sulphate ores in acid and alkaline hydrothermal fluids. In addition, the kinetic features related to some particular transformation reactions will be also addressed, in order to demonstrate the potential of application of the hydrothermal processing coupled with chemical processing for the preparing of single phase or solid solution ceramics compound using raw minerals as reagent precursors.

## 15-6: Hydrothermal Conversion of Brominated Compounds to Alcohols in Aqueous Amphipathic Solution without Catalysts

Toshitaka Funazukuri\*

Department of Applied Chemistry, Chuo University  
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551 Japan, tfunazo@kc.chuo-u.ac.jp

Chemical reactions consisting of hydrophobic and hydrophilic reactants and/or products are significantly affected by contacting conditions for the species in reactors. In such a case, one makes efforts to improve contacting or mixing solvent mixtures using amphipathic solvents, supercritical solvents, and/or surfactants.

Under hydrothermal conditions the mixtures of amphipathic solvents and water consist of two phases such as gas-liquid, and liquid-liquid phases, or a single phase, depending on the compositions as well as temperature and pressure. Using the interesting nature on mixtures of amphipathic solvents and water, high yields of desired products can selectively be obtained in the absence of catalysts. In the presentation conversions of various brominated compounds to alcohols were demonstrated in mixtures of amphipathic solvents and water under hydrothermal conditions.

The experimental apparatus and procedures were described in detail by Goto and Funazukuri as a poster presentation at this conference. The reaction was carried out in a small batch bomb-type reactor (3.6 mL), made of stainless steel tubing and two 1/2 inch Swagelok caps. Certain amounts of amphipathic solvents and brominated compounds were loaded in the reactor at room temperature, the air in it was purged by flowing argon, and then the reactor was plugged by the Swagelok cap. The amphipathic solvents employed were various alcohols and ketones, and brominated compounds were 1-bromoalkyl, 1-bromoalkyl aromatic compounds having different alkyl chain lengths. At time zero the reactor was immersed in a salt bath whose temperature was maintained at the prescribed value with temperature fluctuation within  $\pm 1$  K. After intended time elapsed, the reactor was removed from the bath, and cooled by water. The reactor was opened, and the reaction products were recovered. The reactor was also washed with ultrapure water and acetone. The products in product and washing solution were analyzed by a gas chromatograph equipped with a capillary column. Bromide ion in the solution was measured by an ion chromatograph.

Fig. 1 shows 1-dodecanol yield and debromination against acetone mole fraction at 433 K for 30 min. The yields of 1-dodecanol were almost equal to those of debromination over an entire range of acetone mole fraction, and the highest yield of 1-dodecanol was ca. 80 % at 0.2 mole fraction of acetone. In the presentation the effectiveness of various alcohols and ketones as an amphipathic solvent, and conversions of various brominated compounds were compared. The reaction mechanism is also discussed.

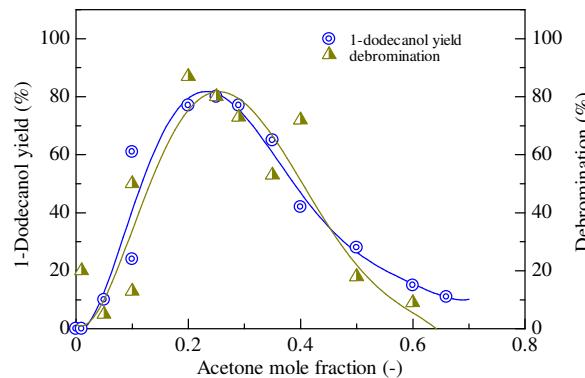


Fig. 1. 1-Dodecanol yield and debromination vs. acetone mole fraction at 433 K for 30 min.

## 16-1: Understanding supercritical CO<sub>2</sub>: from fundamental to industrial applications

L. F. Vega<sup>1,2\*</sup>, F. Llovell<sup>1</sup>, O. Vilaseca<sup>1</sup>, R.M. Marcos<sup>3</sup>, R. Solanas<sup>1</sup>, J. Torres<sup>1,2</sup>, P. López-Aranguren<sup>1,4</sup> and C. Domingo<sup>4</sup>

<sup>1</sup>MATGAS Research Centre. Campus UAB, 08193 Bellaterra, Barcelona, Spain.

<sup>2</sup>Carburos Metálicos/Air Products Group. C/Aragón, 300, 08009 Barcelona, Spain

<sup>3</sup>Dept. d'Enginyeria Mecànica. ETSE. Campus Sescelades. Universitat Rovira i Virgili, 43007 Tarragona, Spain

<sup>4</sup>Institut de Ciència de Materials de Barcelona. Consejo Superior de Investigaciones Científicas, ICMAB-CSIC, Campus UAB, 08193 Bellaterra, Barcelona, Spain.

Carbon dioxide (CO<sub>2</sub>) is finding more and more uses in industry today, from food and water treatment to energy and materials. Among these applications, supercritical carbon dioxide (scCO<sub>2</sub>) is used as an alternative attractive solvent, replacing traditional ones, including hazardous chemicals and precious water resources. scCO<sub>2</sub> offers several advantages versus other solvents: it can be easily recycled, it leaves no residues behind after processing and it is non-flammable, non-toxic and inexpensive. The low process temperature (31 °C) allows for gentle processing, while the low surface tension of scCO<sub>2</sub> and its high diffusivity allows for exceptionally effective penetration. Increased environmental awareness had led to restrictions on some traditional solvents which are now recognized as toxic. Only a few sustainable solvents remain available for future use. Hence, as the society and industry continue to demand more efficient and greener processes, CO<sub>2</sub> remains an attractive alternative.

There are three key issues driving CO<sub>2</sub> applications from labs to industry: the increased fundamental knowledge of CO<sub>2</sub> and its interaction with the materials and other compounds, used to find the best process and operating conditions, the optimization of process equipment to handle the demands of operation at an industrial scale, and the need to use environmentally benign solvents and greener processes. In this context, and thanks to the success of adequate modeling tools, accurate experimental measurements and the optimization of the equipments at industrial scale, the use of scCO<sub>2</sub> has transitioned, over the past twenty-five years, from a laboratory based research to a commercial reality, with applications in high-value products such as in pharmaceuticals, nutraceuticals, foods and flavors, polymers and chemicals, as well as in bulk commodity products such as textiles, biofuels and cement.

After a general overview, we will address some of the recent applications of CO<sub>2</sub> in which our team has been involved, including the recovery of solutes from ionic liquids with CO<sub>2</sub> or separation of ionic liquids from organic solvents by CO<sub>2</sub>, the preparation of organic-inorganic materials by scCO<sub>2</sub> for CO<sub>2</sub> capture and other applications, the use of scCO<sub>2</sub> to extract high added value products and the scCO<sub>2</sub> role in the biofuel arena. Modeling and advanced experimental techniques, from small reactors to pilot plants have been used in order to move the technology forward.

This work is part of the CENIT project SOST-CO<sub>2</sub> belonging to the Ingenio 2010 program financed by CDTI, Spanish Government, aiming at developing new industrial and sustainable uses of CO<sub>2</sub>. The project is lead by the company Carburos Metálicos, from Air Products Group, and it comprises 13 other companies and 31 research institutions.

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## 16-2: CO<sub>2</sub>-expanded solvents: unique media for the synthesis of micro- and nano-particulate molecular materials with high structural homogeneity

N. Ventosa

<sup>a</sup>Department of Molecular Nanoscience and Organic Materials. Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), <sup>b</sup>Networking Research Center on Bioengineering, Biomaterials and Nanomedicine, CIBER-BBN, Campus de la Universitat Autònoma de Barcelona (UAB), 08193-Bellaterra (Spain); E-mail: ventosa@icmab.es

Nano- and micro-particulate molecular materials (micro- and nanocrystals, nanosuspensions, microemulsions, nanovesicles, polymeric particles, etc..) have gained a lot of attention, in particular in the drug delivery field, because they can be used as smart nano-carriers for the temporal and spatial precise delivery of actives in a given site of the body [1].

Despite the potential of these materials, from which polymeric micro/nanoparticles and vesicles are the most thoroughly investigated, a high degree of structural homogeneity is crucial for their optimum performance as functional entities. However, the achievement of homogeneous nanostructured materials with high batch to batch reproducibility is not an easy issue. For instance, novel studies have revealed certain heterogeneity in the encapsulation efficiency [2,3] and the membrane composition and supramolecular organization of individual liposomes within a bulk [4,5]. The method of preparation plays a crucial role in this degree of heterogeneity and therefore, methods that allow a well controlled nanostructuring, not only regarding size but also morphology and supramolecular organization, are necessary for the achievement of homogeneous drug nanocarriers. The scalability of such preparation processes is a usually forgotten issue. However, this aspect is also of high relevance for commercially exploiting the potential of nanocarriers in drug formulations which fulfill standardization and quality requirements imposed by regulatory agencies.

Since conventional precipitation processes usually present difficulties in controlling a homogeneous assembling of the molecules present in a bulk system, especially when scaling-up, “down-stream” operations, such as milling in the case of particles and extrusion or sonication for vesicles, are necessary in order to achieve or isolate the desired structures.

Compressed fluids (CFs), like compressed CO<sub>2</sub>, have a great deal of promise as solvent media for material processing, since their unique characteristics between those of liquid and gases, allow the achievement of materials presenting highly homogeneous structure [6]. In this communication will be shown the influence of the preparation route on the assembly of molecules to form such particulate materials, and the potential of using CO<sub>2</sub>-expanded as solvents for providing more homogeneous crystalline and non-crystalline ordered materials [7,8].

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## 16-3: Fabrication of PVP Micro-Hollow Fiber by Electrospinning Process in Near-Critical CO<sub>2</sub>

Motonobu Goto<sup>1</sup>, Wahyudiono<sup>1</sup>, Koichi Okamoto<sup>1</sup>, Siti Machmudah<sup>1,2</sup>, Satoko Okabayashi<sup>3</sup> and Ryuichi Fukuzato<sup>4</sup>

<sup>1</sup> Department of Chemical Engineering, Nagoya University, Nagoya 464-8603, Japan

<sup>2</sup> Sepuluh November Institute of Technology, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

<sup>3</sup> Department of Advanced Fibro-Science, Kyoto Institute of Technology, Kyoto 606-8585, Japan

<sup>4</sup> SCF Techno-link, Ashiya 659-0033, Japan

Electrospinning is a simple technique that has gained much attention because of its capability in the fabrication of polymer fibers with diameters in the nano- to microscale range. In this work, the one-step generation of PVP hollow fibers by electrospinning with sub- and supercritical CO<sub>2</sub> is described.

Electrospinning chamber is made of PEEK and pressurized CO<sub>2</sub> was supplied. As a starting material, polyvinylpyrrolidone (PVP) was dissolved in dichloromethane (DCM) at a concentration of 4% (w/v) and directly electrospun in the chamber. The voltage applied between the nozzle and collector was set at 17 kV and the distance between nozzles to collector was 8.0 cm [1].

Figure 1 shows the morphology of PVP electrospun produced by electrospinning at pressures 5 MPa and 317 K of CO<sub>2</sub>. As shown in the picture of the cross-section of fibers, hollow structure was clearly observed. The process for polymer hollow fiber formation was estimated as follows. The formation of an outer skin of fiber occurs first by extraction of solvent into CO<sub>2</sub> and then the diffusion of the solvent is subsequently suppressed, and the sorption of CO<sub>2</sub> into the fiber induces the solution trapped inside the fiber to phase separate, allowing CO<sub>2</sub>-rich voids to form and grow.

Therefore, hollow fibers with walls made of organic polymer composites have been formed by electrospinning in a single processing step with near-critical CO<sub>2</sub>. The capability and feasibility of this technique were demonstrated by the production of PVP fibers whose size and wall thickness could be independently varied by controlling a set of experimental parameters. The PVP fibers had an average pore diameter of 2-6 µm. At low pressures (3 MPa), solid fibers were formed, whereas balloon-like structures of fibers were formed with higher pressure (8 MPa) of CO<sub>2</sub>.

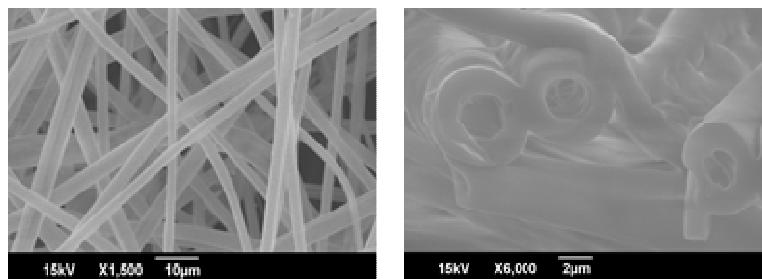


Fig. 1. SEM images of PVP fiber produced by electrospinning in CO<sub>2</sub> at 5 MPa and 317 K.

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## 16-4: Metal Deposition on Porous Supports Using Supercritical CO<sub>2</sub>

A. Cabañas<sup>1\*</sup>, J. Morère<sup>1</sup>, M.J. Tenorio<sup>1</sup>, C. Pando<sup>1</sup>, J.A.R. Renuncio<sup>1</sup>

<sup>1</sup> Dept. Química Física I, Universidad Complutense de Madrid, Spain  
a.cabanas@quim.ucm.es

The deposition of metals into different supports such as mesoporous materials, polymers, carbon nanotubes or patterned wafers has numerous applications in catalysis, microelectronics, photonics, gas separation, hydrogen storage, sensors, and fuel cells. Traditional preparative methods in liquid solution often yield inhomogeneous materials due to the high surface tension of most liquids, the slow diffusion of the metal precursor within the support pores and the potential damage of the support during the drying process. On the other hand, gas based processes such as Chemical Vapour Deposition (CVD) tend to yield non uniform materials mainly because of volatility constraints, which lead to mass transport-limited conditions and poor step coverage. The use of scCO<sub>2</sub> in metallization processes presents several advantages over the conventional techniques. Beside the environmental benefits, its high diffusivity and low viscosity and surface tension favour the penetration of scCO<sub>2</sub> and its solutions into nanostructures and nanopores yielding materials of exceptional properties[1-3].

In our laboratory at UCM we are using scCO<sub>2</sub> to impregnate and/or react metal-organic precursors into different organic and inorganic supports [4-6]. In this presentation we show examples of deposition of Pd, Ni and Ru onto different supports such as mesoporous silica SBA-15, silica inverse opals and mesoporous carbon among others (Fig. 1). In an effort to understand the different steps involved in the process, we have measured the solubility of the precursors in scCO<sub>2</sub> and studied the adsorption isotherms of the precursors on the support. The impregnated material is then decomposed/reduced either in the supercritical mixture or in a reducing atmosphere after depressurization. In most of the examples metal nanoparticles homogeneously dispersed within the support are obtained. Materials are characterized by TGA, XRD, TEM, SEM, EDX, ICP-OES and N<sub>2</sub>-adsorption experiments. Catalytic tests have been also performed in some of these composite materials.

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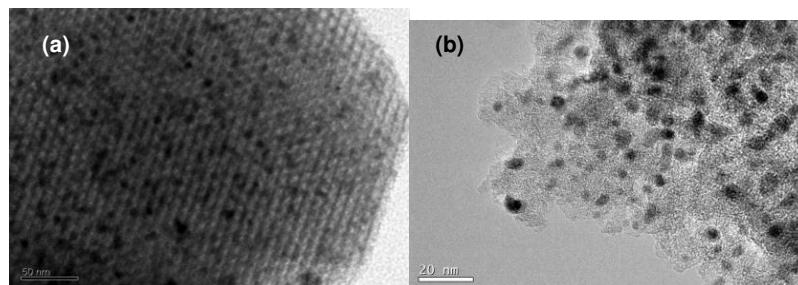


Fig. 1. Ru nanoparticles on mesoporous SiO<sub>2</sub> SBA-15 (a) and carbon (b)

## 16-5: Extraction Kinetics for Dioxins-Contaminated Soil by Supercritical Carbon Dioxide with Methanol

Ming-Tsai Liang<sup>1\*</sup>, Ku-Yuan Liang<sup>1</sup>, Tzu-Chen Kuo<sup>2</sup>, Yung-Ho Chiu<sup>3</sup>, Yan-Min Chen<sup>4</sup>

<sup>1</sup>Dept. of Chem. Eng., I-Shou University, Kaohsiung, 840, Taiwan

<sup>2</sup>Metal Industries Research & Development Centre, Kaohsiung, 811, Taiwan

<sup>3</sup>Taiwan Supercritical Technology Co., LTD, Taichung, 502, Taiwan

<sup>4</sup>Sustainable Environment Res. Center, Cheng-Kung University, Tainan, 709, Taiwan

The extraction of dioxins-contaminated soil from field in Taiwan was conducted in a pilot SFE(supercritical fluid extraction) unit with 0.5 L of extractor. In this study, the extraction kinetics of dioxins from contaminated soil is investigated. Effects of temperature, pressure, and concentration of cosolvent are preliminary investigated and the operating condition for the extraction kinetics study is conducted at 120 C, 35 MPa, and with 10.6 wt% of methanol as cosolvent. The preliminary study revealed that methanol is an appropriate cosolvent for the SFE as compared with isopropanol and toluene, and the extraction solely by liquid methanol is rarely effective. To investigate the extraction kinetics, several experiments with different flow rates of carbon dioxide and duration of extraction time were conducted. For each flow rate of carbon dioxide, the experimental results were fitted by Sovova's model to find the model's parameters. It was found that about 82 % of dioxins in the soil can be classified as easily removable. The left 18% of dioxins is difficult to be extracted, which limits and delays the extraction. By assuming that the carbon dioxide flow rate can only affect the mass transfer coefficient of dioxins in fluid phase, a correlation between the mass transfer coefficient in fluid phase and the carbon dioxide flow rate can be established. Accordingly, the duration of extraction time to clean various levels of the contaminated soil down to local regulation can be predicted, which will provide important information for cost estimation about the contaminated field in Taiwan. The established model is also used to fit the experimental result from large SFE unit with 5 L of extractor. It is concluded that the soil remediation by the supercritical carbon dioxide is technically and economically feasible.

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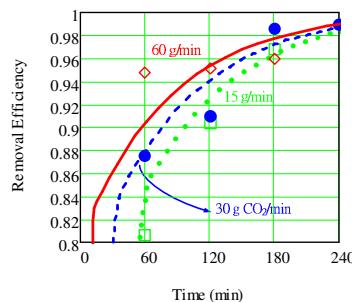


Fig. 1. The curve fitting for dioxins extraction.

## 16-6: Lycopene/Cyclodextrin Nanoparticle Formation Using Solution Enhanced Dispersion by Supercritical Fluid Process

Hazuki Nerome<sup>1\*</sup>, Siti Machmudah<sup>1</sup>, Wahyudiono<sup>1</sup>, Ryuichi Fukuzato<sup>2</sup>,  
Yong-Suk Youn<sup>3</sup>, Youn-Woo Lee<sup>3</sup>, Takuma Higashiura<sup>4</sup>, and Motonobu Goto<sup>1\*</sup>

<sup>1</sup> Graduate School of Engineering, Nagoya University, Aichi 464-8603 Japan

<sup>2</sup> SCF Techno-Link, Hyogo 659-0033 Japan

<sup>3</sup> School of Chemical and Biological Engineering, Seoul National University, Korea

<sup>4</sup> Kagome Co.,Ltd, 329-2762 Japan

Lycopene is a representative of carotenoid that has highly vivid red color. Due to its high antioxidant activity and its color, lycopene generates a great value as feed supplements, nutraceutical, pharmaceutical and cosmetic colorants [1]. However, this natural carotenoid present in several fruits and vegetables such as tomatoes, has low oral bioavailability because of low aqueous solubility and slow dissolution rate.

In order to promote lycopene dispersion in water, nanoparticle formation of lycopene and  $\beta$ -cyclodextrin complex was investigated using the Solution enhanced dispersion by supercritical fluids (SEDS) process in this work. The inclusion complex between lycopene and  $\beta$ -cyclodextrin was prepared with dimethylformamide (DMF) as a liquid solvent and carbon dioxide ( $\text{CO}_2$ ) as a supercritical anti-solvent. The effects of initial concentration of lycopene and  $\beta$ -cyclodextrin,  $\text{CO}_2$  flow rate, solution flow rate, pressure and temperature of the process were examined. Experiments were carried out at pressures of 10-14 MPa and temperatures of 40-50°C. The initial concentrations of lycopene and  $\beta$ -cyclodextrin in DMF solution were 0.35-1.05 mg/mL and 0.74-2.22 mg/mL, respectively.  $\text{CO}_2$  and solution flow rates were 15-25 mL/min and 0.25-0.75 mL/min, respectively. Morphologies of particles generated were observed by scanning electron microscope (SEM) and field emission-scanning electron microscope (FE-SEM). Small sphere-like or agglomerated particles were obtained at the experiment. At high pressure, high temperature, high  $\text{CO}_2$  flow rate and low solution flow rate condition, an average particle size of about 40 nm was obtained. In conclusion, the optimum condition was 50°C, 14MPa, 25 ml/min- $\text{CO}_2$ , 0.25 ml/min-Soltion, and the particle morphology is shown in Fig. 1.

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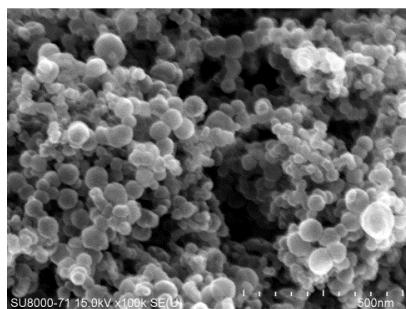


Fig. 1. Lycopene/ $\beta$ -CD particles formed by SEDS  
50°C, 14 MPa, 25 ml/min- $\text{CO}_2$ , 0.25 ml/min-Soltion,

## 16-7: Supercritical fluids for effective particle design processes

Michael Türk

Karlsruhe Institute of Technology, Institute for Technical Thermodynamics and Refrigeration  
Engler-Bunte-Ring 21, D - 76131 Karlsruhe

Numerous results of multitude investigations indicate that the particular properties of supercritical fluids (SCFs) can be conveniently exploited for the preparation of small uniform particles for a large number of applications such as pharmaceutical technology and material science. In case of the former one, the poor dissolution behaviour and therewith bioavailability of drugs in biological media can be enhanced by reduction of the particle size. For catalytic applications, a high dispersion, i.e. the preparation of noble metal nanoparticles on porous catalyst supports improves the activity of the catalyst. Conventional micronization techniques such as milling and grinding, spray-drying, freeze-drying, high-pressure homogenization, and milling have been commonly utilized for pharmaceuticals. These technologies present several disadvantages such as degradation of the product, a broad particle size distribution and cumbersome solids handling. Furthermore, catalysts prepared by the conventional aqueous impregnation of diverse supports yields to metal particles with broad size distribution and to large volumes of waste water. To overcome this, innovative SCF based particle size reduction processes are gaining an importance in material science and pharmaceutical technology. These processes can be classified according to the role of the SCF in the process: it can act as a solvent, as in the Rapid Expansion of Supercritical Solutions (RESS) process. Or even as a solvent, reaction and separation media, as in the Supercritical Fluid Reactive Deposition (SFRD) process.

After an introduction into the basic principles of the processes, including phase behaviour and particle formation and growth, typical results obtained from RESS-experiments with a large number of poorly soluble drugs are presented and discussed [1]. In the RESS process, the solute of interest is dissolved in a SCF (usually scCO<sub>2</sub>), resulting in a solute-laden supercritical solution. By reduction of the pressure across an expansion device, very small particles with narrow size distribution can be obtained. The experimental results show, that the improved dissolution behaviour depends on: a) reduced particle size and hence increased surface area of the processed powders and b) pH value of the dissolution media [1,2].

In the second part of the talk, the basics of the SFRD process and typical results obtained from SFRD experiments are presented and discussed. In the SFRD process, an organometallic complex is dissolved in scCO<sub>2</sub> and decomposed by isobaric hydrogenolysis in scCO<sub>2</sub> induced by the addition of an excess of hydrogen prior to depressurization to ambient conditions. The experimental results show that metallic nanoparticles can directly be deposited on a wide range of solid substrates by SFRD and that the process enables the deposition of small, uniform (< 10 nm) Pt- or Au-particles with improved activity of the Pt catalyst [3,4]. The average particle size and size distribution can be affected by the precursor reduction method and condition, type and amount of the precursor in the system, the surface properties (surface area and chemical nature) and therewith adsorption behaviour of the solid substrate (e.g. uncoated and coated Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>).

At the end of the talk the main conclusions and further perspectives are summarized.

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## **16-8: Supercritical Carbon Dioxide-in-Water Foams Stabilized with Nanoparticle and Surfactant Amphiphiles**

Andrew J. Worthen<sup>a</sup>, Hitesh G. Bagaria<sup>a</sup>, Yunshen Chen<sup>a</sup>, Steven L. Bryant<sup>b</sup>, Chun Huh<sup>b</sup>, and Keith P. Johnston<sup>a</sup>

<sup>a</sup>Department of Chemical Engineering and <sup>b</sup>Department of Petroleum & Geosystems Engineering, The University of Texas at Austin, TX 78712

A relatively new concept for stabilizing supercritical carbon dioxide-in-water foams for enhanced oil recovery and CO<sub>2</sub> sequestration is to design a mixture of nanoparticle and surfactant amphiphiles that adsorb at the CO<sub>2</sub>-water interface. A concept of hydrophilic/CO<sub>2</sub>-philic balance (HCB) may be defined to describe the surface chemistry on the amphiphiles, which influences stabilization of supercritical carbon dioxide-in-water (C/W) foams. Surfactant can adsorb on the nanoparticle surface to alter the HCB as well as adsorb at the CO<sub>2</sub>-water interface to lower the interfacial tension. The apparent viscosity of C/W foams with fine texture (bubble sizes less than 100 µm) increased over 100 times the value without nanoparticles or surfactant upon foam generation by shearing CO<sub>2</sub> and water phases in a beadpack. Long-term stability of C/W foams was also demonstrated in terms of foam resolution. The ability to achieve viscous and stable C/W foams with properly designed nanoparticle and surfactants could provide more stable foams than conventional surfactants.

## **16-9: Switchable Ethoxylated Nonionic to Cationic Amine Surfactants for CO<sub>2</sub> Enhanced Oil Recovery in High Temperature, High Salinity Carbonate Reservoirs**

Yunshen Chen<sup>a</sup>, Amro S. Elhag<sup>a</sup>, Benjamin M. Poon<sup>a</sup>, Leyu Cui<sup>b</sup>, Kun Ma<sup>b</sup>, Sonia Y. Liao<sup>b</sup>, Prathima P. Reddy<sup>a</sup>, Andrew J. Worthen<sup>a</sup>, George J. Hirasaki<sup>b</sup>, Quoc P. Nguyen<sup>c</sup>, and Keith P. Johnston\*<sup>a</sup>

<sup>a</sup>Dept. of Chemical Eng., The University of Texas at Austin;

<sup>b</sup>Dept. of Chemical & Biomolecular Eng., Rice University;

<sup>c</sup>Dept. of Petroleum & Geosystems Eng., The University of Texas at Austin

The sweep efficiency for CO<sub>2</sub> enhanced oil recovery can be improved by forming CO<sub>2</sub>/water (C/W) foams up to 120 °C with ethoxylated amines. These surfactants are nonionic in CO<sub>2</sub> and quite soluble, but are protonated in brine at pH 4-6. The ionic character results in high cloud point temperatures above 120 °C. C/W foams with viscosities up to on the order of hundreds of times of that of pure CO<sub>2</sub> at the same conditions were produced by injecting the surfactant either in the CO<sub>2</sub> or the brine. The ethoxylated cocoamine with 2 EO groups was shown to stabilize C/W foams with high salinity brine with NaCl concentrations up to 182 g/L at 120 °C, 3400 psia. In summary, the switchable ethoxylated amines surfactants combine the high cloud points of ionic surfactants in water with high solubility in CO<sub>2</sub> for nonionic surfactants, while providing for C/W foam generation at 120 °C.

## P-1: Silanization of Silica SBA-15 using Supercritical Carbon Dioxide

Yolanda Sánchez-Vicente<sup>1</sup>, Concepción Pando<sup>1</sup>, Juan A.R. Renuncio<sup>1</sup> and Albertina Cabañas<sup>1,\*</sup>

<sup>1</sup> Dept. Química Física I, Universidad Complutense de Madrid, 28040 Madrid, Spain  
a.cabanas@quim.ucm.es

In many technological applications, the control of the physical and chemical properties of material surfaces is crucial. Therefore, in recent years, the surface modification of porous materials with organic functional molecules has received considerable attention [1,2]. Silanization is one of the most successful synthetic methods for chemical modification of the material surface using functional organosilanes such as alkyl, aryl and chloro silanes[3]. This process is commonly used to protect fine metal particles against corrosion or to protect nanoparticles of labile biomolecules against denaturalization as well as to obtain materials capable of absorbing metals [4].

In the silanization process, the most easy and conventionally used method is the reactive deposition of the silane agent either from an aqueous-alcohol solution or an organic solvent when the agent is highly reactive with water [5,6]. However, the drawbacks of this method include non-uniform surface coverage, pore blocking, and pore collapse and crumbling due to the large capillary forces exerted by the liquid in the pores. On the other hand, supercritical carbon dioxide ( $\text{scCO}_2$ ) has been recently used in the surface modification of a wide variety of inorganic surfaces such as those of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  nanoparticles and aerogels [7,8]. The low viscosity, high diffusivity and very low surface tension of  $\text{scCO}_2$  as well as its adjustable density with small changes of pressure and temperature, turn  $\text{scCO}_2$  into an attractive medium for surface modification. Furthermore,  $\text{scCO}_2$  is considered a green solvent and does not leave any residue in the materials.

In this work, the surface modification of mesoporous silica SBA-15 with (*N,N*-dimethylaminopropyl)trimethoxysilane (DMAPTS) has been carried out for the first time in  $\text{scCO}_2$ . The effects of the reaction conditions (pressure, temperature and time) on the surface modification have been studied. Besides, the surface coverage, thermal stability, pore structure and type of silane-silica interactions have been determined using FTIR spectroscopy, thermogravimetric analysis, and  $\text{N}_2$  adsorption-desorption isotherms. The performance of the  $\text{scCO}_2$  silanization is compared to that of the conventional method using toluene. Results indicate that  $\text{scCO}_2$  is a good solvent to carry out the silanization of silica SBA-15, comparable or better than common liquid organic solvents.

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## P-2: Synthesis of Carbonated Doped Hydroxyapatite Powders by Urea Decomposition Under by Hydrothermal Method.

J. R. Escalona-González<sup>1,5\*</sup>, J. C. Rendón-Angeles<sup>2,1</sup>, Z. Matamoros-Veloza<sup>3</sup>, K. Yanagisawa<sup>4</sup>, and D. Jaramillo-Vigueras<sup>5</sup>.

<sup>1</sup>Department of Nanoscience & Nanotechnology, Research Institute of Advanced Studies of the NPI, Campus Mexico City, U. Profesional Adolfo López Mateos, México.

<sup>2</sup>Research Institute of Advanced Studies of the National Polytechnic Institute, Saltillo Campus, Ramos Arizpe, 25900, Coahuila México.

<sup>3</sup>Technological Institute of Saltillo, Faculty of Metal-Mechanics, Saltillo 25280, México.

<sup>4</sup>Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Kochi 780-8073.

<sup>5</sup>Research Institute for Technology Innovation and Development of the NPI (CIITEC-IPN), Azcapotzalco

Carbonated hydroxyapatite have particular advantages based on its chemical properties, in particular osteoclast dissolve faster CO<sub>3</sub>HAp in comparison with other Ca-HAp materials, therefore; new bone is form around the implanted CO<sub>3</sub>HAp material. The continue interaction of the implant by the biological environment yield the complete implant transformation and new living bone is formed. The feasibility for preparing CO<sub>3</sub>-HAp under hydrothermal conditions via urea decomposition has recently been reported to a very reduced CO<sub>3</sub> contents, below 2 w%. Therefore, in the present work we evaluated the chemical compositional control, from 1 – 6 wt% of C; of CO<sub>3</sub> ions incorporated on the HAp structure and the morphological differences as well. Hydrothermal experiments were conducted in a large (2 L) autoclave vessel with an inner Teflon container and stirring propel. The CO<sub>3</sub>-HAp powders were prepared using a precursor 1 M Ca(NO<sub>3</sub>)<sub>2</sub> and 0.2 M Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> solutions, which were mixed in a volume ratio 1:1 to keep the stoichiometric molar ratio Ca/P=1.67. 2-Propanol (30 vol%, 240 ml) was poured to complete total volume of the precursor solutions (800 ml) and three different urea (NH<sub>2</sub>)<sub>2</sub>CO contents of 62.5, 200 and 300 mmol/L were added to the mother solution. All the hydrothermal treatments were conducted at a constant slow heating speed of 24 °/h in order to reach the desired treatment temperature of 150 °C, the vessel was keep at this temperature for 10 h and stirring of the precursor mother solution proceeded during the heating and cooling stages at a constant speed of 150 rpm. The specimens were characterized by X-ray powder diffraction, field emission SEM, FT-IR, and the chemical composition was measured by ICP-AES, CHNS thermal decomposition apparatus was used to determine carbon content on the reaction product.

In general, the results demonstrated that powders corresponding to the following solid solutions Ca<sub>9.98</sub>(PO<sub>4</sub>)<sub>5.94</sub>(CO<sub>3</sub>)<sub>0.06</sub>(OH)<sub>1.62</sub>(CO<sub>3</sub>)<sub>0.20</sub>, Ca<sub>9.93</sub>(PO<sub>4</sub>)<sub>5.81</sub>(CO<sub>3</sub>)<sub>0.19</sub>(OH)<sub>0.91</sub>(CO<sub>3</sub>)<sub>0.57</sub> and Ca<sub>9.91</sub>(PO<sub>4</sub>)<sub>5.71</sub>(CO<sub>3</sub>)<sub>0.29</sub>(OH)<sub>0.63</sub>(CO<sub>3</sub>)<sub>0.74</sub> were produced with different urea contents of 62.5, 200 and 300 mmol/L under hydrothermal conditions, respectively. A coupled process that involved the dissolution of the precursor Ca<sub>5</sub>P<sub>3</sub>O<sub>10</sub> amorphous gel and the decomposition of urea producing CO<sub>3</sub><sup>2-</sup> promoted the crystallization of the CO<sub>3</sub>-HAp powders by means of the dissolution-precipitation mechanism. Moreover, the CO<sub>3</sub>-HAp particles exhibited a rod-like morphology with various particles sizes varying from 50 nm X 200 nm to 0.5 μm X 10 μm on width and length, respectively. The variation on the excessive particle size exhibited on the particles prepared with low urea contents are discussed on terms of the alkalinity grade of the hydrothermal media produced by the decomposition of urea, which promoted the increase of the pH of the hydrothermal media due to the presence of NH<sub>4</sub> mainly on those treatments conducted at contents of urea above 200 mmol/L.

### P-3: Hydrothermal Conversion of 1-Bromododecane to 1-Dodecanol in Aqueous 2-Butanone Solution without Catalysts

Yuki Goto, Toshitaka Funazukuri\*

Department of Applied Chemistry, Chuo University  
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551 Japan

Chemical reactions for hydrophobic species are usually carried out in organic solvents. When some of reactants and/or products are hydrophobic, the selection of solvent is important because reaction rates/conversions are often affected significantly. In such a case the addition of amphipathic solvents such as lower molecular weight mono-alcohols, diols, ketones etc. to an aqueous phase is effective.

In this presentation conversion of 1-bromododecane (1-C12Br) to 1-dodecanol (1-C12OH) was carried out in a mixture of water and 2-butanone (methyl ethyl ketone, MEK) under hydrothermal conditions. As a result, the reaction proceeded selectively without catalysts, and the reaction rates and conversions were significantly affected by the composition of aqueous solvent as well as temperature and time. 1-Dodecanol of 80 % was yielded at 433 K and 0.2 mole fraction of MEK for 90 min.

The reaction was carried out in a small batch bomb-type reactor (3.5 mL), made of stainless steel tubing and two 1/2 inch Swagelok caps. Certain amounts of solvent mixtures and 1-bromododecane were loaded in the reactor at room temperature, the air in it was purged by flowing argon, and then the reactor was plugged by the Swagelok cap. At time zero the reactor was immersed in an oil bath whose temperature was maintained at the prescribed temperature with temperature fluctuation within  $\pm 1$  K. After intended time elapsed, the reactor was removed from the salt bath, and cooled by water. The reactor was opened, and the reaction products were recovered. The reactor was also washed with acetone. The products in product and washing solution were analyzed by a gas chromatograph equipped with a capillary column. Bromide ion in the solution was measured by an ion chromatograph.

As shown in Fig. 1, the conversion of 1-C12Br to 1-C12OH selectively proceeded because debromination was almost equal to 1-C12OH yield over an entire range of MEK mole fraction. At MEK mole fractions around 0.2 the conversion was the highest, and the conversions were so low at zero and in MEK rich region. In the presentation the effects of various experimental variables on conversions will be shown, and the reaction mechanism will be discussed.

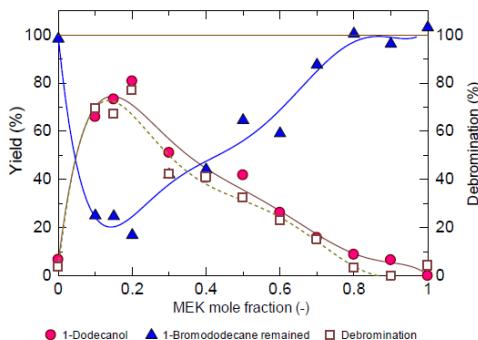


Fig. 1 Dependence of 1-dodecanol yield, 1-bromododecane remained, and debromination on MEK mole fraction at 433 K for 90 min.

## P-4: Influence Of Hydrothermal Alkaline Activation on the Co-Cr-Mo Biodur CCmplus 799 Alloy Compacts

Z. Matamoros-Veloza<sup>\*,1</sup>, J. C. Rendón-Angeles<sup>2,3</sup>, K. Yanagisawa<sup>4</sup> and B. Moreno Pérez<sup>1</sup>

<sup>1</sup>Technological Institute of Saltillo, Research and Graduate Division, Saltillo 25280, México.

<sup>2</sup>Research Institute for Advanced Studies of the NPI, Campus Saltillo, Saltillo 25900, México.

<sup>3</sup>Department of Nanoscience & Nanotechnology at the Research Institute for Advanced Studies of the NPI, Campus Mexico City, U. Profesional Adolfo Lopez Mateos, México.

<sup>4</sup>Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Kochi 780-8520, Japan

In the present work Co-Cr-Mo BioDur CCMPlus 799 alloy compacts had been prepared by means of spark plasma sintering (SPS), in order to obtain nanostructured pellets that exhibit excellent mechanical properties and corrosion resistance, however, still a lack information of their bioactivity in spite of there are a few investigations related to this topic[1]. In this study we investigated the influence of the alkaline hydrothermal activation of the SPS compacted Co-Cr-Mo BioDur pellets and its biomimetic behavior. Thus, the sintered specimens underwent to a surface activation process, which was carried out under hydrothermal treatment by using a sodium hydroxide solution (5 M) at temperature of 240 °C for 12 h. Subsequently, the biomimetic study was conducted by submerging the hydrothermally activated compacts into a simulated body fluid (1.5 SBF) [2] for different periods of time (7, 14, 21 and 28 days) at a constant temperature of 37 °C and pH of 7.4. The characterization results conducted by low angle X-ray diffraction and EDX analyses confirmed the formation and growth of a hydroxyapatite layer, which was achieved during the biomimetic process; this layer was formed on the surface of the hydrothermally treated SPS pellets, the thickness was increased as immersion time increased.

In general, calcium deficient coatings were produced, the average molar ratio Ca/P determined on the coatings prepared after 28 days was of 1.58, and this value is lower than the value for stoichiometric pure hydroxyapatite. The present results indicate that the proposed hydrothermal method might be useful for preparing implants with good biocompatible properties for bone substitution.

### Acknowledgement

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## P-5: Effect of Phosphate Precursor on the Crystallization of $\text{Ca}_{10-x}\text{Mg}_x(\text{PO}_4)_6(\text{OH})_2$ Solid Solutions Under Hydrothermal Conditions

K.L. Montoya-Cisneros<sup>1</sup>, J.C. Rendón-Ángeles<sup>1</sup>, Z. Matamoros-Veloza<sup>2</sup>, K. Yanagisawa<sup>3</sup> and M.I. Pech-Canul<sup>1</sup>

<sup>1</sup>Research Institute of Advanced Studies of the National Polytechnic Institute, Saltillo Campus,  
Ramos Arizpe, 25900, Coahuila México, alrak.montoya188@gmail.com

<sup>2</sup>Technological Institute of Saltillo, Faculty of Metal-Mechanics, Saltillo 25280, México.

<sup>3</sup>Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, Kochi  
780-8073.

The hydroxyapatite (HAp:  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) is a compound used as bone grafting material in hard tissues implants, due to its excellent biocompatibility. The HAp structure easily incorporates a wide variety of cationic and anionic ions. The ions are incorporated depending on its electric valence in a particular site (A, B, and X) of the hexagonal structure of the  $\text{A}_{10}(\text{BO}_4)_6\text{X}_2$  [1]. Mg has been known as one of cationic substitutes for Ca in the HAp, but increasing Mg concentration has some effects in the properties, such as: crystallinity and dissolution. In addition, the Mg is associated with mineralization process; the content in human bodies is up to 6 mol% [2]. Recently, a microwave-hydrothermal (M-H) method has been employed for the synthesis of inorganic materials; this method had proved to be effective for preparing nanoparticles including oxides. In comparison with other methods, M-H synthesis has many features and advantages, such as fast heating to crystallization temperature, high chemical reaction rates, this lead to enhancing crystallinity and decreasing the formation of secondary crystalline phases [3].

In the present study, powders of three different solid solutions of Mg-substituted hydroxyapatite ( $\text{Ca}_{10-x}\text{Mg}_x(\text{PO}_4)_6(\text{OH})_2$ ) were synthesized using two compounds as phosphate ions source; namely  $(\text{Na}_5\text{P}_3\text{O}_{10})$  and  $(\text{NH}_4)_2\text{HPO}_4$  by microwave-hydrothermal conditions, in order to investigate the effect of  $\text{PO}_4^{3-}$  precursor on the crystallization of Mg doped HAp powders. The powders were prepared in the temperature interval of 100 – 150 °C for different intervals in the range of 0.08 – 5 h. The effect of experimental parameters such as temperature, reaction interval and pH of the suspension were evaluated. The reaction products obtained were characterized by XRD, FT-IR, ICP and FE-SEM techniques.

The results showed that the formation of HAp particles doped with 2, 4 and 6 wt% in  $\text{Na}_5\text{P}_3\text{O}_{10}$  and  $(\text{NH}_4)_2\text{HPO}_4$  was achieved by the dissolution-precipitation mechanism, and was possible to observe that the particles obtained in these two precursors exhibited a rod-like shape morphology. In addition, the powders prepared with  $\text{Na}_5\text{P}_3\text{O}_{10}$  had a particle size (1.2  $\mu\text{m}$ ) ten times larger than those prepared with  $(\text{NH}_4)_2\text{HPO}_4$  which exhibited nanometer sizes from 70 to 300 nm, these marked differences are mainly associated to the presence of a high concentration of alkaline ions  $\text{NH}_4^+$ , which might accelerate the dissolution-precipitation mechanism that promotes the crystallization of these particles under hydrothermal conditions, because the presence of these ions might accelerate the dissolution of the precursor gel resulting on a fast solvent saturation, these factors might control the particle growth process under M-H conditions.

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## P-6: Hydrothermal Conversion of Celluloses to Glucose and Cellooligosaccharides in Dilute Aqueous Formic Acid Solution

Shingo Ozawa, Toshitaka Funazukuri\*

Department of Applied Chemistry, Chuo University  
1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551 Japan, tfunazo@kc.chuo-u.ac.jp

Cellulose is one of major constituents of biomass, and abundant on the earth. Recently conversion of cellulose to energy or chemicals has become focus of attention, in particular, via fermentative production from glucose. In the process effective conversion of cellulose to glucose is essential, and hydrothermal conversion is attractive in the absence of acids or catalysts. In fact, a large number of studies have been reported. When no acids are used, e.g. under conditions of supercritical water, extremely short contact times should be regulated due to high reaction rates. To prevent further decomposition of products such as glucose and oligomers having lower degree of polymerization, longer contact times are easily controlled at lower temperatures. However, reaction rates are so slow. To obtain moderate reaction rates and prevent further decomposition of desired products at mild reaction conditions, the addition of acids may be required. A dilute aqueous acid solution under hydrothermal conditions is one of the candidates.

In this study various celluloses were subjected to dilute aqueous formic acid solution up to 1 wt% under hydrothermal conditions, at temperatures from 503 to 533 K and 5 to 10 MPa, in a small semi-batch reactor. The celluloses studied were cotton cellulose, filter papers and microcrystalline cellulose powder. The yields of glucose, cellooligosaccharides up to DP = 9, fructose and further decomposition products such as 1,6-anhydroglucose and 5-hydroxymethylfurfural were measured over time. As a result, the maximum yields of monomer and oligomer were 67 and 71 % (on carbon weight basis of initial cellulose loaded) for cotton cellulose and filter paper, respectively at 533 K, 5 MPa in a 0.1 wt% aqueous formic acid solution. The glucose yields for filter papers were higher than those for cotton cellulose, and the yields of oligomers were lower. The yields of mono- and oligosaccharides up to DP = 9 were well represented by the first order reaction kinetics. The apparent reaction rate constants increased with increasing formic acid concentration. In the presentation the differences in yields from various cellulose types were discussed.

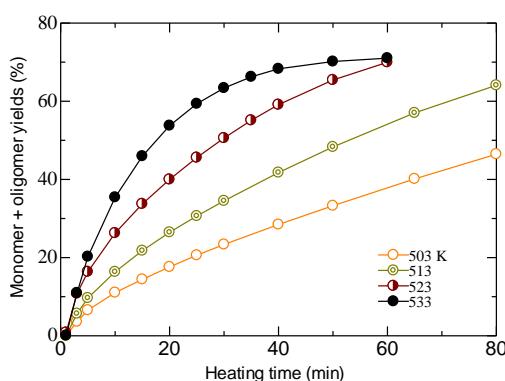


Fig. 1 Yields of monomer and oligomers having up to DP = 9 over heating time at 5 MPa various temperatures in a 0.1 wt% aqueous formic acid solution.

## P-7: Phase Transformation and Photoluminescence of CePO<sub>4</sub> Nano-wires

Pengfei Xu, Ranbo Yu\*, Lingbo Zong, Jiali Wang, Jinxia Deng, Jun Chen, and Xianran Xing

Department of Physical Chemistry, University of Science and Technology Beijing, Beijing  
100083, China

\* E-mail: ranboyu@ustb.edu.cn

As an pivotal rare earth phosphate, CePO<sub>4</sub> whose phase structure unusually behaves as hexagonal or monoclinic phase, has been explored extensively in the past few years[1-3]. In this paper, uniform CePO<sub>4</sub> nanowires have been successfully fabricated under various phosphate concentration through a single-step hydrothermal process. Its SEM images is shown in Fig. 1. The phase of these nanowires were confirmed by XRD and the results showed these nanowires underwent phase evolution from mixed phase of hexagonal and monoclinic to pure monoclinic phase accompanying with the change of the initial molar ratio between cerium source and phosphate source (denoted as Ce/P). With the analysis of photoluminescent spectra, it was uncovered that CePO<sub>4</sub> nanowires with optimized Ce/P equal to 4 showed the best PL properties. We also established the growth process of CePO<sub>4</sub> nanowires based on well-designed experiments which might consist of three main steps: (I) abrupt nucleation; (II) dissolution and recrystallization; and (III) Ostwald ripening. Based on proper hypothesis, the possible mechanism of the enhanced optical properties was proposed.

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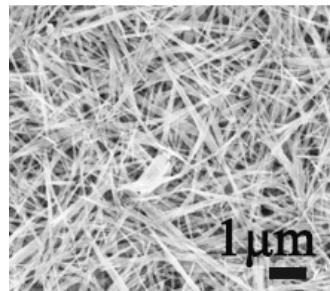


Fig. 1. SEM images of as-synthesized CePO<sub>4</sub> nanowires.

## P-8: Superparamagnetic Iron Oxide Nanoparticles Grafted with Sulfonated Copolymers are Stable in Concentrated Brine at Elevated Temperatures and Weakly Adsorb on Silica

Zheng Xue<sup>a#</sup>, Hitesh G. Bagaria<sup>a#</sup>, Bethany M. Neilson<sup>b</sup>, Andrew J. Worthen<sup>a</sup>, Ki Youl Yoon<sup>a</sup>, Susheela Nayak<sup>a</sup>, Victoria Cheng<sup>a</sup>, Jae Ho Lee<sup>a</sup>, Christopher W. Bielawski<sup>b</sup>, and Keith P. Johnston<sup>a\*</sup>

<sup>a</sup>Department of Chemical Engineering and <sup>b</sup>Department of Chemistry and Biochemistry, The University of Texas at Austin, TX 78712

Magnetic nanoparticles that can be transported in subsurface reservoirs at high salinities and temperatures are expected to have a major impact on enhanced oil recovery, carbon dioxide sequestration, and electromagnetic imaging. Herein we report a rare example of steric stabilization of superparamagnetic iron oxide (IO) nanoparticles (NPs) grafted with poly(2-acrylamido-2-methylpropanesulfonate-*co*-acrylic acid) (poly(AMPS-*co*-AA)) that not only display colloidal stability in standard American Petroleum Institute (API) brine (8% NaCl + 2% CaCl<sub>2</sub> by wt.) at 90 °C for 1 month, but also resist undesirable adsorption on silica surfaces (0.4% monolayer NPs). Nanoclusters of superparamagnetic iron oxide nanoparticles were synthesized in water at 90 °C with controlled size. Since the AMPS groups interacted weakly with Ca<sup>2+</sup>, they were sufficiently well solvated to provide steric stabilization. The PAA groups, in contrast, enabled covalent grafting of the poly(AMPS-*co*-AA) chains to amine-functionalized IO NPs via formation of amide bonds and prevented polymer desorption even after a 40,000-fold dilution. The aforementioned methodology may be readily adapted to stabilize a variety of other functional inorganic and organic NPs at high salinities and temperatures.

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| Kawasaki            | Shin-ichiro         | AIST                                | <b>9-6</b>  |
| KeerthiRaj          | Namratha            | University Of Mysore                | <b>14-4</b>                                       |
| Kolis               | Joseph              | Clemson University                  | <b>12-5</b>                                       |
| Komarneni           | Sridhar             | Penn State University               | <b>Plenary, Session 14 Chair</b>                  |
| Korgel              | Brian               | University of Texas                 | <b>Welcome Remarks,<br/>Session 16 Chair</b>      |
| Lester              | Edward              | University of Nottingham            | <b>Roy-Somiya Award, 9-3,<br/>Session 5 Chair</b> |
| Li                  | Jing                | Rutgers University                  | <b>3-6</b>  |
| Li                  | Guangshe            | Fujian Institute of Research        | <b>13-7</b>                                       |
| Liang               | Ming-Tsai           | I-Shou University                   | <b>16-5</b>                                       |
| Liu                 | Yunling             | Jilin University                    | <b>12-3</b>                                       |
| Liu                 | Chengxiang          | Tsinghua University                 | <b>14-5, 14-6</b>                                 |
| Long                | Jeffrey             | University of California, Berkeley  | <b>3-4</b>  |
| Lotty               | Olan                | University College Cork             | <b>7-5</b>  |
| Lu                  | Fu-Hsing            | National Chung-Hsing University     | <b>4-2</b>  |
| Lu                  | Xianmao             | National University of Singapore    | <b>4-3</b>  |
| Lu                  | Xiaotang            | University of Texas at Austin       | <b>7-4</b>  |
| Manthiram           | Arumugam            | University of Texas at Austin       | <b>1-1</b>  |
| Mao                 | Jiang-Gao           | Fujian Institute of Research        | <b>14-3</b>                                       |
| Marre               | Samuel              | University of Bordeaux              | <b>5-3</b>  |
| Matamoros<br>Veloza | Zully               | Technological Institute of Saltillo | <b>P-4</b>  |

| Attendee Last Name | Attendee First Name | Affiliation                                    | Session Info                  |
|--------------------|---------------------|--|-------------------------------|
| Montoya            | Karla               | Cinvestav                                      | <b>P-5</b>                    |
| Morita             | Takeshi             | University of Tokyo                            | <b>8-3</b>                    |
| Nerome             | Hazuki              | Nagoya University                              | <b>16-6</b>                   |
| Ohara              | Satoshi             | Osaka University                               | <b>1-6</b>                    |
| Onoki              | Takamasa            | Osaka University                               | <b>6-2</b>                    |
| Ozawa              | Shingo              | Chuo University                                | <b>P-6</b>                    |
| Pang               | Guangsheng          | Jilin University                               | <b>7-6</b>                    |
| Patzke             | Greta               | University of Zurich                           | <b>12-2</b>                   |
| Playford           | Helen               | University of Warwick                          | <b>6-4</b>                    |
| Poeppelmeier       | Kenneth R.          | Northwestern University                        | <b>12-1</b>                   |
| Ravinder           | Dachepalli          | Osmania University                             | <b>13-8</b>                   |
| Rendón-Angeles     | Juan Carlos         | Cinvestav                                      | <b>15-5, Session 11 Chair</b> |
| Richards           | Benjamin            | Cornell University                             | <b>1-5</b>                    |
| Riman              | Richard (Rik)       | Rutgers University                             | <b>15-2, Session 3 Chair</b>  |
| Sankar             | Gopinathan          | University College London                      | <b>11-1</b>                   |
| Savage             | Phillip             | University of Michigan                         | <b>3-1</b>                    |
| Schaef             | Todd                | Pacific Northwest National Laboratory          | <b>5-5</b>                    |
| Senthilnathan      | Jaganathan          | National Cheng Kung University                 | <b>11-4</b>                   |
| Shuai              | Min                 | Texas A&M University                           | <b>5-7</b>                    |
| Soga               | Kohei               | Tokyo University of Science                    | <b>14-2</b>                   |
| Stevenson          | Keith               | University of Texas at Austin                  | <b>1-2</b>                    |
| Stride             | John                | University of New South Wales                  | <b>11-2</b>                   |
| Suchanek           | Wojciech            | Sawyer Technical Materials, LLC                | <b>8-6</b>                    |
| Takami             | Seiichi             | Tohoku University                              | <b>5-2</b>                    |
| Tang               | Zhiyong             | National Center for Nanoscience and Technology | <b>2-1</b>                    |
| Tilley             | Richard             | Victoria University of Wellington              | <b>4-4, Session 7 Chair</b>   |
| Ting               | Jyh-Ming            | National Cheng Kung University                 | <b>10-3</b>                   |
| Tuan               | Hsing-Yu            | National Tsing Hua University                  | <b>4-5</b>                    |
| Türk               | Michael             | Karlsruhe Institute of Technology              | <b>16-7</b>                   |
| Vega               | Lourdes             | MATGAS   | <b>16-1</b>                   |
| Ventosa            | Nora                | ICMAB-CSIC                                     | <b>16-2</b>                   |
| Vilarinho          | Paula               | University of Aveiro                           | <b>8-4</b>                    |
| Walton             | Richard             | University of Warwick                          | <b>4-1, Session 9 Chair</b>   |
| Wang               | Dan                 | Institute of Process Engineering               | <b>10-6, Session 8 Chair</b>  |
| Wang               | Xun                 | Tsinghua University                            | <b>2-2</b>                    |
| Watkins            | Jim                 | University of Massachusetts                    | <b>4-6, Session 2 Chair</b>   |
| Whalen             | Terence             | Rutgers University                             | <b>11-5</b>                   |
| Worthen            | Andrew              | University of Texas at Austin                  | <b>16-8</b>                   |

| Attendee Last Name | Attendee First Name | Affiliation                                  | Session Info                                |
|--------------------|---------------------|--|---|
| Wu                 | Yuen                | Tsinghua University                          | <b>6-8</b>                                  |
| Xiang              | Lan                 | Tsinghua University                          | <b>2-3</b>                                  |
| Xu                 | Pengfei             | University of Science and Technology Beijing | <b>P-7</b>                                  |
| Xue                | Zheng               | University of Texas at Austin                | <b>P-8</b>                                  |
| Yanagisawa         | Kazumichi           | Kochi University                             | <b>8-5</b>                                  |
| Yoshida            | Hiroyuki            | Osaka University                             | <b>6-9</b>                                  |
| Yoshimura          | Masahiro            | National Cheng Kung University               | <b>ISHA Lifetime Achievement Award, 2-4</b> |
| Yu                 | Shu-Hong            | Hefei National Laboratory (HFNL)             | <b>2-5, Session 13 Chair</b>                |
| Yu                 | Ranbo               | University of Science and Technology Beijing | <b>14-1</b>                                 |
| Zhao               | Huijun              | Griffith University                          | <b>11-8</b>                                 |

## **Notes**

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**The University of Texas at Austin  
Cockrell School of Engineering, McKetta Department of Chemical  
Engineering**

200 E. Dean Keeton St. Stop C0400  
Austin, TX 78712-1589

Phone: +1 512.471.5633 Fax: +1 512.471.7060

Email: isha2013@austin.utexas.edu

<http://www.che.utexas.edu/korgel-group/isha/>