

CHEM 30200 (Synthesis and Physical Methods in Inorganic Chemistry) Notes

Steven Labalme

January 7, 2023

Weeks

1	???	1
1.1	Nanomaterials	1

List of Figures

1.1	Kirkendal effect.	3
1.2	Top-down synthesis of MoS ₂	3

Week 1

???

1.1 Nanomaterials

- 1/3:
- Contact Dr. Shevchenko at eshevchenko@anl.gov or eshevchenko@uchicago.edu.
 - How to make nano.
 - Top-down approach: Start with large, end with nano. Includes nanofabrication.
 - Bottom-up approach: Solution-based approach.
 - Scalable and cheap.
 - Use an inorganic core with a coating.
 - What nanoparticles look like.
 - Differences in size, size distribution, shape, chemical composition, and structures.
 - Different sizes (like atoms) and different shapes (like bacteria and viri).
 - Ancient nanoscience.
 - The Lycurgus cup.
 - A 4th-century Roman glass cage cup.
 - Currently housed at the British Museum.
 - Contains ~ 70 nm gold/silver nanoparticles.
 - When front-lit, it appears green (light is scattered by larger NPs).
 - When back-lit, it appears red (light is absorbed by NPs).
 - Hair dye.
 - 2000 years ago from Greco-Roman times.
 - Made of lead oxide (PbO), slaked lime (Ca(OH)_2), and water (H_2O).
 - The lead oxide combines with sulfur-rich peptides in the hair to make ~ 5 nm PbS NPs.
 - Applications of nanoparticles: Catalysis.
 - Refining of petroleum (transformation of crude oil into gasoline, jet fuel, diesel oil, and fuel oils).
 - Converter of automobile exhaust (reduction of nitrogen oxides $[\text{NO}_x]$ to N_2 and O_2 ; oxidation of CO to CO_2 ; oxidation of unburnt hydrocarbons to $\text{CO}_2 + \text{H}_2\text{O}$).
 - Hydrogenation of CO (synthesis of fuels such as methane or methanol).
 - Selective oxidation of hydrocarbons (synthetic fibers, plastics, and fine chemicals).
 - Methods of NP analysis: XRD, TEM, XANES, and XPS.

- Applications of nanoparticles: Displays.
 - Semiconductor nanoparticles (e.g., solutions of CdSe or InP nanoparticles) emit different colors.
 - Sony has announced that it will embed quantum dots in its latest flat-screen TV.
 - QLEDs can be made out of CdSe, CdS, InP coatings with silica, perovskite (CsPbX where $\text{X} = \text{Cl, Br, I}$), and cesium lead halide salts.
- Milestones in the synthesis of nanomaterials (a subjective and incomplete POV).
 - Alexei Ekimov (late 1970s-1981, USSR): CuCl_x and CdSe in molten glass matrix (fluorescence, gradient colors).
 - Alexander Afros (1982): Theoretical description of size effect.
 - Louis Brus (1983, Bell Labs, US): CdS in solution.
 - Paul Alivisatos (UChicago) and Moungi Bawendi (MIT).
 - Moungi Bawendi et al. (1993): Synthesis of monodisperse CdSe nanoparticles — a big one!
 - Philippe Guyot-Sionnest (1996): Synthesis of core/shell nanoparticles.
 - Paul Alivisatos (1997 and 2003): Synthesis of nanorods and tetrapods.
 - Chris Murray and Shouheng Sun (2000): Synthesis of magnetic FePt nanoparticles.
 - Benoit Dubert (2007, France): Synthesis of CdSe nanoplates (more stable, emission is polarized and directional).
 - Maksym Kovalenko (2015): Synthesis of perovskites.
 - Mostafe El-Sayed, Catherine Murphy, Peidong Yang, and Yunan Xia: Synthesis of Au and Ag nanoparticles.
- Synthesis of nanoparticles.
 - The 1993 Bawendi paper.
 - The innovation was the synthesis of NPs in organic solvents, still widely used today.
- LaMer model.
 - Precursors under go nucleation, focusing, and “nano”-Ostwald ripening.
 - Key idea: Separation of nucleation and growth in time.
- Nanomaterials: State-of-the-art.
 - The chemistry behind QD synthesis is rather simple compared to what is used by organic or coordination chemists, but the field sometimes lacks depth and chemical understanding.
 - Indeed, only a fraction of reported results have been reproduced, and only a fraction of those have been understood and optimized.
 - This is a big problem for AI/ML approaches.
 - During the next 5-10 years, nanomaterials synthesis will progress mostly through systematic mechanistic studies.
- Synthesis of nanocrystals without Ostwald Ripening.
 - The nanocrystals form and grow during 0.1-1 minute after the start of the reaction.
 - Annealing at high temperatures (250-280 °C) is required to improve crystallinity.
 - No change in particle size takes place upon the annealing.
 - Tune particle size with nucleation, since growth proceeds until all monomer is consumed — fast nucleation leads to many particles, which can only grow so large; slow nucleation leads to a few particles which can grow very large (conservation of end volume).

- Synthesis with “artificial molecules.”
 - Rearrangement, addition, substitution, and elimination.
- Hollow nanocrystals: Kirkendal Effect at Nanoscale.
 - Uniform spherical cobalt nanocrystals can be synthesized by rapid pyrolysis of cobalt carbonyl in hot solvent.
 - Hollow nanocrystals form after sulfidation reaction.
- Kirkendal effect.

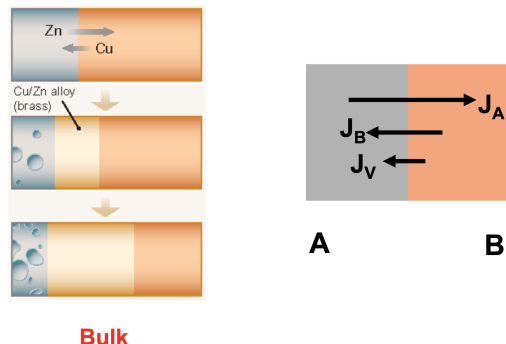
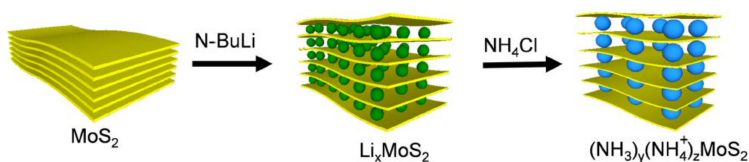


Figure 1.1: Kirkendal effect.

- Occurs when the diffusion rates of two species are different.
- When vacancies become supersaturated, they condense into voids in the fast diffusion species side.
- The Kirkendall voids result in weak bonding and lead to brittle fracture at the bonding interface.
- Top-down approaches for the synthesis of MoS_2 .

Figure 1.2: Top-down synthesis of MoS_2 .

- This is the synthesis of interlayer expanded (IE) MoS_2 through chemical intercalation of Li and the following exchange with NH_3 and NH_4 .
- Each MoS_2 layer is composed of an atomic layer of Mo sandwiched between atomic layers of S through strong ionic/covalent bonds. Weak van der Waals forces link individual MoS_2 layers with an interlayer spacing of 0.615 nm.
- Procedure.
 - Electron-donating species, e.g., alkali metals, Lewis bases, and organolithium compounds can intercalate between layers.
 - Alkali metals can after that be evaporated or react with water.
 - **Exfoliation** with ultrasound (mechanical exfoliation).
- Useful characterization methods: TEM, XRD, XPS.
- **Exfoliation:** The complete separation of the layers of a material.

- Bottom-up approaches for the synthesis of MoS_2 .
 - Chemical synthesis of interlayer expanded (IE) MoS_2 .
 - Chemical Vapor Deposition (CVD).
- MXene = 2D metal and surface chemistry.
 - Applications to supercapacitors, batteries, conductors, catalysts, and composites.
 - Most made out of Ti_3AlC_2 .
- MXenes: Solution processed 2D transition metal carbides and nitrides.
 - Scanning electron microscopy (SEM) and HRTEM images shown.
 - Etching and delamination phases.
- MXenes: Variable termination groups.
 - Ask in OH??
- MXenes are solution processable 2D transition metal carbides and nitrides.
 - Lists various experimentally synthesized structures.
- What can and cannot be synthesized in solution?
 - Current solution synthesis methodology can be applied to materials that crystallize below 400°C . Many materials that require higher temperatures to form, e.g., nitrides, carbides, GaAs.
 - Higher temperatures: Gas phase and solid state synthesis, as well as synthesis in molten salts.
- Nanocrystals in molten salts.
 - QDs are synthesized at high T in molten salts.
 - There is typically a postpreparative treatment phase still in molten salts.
- Nanoparticles as building blocks to make new materials.
 - The idea behind nanoparticles is encapsulated by the synthesis of NaCl from Na° and Cl_2° : Two substances with certain properties combine to form a new material with very different properties.
 - Assembly of atoms leads to new materials and new properties!
- Self-assembly of nanoparticles.
 - Can be multilayered (up to five).
- Crystals of nanocrystals.
 - Example: 3D crystals ($\sim 30\text{ }\mu\text{m}$) have been assembled from 3.3 nm CdSe nanocrystals.
 - Example: 3D crystals ($\sim 10\text{ }\mu\text{m}$) have been assembled from 6 nm CoPt_3 nanocrystals.
 - More conventional example: Crystals of quartz (made by atoms).
- Binary nanoparticle superlattices.
 - Natural opal vs. synthetic opals (very similar appearance and properties).
 - Formation of binary superlattices depends on the ratio of nanoparticle radii (γ), the concentration of nanoparticles, the size distribution of nanoparticles, the nature of the capping ligand, and the substrate.
 - Evaporating colloidal solutions of binary nanoparticle mixtures at 45°C leads to the formation of binary nanoparticle superlattices.

- Periodic table of nanocrystals.
 - Different types of unit cells listed.
 - Examples include AlB_2 , MgZn_2 , Cu_3Au , Fe_4C , CaCu_5 , and CaB_6 .
- Directing of self-assembly of nanocrystals.
 - Various additives can be mixed in.
- Metal organic frameworks (MOFs).
 - MOFs (also called porous coordination polymers or PCPs) are two- or three-dimensional porous crystalline materials with infinite lattices synthesized from secondary building units (SBUs) — metal cations, salts, or clusters — and polydentate organic ligands with coordination type connections.
 - Common SBUs pictured.
 - From single-metal nodes to SBUs: More than 20,000 MOF structures have been reported so far.
 - Characterization methods: TEM, SEM, XRD, XANES, XPS, and electron paramagnetic resonance (EPR).
- Summary.
 - Structural information (XRD, ED).
 - Compositional information (XRD, ED, energy dispersive X-ray analysis [EDX], and X-ray fluorescence [XRF]).
 - Size and morphology of materials (TEM, SEM, and XRD).
 - Redox states of bulk and surface (XANES, XPS).
 - Important variables: Quality of synthesized materials, stability of materials during processes, and structure-property correlations.