

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263955143>

# ChemInform Abstract: Perspectives on Electron-Assisted Reduction for Preparation of Highly Dispersed Noble Metal Catalysts

ARTICLE *in* CHEMINFORM · NOVEMBER 2013

Impact Factor: 0.74 · DOI: 10.1021/sc400376m

---

CITATIONS

18

---

READS

49

## 6 AUTHORS, INCLUDING:



Chang-Jun Liu

Tianjin University

153 PUBLICATIONS 3,424 CITATIONS

[SEE PROFILE](#)



Ze Chang

Nankai University

74 PUBLICATIONS 1,407 CITATIONS

[SEE PROFILE](#)

## Perspectives on Electron-Assisted Reduction for Preparation of Highly Dispersed Noble Metal Catalysts

Chang-Jun Liu,\*<sup>†,§</sup> Yue Zhao,<sup>†</sup> Yingzhi Li,<sup>†</sup> Da-Shuai Zhang,<sup>‡</sup> Ze Chang,<sup>‡</sup> and Xian-He Bu\*,<sup>‡,§</sup>

<sup>†</sup>Advanced Nanotechnology Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>‡</sup>Department of Chemistry, Nankai University, Tianjin 300071, China

<sup>§</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

**ABSTRACT:** Electrons are the greenest reducing agent for the preparation of highly dispersed noble metal catalysts. Two methods have been developed with electrons as the reducing agent: electron beam irradiation and room-temperature electron reduction with glow discharge or radio frequency discharge as the source of electrons. In this perspective, we attempt to summarize the current status of electron reduction with those non-hydrogen discharges as the electron source. Future developments have been addressed, too. The room-temperature electron reduction via discharges is excellent for size control with fast nucleation and slow crystal growth. It is a simple, easy, cheap, and energy efficient way to reduce metal ions. It is also worthwhile to load noble metal particles into channels of ordered porous materials, like SBA-15, with no need for complex chemical modification. The room-temperature operation makes it very useful for the preparation of noble metal catalysts supported on thermal sensitive substrates like porous organic materials, conducting polymers, ultrahigh surface area carbon, peptides, and proteins.



**KEYWORDS:** Reduction, Electron, Catalyst, Porous organic polymer, Noble metal, Gas discharge, Plasma

### INTRODUCTION

The use of catalysts is considered one of the principles of green chemistry.<sup>1–3</sup> With more concerns on the utilization of renewable sources, CO<sub>2</sub> conversion, and environmental protection, catalysis will play even more important role in the future.<sup>4,5</sup> Among the catalysts developed, the metal catalyst supported on various supporting materials is extremely important.<sup>6–8</sup> Specifically, many reactions require metallic nanoparticles as the active species. Particle size (or dispersion) and structure have significant influence on catalytic properties like selectivity and conversion.<sup>8</sup> One of the basic operations for this kind of metal catalyst is the reduction of catalyst. The conditions of catalyst reduction normally determines the size and structure of the obtained catalyst. Nowadays, the catalysts are normally reduced by flowing hydrogen at elevated temperatures or by chemical reductants, like formaldehyde and hydrazine. Generally, hydrogen is explosive. Special care is required for production, transportation, storage, and use of hydrogen. Also, the present production of hydrogen requires a huge consumption of energy and a large amount of emissions of CO<sub>2</sub> and other pollutants. On the other hand, most chemical reducing agents currently used are hazardous to both the human body and the environment. The production of chemical reducing agents is also not cheap with many wastes generated as byproducts. Thus, alternative reduction technologies must be developed.<sup>6,7</sup>

From the pointview of green chemistry principals, electrons are the best reducing agent. Specifically, electron-based reduction

methodologies have been exploited.<sup>9–27</sup> The methods reported include electron beam irradiation<sup>9–12</sup> and electron-assisted reduction (EAR) using glow discharge<sup>13–25</sup> or radio frequency<sup>26–28</sup> plasmas as the souce of electrons. The electron beam is an excellent candidate for reduction of metal ions. It has a great potential for the future application of 3D printing. However, the present technology for large-scale electron beams is still too expensive. Another way to reduce metal ions employs cold plasma technology (normally glow discharge plasma) that can operate at low temperature (as low as room temperature) with a plentiful of highly energetic electrons. The EAR using glow discharge or radio frequency plasmas is a very promising and straightforward way to prepare metal nanoparticles because it is an environmentally friendly, fast, and simple methodology and also is a promising alternative to hydrogen reduction at high temperatures.<sup>6</sup> Plasma is the fourth fundamental state of matter beyond solid, liquid, and gas. By application of energy (via heating or electric field) on a gas, the gas may ionize its molecules or atoms and becomes “plasma”. The plasma contains electrons, positive ions, negative ions, radicals, excited species, and neutral species. On the basis of the relative energies (or temperatures) of the electrons, ions, and neutral species, plasmas

**Special Issue:** Sustainable Chemical Product and Process Engineering

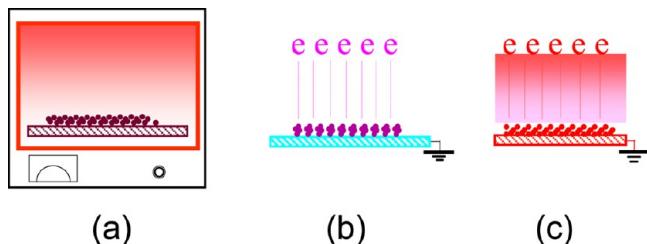
**Received:** September 23, 2013

**Revised:** October 29, 2013

**Published:** November 2, 2013

can be classified as “thermal” or “nonthermal (or cold)” plasmas. With the thermal plasmas, electrons and heavy particles have almost the same temperature. They are in a kind of thermal equilibrium with each other. Different from thermal plasmas, cold plasmas contain highly energetic electrons, but the ions and neutrals remain “cool”. They can be operated at a much lower temperature (as low as room temperature). The glow discharge and radio frequency discharge are two conventional cold plasma phenomena. Glow discharge can be easily created in a vacuum (e.g., 100 Pa) by putting two electrodes into a gas. One electrode is connected to a high voltage generator (several hundreds volts will be enough), while another electrode is grounded. Radio frequency discharge needs a higher vacuum. Details of the setups have been described in refs 13–27. Most of the reported works employed glow discharge as the source of electrons for EAR. For the reduction of metal ions or the catalyst, argon, helium, nitrogen, or even air can be used as the plasma-generating gas. In this perspective, we do not include the reduction using hydrogen plasmas. One can easily find many papers on catalyst reduction using hydrogen plasmas with hydrogen active species and electrons as the reducing agent. From the pointview of green chemistry, hydrogen plasma is not very green as discussed above, although it is a very effective way to reduce catalysts. An advantage of hydrogen plasma is that it can be operated at lower temperature compared to hydrogen reduction thermally.

The mechanism for EAR is still not very clear because of the difficulty in the measurement of electrons and other active species within cold plasmas. From the present experimental studies, electrons play the most important role in the reduction of metal ions. Electrons can be the reducing agent directly. Some species generated by the electron-induced reactions can be also effective and efficient reducing agents.<sup>29</sup> This is the reason that we assign “plasma reduction” as EAR.



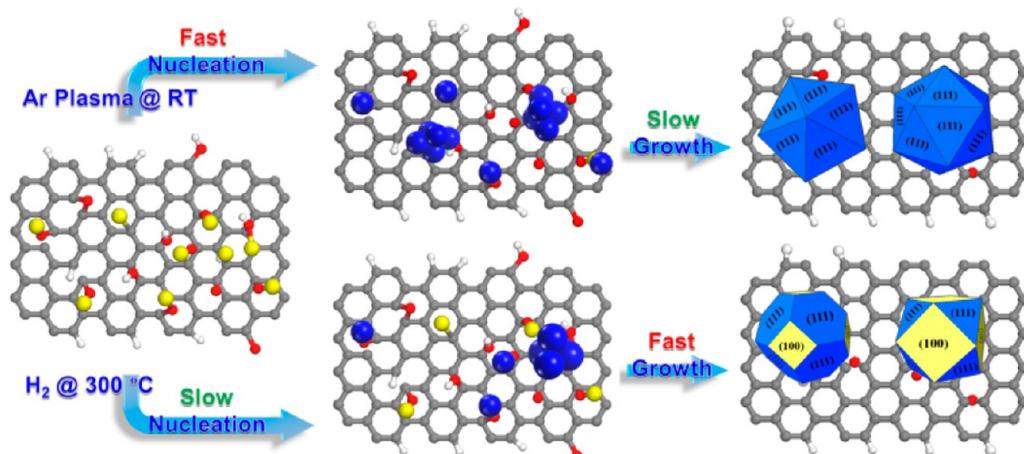
**Figure 1.** Schematic representations of catalyst preparation by thermal treatment (a), cold plasma (EAR) (b), and thermal plasma treatment (c).<sup>8</sup>

EAR is normally operated at ambient temperature. It is excellent for the fabrication of metal nanoparticles or catalysts with thermal sensitive substrates. According to the energy balance, the EAR approach significantly reduces energy consumption and economic cost as well as emissions of the toxic or hazardous materials. The reducibility of metal ions by non-hydrogen plasma can be determined by the value of the standard electrode potential of the metal ions.<sup>14</sup> Those metal ions with positive standard electrode potentials can be easily reduced by non-hydrogen plasma at ambient temperature, such as Pd, Pt, Au, Ag, Rh, Ir, etc.<sup>14</sup> For those ions with negative standard electrode potentials, a combination of glow discharge or radio frequency plasma treatment and thermal calcination can be applied, too.<sup>30–32</sup> The catalytic performance can be significantly improved with this combination. Moreover, hydrogen plasma can be employed directly if necessary.<sup>33</sup>

In this perspective, we attempt to summarize the recent progress in the application of EAR with non-hydrogen plasmas; normally glow discharge and radio frequency discharge are the sources of electrons for the preparation of noble metal catalysts. The future development will be discussed.

## ■ NUCLEATION AND CRYSTAL GROWTH UNDER THE EAR MODE

The first step of catalyst preparation is the nucleation of the catalyst crystal. Under the EAR mode, the nucleation (and then crystal growth) occurs normally at room temperature. It is very different from the conventional thermal way. The nucleation under the EAR mode is initiated by electrons or by the active species via electrons with no thermal effect. Therefore, nucleation is fast under the EAR mode. However, crystal growth after nucleation under the EAR mode is complex. It depends on the supporting material applied, electron density (or the density of active species), electron energy, and probably others. Because of the lack of on-site characterization technology, the crystal growth mechanism is still unclear. In general, EAR is carried out at room temperature. Crystal growth is slower compared to the conventional thermal way. Figure 1 shows schematic representations of catalyst preparations by thermal treatment, EAR (cold plasma), and thermal plasma treatment.<sup>8</sup> Figure 2 shows the comparison of nucleation and crystal growth under EAR and thermal modes. We have to acknowledge that nucleation and crystal growth under the EAR mode is new. Many unknown issues, opportunities, and challenges exist. We will report more progresses in the near future.



**Figure 2.** Nucleation and crystal growth under EAR and thermal modes.

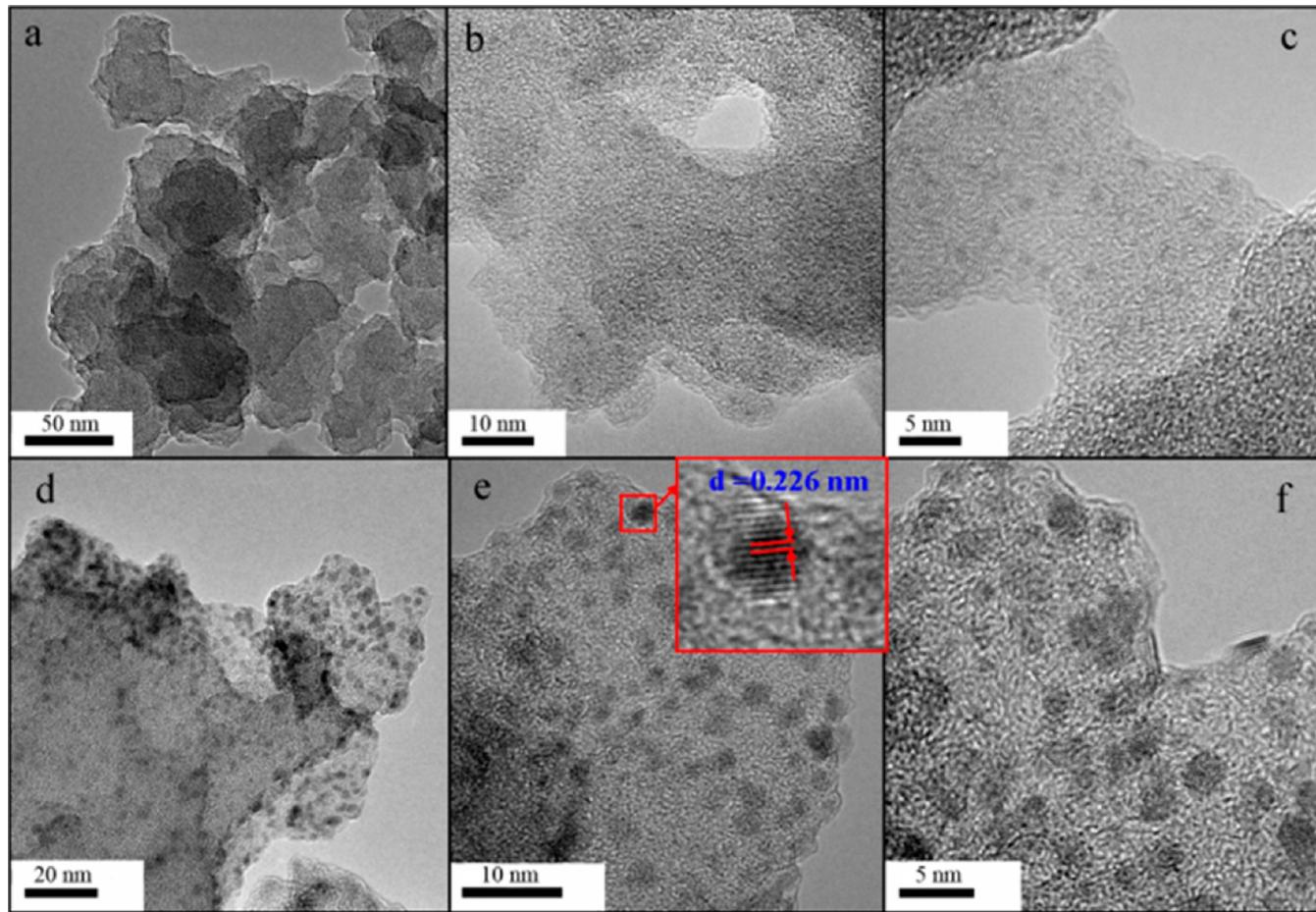


Figure 3. TEM images of COP-4 (a), Pd/COP-4-DE (b and c), Pd/COP-4-WE (d, e, and f). COP-4 is the COP material applied in this work.<sup>37</sup>

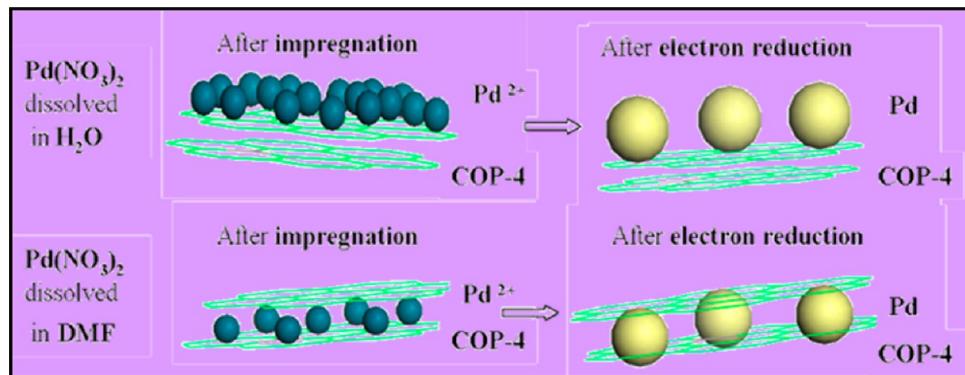


Figure 4. Synthesis process of COP-4-supported Pd catalysts in different solvents.<sup>37</sup>

#### ■ EAR FOR PREPARATION OF CATALYSTS SUPPORTED ON POROUS ORGANIC POLYMERS

Recently, the use of porous organic polymers (POPs) as catalyst supports has attracted much attention.<sup>34–37</sup> A major advantage of POPs is that one can design the functions or properties of POPs before syntheses. It has been expected that POP-supported catalysts will find promising applications in the chemical industries and others. However, many POPs have poor thermal stability. It is difficult to use the conventional hydrogen reduction to load the metal catalyst. In this regard, EAR is excellent for the preparation of POP-supported catalysts.

In order to demonstrate the effectiveness of EAR, we first tested covalent organic polymers (COPs) with good hydrothermal

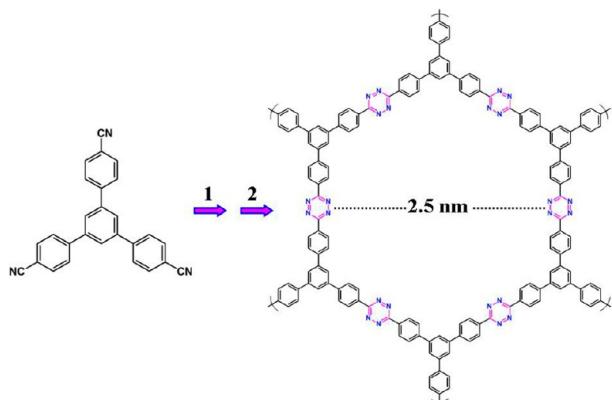
stability (because of the composition of relatively stable covalent C–C, C–H, and C–N bonds).<sup>37</sup> Two COP-supported palladium (Pd) catalysts were prepared using EAR via impregnation with distilled water and DMF. The obtained COP-supported Pd catalysts show excellent Pd dispersion with EAR. No diffraction peaks ascribed to the Pd species can be found in the XRD patterns. This indicates that the particles are highly dispersed on the support with a smaller size than the detection limit of 3 nm. The above observation is confirmed by TEM images of the samples in Figure 3. The particles are very clear and show uniform distribution. The inset image in Figure 2e shows lattice fringes with  $d = 0.226 \text{ nm}$ , which can be attributed to the Pd (111) planes. This indicates that Pd<sup>0</sup> is formed on COP. In addition, it was confirmed that the solvent has a

significant effect on the Pd dispersion. As shown in Figure 4, DMF can easily infiltrate to the pores of COP-4, while water is kept outside the pores. Therefore, the Pd particles will be confined into the pores after the metal ions in DMF are reduced. In contrast, the Pd ions in water transfer to the Pd particles outside the pores without confinement in the pores. DMF is obviously better than water for higher Pd dispersion.<sup>37</sup>

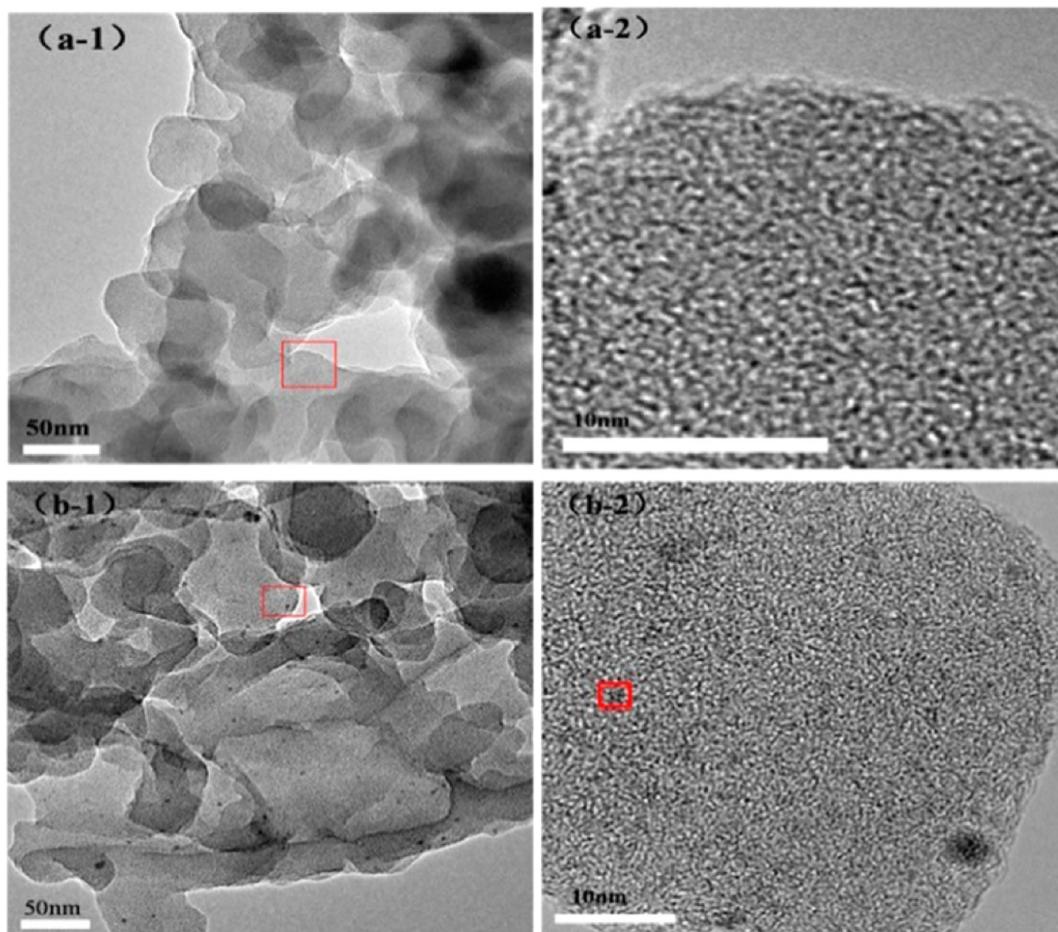
The isotherms of the two Pd/COP samples have similar shapes with that of COP. Moreover, they have nearly the same

pore size distribution calculated by the HK method. This suggests that the pore structure of COP does not show change after Pd loading and electron reduction. The EAR-made catalysts have shown good activities for CO oxidation.<sup>37</sup>

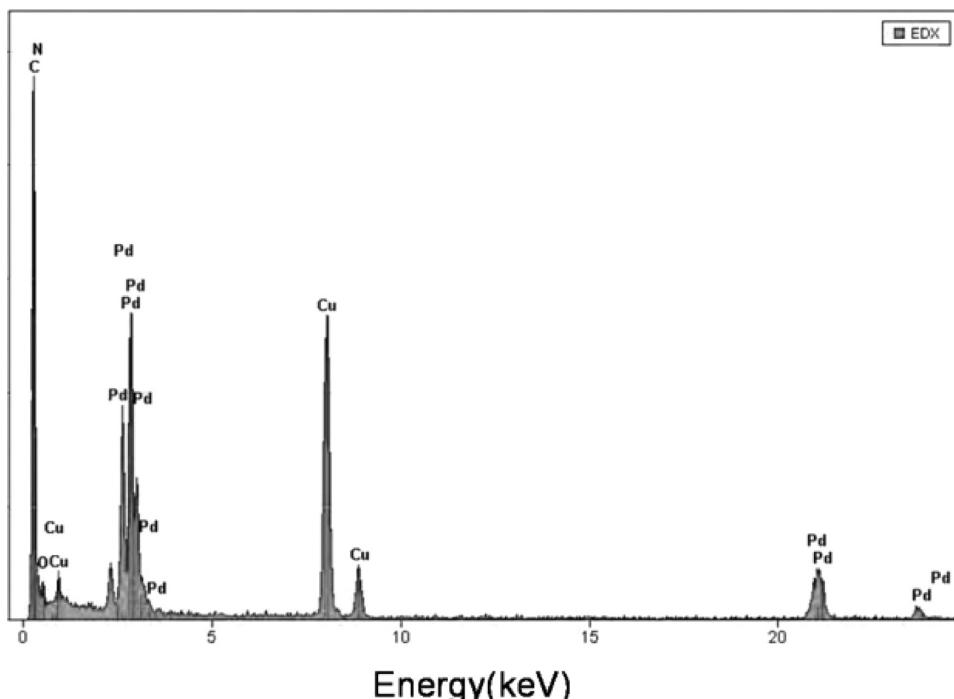
However, there are many POPs with poor thermal stability. It still remains a big challenge to use these thermally sensitive POPs as the catalyst support. It limits the application of POPs, too. It is highly necessary to develop novel techniques that can be operated at low temperature conditions (less than 200 °C normally) for the preparation of POP-supported catalysts. Also, efficient loading of the metal catalyst is another factor to consider. The pore dimension and surface characteristic of POPs could affect the particle size and distribution of the catalyst, which determines the performances of POP-based catalysts. An impregnation is always preferred for the high metal loading catalysts. In this perspective, we extend the use of EAR for the preparation of covalent organic framework (COF)-supported Pd catalysts. We chose an ingeniously constructed conjugated tetrazine-based organic framework (TzF) as the example.<sup>38</sup> TzF possesses permanent microporous structures and can be a good candidate for the porous support. The nitrogen-rich pore surface provides suitable binding sites for the anchoring of metal ions. The unique tetrazine linkage between building blocks (Figure 5) reduces the stability of the framework as well as the pore surface. The tetrazine ring would gradually decompose into nitriles and N<sub>2</sub> molecules upon heating above 200 °C, which limits the treatment of material under elevated temperature. Fortunately, with the room-temperature EAR technology, the framework of TzFs can be persevered during the reduction of metal ions. TzFs can be then employed as the catalyst



**Figure 5.** Synthetic routes of TzF-9. TzF-9 is the TzF material applied in this work. (1) Hydrazine hydrate and sulfur/solvent. (2) AcOH and NaNO<sub>2</sub> solution.



**Figure 6.** TEM images of (a) TzF-9 and (b) 10% Pd/TzF-9. 1 stands for low resolution TEM images, and 2 stands for HRTEM images.



**Figure 7.** EDX intensity profile of Pd nanoparticle.

support. An ultrahigh dispersion of palladium nanoparticles has been achieved even with a high metal loading (10 wt %). The obtained catalyst shows a good activity for oxidation of benzyl alcohol. Figure 6 presents the TEM images of a TzF-supported Pd catalyst. From Figure 6b, highly dispersed palladium nanoparticles with narrow size distribution have been formed. The mean size of palladium nanoparticles is smaller than 1.5 nm, which is in good agreement with the pore width of 1.4 nm of TzF. The EDX spectra (Figure 7) confirm the formation of Pd nanoparticles, whereas the content of element O is very low. Therefore, we can deduce that the Pd nanoparticles are mainly metallic. The porous structure of the TzF support plays an important role in the size control and dispersion of Pd species.

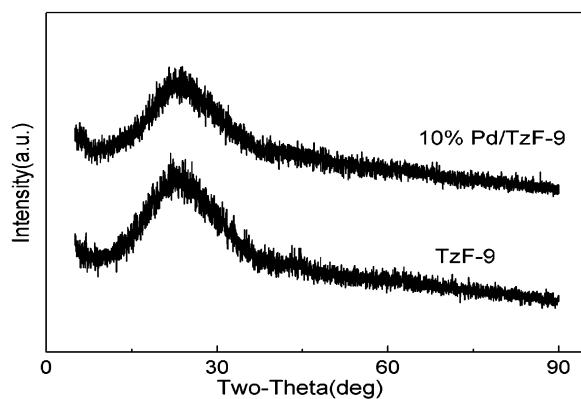
Figure 8 shows the XRD patterns of TzF and Pd/TzF. A broaden peak located at about  $2\theta = 23^\circ$  is observed over TzF. XRD

particle size. This confirms the TEM result. The obtained Pd/TzF-9 catalyst shows a good activity for aerobic benzyl alcohol oxidation using dioxygen as oxidant. The highest TOF ( $7728 \text{ h}^{-1}$ ) was achieved at the reaction temperature of  $120^\circ\text{C}$ .

From the discussions above, the EAR method is indeed excellent for catalyst preparation with a thermally sensitive substrate. In this regard, Buitrago-Sierra et al.<sup>39</sup> reported another good example with polypyrrole as the supporting material. This material is even less stable compared to porous organic materials. They had to use EAR to load Pt on it. They found that platinum in the metal precursor ( $\text{H}_2\text{PtCl}_6$ ) is partially reduced to Pt(II) species upon the impregnation of polypyrrole, with  $-\text{NH}-$  groups being subsequently oxidized to  $\text{N}^+$ . This provides anchoring sites for the metal precursor that results in a high dispersion of the active metal. The particle sizes of EAR-made samples are between 2.5 and 4.5 nm, while 4.5 nm is the particle size for the sample reduced with borohydride. EAR leads to a more effective reduction of platinum ions in the chloroplatinum complex to metallic platinum compared to reduction with borohydride because of direct transfer of the abundant electrons in the plasma to platinum ions. The EAR-made sample effectively catalyzes the reaction of reduction of nitrates in water with  $\text{H}_2$  up to  $\text{N}_2$ , producing very low amounts of nitrite and ammonium ions.

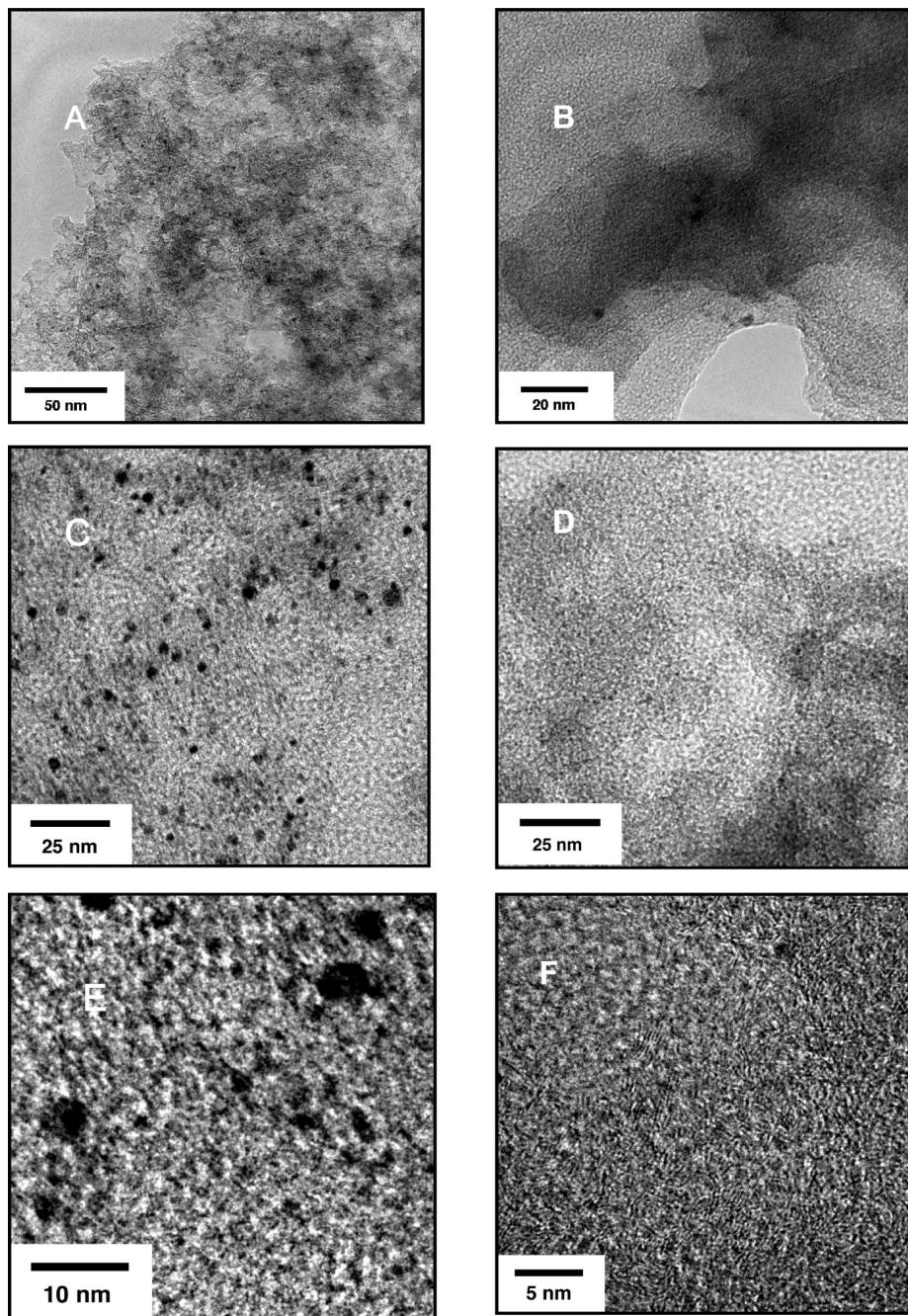
#### ■ EAR FOR PREPARATION OF CARBON-SUPPORTED NOBLE METAL CATALYSTS

Carbon is a very important supporting material for many applications like fuel cells, hydrogen storage, and fine chemical production. Doping of metal on carbon can be significantly improved by EAR,<sup>22,23</sup> especially for those carbon with ultrahigh surface areas. Increased dispersion and stronger interactions between metal particles and the substrate can be achieved. For the case of hydrogen storage, both improvements lead directly to enhanced hydrogen spillover, thereby increasing hydrogen storage. A high dispersion of metal particles will lead to a high storage capacity because highly dispersed metal will have a large



**Figure 8.** XRD patterns of TzF-9 and 10% Pd/TzF-9 catalysts.

patterns indicate the amorphism of TzF and Pd/TzF. No peaks assigned to palladium can be detected in the patterns of Pd/TzF even with a high metal loading of 10 wt %. This means that palladium has been highly dispersed in the support with a very small

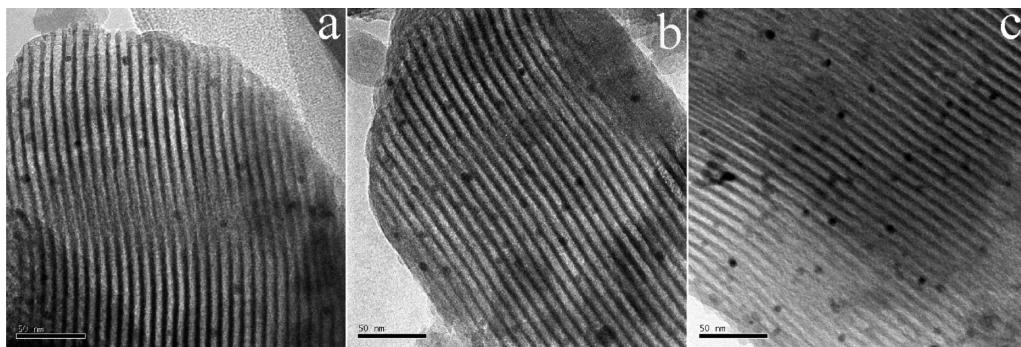


**Figure 9.** TEM images of the hydrogen-reduced Pt/AC (A, C, E) and EAR-made Pt/AC (B, D, F) samples.<sup>23</sup> (A, B) As synthesized and (C, D, E, F) after sintering at 773 K (in Ar) for 3 h.

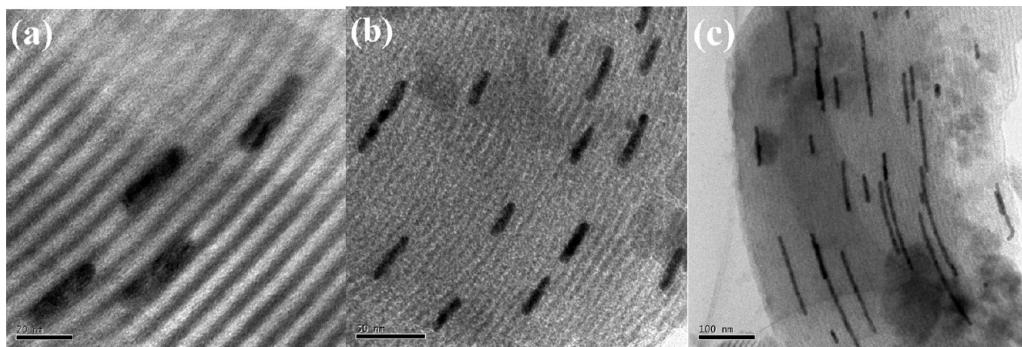
metal surface area that enables the maximum contacts with the carbon structures and also with hydrogen molecules. Therefore, it could facilitate the dissociation of hydrogen and the diffusion of atomic hydrogen on the carbon surface.<sup>22,23</sup> Sui et al.<sup>16</sup> have also demonstrated that EAR improves Pt dispersion, leading to a significant improvement in fuel cell performance.

Hydrogen energy is considered as an alternative energy to fossil fuels. An effective hydrogen storage technique is one of the key barriers for realization of fuel cell-powered vehicles using hydrogen as the energy carrier. Using EAR with 3 wt % Pt loading, the hydrogen storage capacity of activated carbon at 298 K is increased nearly 3-fold.<sup>23</sup> Without EAR but with hydrogen reduction, the increase in hydrogen storage is only 54% by doping 3 wt % Pt.<sup>23</sup> This EAR made Pt sample possesses an

excellent thermal stability. As shown in Figure 9C and E, very large Pt particles with sizes of ~6 nm are observed on the thermally treated sample. The particles of Pt are sintered upon heating at 500 °C for 3 h. However, for the EAR-made sample, no significant changes in the particle size of Pt are observed as shown in Figure 9D and F.<sup>23</sup> The excellent thermal stability of the EAR-made Pt sample is also confirmed by low-pressure H<sub>2</sub> adsorption measurements.<sup>23</sup> From the low-pressure H<sub>2</sub> isotherms on the EAR-made and thermally treated samples before and after a sintering test, one can observe that the hydrogen adsorption capacity at zero pressure by extrapolating the isotherm is clearly reduced on the thermally prepared sample after thermal treatment, showing considerable sintering. However, no significant difference is observed between the



**Figure 10.** Typical TEM images of Pd/SBA-15 composites with different Pd loading: (a) 0.5 wt % Pd/SBA-15, (b) 2.0 wt % Pd/SBA-15, and (c) 5.0 wt % Pd/SBA-15.<sup>40</sup> Scale bar: 50 nm.



**Figure 11.** Typical TEM images of Au/SBA-15 composites with different Au loading: (a) 0.5 wt % Au/SBA-15; scale bar, 20 nm; (b) 1.0 wt % Au/SBA-15; scale bar, 50 nm; and (c) 5.0 wt % Au/SBA-15;<sup>40</sup> scale bar, 100 nm.

EAR-made samples before and after the thermal treatment. These results indicate stronger interactions between the Pt particles and carbon on the EAR-made sample. The stronger interactions enable more intimate connectivities between Pt and carbon, thereby facilitating more spillover of hydrogen from Pt to the surface of the carbon.<sup>23</sup>

Reversibility is evaluated on the EAR-made Pt sample by measuring the desorption branch down to 1 atm. It can be seen that the desorption branch nearly follows the adsorption branch, although there appeared to be a slight hysteresis. The sample is then evacuated to a pressure of 1 Pa for 12 h at 298 K, and total desorption occurs. The second adsorption isotherm is in complete agreement with the first adsorption isotherm. These results show that hydrogen adsorption in the EAR-made Pt sample is fully reversible.<sup>23</sup>

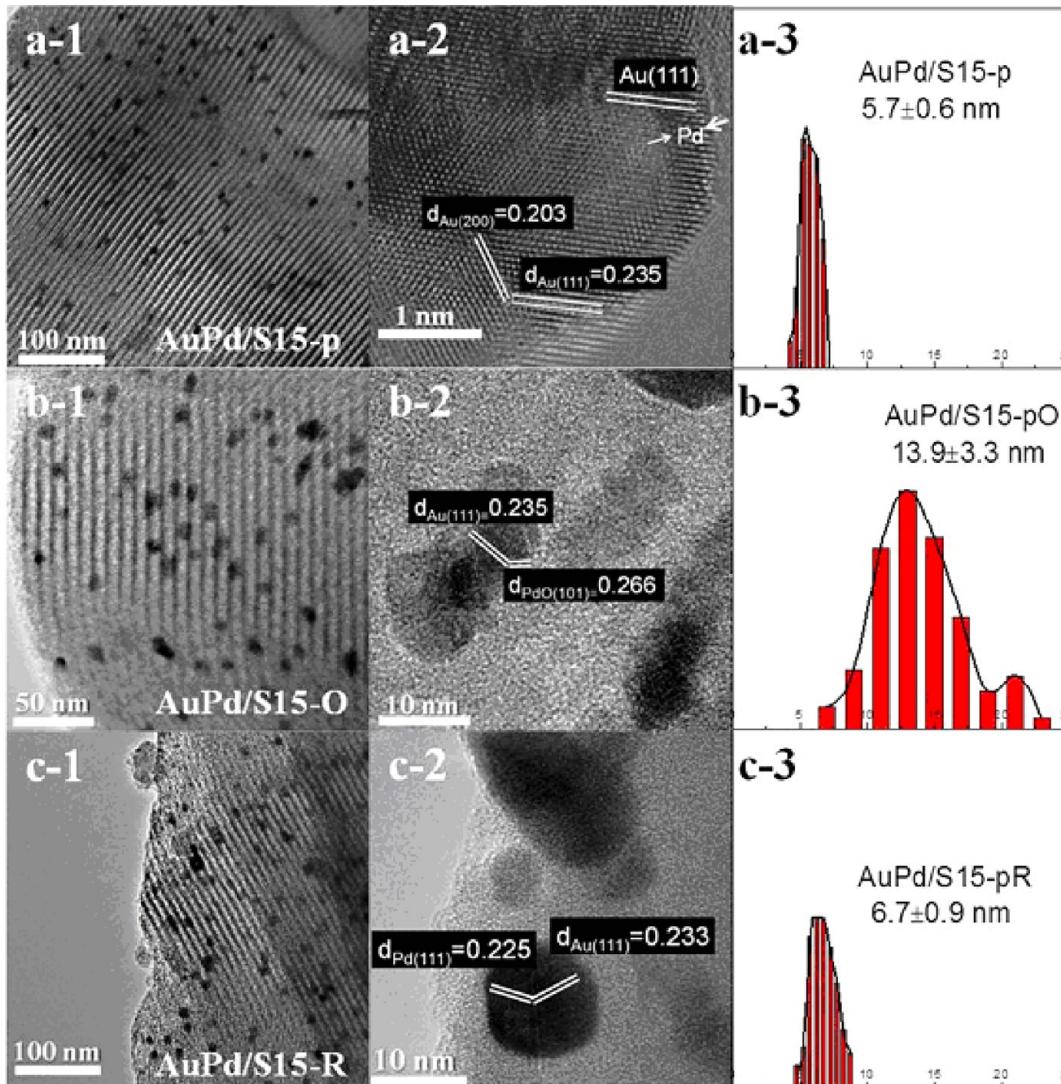
### ■ EAR FOR DISPERSION OF NOBLE METAL NANOPARTICLES INTO CHANNELS OF SBA-15

Metal or multi-metal/mesoporous material composites (e.g., noble metal/SBA-15 composites) are promising in catalysis, drug delivery, and many other processes. Because of the charge characteristic of SBA-15, modification of SBA-15 is normally needed by adding functional groups before impregnation. We have demonstrated that chemical modification is unnecessary if EAR is employed after conventional impregnation.<sup>40</sup> Pd and Pt nanoparticles can be easily loaded into SBA-15. The increasing metal content does not make larger nanoparticles (Figure 10). However, Au and Ag nanowires are formed during EAR.<sup>40</sup> The increasing metal content leads to longer nanowires (Figure 11). EAR provides an easy way to load metallic nanoparticles into SBA-15.

We have extended the use of EAR to prepare Au–Pd bimetal/SBA-15 composites.<sup>41</sup> Different from the monometal/SBA-15 composites discussed above, the obtained bimetallic Au–Pd nanocomposites well retains the morphology of spherical nanoparticles with a similar particle size distribution. The size of the metal nanostructure (diameter of metal nanoparticles/nanorods) can be effectively controlled and tailored by the highly ordered mesopores of SBA-15 silica. Uniform particle dispersions and size distributions are obtained. Specifically, a Pd-rich shell/Au-rich core structure with abundant surface coordination of unsaturated Pd atoms for effectively reduced Au–Pd bimetallic nanoparticles has been formed. These Au–Pd bimetallic nanoparticles show high activity in the selective oxidation of benzyl alcohol. The reaction rate of the bimetallic nanoparticles is 12.5- and 2-fold higher than that over Au and Pd monometallic catalysts, respectively. The enhancement in both activity and selectivity has been attributed to the Pd-rich shell/Au-rich core structure with abundant surface coordination of unsaturated Pd atoms of those effectively confined and well-dispersed Au–Pd nanoparticles.<sup>41</sup> Figure 12 shows TEM images of different bimetallic Au–Pd catalysts. Further oxidation and re-reduction of the plasma reduced Au–Pd catalyst result in atomic rearrangement of nanoparticles, leading to an inferior catalytic performance.<sup>41</sup>

### ■ OUTLOOK

We confirm here that EAR has many promising applications in the fabrication of metallic nanoparticles, nanocomposites, and catalysts. Specifically, it is very promising to use EAR for the preparation of supported catalysts or composites on thermally sensitive substrates like porous organic polymers, peptides, and ultrahigh surface area carbon. We previously demonstrated a hydrated electro-induced self-assembly of peptides.<sup>42</sup> EAR has



**Figure 12.** TEM images of different bimetallic Au–Pd catalysts. (a) EAR-made AuPd/SBA-15. (b) EAR-made AuPd/SBA-15 after oxidation at 773 K in oxygen. (c) EAR-made AuPd/SBA-15 after oxidation at 500 °C in oxygen and re-reduction at 773 K in hydrogen. 1 stands for low-resolution TEM images, 2 stands for HRTEM images, and 3 stands for the corresponding size distribution.<sup>41</sup>

great potential for loading noble metal nanoparticles on peptides and also on proteins and other related soft materials.

With the present glow discharge or radio frequency discharge technology, the non-hydrogen-based EAR can only reduce metal ions with positive standard electrode potentials.<sup>14</sup> For those with negative standard electrode potentials, the glow discharge or radio frequency discharge treatment can modify the hydrate and the interaction between the precursor and the supporting material. With a combination of thermal treatment, an excellent catalyst can be still prepared in an efficient and effective way.<sup>8,30,31</sup>

Because EAR is operated at room temperature, a fast nucleation has been observed, normally induced by the reaction with electrons. With the effect of the supporting material, one can make the nanoparticles in a size controllable way using EAR. A narrow size distribution has been achieved with EAR on several supporting materials, like COP,<sup>37</sup> conducting polymers,<sup>39</sup> and carbon.<sup>22,23</sup> Specifically, EAR can easily load the metallic nanoparticles into the pores of mesoporous materials like SBA-15 via conventional impregnation. No chemical modification is needed. A significant advantage of EAR is that site control or region control becomes possible. This means that we can precisely and

easily control the site or the area where the nanoparticle will be deposited. No complex processing is needed. An atmospheric pressure microplasma EAR has been recently developed.<sup>43</sup> This microplasma will make the site or region control easier. More progress is expected with the applications of EAR.

The mechanism of EAR-related reactions is still not clear. Within the glow discharge or radio frequency discharge, the electrons are energetic and “very hot” (up to  $10^5$  K), but the heavy particle temperature remain as low as room temperature. This “nonequilibrium” characteristic makes the cold plasma very useful for the reduction of metal ions in an easy and rapid way with the electrons or electron-induced active species as the reducing agent. Therefore, argon, helium, and even air can be used as the plasma-generating gas for plasma reduction. No hydrogen is needed. No hazardous chemicals are needed. However, it is still very difficult to measure the density and energy of electrons and other active species within the glow discharge or radio frequency discharge. It is also very difficult to detect the charge and active species involved in the electron-induced reactions, especially on the surface of the catalyst. This generates many important fundamental issues not only in

chemistry and physics. We can expect rapid progress in the technical or experimental aspects with more products fabricated using EAR.<sup>3,8,13,44,45</sup> However, a challenge remaining is the poor theoretic understanding. Because of the nonequilibrium characteristic, we are still waiting for a breakthrough in thermodynamics, physics, and chemistry regarding cold plasmas. A multidisciplinary effort is immediately needed.

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: ughg\_cjl@yahoo.com. Tel: +86 22 27406490. Fax: +86 22 27406490 (C.-J. Liu).

\*E-mail: buxh@nankai.edu.cn. Tel: +86 22 23502809. Fax: +86 22 23502458 (X.-H. Bu).

### Notes

The authors declare no competing financial interest.

### Biographies



Dr. Chang-Jun Liu received his Ph.D. degree from Tianjin University in 1993. After postdoctoral positions at the University of Oklahoma (2.5 years) and Prairie View A&M University (1 year), he joined ABB Cooperative Research, Switzerland. He became a Professor at Tianjin University in 1999. Prof. Liu's research interests include catalysis, CO<sub>2</sub> utilization, and plasma nanoscience. He served as 2010 Program Chair of the Fuel Chemistry Division of the American Chemical Society and Chair of the 10th International Conference on CO<sub>2</sub> Utilization. He was a guest editor for the ACS Symposium Series, Catalysis Today, Green Chemistry, ChemCatChem, and Energy & Environmental Science. He is now an advisory board member for Greenhouse Gases: Science & Technology and an editorial board member for Applied Catalysis B, Journal of Energy Chemistry, and Journal of CO<sub>2</sub> Utilization. He became a Fellow of the Royal Society of Chemistry in 2011.



Ms. Yue Zhao obtained her M.S. degree in Chemical Technology from Tianjin University in 2013 under the supervisor of Prof. Chang-Jun Liu.

During her graduate studies, she focused on the synthesis of noble metal catalysts based on porous organic materials. She is now an engineer at Tianjin Sigma Innova Technology Co, Ltd.



Ms. Yingzhi Li obtained her science degree from Nankai University and engineering degree from Tianjin University in 2009. After that, she became a graduate student of Prof. Chang-Jun Liu. She focused on the research of graphene-supported noble metal catalysts. In 2012, she received her M.S. degree at Tianjin University and joined PPG coatings (Tianjin) Co. Ltd as a quality engineer.



Mr. Da-Shuai Zhang received his B.S. degree in 2009 from Liaocheng University, China, and is now a Ph.D. candidate at Nankai University under the supervision of Professor Xian-He Bu. His research interests include the rational design and synthesis of metal organic frameworks and their applications in gas storage and separation.



Dr. Ze Chang received his B.S. degree at Nankai University in 2006 and his Ph.D. degree in 2011 under the direction of Prof. Xian-He Bu. Then, he became a lecturer at Nankai University and joined Prof. Bu's group. His research interest focuses on the construction and properties

investigation of functional porous metal organic frameworks and porous organic polymers.



Prof. Xian-He Bu received his B.S. degree and Ph.D. degree at Nankai University in 1986 and 1992, respectively. He is now a professor (Chang-Jiang Scholar) at Nankai University and serves as the head of the Department of Chemistry and is a director of the Tianjin Key Lab on Metal and Molecule-based Materials Chemistry. His current research interests include coordination chemistry, MOFs, COFs, magnetic materials, etc. He has coauthored over 300 research papers (H index 52) and received several scientific awards.

## ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (#51174276) the 973 program of China (2012CB821700) is greatly appreciated.

## REFERENCES

- (1) Anastas, P. T.; Bartlett, L. B.; Kirchhoff, M. M.; Williamson, T. C. The role of catalysis in the design, development, and implementation of green chemistry. *Catal. Today* **2000**, *55* (1–2), 11–22.
- (2) Polshettiwar, V.; Varma, R. S. Green chemistry by nano-catalysis. *Green Chem.* **2010**, *12* (5), 743–754.
- (3) Liu, C. J.; Burghaus, U.; Besenbacher, F.; Wang, Z. L. Preparation and characterization of nanomaterials for sustainable energy production. *ACS Nano* **2010**, *4* (10), 5517–5526.
- (4) Ramsurn, H.; Gupta, R. B. Nanotechnology in solar and biofuels. *ACS Sustainable Chem. Eng.* **2013**, *1* (7), 779–797.
- (5) Lee, G. G. W.; Minteer, S. D. Greener method to a manganese oxygen reduction reaction electrocatalyst: Anion electrolyte effects on electrocatalytic performance. *ACS Sustainable Chem. Eng.* **2013**, *1* (3), 359–363.
- (6) Campelo, J. M.; Luna, D.; Luque, R.; Marinas, J. M.; Romero, A. A. Sustainable preparation of supported metal nanoparticles and their applications in catalysis. *ChemSusChem* **2009**, *2* (1), 18–45.
- (7) White, R. J.; Luque, R.; Budarin, V. L.; Clark, J. H.; Macquarrie, D. J. Supported metal nanoparticles on porous materials. Methods and applications. *Chem. Soc. Rev.* **2009**, *38* (2), 481–494.
- (8) Liu, C. J.; Ye, J. Y.; Jiang, J. J.; Pan, Y. X. Progresses in the preparation of coke resistant Ni-based catalyst for steam and CO<sub>2</sub> reforming of methane. *ChemCatChem* **2011**, *3* (3), 529–541.
- (9) Ohkubo, Y.; Hamaguchi, Y.; Seino, S.; Nakagawa, T.; Kageyama, S.; Kugai, J.; Nitani, H.; Ueno, K.; Yamamoto, T. A. Preparation of carbon-supported PtCo nanoparticle catalysts for the oxygen reduction reaction in polymer electrolyte fuel cells by an electron-beam irradiation reduction method. *J. Mater. Sci.* **2013**, *48* (14), 5047–5054.
- (10) Pai, Y. H.; Huang, H. F.; Chang, Y. C.; Chou, C. C.; Shieh, F. S. Electron-beam reduction method for preparing electrocatalytic particles for membrane electrode assemblies (MEA). *J. Power Sources* **2006**, *159* (2), 878–884.
- (11) Song, K.; Sauter, D. J.; Wu, J. S.; Dravid, V. P.; Stair, P. C. Evolution of high-energy electron beam irradiation effects on zeolite supported catalyst: Metal nanoprecipitation. *ACS Catal.* **2012**, *2* (3), 384–390.
- (12) Kugai, J.; Moriya, T.; Seino, S.; Nakagawa, T.; Ohkubo, Y.; Nitani, H.; Mizukoshi, Y.; Yamamoto, T. A. Effect of support for Pt–Cu bimetallic catalysts synthesized by electron beam irradiation method on preferential CO oxidation. *Appl. Catal., B* **2012**, *126*, 306–314.
- (13) Liu, C. J.; Zou, J. J.; Yu, K. L.; Cheng, D. G.; Han, Y.; Zhan, J.; Ratanatawanate, C.; Jang, B. W. L. Plasma application for more environmentally friendly catalyst preparation. *Pure Appl. Chem.* **2006**, *78* (6), 1227–1238.
- (14) Wang, Z. J.; Zhao, Y.; Cui, L.; Du, H.; Yao, P.; Liu, C. J. CO<sub>2</sub> reforming of methane over argon plasma reduced Rh/Al<sub>2</sub>O<sub>3</sub> catalyst: A case study of alternative catalyst reduction via non-hydrogen plasmas. *Green Chem.* **2007**, *9* (6), 554–559.
- (15) Liang, X.; Liu, C. J.; Kuai, P. Y. Selective oxidation of glucose to gluconic acid over argon plasma reduced Pd/Al<sub>2</sub>O<sub>3</sub>. *Green Chem.* **2008**, *10* (12), 1318–1322.
- (16) Sui, S.; Ma, L. R.; Zhai, Y. C. TIC supported Pt–Ir electrocatalyst prepared by a plasma process for the oxygen electrode in unitized regenerative fuel cells. *J. Power Sources* **2011**, *196* (13), 5416–5422.
- (17) Zhou, C. M.; Chen, H.; Yan, Y. B.; Jia, X. L.; Liu, C. J.; Yang, Y. H. Argon plasma reduced Pt nanocatalysts supported on carbon nanotube for aqueous phase benzyl alcohol oxidation. *Catal. Today* **2013**, *211*, 104–108.
- (18) Yang, F.; Li, Y. F.; Liu, T.; Xu, K.; Zhang, L. Q.; Xu, C. M.; Gao, J. S. Plasma synthesis of Pd nanoparticles decorated-carbon nanotubes and its application in Suzuki reaction. *Chem. Eng. J.* **2013**, *226*, 52–58.
- (19) Meiss, S. A.; Rohnke, M.; Kienle, L.; El Abedin, S. Z.; Endres, F.; Janek, J. Employing Plasmas as gaseous electrodes at the free surface of ionic liquids: Deposition of nanocrystalline silver particles. *ChemPhysChem* **2007**, *8* (1), 50–53.
- (20) Kaneko, T.; Takahashi, S.; Hatakeyama, R. Control of nanoparticle synthesis using physical and chemical dynamics of gas-liquid interfacial non-equilibrium plasmas. *Plasma Phys. Controlled Fusion* **2012**, *54* (12), 124027.
- (21) Chen, Q.; Kaneko, T.; Hatakeyama, R. Rapid synthesis of water-soluble gold nanoparticles with control of size and assembly using gas-liquid interfacial discharge plasma. *Chem. Phys. Lett.* **2012**, *521*, 113–117.
- (22) Wang, Z.; Yang, R. T. Enhanced hydrogen storage on Pt-doped carbon by plasma reduction. *J. Phys. Chem. C* **2010**, *114* (13), 5956–5963.
- (23) Li, Y.; Yang, R. T.; Liu, C. J.; Wang, Z. Hydrogen storage on carbon doped with platinum nanoparticles using plasma reduction. *Ind. Eng. Chem. Res.* **2007**, *46* (24), 8277–8281.
- (24) Yu, Y.; Li, Y. Z.; Pan, Y. X.; Liu, C. J. Fabrication of palladium/graphene oxide composite by plasma reduction at room temperature. *Nanoscale Res. Lett.* **2012**, *7*, 234.
- (25) Zhou, C. M.; Wang, X.; Jia, X. L.; Wang, H. P.; Liu, C. J.; Yang, Y. H. Nanoporous platinum grown on nickel foam by facile plasma reduction with enhanced electro-catalytic performance. *Electrochim. Commun.* **2012**, *18*, 33–36.
- (26) Zhou, T.; Jang, K.; Jang, B. W. L. Ionic liquid and plasma effects on SiO<sub>2</sub> supported Pd for selective hydrogenation of acetylene. *Catal. Today* **2013**, *211*, 147–155.
- (27) Wang, Q.; Song, M. M.; Chen, C. L.; Wei, Y.; Zuo, X.; Wang, X. K. Synthesis of graphene-based Pt nanoparticles by a one-step in situ plasma approach under mild conditions. *Appl. Phys. Lett.* **2012**, *101* (3), 033103.
- (28) Li, Y.; Jang, B. W. L. Non-thermal RF plasma effects on surface properties of Pd/TiO<sub>2</sub> catalysts for selective hydrogenation of acetylene. *Appl. Catal., A* **2011**, *392* (1–2), 173–179.
- (29) Patel, J.; Němcová, L.; Maguire, P.; Graham, W. G.; Mariotti, D. Synthesis of surfactant-free electrostatically stabilized gold nanoparticles by plasma-induced liquid chemistry. *Nanotechnology* **2013**, *24*, 245604.

- (30) Zhu, X. L.; Huo, P. P.; Zhang, Y. P.; Cheng, D. G.; Liu, C. J. Structure and reactivity of plasma treated Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for CO<sub>2</sub> reforming of methane. *Appl. Catal., B* **2008**, *81* (1–2), 132–140.
- (31) Pan, Y. X.; Liu, C. J.; Shi, P. Preparation and characterization of coke resistant Ni/SiO<sub>2</sub> catalyst for carbon dioxide reforming of methane. *J. Power Sources* **2008**, *176* (1), 46–53.
- (32) Wang, N.; Shen, K.; Yu, X. P.; Qian, W. Z.; Chu, W. Preparation and characterization of a plasma treated NiMgSBA-15 catalyst for methane reforming with CO<sub>2</sub> to produce syngas. *Catal. Sci. Technol.* **2013**, *3* (9), 2278–2287.
- (33) Xu, Y.; Long, H. L.; Wei, Q.; Zhang, X. Q.; Shang, S. Y.; Dai, X. Y.; Yin, Y. X. Study of stability of Ni/MgO/gamma-Al<sub>2</sub>O<sub>3</sub> catalyst prepared by plasma for CO<sub>2</sub> reforming of CH<sub>4</sub>. *Catal. Today* **2013**, *211*, 114–119.
- (34) Jiang, H. L.; Liu, B.; Akita, T.; Haruta, M.; Sakurai, H.; Xu, Q. Au@ZIF-8: CO Oxidation over gold nanoparticles deposited to metal-organic framework. *J. Am. Chem. Soc.* **2009**, *131* (32), 11302–11303.
- (35) Xie, Z. G.; Wang, C.; deKrafft, K. E.; Lin, W. B. Highly stable and porous cross-linked polymers for efficient photocatalysis. *J. Am. Chem. Soc.* **2011**, *133* (7), 2056–2059.
- (36) Kraft, S. J.; Sanchez, R. H.; Hock, A. S. A remarkably active iron catecholate catalyst immobilized in a porous organic polymer. *ACS Catal.* **2013**, *3* (5), 826–830.
- (37) Zhou, Y.; Xiang, Z. H.; Cao, D. P.; Liu, C. J. Covalent organic polymer supported palladium catalysts for CO oxidation. *Chem. Commun.* **2013**, *49* (50), 5633–5635.
- (38) Zhang, D. S.; Chang, Z.; Lv, Y. B.; Hu, T. L.; Bu, X. H. Construction and adsorption properties of microporous tetrazine-based organic frameworks. *RSC Adv.* **2012**, *2* (2), 408–410.
- (39) Buitrago-Sierra, R.; García-Fernández, M. J.; Pastor-Blas, M. M.; Sepúlveda- Escribano, A. Environmentally friendly reduction of a platinum catalyst precursor supported on polypyrrole. *Green Chem.* **2013**, *15*, 1981–1990.
- (40) Wang, Z. J.; Xie, Y. B.; Liu, C. J. Synthesis and characterization of noble metal (Pd, Pt, Au, Ag) nanostructured materials confined in the channels of mesoporous SBA-15. *J. Phys. Chem. C* **2008**, *112* (50), 19818–19824.
- (41) Chen, Y. T.; Wang, H. P.; Liu, C. J.; Zeng, Z. Y.; Zhang, H.; Zhou, C. M.; Jia, X. L.; Yang, Y. H. Formation of monometallic Au, Pd and bimetallic Au-Pd nanoparticles confined in mesopores via Ar glow discharge plasma reduction and their catalytic applications in aerobic oxidation of benzyl alcohol. *J. Catal.* **2012**, *289*, 105–117.
- (42) Pan, Y. X.; Liu, C. J.; Zhang, S.; Yu, Y.; Dong, M. D. 2D Oriented self-assembly of peptide induced by hydrated electrons. *Chem.—Eur. J.* **2012**, *18* (46), 14614–14617.
- (43) Lee, S. W.; Kumpfer, J. R.; Lin, P. A.; Li, G.; Gao, X. P. A.; Rowan, S. J.; Sankaran, R. M. *In situ* formation of metal nanoparticle composites via “soft” plasma electrochemical reduction of metallosupramolecular polymer films. *Macromolecules* **2012**, *45* (20), 8201–8210.
- (44) Ostrikov, K.; Neyts, E. C.; Meyyappan, M. Plasma nanoscience: From nano-solids in plasmas to nano-plasmas in solids. *Adv. Phys.* **2013**, *62* (2), 113–224.
- (45) Ostrikov, K.; Cvelbar, U.; Murphy, A. B. Plasma nanoscience: Setting directions, tackling grand challenges. *J. Phys. D - Appl. Phys.* **2011**, *44* (17), 174001.