ND*nano* Undergraduate Research Fellowship (NURF)
2012 Project Summary

1) Student name: Qiuting Guo

2) Faculty mentor name: Franklin Tao

3) Project title: Synthesis of PdxCu1-x nanocatalysts with well controlled size and shape

4) Briefly describe any new skills you acquired during your summer research:

Learn wet chemistry synthetic methods of nanocrystals (e.g., hydrothermal, polylol, etc.) and fundamental analytical procedure of transmission electron microscope (TEM) characterization.

5) Please briefly share a practical application/end use of your research:

The research provides not only materials platform but also a possible route for synthesis of efficient catalysts for clean energy.

Project summary:

Concerning the shortage of energy and increasing environment problems, developing efficient catalysts is a valid way to resolve these issues we encounter. Noble metal nanocatalysts are widely applied as active components in various crucial catalytic processes. Easy-poisoned and low abundance put off the development of noble metal catalysts. Compared with mono-metal catalysts, alloying precious a metal with non-precious metal not only reduce the cost, but also improve the catalytic performance due to the synergstic effect between the two metals (i.e., ligand effect or/and ensemble effect). Pd and Cu exhibit superior catalytic performance in many industrial catalysis processes, especially in the selective hydrogen production (e.g., water-gas shift, methanol steam reforming, etc.). Alloying Cu to Pd lattice could reduce the cost of producing and recycling the catalysts, as well as increase their performance. Thus, the purpose for my summer research is to prepare Pd_xCu_{1-x} NCs with different morphologies and compositions and further study their catalytic performance and surface chemistry under reaction condition toward building a coorelation surface chemistry of bimetallic catalysts to their catalytic performance. By the finely control over their composition or morphology, the correatlation between the catalytic performance (e.g., activity, selectivity, durability, etc.) and their in-situ surface chemistry and structure including surface composition and oxidation state of the metals could be built. This correation will guide the understaindg of catalytic mechaneism and provide insights for further synthesis toward catalysts with better performance.

We initially applied hydrothermal method for synthesis of PdxCu1-x NCs, but only large NCs without well-defined morphology were obtained. Thus, we switched the synthetic routes to polyol method. In this case, ethylene glycol (EG) serves as both the solvent and primary reductant at the temperature commonly used for Pd-related NCs synthesis. Bromine ions and

polyvinylpyrrolidone (PVP) were used as stabilizers to confine the size of obtained NCs. Furthermore, bromine ions serve as a shape inducing agent by selectively decreasing the surface energy of certain facets as they prefernetailly bind in this surface. As illustrated in Figure 1, a series of 5 nm PdxCu1-x alloy nanoparticles with Cu content range from 20% to 55% were acquired by control of molar ratio of acetylacetone precursor of Pd to Cu. With the assistance of bromine ions, the size distribution of Pd-Cu NCs were refined to a narrow interval. High resolution transmission electron microscopy (HRTEM) image showed the geometry structure of obtained NCs were primarily spheres and multiply twinned particles. High angle annular dark filed scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) line-scan profiles suggested the PdCu NCs are in an alloy structure rather than core-shell structure. The contrast of the NCs in STEM images also supported the alloy structure.

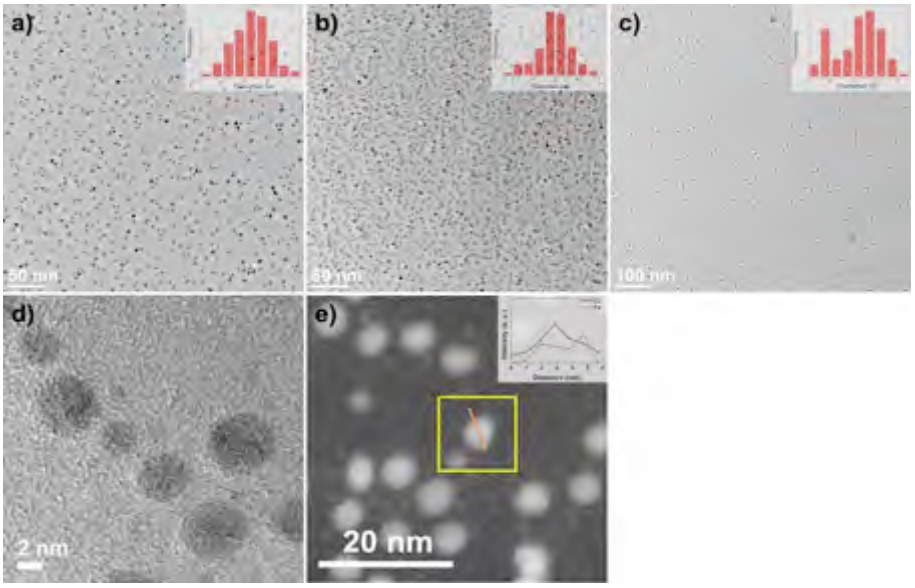

Fig. 1 a-c) TEM images of PdCu bimetallic NCs with different compositions. Respectively the atomic percentage of copper was 20.6%, 48.4%, and 55.1% (EDS); d) HRTEM image of PdCu NCs; e) HAADF-STEM-EDS line scan profile of PdCu NCs.

More interestingly, after changing the precursors from acetylacetone salts to halides, regular Pd-Cu bimetallic nanocubes with the Cu content of 11% were obtained in a relative high selectivity by injecting $PdCl_2$ and $CuCl_2$ precursors in a 1:1 molar ratio under 197 °C. HRTEM image showed the nanocubes were bounded with six {100} facets. The synthesis of composition-tunable PdCu nanocubes is still in progress.

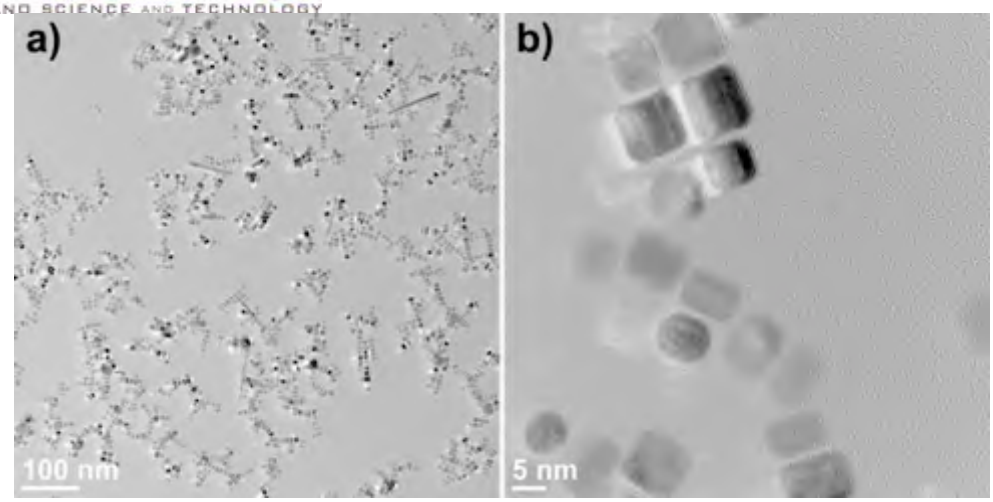

Fig. 2 a) TEM image and b) HRTEM image of Pd-Cu nanocubes .

So far a series of 5 nm Pd-Cu alloys with Cu content range from 20% to 55% and 8 nm Pd-Cu nanocubes were successfully synthesized by the co-reduction of metal salts in ethylene glycol. These series of PdCu NCs provide a material platform for the study on the structure- and composition-dependent catalytic property. Further investigations will focus on the catalytic performance of these synthesized Pd_xCu_{1-x} bimetallic NCs in hydrogen generation through methanol partial oxidation and their in-situ surface chemistry using ambient prerssure XPS in Tao group so as to unveil the catalytic mechanism and boost the rational design of catalysts with superior performance in the future.

Publications (papers/posters/presentations):

Composition- and Size-controlled Synthesis of PdCu Nanocrystals

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Introductions

Energy crisis becomes one of the most serious problems in the 21st century. Developing efficient catalysts is one valid solution to resolve the environmental and energy problems we encounter. Due to high power conversion and non-pollution, hydrogen-oxygen proton exchange membrane fuel cell (PEMFC) is one excellent system to replace many energy supplies. Providing CO-free H_2 and the storage of H_2 are two urgent issues in PEMFC.[1]

Strategy

Pd ,Cu and supported catalysts are the efficient materials in many hydrogen generation reactions (e.g., water-gas shift, methanol steam reforming, etc.).[2] Hence, we propose to fabricate PdCu bimetallic nanocrystals (NCs) by wet chemical synthetic routes. By the control over the additives and ratio of precursors, we can synthesize PdCu NCs with various morphologies and compositions. These series of PdCu NCs provide a material platform for the study on the structure- and composition-dependent catalytic property.

Results and Conclusions

As illustrated in Figure 1, we acquired near-monodispersed 5 nm PdCu NCs with three different compositions by the co-reduction of acetylacetone salts in ethylene glycol. High resolution transmission electron microscopy (HRTEM) image showed the geometry structure of obtained NCs were primarily spheres and multiply twinned particles. High angle annular dark filed scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (HAADF-STEM-EDS) line-scan profiles suggested the PdCu NCs was in an alloy structure rather than core-shell structure. The contrast of the NCs in STEM images also supported the alloy structure.

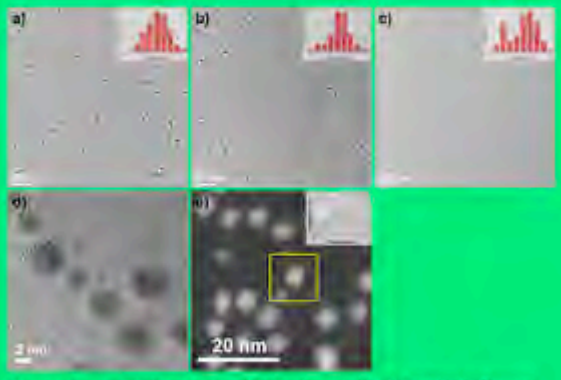

Figure 1. a-c) TEM images of PdCu bimetallic NCs with different compositions. Respectively the atomic percentage of copper was 20.6%, 48.4%, and 55.1% (EDS); d) HRTEM image of PdCu NCs; e) HAADF-STEM-EDS line scan profile of PdCu NCs.

Furthermore, PdCu nanocubes were synthesized by altering acetylacetone precursors to chlorides.

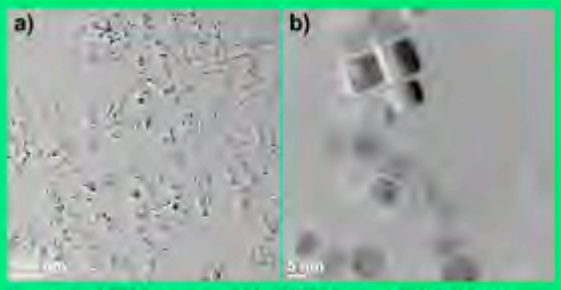

Figure 2. a) TEM image and b) HRTEM image of PdCu bimetallic nanocubes.

Acknowledgements

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References

[1] W. Wiese, B. Emonts, R. Peters, *J Power Sources*, **1999**, 84, 187-193

[2] a) A. Kulprathipanja, G. O. Alptekin, J. L. Falconer, J. D. Way, *Ind. Eng. Chem. Res.*, **2004**, 43, 4188-4198; b) C. Rameshan, M. W. Stadlmayr, S. Penner, et al., *Angew. Chem. Int. Ed.*, **2012**, 51, 3002-3006.