

Electrochemical Characterization of Nanoparticles with Different Morphologies

Mengjia Hu, Eric Taylor, Benjamin Jones, Jingyi Chen and Ingrid Fritsch

Department of Chemistry and Biochemistry
University of Arkansas
Fayetteville, AR 72701 USA

Nanoparticles have been used as electrode modification materials and applied to multiple fields such as electrochemical sensors and fuel cells.^{1,2} A variety of shapes, dimensions, and compositions have been reported. The electrode surfaces can be modified with them either in situ using electrochemical methods or post synthesis via drop-casting or entrapment with polymers. The nanoparticles provide higher surface area and therefore presumably greater catalytic activity than the unmodified electrodes. However, the composition of the nanoparticles is often electrochemically active and may interfere with the target electrochemistry. Therefore, thorough electrochemical characterization of these materials is of great interest.

A relatively new class of nanoparticles in the shape of cages is being synthesized, and is just now being investigated in different applications.^{3, 4} Their unique features are that they are hollow, providing an even higher surface area than cubes or spheres, in comparison, and may deliver or store substances in the interior that are different than the surrounding chemical environment. Electrochemical evaluation of nanocages will be presented. We are exploring ways of modifying electrodes with these cages for the purpose of sensor and catalyst development that include drop casting, covering with electrochemical polymerized polymer (poly (3, 4-ethylene dioxythiophene), PEDOT) and co-deposition with electropolymerization.

In the initial study, anodic stripping voltammetry of gold nanocages and silver nanocubes drop casted onto commercially available platinum disk electrodes was performed in different electrolytes, including 0.1 M KCl solution, with a three electrode experiment (Ag/AgCl saturated KCl as the reference and a Pt flag as the auxiliary electrodes). Characteristic stripping waves appear to vary with size, facets, and amount of nanoparticles deposited on the electrode. Preliminary results show that gold nanocages and silver nanocubes having the same size (~40 nm of edge length) share similar stripping waves. Silver nanocubes with a smaller size (33.3 ± 6.7 nm of edge length) have a shift in peak potential of the stripping wave that is about +0.015 V from the peak potential of the larger size (50.1 ± 8.7 nm of edge length). Stripping peaks for silver cuboctahedrons exhibit a negative potential shift compared to silver nanocubes of the same size. These results indicate that differentiation of nanoparticles having different sizes and crystal facets by their peak potentials and peak wave shapes in the stripping voltammograms may be possible.

We are also investigating the electrochemical characteristics of nanoparticles embedded in a conducting polymer. For example, nanoparticles were drop-casted and then covered by subsequent electropolymerizing of PEDOT, and immobilized onto the electrode by copolymerization with PEDOT. In both cases, they showed similar electrochemical stripping characteristics. However, as the nanoparticles are embedded in a relatively thick film of conducting polymer, some of the wave structure is lost.

ACKNOWLEDGEMENTS

This work was supported in part by the Ralph E. Powe Jr. Faculty Enhancement Award and startup funds from the University of Arkansas to J.C. Support has also been provided in part by the Arkansas Biosciences Institute, the major research component of the Arkansas Tobacco Settlement Proceeds Act of 2000.

REFERENCES

1. Saha, K.; Agasti, S. S.; Kim, C.; Li, X.; Rotello, V. M., *Gold Nanoparticles in Chemical and Biological Sensing*. *Chemical Reviews* **2012**, 112, 2739-2779.
2. Rabis, A.; Rodriguez, P.; Schmidt, T. J. *ACS Catalysis*, **2012**, 2, 864.
3. Chen, J.; Yang, M.; Zhang, Q.; Cho, E. C.; Cogley, C. M.; Claus, C.; Kim, C.; Wang, L. V.; Welch, M. J. and Xia, Y. *Gold Nanocages: A Novel Class of Multifunctional Nanomaterials for Theranostic Applications*, *Adv. Funct. Mater.* **2010**, 20, 3684-3694.
4. Chen, J.; Wiley, B.; McLellan, J.; Xiong, Y.; Xia, Y. *Optical Properties of Pd-Ag and Pt-Ag Nanoboxes Synthesized via Galvanic Replacement*, *Nano Lett.* **2005**, 5, 2058-2062.