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doi:10.1017/S1431927611009354
Microsc. Microanal. 17 (Suppl 2), 2011

Nanostructured Alloy Catalysts: Control of Size, Shape and Composition

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The successful synthesis of catalyst particles with the desired size, composition, and structure/morphology offers a practical connection between theory and experiments and will help to promote the design of active and stable catalysts. Palladium alloyed with base metals such as Cu, and W have been predicted to modify the electronic structure of palladium with palladium forming a surface skin over the alloy, leading to enhancement of oxygen reduction reaction (ORR) activity and catalyst stability.[1] Colloidal preparation methods [2] that utilize organic capping agents offer an attractive approach to prepare alloy compositions with a high degree of homogeneity and controlled particle size and morphology. This paper presents results of the synthesis of palladium alloy catalysts with controlled size, shape and composition, using colloidal preparation and post-deposition approaches. The results of characterization using transmission electron microscopy with energy dispersive X-ray analysis (TEM-EDX) are discussed.

The general synthesis of bimetallic nanoparticles involved the use of metal precursors in controlled molar ratios. Organic solvents were used, which in some cases functioned as the reducing agent for the metal precursors. A mixture of long chain alkyl molecules with amine and carboxylic acid functional groups were used as coordinating as well as capping agents. Formation of alloy particles was achieved at relatively low temperatures with an upper limit of 140 ^{o}C. Philips CM30T electron microscope (200 kV) equipped with an energy-dispersive X-ray analyzer (EDX) was used for analysis of the formed particles. Samples for TEM analysis were made into dilute suspensions in hexane (for unsupported particles) or isopropanol (for carbon-supported particles) and were drop-cast onto a carbon-coated grid followed by solvent evaporation in air at room temperature.

In previous studies, palladium-copper (PdCu) alloy nanoparticles of controlled size (3-5 nm) and composition were prepared using the colloidal method.[2] Once heat treated in a reducing atmosphere, the catalyst particles supported on carbon black showed high activity for the oxygen reduction reaction (ORR) in aqueous electrochemical tests. The alloys had varying degrees of ORR activity stability which was highly dependent on the palladium to copper ratio and the alloy phases formed. Post-deposition of palladium on the carbon-supported PdCu nanoparticles was carried out to selectively deposit palladium on the pre-formed particles. TEM analysis showed lateral elongation of the particles with successive deposition of palladium (Figure 1). These results indicated that factors, such as bonding characteristics of the metal were in play during the deposition process. The prepared Pd-PdCu catalysts showed ORR activities that were within the range observed for Pd-alone catalyst, suggesting a dominating effect of the deposited Pd.

In the preparation of palladium-tungsten (Pd-W) alloy nanoparticles, optimization of synthesis parameters was carried out by varying reaction conditions including the choice of solvent, reducing agent, and concentration of metal precursors and capping agents. Characterization by TEM-EDX showed formation of monodisperse Pd-W alloy nanoparticles with an average particle diameter of 7

nm and controlled composition consistent with feed ratio of the metal precursors. The shape of the particles was affected by the type of solvent used, indicated by formation of Pd-W polypods in octyl ether solvent, and spherical and triangle shapes in ortho-xylene. (Figure 2) The observation of solvent effects on the shape of the catalyst particle is very helpful in designing catalysts with desired properties through anisotropic growth of multifaceted structures/shapes in solution phase. This information is of great interest to the materials science community, as it impacts the rationale for selection and control of factors and parameters in catalyst designs.

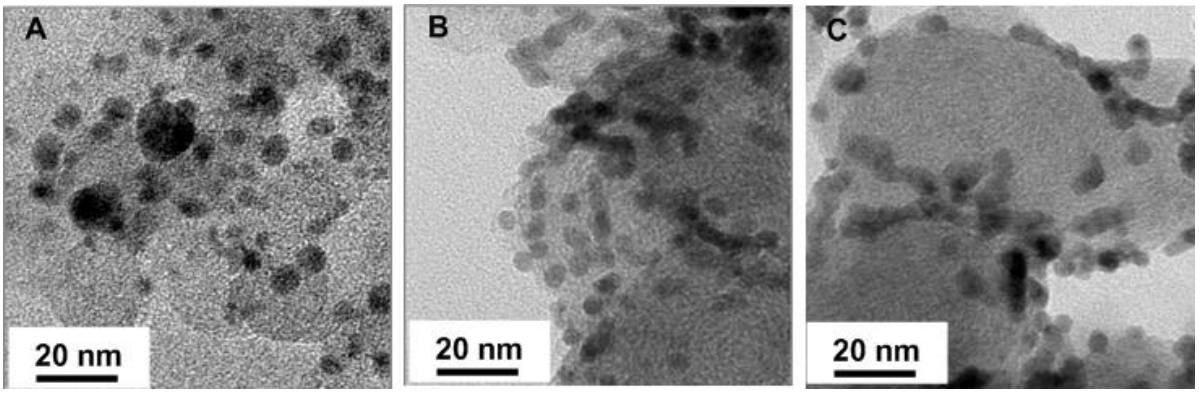

FIG. 1. TEM images of the Pd-PdCu/C samples corresponding to varying amounts of deposited palladium. A (control, no added Pd); B (2 monolayers equivalent), C (3 monolayers deposited)

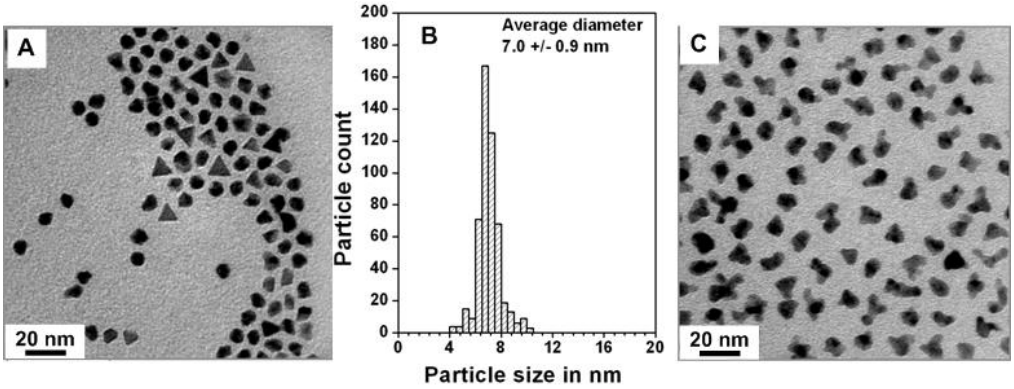

FIG. 2. TEM images of Pd-W nanoparticles prepared in octyl ether (A) and ortho-xylene (C) as solvent. Size distribution (B) is shown for the particles of image (A).

References

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3) This research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program. The electron microscopy was performed at the Electron Microscopy Center for Materials Research at Argonne National Laboratory, a U.S. Department of Energy Office of Science Laboratory operated under Contract No. DE-AC02-06CH11357 by UChicago Argonne, LLC.