Effect of Transition Metals (M) in M@Pd core@shell nanoparticles for Direct Formic Acid Fuel Cells

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The study of Pd-based core@shell nanoparticles that consist of one transition metal as the core and Pd as the shell has generated great interest in the field of electrochemical catalysis, especially in direct formic acid fuel cells (DFAFCs), because their electronic and chemical properties are completely different from those of pure Pd. The current DFAFC technology uses Pd as the anode catalyst, on which formic acid is oxidized to CO_2 and releases electrons. An enhanced activity has been obtained for these Pd-based core@shell nanoparticles compare to pure Pd for formic acid oxidation. However, there is a lack of understanding of how these added transition metals interact with Pd, namely by influencing their electronic structure and electrochemical property toward electrochemical oxidation of formic acid. It is important to fill this knowledge gap and find out a trend between the effect of adding the transition metals and the electrochemical activity of Pd-based core@shell nanoparticles. This will help developing DFAFCs with higher efficiency. In addition, the cost of DFAFCs can be reduced by using the Pd-based core@shell nanoparticles since less-expensive transition metals can be used as the core and less Pd is required compare to the DFAFCs with pure Pd anodes.

In this study, M@Pd (M = Au, Cu, Ru, Pt, etc.) core@shell nanoparticles with same thickness of Pd are synthesized via a two-step process. Non-supported nanoparticles are used for TEM analysis to characterize the structure and morphology of the nanoparticles. XPS is used to differentiate the chemical shifts due to charge transfer between Pd and M. XPS analysis shows a different binding energy shift for Pd peak for M@Pd core@shell nanoparticles compare to that of pure Pd nanoparticles. In addition, a change of the XPS valence band shape and down-shift of the d-band center are also observed. These different binding energy shifts indicate that the core metals (M) interact with Pd shell and significantly influence the electronic structure of Pd. This electronic perturbation changes the bond strength between Pd and the adsorbate. Thus, the electrochemical performance of M@Pd core@shell nanoparticles is altered, which can be detected by cyclic voltammetry (CV) and chronoamperometry (CA) experiments. Based on the CV and CA results, M@Pd core@shell nanoparticles show different Pd-H bond strength and activity toward formic acid oxidation with different transition metals as the core. The relationship between the electronic perturbation and electrochemical activity can be elucidated.