Core-shell Nanomaterials: Synthesis and Applications in Catalysis

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Abstract: Core-shell nanocomposites are among the classes of advanced nanomaterials that have recently recognized rising consideration because of their fascinating properties as well as an extensive range of applications in various fields. Notably, core-shell nanomaterials for catalysis can now be synthesized with distinctive structure, morphology and composition for precise catalytic applications via more benign pathways. Some of the as-prepared core-shell nanomaterials can be further modified with magnetic nanocomposites or other metallic and metal oxides nanoparticles. In the present study, our recent activity in this area comprising some catalytic and electrocatalytic applications of core-shell nanoparticles is highlighted.

Keywords: Pt@Pd, reduced graphene oxide-Pd@Pt, Ag@CoxP core-shell nanoparticles

1. Introduction

The preparation of well-defined metal nanoparticles (NPs) with well-ordered morphology has been the principal focus of nanomaterials research, owing to their fascinating catalytic, electronic, photonic, and sensing properties.[1] Various NPs with complex morphologies containing multiple compositions and high-index facets have been measured for both theoretical and experimental studies, revealing that the activity of NPs is dependent on their size, shape, composition, and microstructure. Recently, several efforts have been engaged for the assembly of bimetallic NPs with a core–shell or an alloyed structure for the investigation of their catalytic and other properties that are often superior to those of their monometallic counterparts. Often, the addition of a second metallic component has a greater potential for enhancing the functionalities and performance of pure metal components due to momentous synergistic effects.[4]

2. Experimental

A one-pot microwave (MW)-assisted approach was designed to synthesize the reduced graphene oxide (rGO)-supported Pd−Pt core−shell nanoparticles, (Pd@Pt/rGO); spherical core-shell nanomaterials (~95 nm) with Pd core (~80 nm) and 15 nm Pt shell were attractively distributed on the rGO matrix based on the choice of reductant and reaction conditions. In another example, a core−shell Ag@CoxP OER (Oxygen Evolution Reaction) nanoelectrocatalysts were synthesized *via* in situ growth of TMP (transition-metal phosphides) using Ag NPs as seed. The unique Ag core permits successful development of the surrounding Co_xP shell and improves the OER performance, owing to its distinct electronic nature. The possible surface interactions and catalytically active sites are recognized using numerous experimental methods that allow correlating these interactions and sites with the electrocatalytic properties.

3. Results and Discussion

The well-characterized Pd@Pt/rGO endowed with synergism among its components and rGO support, served as catalysts in aromatic dehalogenation reactions and for the reduction of olefins with high yield (>98%), excellent selectivity (>98%) and reusability (up to 5 times). Notably, both Pt/rGO and Pd/rGO and even their physical mixtures displayed considerably lower conversions (20 and 57%) in dehalogenation of 3-bromoaniline. Likewise, in the reduction of styrene to ethylbenzene, Pd@Pt core−shell nanoparticles (without rGO support) yielded considerably lower conversion (60%) compared to Pd@Pt/rGO (Figure 1a). The mechanism of dehalogenation reactions with Pd@Pt/rGO catalyst was also discussed with the explicit premise that rGO matrix facilitates the adsorption of the reducing agent, thus enhancing its local concentration and expediting the hydrazine (the reducing agent) decomposition rate. The versatility of the catalyst has been validated *via* diverse substrate scope for both reduction and dehalogenation reactions. The recyclability and leaching studies also confirmed that the efficiency and structural integrity of the nanocatalysts did not change even after multiple cycles of reaction.

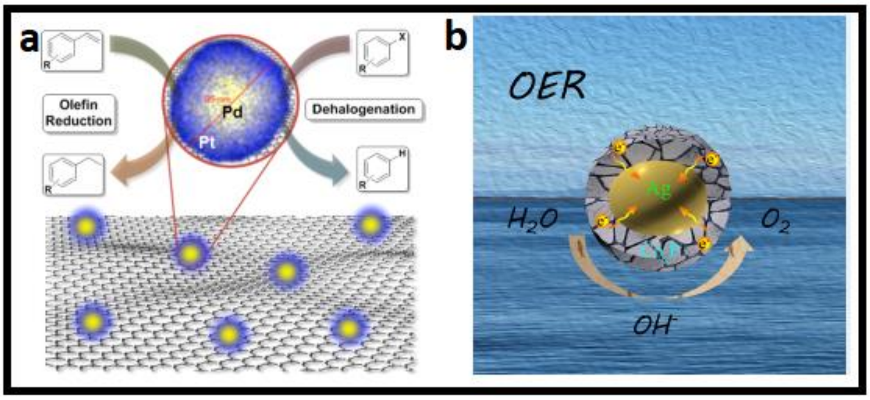

Figure 1. Applications of a) Pt-Pd Core-shell nanoparticles for reduction and dehalogenation reactions [5] and b) Ag@Co$_x$P core−shell for OER[6].

The other novel Ag@Co$_x$P core−shell type heterogeneous nanostructures was explored for oxygen evolution reaction (OER) activity (Figure 1b). This nanocatalyst could deliver a current density of 10 mA/cm^2 at a small overpotential of 310 mV and displayed high catalytic stability. Furthermore, the catalytic efficiency of Ag@Co$_x$P was 8 times higher than that of the Co$_2$P nanoparticles, owing primarily to the strong synergistic electronic interaction between the Ag core and the Co$_x$P shell.

4. Conclusions

We have demonstrated a simple MW-assisted, one-pot scalable synthesis of rGO-entrenched Pd@Pt core-shell nanoparticles and established their efficacy as nanocatalysts for the reduction of olefins and in aromatic dehalogenation reactions. The dominance of the catalysts can be accredited to the synergistic effect among the individual components. Notably, the sustainable nanocatalytic system is versatile, very stable, can be easily separated by centrifugation, and could be recycled numerous times without loss of activity. The other Ag@Co$_x$P core-shell electrocatalyst is prepared through the controlled addition of Co(OAc)$_2$ to a AgNO$_3$ solution, where the uniform Co$_x$P shell, formed around the Ag core allows OER activity. This story delivers a simple and straightforward synthetic strategy for the synthesis of Ag@Co$_x$P phosphide catalysts, permitting the exploration of synergistic interactions between the Ag core and the shell. The Ag@Co$_x$P core−shell nanoparticles are efficient and sturdy catalysts for the OER than most of the reported catalysts.

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