



Understanding the formation of nanocomposites consisting of silver sulfide and platinum hollow nanostructures



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ABSTRACT

Structural conversion using core-shell silver (Ag)-platinum (Pt) nanoparticles as starting materials is a promising way to produce nanocomposites consisting of silver sulfide (Ag₂S) and hollow Pt nanostructures (Ag₂S-hPtNCs). However, the mechanism behind the structural conversion process is yet to be understood. In this study, we use transmission electron microscope (TEM) as a typical tool to characterize the products formed in different structural conversion processes, and interpret the experimental observations by proposing mechanisms behind the reactions between core-shell Ag-Pt nanoparticles and sulfur precursors from different sources. We then design additional experiments to rationalize the formation mechanism we proposed. The mechanistic understanding of the structural conversion from bimetallic core-shell nanostructures to heterogeneous nanocomposites may extend the fabrication of heterogeneous nanocomposites for a given technological application.

1. Introduction

In the field of nanomaterials synthesis, there has been increasing interest in scientific community to develop nanocomposites that consist of different kinds of materials [1–9]. It has been well documented that these composite nanomaterials have tunable physical/chemical properties due to the integration of distinctly different materials within same nanostructures [10–15]. In particular, the nanocomposites consisting of silver sulfide and platinum (Ag₂S-PtNCs) exhibit excellent performance in catalyzing methanol oxidation reaction (MOR), the anode reaction of direct methanol fuel cells (DMFCs), due to the electronic coupling effect between the Ag₂S domain and Pt sites [16–22]. In brief, the alignment of energy levels in the nanocomposites could induce electron transfer from Ag₂S domain to Pt sites, leading to increase of electron density around the Pt atoms, which weakens the chemisorption of carbon monoxide (CO)-like intermediates generated from MOR on the Pt surfaces, and promote MOR [16,18,23]. Considering the apparent shortcomings for the synthesis of Ag₂S-PtNCs in aqueous phase, such as expensive chemical agents and low concentration requirement [16], the production of Ag₂S-PtNCs in an organic medium through a structural conversion process might be a promising strategy [24,25]. This approach involves the preparation of core-

shell Ag-Pt nanoparticles and the subsequent reaction with element sulfur (S) or sodium sulfide (Na₂S) to convert the core-shell Ag-Pt nanostructures into nanocomposites consisting of Ag₂S and Pt with hollow interiors (Ag₂S-hPtNCs). This synthesis is conducted in an organic phase and can be performed in very large-scale. However, we experimentally found that reacting core-shell Ag-Pt nanoparticles with Na₂S often results in the formation of only hollow Pt nanostructures (hPtNSs) instead of Ag₂S-hPtNCs. The observation is closely associated with the detailed mechanism behind the synthesis of Ag₂S-hPtNCs through the structural conversion, which is yet to be explored.

Herein, we use transmission electron microscope (TEM) as a typical tool to characterize the products formed by the structural conversion process, e.g. by reacting core-shell Ag-Pt nanoparticles with element sulfur or sodium sulfide in toluene. We will interpret the experimental observations by proposing mechanisms behind the reaction between core-shell Ag-Pt nanoparticles and sulfur precursors from different sources. We then design additional experiments to rationalize the formation mechanism we proposed. We believe that the mechanistic understanding of the structural conversion from bimetallic core-shell nanostructures to heterogeneous nanocomposites may shed some light for designing and fabricating more heterogeneous composite nanostructures for technological applications.

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2. Materials and methods

2.1. Chemicals

Silver nitrate (AgNO_3 , 99%), potassium tetrachloroplatinate(II) (K_2PtCl_4 , 98%), sodium sulfide nonahydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, $\geq 98\%$) and element sulfur (S , $\geq 99.5\%$) from Aladdin Reagents, oleylamine (70%, technical grade) from Sigma-Aldrich, methanol (99%), ethanol (99%) and toluene (99.5%) from Beijing Chemical Works, were used as received. All glassware and Teflon-coated magnetic stir bars were cleaned with *aqua regia*, followed by copious washing with de-ionized water before drying in an oven.

2.2. Synthesis of core-shell Ag-Pt nanoparticles with different Ag/Pt molar ratios

To synthesize core-shell Ag-Pt nanoparticles, we added 0.6 mmol of AgNO_3 to 20 mL of oleylamine in a three-necked flask, which was fitted with a condenser and a stir bar. The mixture was heated at 150 °C for 1 h to obtain Ag seed particles. Then, 0.2, 0.3, or 0.6 mmol of K_2PtCl_4 (corresponding to Ag/Pt molar ratio of 3/1, 2/1, or 1/1, respectively) was introduced swiftly. The temperature was increased to 160 °C and kept there for another 1 h to reduce the Pt precursors in the presence of Ag seeds. Afterwards, we collected the core-shell Ag-Pt nanoparticles by methanol precipitation, purified them twice by methanol washing, and re-dispersed them in 20 mL of toluene.

2.3. Reacting core-shell Ag-Pt nanoparticles with sodium sulfide or element sulfur and sample characterizations

For the treatment of core-shell Ag-Pt nanoparticles by Na_2S , we firstly dissolved 2 mmol of Na_2S into 20 mL of water to generate

aqueous Na_2S solution with concentration of 100 mM. Then we mixed 10 mL of core-shell Ag-Pt organosol in toluene with 6 mL of aqueous Na_2S solution to render a 2/1 M ratio for S/Ag in the mixture. We subsequently collected the toluene phase after agitating the mixture for 3 h. Analogously, for reacting core-shell Ag@Pt nanoparticles with element sulfur, we added 20 mg of element sulfur to 10 mL of core-shell Ag-Pt organosol in toluene (the S/Ag molar ratio in the mixture is approximate 2/1). We aged the mixture for 5 h under vigorous stirring at room temperature, and then collected the products by precipitation with methanol and centrifugation.

Powder X-ray diffraction (XRD) patterns were gained on a Rigaku D/Max-3B diffractometer with $\text{Cu K}\alpha$ as radiation. The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations for all samples were performed on the JEOL JEM-2100F electron microscope, which is operated at 200 kV with supplied software for automated electron tomography. The samples for TEM and HRTEM observations were prepared by dispensing a drop of nanoparticle solution onto a 3-mm carbon-coated copper grid, which was placed on an absorbent paper. The copper grids with sample loading were then dried in air at room temperature. The average particle diameter and the standard deviations were determined from a few randomly chosen areas in the TEM image containing 200 nanoparticles each.

3. Results and discussion

3.1. Core-shell Ag-Pt nanoparticles with different Ag/Pt molar ratios

Fig. 1a shows the TEM image of the as-prepared Ag nanoparticles, which were used as seeds for the subsequent deposition of Pt shells. As indicated, the Ag seed particles are spherical, nearly monodispersed,

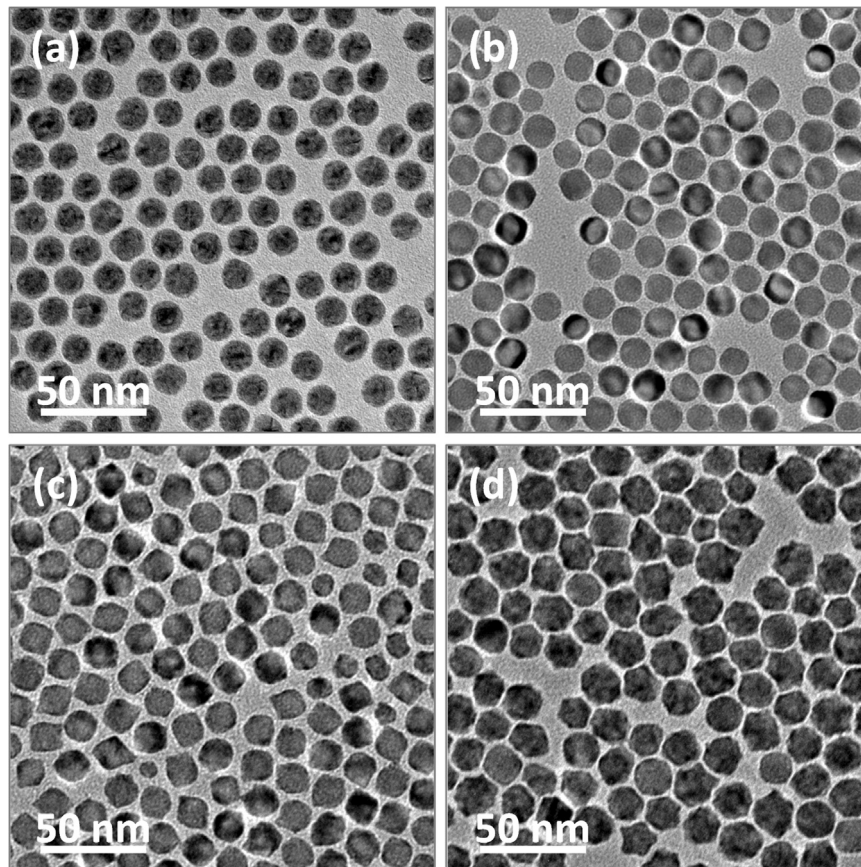


Fig. 1. TEM images of **a** Ag seed particles, **b** core-shell Ag-Pt nanoparticles with Ag/Pt molar ratio of 3/1, **c** core-shell Ag-Pt nanoparticles with Ag/Pt molar ratio of 2/1, and **d** core-shell Ag-Pt nanoparticles with Ag/Pt molar ratio of 1/1.

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