

Effect of ionic liquid on the synthesis and electrocatalytic property of platinum-based bimetallic nanoparticles



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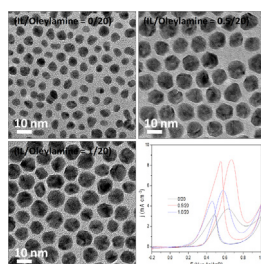
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HIGHLIGHTS

- The effect of IL on the synthesis of Pt-based nanoparticles has been investigated.
- Core-shell Ag–Pt and Au–Pt nanoparticles have been prepared in the presence of IL.
- IL has significant effect on the size/morphology of core-shell Ag–Pt nanoparticles.
- IL mainly affects the electrochemical property of core-shell Au–Pt nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

Because of their many distinct advantages, the application of ionic liquids (ILs) for the synthesis and tailoring of nanoscale metal catalysts represents a burgeoning direction in materials chemistry. We herein depict the using of ammonium dibutyl phosphate ($[AD]PO_4$), an organic soluble ionic liquid as an additive for the synthesis of Pt-based nanoparticles at elevated temperature in oleylamine. The experimental results reveal that not only the size/morphology, but also the electrocatalytic property of the platinum (Pt)-based bimetallic nanoparticles could be significantly tuned by a small amount of ionic liquid added in the reaction systems. For the silver (Ag)-Pt bimetallic system, core-shell Ag–Pt nanoparticles with dense or dendritic Pt shells are obtained at IL/oleylamine volume ratio of 0.25/10 and 0.5/10, while for gold (Au)-Pt bimetallic system, although the tuning of IL on the size/morphology of the particles are not apparent, the core-shell Au–Pt nanoparticles synthesized at IL/oleylamine volume ratio of 0.5/20 exhibit superior catalytic activity and durability for methanol oxidation reaction (MOR), compared to those prepared at other volume ratios.

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1. Introduction

Direct methanol fuel cell (DMFC) has become a promising power source in recent years due to its high conversion efficiency, high energy density, environmentally friendliness, long life, and so forth

[1–5]. The key factor that determines the performance of a DMFC is the electrocatalyst. Currently, Pt nanoparticles are electrocatalytically active for both the anodic (methanol oxidation reaction, MOR) and cathodic (oxygen reduction reaction, ORR) reactions of the DMFC [6–8]. However, pure Pt particles as electrocatalyst have some drawbacks including high cost, low utilization efficiency, and poor carbon monoxide (CO) tolerance [9–11]. Hence, the synthesis of nanostructured Pt-based materials with superior catalytic performance and better CO-tolerant property is of great importance

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[12]. As has been demonstrated in a number of literatures, mastery over the structure and/or composition of metal nanoparticles is an effective way to improve their catalytic activity on a mass basis [13,14]. In addition, there is also increasing interest in combining morphology engineering and the synergistic effects of an adjuvant metal to enhance the Pt catalytic properties [15–18].

In recent years, ionic liquids (ILs) have been recognized as stabilizers and green media in the preparation of metallic nanoparticles [19–21]. Indeed, in comparison with the traditional aqueous or organic solvents, ILs have many distinct advantages for the synthesis of metal nanoparticles with controlled sizes/morphologies, such as good thermal stability, high ionic conductivity, broad electrochemical potential windows, high synthetic flexibility, and environmental benefits deriving from the negligible vapor pressures [22,23]. The most interesting thing for the fabrication of metal nanoparticles using ILs is that they may provide possible pathways to furnish the nanoparticles with new properties that cannot (or only with great difficulty) be made via conventional processes [24–28].

Based on our recent progress in synthesizing monometallic nanoparticles in or in the presence of ionic liquids, we found the size/morphology of the noble metal nanoparticles could be significantly tuned by the ionic liquids [29]. For example, the Pt nanoparticles with irregular shape prepared in pure water are evolved into Pt nanospheres in an IL, and the average size of the particles was also decreased from 4.6 nm in water to 1.2 nm in IL. In particular, the electrochemical measurements illustrated that the Pt nanoparticles prepared in ionic liquid have better CO-tolerant property in catalyzing methanol oxidation reaction.

Hence, in this work, we investigate the effect of ILs on the synthesis and electrocatalytic property of platinum-based bimetallic nanoparticles. We use ammonium dibutyl phosphate ([AD]PO₄), an organic soluble ionic liquid as an additive to direct the one-pot synthesis of bimetallic Ag–Pt and Au–Pt nanosystems in oleylamine at elevated temperature. We hypothesize that this strategy may combine the synergistic effect between the Pt and an adjuvant metal with the distinct advantages of ILs for the synthesis of Pt-based nanoparticles with desired physical/chemical properties. As expected, the experimental results reveal that not only the size/morphology, but also the electrocatalytic property of the Pt-based bimetallic nanoparticles could be significantly tuned by adding a small amount of ionic liquid in the reaction media. For the Ag–Pt bimetallic system, core–shell Ag–Pt nanoparticles with dense or dendritic Pt shells are the dominant product at IL/oleylamine volume ratio of 0.25/10 and 0.5/10, respectively, while for Au–Pt bimetallic system, although the tuning of IL on the size/morphology of the particles are not apparent, the core–shell Au–Pt nanoparticles synthesized at IL/oleylamine volume ratio of 0.5/20 exhibit much higher MOR catalytic activity and durability than those prepared at other volume ratios.

2. Experimental

2.1. Chemicals

The organic soluble ionic liquid (ammonium dibutyl phosphate, [AD]PO₄, 98%) from Linzhou Keneng Material Technology Co., silver nitrate (AgNO₃, ACS reagent, 99.0%), platinum(II) acetylacetonate (Pt(acac)₂, 99%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99.9%), oleylamine (80%, technical grade) and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Sigma–Aldrich, ethanol (>99.7%), methanol (>99%), toluene (>99.5%) and perchloric acid solution (70%) from Beijing Chemical Works, and Vulcan XC-72 carbon powders (XC-72C with BET surface area of 250 m² g⁻¹ and average particle size

of 40–50 nm) from Cabot were used as received. Deionized water was distilled by a Milli-Q Ultrapure-water purification system. All glassware and Teflon-coated magnetic stirring bars were cleaned with aqua regia, followed by copious rinsing with deionized water before drying in an oven.

2.2. Synthesis of bimetallic Ag–Pt nanoparticles in the presence of organic soluble IL

The bimetallic Ag–Pt nanoparticles were prepared using an one-pot approach. In detail, 17 mg of AgNO₃ and 40 mg of Pt(acac)₂ were dissolved in 10 mL of oleylamine with the addition of 0, 0.25, and 0.5 mL of [AD]PO₄, respectively. The solution was heated to 180 °C and kept at this temperature for 3 h. Oleylamine serves as both capping and reducing agent. No other reducing agent and stabilizer were used to form bimetallic Ag–Pt nanoparticles. After reaction, the bimetallic Ag–Pt nanoparticles were purified by precipitation with methanol, followed by centrifugation and washing with methanol, then re-dispersed in 10 mL of toluene.

2.3. Synthesis of bimetallic Au–Pt nanoparticles in the presence of organic soluble ILs

Analogous to the synthesis of bimetallic Ag–Pt nanoparticles, for the synthesis of bimetallic Au–Pt nanoparticles using an one-pot approach, 41 mg of HAuCl₃ and 79 mg of Pt(acac)₂ were dissolved in 20 mL of oleylamine with the addition of 0, 0.5, and 1 mL of [AD]PO₄, respectively. The solution was heated to 180 °C and kept at this temperature for 3 h. Subsequently, the solution was cooled down to room temperature, and the bimetallic Au–Pt nanoparticles were purified by precipitation with methanol, followed by centrifugation and washing with methanol, then re-dispersed in 20 mL of toluene.

2.4. Particle characterizations

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) were performed on a JEOL JEM-2100 and JEOL JEM-2010F electron microscope operated at 200 kV with the supplied software for automated electron tomography. For the TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3 mm carbon-coated copper grid, and excessive solution was removed by an absorbent paper. Then the sample was dried under vacuum at room temperature.

2.5. Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode cell connected to a Bio-logic VMP3 (with EC-lab software version 9.56) potentiostat. A leak-free Ag/AgCl (saturated with KCl) electrode was used as the reference electrode. The counter electrode was a platinum mesh (1 × 1 cm²) attached to a platinum wire. For the loading of the Pt-based nanoparticles on Vulcan XC-72 carbon support, a calculated amount of carbon powder was added to the toluene solution of Pt-based nanoparticles. After stirring the mixture for 24 h, the Pt/C (20 wt% Pt on carbon support) was collected by centrifugation, washed thrice with methanol, and then dried at room temperature in vacuum.

The working electrode was a thin layer of Nafion-impregnated catalyst cast on a vitreous carbon disk. This electrode was prepared by ultrasonically dispersing 5 mg of the nanoparticles/C in 1 mL of ethanol containing 0.05 mL of Nafion solution. A calculated volume of the ink was dispensed onto the 5 mm glassy carbon disk electrode to produce a nominal catalyst loading of 25 μg cm⁻² (Pt basis). The carbon electrode was then dried in a stream of warm air at 70 °C for 1 h.

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