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Short communication

Synthesis of porous PdAg nanoparticles with enhanced electrocatalytic activity

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ABSTRACT

A facile synthesis of PdAg alloyed bimetallic nanocrystals with flower-shaped porous morphology is demonstrated. The whole synthetic process is very simple just by mixing palladium nitrate, silver nitrate, polyvinylpyrrolidone and hydroquinone and heated at 70 °C for 15 min. The prepared flower-shaped porous PdAg nanoparticles exhibit superior electrocatalytic activity toward ethanol electrooxidation in alkaline condition, and the catalytic performance could be easily tuned by the Pd/Ag ratio.

1. Introduction

In recent years, Pd-based nanomaterials have become a hot topic of interest in the ethanol oxidation reaction (EOR) because of their relatively lower cost and good catalytic performance as compared to Pt-based catalysts [1–3]. In this regard, considerable efforts have been devoted to developing simple and practical techniques to prepare Pd electrocatalysts with controllable nanostructures and enhanced performance for the EOR applications [4]. Previous studies have demonstrated that the shape, size and composition are the important factors governing the catalytic performance of the nanomaterials [5]. Thus, controlled synthesis of Pd-based catalysts with optimized composition and morphology is a promising approach to achieve high catalytic performance.

Introducing a second transition metal with cheaper price into Pd-based nanomaterials has been proved to be an effective way to improve its catalytic performance and reduce the cost [6]. On the other hand, in recent years, dendritic materials have received much attention. Because they are porous, their branches provide many high-index facets, and hence lead to the high performance during the catalysis [7,8]. Up to now, a variety of Pd-based porous nanomaterials, such as Pd-on-Pt [9], Pd–Au nanodendrites [10]. However, these materials are not economical, because of Pt and Au are very expensive. Introducing a less expensive metal (such as Ag) into Pd-based porous materials is highly desired both for improving the utilization efficiency of Pd and cutting down the cost. Although a few group employed cetyltrimethyl ammonium chloride to prepare porous PdAg nanospheres through a two-stepped seed growth method [11], the process would inevitably lead to the formation of AgCl precipitates in the products and thus the further removal procedures. Therefore, developing a facile method to synthesize porous PdAg nanoparticles with high electrocatalytic activity is still highly important.

In this work, we developed a very simple and rapid method to synthesize flower-shaped porous PdAg nanoparticles (PdAg FPNPs) with high yield in aqueous solution. The whole synthetic process is just by mixing palladium nitrate, silver nitrate, polyvinylpyrrolidone (PVP) and hydroquinone (HQ) and sequentially heated at 70 °C for 15 min. The prepared PdAg FPNPs exhibit superior electrocatalytic performance toward ethanol electrooxidation in alkaline condition.

2. Experimental

$Pd(NO_3)_2$, HQ and PVP (K30, molecular weight: 50000–58000) were bought from Sinopharm (Shanghai, China). Nafion ethanol solution (5 wt.%) was obtained from Aldrich. Other chemicals used were commercially obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). All chemicals were of analytical grade and used as received. Milli-Q ultrapure water (Millipore, $\geq$18.2 MΩ cm) was used throughout the experiments.

To synthesize PdAg FPNPs, 70 μL fresh prepared $Pd(NO_3)_2$ (5 mg mL^{-1}), 70 μL 0.1 mol L^{-1} $AgNO_3$ and 20 mg PVP were mixed into 15 mL water and stirred to form a homogeneous solution. After that, 1 mL HQ (0.03 mol L^{-1}) was quickly injected to

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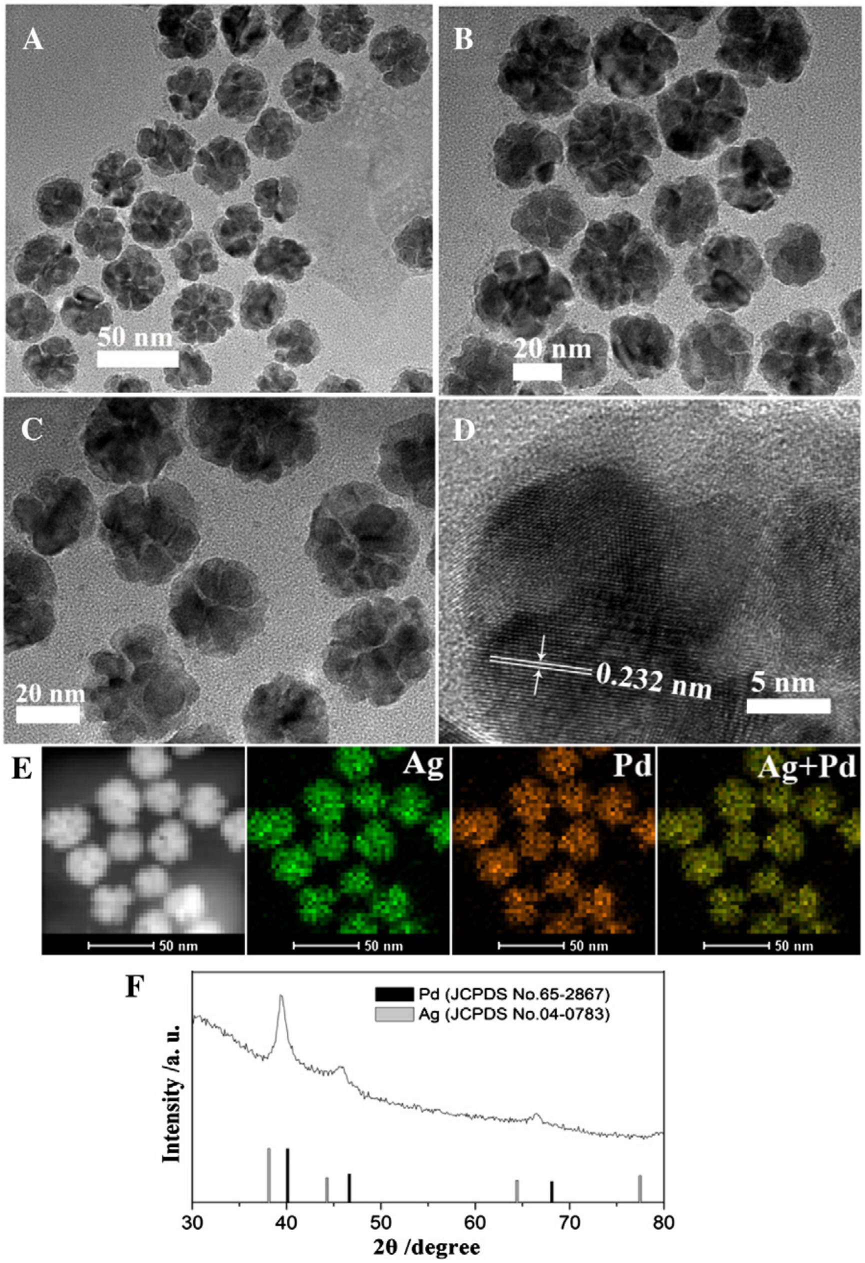

Fig. 1. (A, B, C) Typical TEM images of the prepared PdAg FPNPs with different magnifications. (D) HRTEM images of PdAg FPNPs. (E) HAADF-STEM and elemental mapping of PdAg FPNPs. (F) XRD pattern of the as-prepared PdAg FPNPs.

the mixture and sequentially heated at 70 °C for 15 min in a water bath. Finally, the products were collected by centrifugation and washed several times by water. The exact composition of as prepared catalysts was determined by inductively coupled plasma optical emission spectrometer (ICP-OES) and calculated to the mole ratio.

For electrochemical catalytic measurements, a glassy carbon electrode (GCE) was employed as working electrode. A platinum wire and KCl saturated Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The GCE was polished carefully with alumina powder and followed by sonication in ethanol and water successively before experiment. For electrooxidation test, commercial Pd/C or PdAg FPNP catalyst solution was dropped on the surface of the GC electrode and dried with an infrared lamp carefully, the Pd loading mass of PdAg FPNPs and commercial Pd/C catalyst was 19.1 μg cm^{-2} and 30.8 μg cm^{-2}, respectively. Then, 5 μL of Nafion (0.5%) was coated on the surface of the above material modified GCE and dried before electrochemical tests. All the electrochemical experiments were carried out on a CHI 832B electrochemical workstation, Chenhua Instruments Corp (Shanghai, China).

3. Result and discussion

Transmission electron microscopy (TEM) was used to characterize the morphology and structure of the as-synthesized samples. Fig. 1(A, B, C) shows the typical TEM images of the prepared PdAg nanocrystals with different magnifications. The TEM images obviously show that the resulting samples are definitely endowed with flower-shaped porous nanoparticles, indicating the high yield production of PdAg FPNPs. The average diameter of the PdAg FPNPs is about 34.8 nm. The high-resolution TEM (HRTEM) image (Fig. 1D) indicates that the PdAg FPNPs are dominant formation of the face-centered cubic (fcc) (111) lattice image. The lattice spacing is observed to be 0.232 nm, which is between the lattice spacing of (111) plane of fcc Ag (0.236 nm) and (111) plane of fcc Pd (0.226 nm), suggesting the well alloyed Pd and Ag atoms [12]. The