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Shape-controlled synthesis of Pt–Pd core–shell nanoparticles exhibiting polyhedral morphologies by modified polyol method

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Abstract

Pt–Pd core–shell nanoparticles were synthesized by a simple synthetic method. First, Pt nanoparticles were synthesized in a controlled manner via the reduction of chloroplantinic acid hexahydrate in ethylene glycol (EG) at 160 °C in the presence of silver nitrate and the stabilization of polyvinylpyrrolidon. $AgNO_3$ used acts as a structure-modifying agent to the morphology of the Pt nanoparticles. These Pt nanoparticles function as the seeds for the successive reduction of sodium tetrachloropalladate (II) hydrate in EG under stirring for 15 min at 160 °C in order to synthesize Pt–Pd core–shell nanoparticles. To characterize the as-prepared Pt–Pd nanoparticles, transmission electron microscopy (TEM) and high-resolution TEM are used. The high-resolution elemental mappings were carried out using the combination of scanning TEM and X-ray energy-dispersive spectroscopy. The results also demonstrate the homogeneous nucleation and growth of the Pd metal shell on the definite Pt core. The synthesized Pt–Pd core–shell nanoparticles exhibit a sharp and polyhedral morphology. The epitaxial growth of the controlled Pd shells on the Pt cores via a polyol method was observed. It is suggested that Frank–van der Merwe and Stranski–Krastanov growth modes coexisted in the nucleation and growth of Pt–Pd core–shell nanoparticles.
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Keywords: Pt–Pd core–shell nanoparticles; Pt cores; Pd shells; Polyol method; $AgNO_3$

1. Introduction

The chemical synthesis and morphology control of nanoparticles of noble metals such as platinum are attracting increasing attention [1,2]. Single nanoparticles and their bimetal nanoparticles are utilized as active catalysts because of their possible applications in fuel cell technologies [1–9]. Despite the significant catalytic properties of Pt nanoparticles, there are some limitations faced in the application of Pt nanoparticles as catalysts because of their fast degradation, limited amounts of natural resources and high cost [10]. To overcome these limitations, Pt-based alloy structures that exhibit catalytic activity greater than that of Pt nanoparticles have been developed [4,9]. However, the underlying mechanism of the enhanced catalytic activity is controversial. For example, the nature of the nanoparticle surface determines the catalytic activity and selectivity [11].

Both bimetallic Pt-based alloy nanoparticles and core–shell catalysts have been studied for proton exchange membrane fuel cells (PEMFCs) [9,12]. The synthesis of Pt-based alloy nanoparticles via the chemical reduction of their salts is much simpler than that of Pt-based core–shell nanoparticles. Therefore, various methods have been developed for the synthesis of bimetal nanoparticles [13].

The Pt-based core–shell structure is an excellent way of reducing the Pt catalyst loading. The electrochemical synthesis of core–shell catalysts for electrocatalytic applications has been reported [14]. The synthesis of core–shell nanoparticles via a photochemical reduction process that reduces Keggin ions $[(SiW_{12}O_{40})^{4-}]$ in aqueous solutions

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has also been studied [15]. Recently, Pt–Pt core–shell catalysts have demonstrated their enhanced electrocatalytic activity toward oxygen reduction reactions (ORR) and methanol oxidation reactions (MOR) [16]. This enhanced activity is due to a synergetic characterization between the layers of the core, the shell and their interfaces in the specific core–shell geometry, as well as their high surface-to-volume ratio and quantum size [13].

The synthesis of Pt–Pd nanoparticles has been considered in particular via a polyol method [12,17]. The alternative method of depositing a Pt monolayer on metal nanoparticles has also been presented [18]. Most cases report that, in comparison to the oxide shell, the layers of the metal shell grew uncontrollably and irregularly on the metal core [19]. Therefore, controlling the nucleation and growth of the metal shell layer is crucial. The two fundamental mechanisms of nucleation and growth were observed in the epitaxial growth of a metal shell and in the non-epitaxial growth of an oxide shell [19,20]. However, the overgrowth of the shell layer on the core with a lattice match and mismatch requires further clarification. In fact, the synthesis of a homogeneous system of core–shell bimetal nanoparticles, which relies on synthetic procedures and experimental conditions, is difficult. On the other hand, the fabrication procedure of core–shell shaped bimetal nanoparticles via a bottoms-up approach has been very challenging because of random alloying and the large lattice mismatches that occur between the core and the shell of two different metals, especially the melting phenomenon of the core and/or shell [21–31].

The controlled synthesis of Pt–Pd core–shell catalysts has been much studied because of their practical applications in direct methanol fuel cells and PEMFCs for the realization of sustainable power sources [21–31]. At present, the control of core–shell bimetal nanoparticles <30 nm in size is very difficult, especially the preparation of a practical homogeneous core–shell particle system. Therefore, researchers usually focus on controlling strategies (various chemical and physical synthetic methods and experimental conditions) and on the selection of metal precursors, reducing agents (weak, mild, moderate or strong) and controlling reagents such as additives and impurities. During synthesis and testing, the nucleation and growth mechanisms of nanostructures were studied in order to optimize the entire process [2].

Recently, Pt–Pd core–shell nanoparticles exhibiting a spherical porous structure of diameter 30–40 nm have been synthesized by a one-step microwave heating method. Their morphology, structure and composition were controlled by merely adjusting the $PdCl_2/K_2PtCl_4$ molar ratio. These Pt–Pd catalysts exhibit greater catalytic activity than pure Pd or Pt catalysts for both ORR and MOR in fuel cells. As a result, the highest activity obtained had a Pt/Pd molar ratio of 1:3 [16]. Better performance of ORR and MOR could be realized using the novel core–shell electrocatalyst, while Pt utilization could also be diminished. In the present study, we present a simple strategy for the shape-controlled synthesis of Pt–Pd core–shell nanoparticles via a modified polyol method, in the presence of silver nitrate as a modifying agent at a high synthesis temperature. By using this approach, the overgrowth of thin and uniform layers of single-crystal Pd nanoshells on the surfaces of the shape-controlled Pt cores is observed.

2. Experimental section

2.1. Chemicals and materials

The chemicals used in our process were from Aldrich and Sigma–Aldrich. They were polyvinylpyrrolidone (PVP, a stabilizer), sodium tetrachloropalladate (II) hydrate (ACS reagent) and chloroplantinic acid hexahydrate (ACS reagent) as precursors for Pt and Pt–Pd core–shell nanoparticles. Ethylene glycol (EG) was used as both the solvent and the reducing agent. Silver nitrate (metal basis) was used as a modifying agent. Ethanol, acetone and hexane were used for washing and cleaning. Ionized water and distilled water were prepared using a Narnstead nanopure H_2O purification system. All chemicals used were of analytical grade and were used without any further purification.

2.2. Synthesis of Pt nanoparticles as Pt core particles

During the controlled synthesis of the Pt nanoparticles, 3 ml of EG, 1.5 ml of 0.0625 M H_2PtCl_6, 3 ml of 0.375 M PVP and 0.5 ml of 0.04 M $AgNO_3$ were used. Volumes of 3 ml EG and 0.5 ml 0.04 M $AgNO_3$ were mixed in a flask and heated to 160 °C. After the solution was mixed for 15 min, argon gas was bubbled for 20 min to purge the oxygen present in the flask prior to the synthesis. The solution was refluxed for 2 h in an Ar gas atmosphere and sealed to avoid air from entering the flask. Next, 30 μl of 0.0625 M H_2PtCl_6 was added to the flask at 160 °C followed by 60 μl of 0.375 M PVP, this process being repeated until their total volumes (1.5 ml of 0.0625 M H_2PtCl_6 and 3 ml of 0.375 M PVP) had been added and allowed to reacted thoroughly under continuous stirring for 15 min. The reduction of H_2PtCl_6 occurred because of the EG present. The resultant mixture was stirred in the flask at 160 °C for 15 min. As a result, a dark brown solution containing Pt nanoparticles that exhibit a polyhedral morphology was obtained.

2.3. Synthesis of Pt–Pd core–shell nanoparticles

First, Pt nanoparticles were synthesized by the above procedure. These Pt nanoparticles were then used as the cores of the Pt–Pd core–shell nanoparticles. Both 3 ml of EG and 0.5 ml of 0.04 M $AgNO_3$ were added to a flask, and the mixture was refluxed at 160 °C for 15 min. Then 30 μl of 0.0625 M Na_2PdCl_4 solution was added to the flask followed by the addition of 60 μl of 0.375 M PVP, until their total volumes (1.5 ml of 0.0625 M Na_2PdCl_4 and

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