



Large faceted Pd nanocrystals supported small Pt nanoparticles as highly durable electrocatalysts for oxygen reduction



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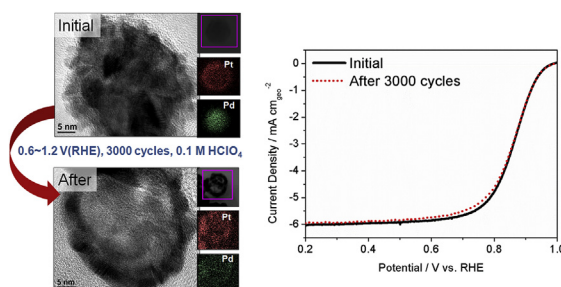
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HIGHLIGHTS

- Large Pd nanocrystal supported small Pt nanocrystals are prepared by a facile method.
- The Pd core shows well-defined cuboctahedral and icosahedral morphology.
- An excellent durability against potential cycling is presented by Pd@Pt.
- Pd@Pt is converted to hollow PdPt alloyed nanocages after potential cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

The reduction of Pt content together with the improvement of the durability of the catalyst for oxygen reduction reaction (ORR) is required to the large-scale commercialization of proton exchange membrane fuel cells. In this work, a novel ORR catalyst consisting of large Pd nanocrystal as the core with small Pt nanoparticles supported on the Pd core is prepared by a facile one-step synthesis method. The Pd substrate is presented in the form of well-defined cuboctahedrons and icosahedrons. The type of metal precursors and Pt/Pd molar ratio are important factors to obtain this Pd-supporting-Pt structure. The Pd₂-s-Pt₁ catalyst with a nominal Pt/Pd atomic ratio at 1/2 shows improved ORR activity: its mass specific activity and area specific activity is 2.5 and 3.5 times that of commercial Pt/C, respectively. More importantly, the Pd₂-s-Pt₁ catalyst demonstrates outstanding durability against potential cycling which can be ascribed to the slow dissolution of Pd core and the structure transformation from Pd@Pt to hollow PdPt alloyed nanocages. This exciting result provides a new pathway to the design of ORR catalyst with excellent durability.

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1. Introduction

The degradation of cathode catalyst for oxygen reduction reaction (ORR) during long-term operation is one of essential reasons

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causing the performance decline of proton exchange membrane fuel cells (PEMFCs) [1,2]. Therefore, in addition to the reduction of Pt content in ORR catalyst, the simultaneous enhancement of the durability is also indispensable for the large-scale commercialization of PEMFCs [1–3].

In order to hold the ORR activity stable, many strategies have been developed to suppress the alteration of morphology and composition in catalyst under dynamic working conditions, such as the fabrication of non-zero-dimensional nanostructure (e.g., nanowires [4], nanoflowers [5], well defined faceted nanocrystals [6]), deposition of other element on the surface of Pt to inhibit the oxidation of Pt atoms [7,8] and encapsulation of Pt catalyst with inert shells (e.g., PANI shell [9] and carbon shell [10]). However, it should be kept in mind that the ultimate goal of designing durable catalyst is to stabilize the catalytic activity instead of morphology or composition. It is well-known that the ORR activity is dependent on the structure of catalyst. Strasser's group reported that the dealloying of PtM (M = Cu, Co, Ni, etc.) alloy during potential cycling produced a structure with Pt enriched surface, giving rise to a promotion of ORR activity [11,12]. Chen et al. [13] found that hollow Pt₃Ni nanoframes transformed from solid PtNi₃ nanocrystals after Ni leaching presented an unexpected outstanding ORR activity. The above results implied that it is possible to utilize the structure transformation of catalyst to improve the ORR activity.

Pd@Pt core-shell nanostructure has attracted much interest in the application of ORR catalyst due to the high Pt utilization and enhanced ORR activity [14–19]. Traditionally, compact Pt shell with a few atomic layers were prone to be fabricated instead of porous or dendritic Pt shell with a larger thickness from the point of enhancing catalytic performance and protecting Pd core [20,21]. However, in the Pd@Pt catalyst with imperfect Pt shell (e.g., having pin holes), the preferential oxidation of exposed Pd core will protect the Pt shell from dissolution [16]. Additionally, in the Pd@Pt with dendritic Pt shell, the dissolution of Pd core and the subsequent *in-situ* alloying occurred between Pd core and Pt shell during repeated potential variation can produce a PdPt alloy with enhanced ORR activity [22,23]. These experiment results inspired us that we can make use of the structure transformation of Pd@Pt under dynamic operation conditions to maintain the activity of catalyst, i.e., improving the durability of ORR catalyst.

Based on the above ideas, a Pd@Pt catalyst with large Pd nanocrystal as the substrate supporting small Pt nanoparticles (denoted as Pd-s-Pt) was synthesized by a facile one-step synthesis method. The large Pd nanocrystal existed in the shape of well-defined cuboctahedron and icosahedron, while small Pt nanoparticles grew on the surface of Pd core by the Volmer-Weber mode [24]. It was found that the durability of catalyst against potential cycling was remarkably enhanced in comparison with Pt/C due to a slow dissolution of Pd core and the transformation from solid Pd@Pt structure to hollow PdPt alloyed nanocages.

2. Experimental section

2.1. Chemicals

Pluronic F127 copolymers came from Sigma Aldrich. Na₂PdCl₄ was bought from Aladdin (Shanghai, China). H₂PtCl₆·6H₂O and K₂PtCl₄ were provided by Shenyang Research Institute of Nonferrous Metal (Shenyang, China). Other chemicals used were commercially available with analytical grade. All chemicals were used as-received without further treatment.

2.2. Material synthesis

The Pd-s-Pt nanomaterials were prepared by a one-step

synthesis method. Typically, 1.0 g Pluronic F127 copolymers were added into 7.55 mL deionized water in a 25 mL round bottom flask with stirring. After complete dissolution, the flask was put into an oil bath at 80 °C followed by injecting the mixture of 1.0 mL Na₂PdCl₄ aqueous solution (34.2 mM) and 0.45 mL H₂PtCl₆ aqueous solution (37.9 mM) with the nominal Pt/Pd atomic ratio at 1/2. The reaction mixture was kept at 80 °C for 3 h in air under stirring and the nanoparticles (NPs) obtained were denoted as Pd₂-s-Pt₁ NPs. When the volume of H₂PtCl₆ solution was changed to 0.225 mL, 0.30 mL and 1.8 mL (the volume of water was adjusted correspondingly to keep the final volume of the mixed solution at 9.0 mL), i.e., the nominal Pt/Pd molar ratio was 1/4, 1/3 and 2/1, the product obtained finally was named as Pd₄-s-Pt₁, Pd₃-s-Pt₁ and Pd₁Pt₂ NPs, respectively. In comparison, the H₂PtCl₆ was replaced by K₂PtCl₄ (38.2 mM aqueous solution) to prepare the NPs (named as Pd₂Pt₁-K₂PtCl₄ NPs) at the nominal Pt/Pd molar ratio of 1/2 with other reaction conditions unchanged.

For the electrochemical testing, the NPs were loaded onto Vulcan XC-72R carbon blacks. Firstly, 16.5 mg carbon black was uniformly dispersed in ethanol by sonication, and the suspension was added into the above mixture containing Pt-Pd NPs. After stirring overnight, the product was collected by centrifugation and washed by ethanol and water. The centrifugate obtained was dried at 60 °C under vacuum overnight. The true metal loading of various catalyst evaluated by thermogravimetric (TG) analysis was 19%, 27% and 52% for Pd₄-s-Pt₁/C, Pd₂-s-Pt₁/C and Pd₁Pt₂/C, respectively.

2.3. Physical characterizations

A JEOL JEM-2000EX transmission electron microscope (TEM) was used to take the TEM images of catalysts. A JEOL JEM-2100F microscope was utilized to perform the high-resolution TEM (HRTEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) analysis. The scanning electron microscopy (SEM) images were recorded by a JEOL JSM-7800F field-emission SEM. The composition of catalyst was measured by energy dispersive spectroscopy (EDS), which was performed by Oxford Inca EDX detector equipped on an FEI Quanta 450 SEM. The crystalline structure of catalysts was studied by X-ray diffraction (XRD) analysis on a Rigaku D/MAX-2500/PC X-ray diffractometer using Cu K α radiation. The thermogravimetric (TG) curves of catalysts were tested from room temperature to 600 °C at a heating rate of 10 °C min⁻¹ under air flow on a NETZSCH TG 209 TG analyzer. X-ray photoelectron spectra (XPS) of catalysts were obtained from an ESCALAB 250Xi (Thermo Scientific) spectrometer using Al K α radiation. UV–vis spectra of solutions were recorded on a Shimadzu UV2550 spectrometer.

2.4. Electrochemical studies

Electrochemical analyses were performed in a conventional three-electrode system connected with a CHI-730D electrochemical station (CH Instruments, Inc.). A rotating disk electrode (RDE) with a glassy carbon disk (4 mm in diameter) was adopted as the working electrode, which was installed on a RDE system (Pine Instrument, US). Pt foil was counter electrode; saturated calomel electrode (SCE) was reference electrode, but all electrode potentials in this work were given versus reversible hydrogen electrode (RHE). HClO₄ aqueous solution (0.1 M) was used as an electrolyte for the electrochemical analyses.

The electrocatalyst slurry was prepared as follows: 5 mg electrocatalysts were sonicated in a mixture (2.5 mL) of isopropanol and 5% Nafion solution (DuPont) for 30 min. The working electrode was prepared by dropping a given volume of the catalyst ink onto the glassy carbon disk of RDE followed by drying in air at room

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