Functional palladium tetrapod core of heterogeneous palladium–platinum nanodendrites for enhanced oxygen reduction reaction

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HIGHLIGHTS

- A hydrothermal synthesis for preparing Pd nanotetrapods without toxic chemicals.
- Formation of Pd nanocrystals under different conditions was discussed.
- Pd-core of stepped surfaces ideal for growing dendritic Pt-shell with high activity.
- Pd tetrapods are as a functional morphology to enhance Pt shell's ORR activity.
- $Pd_{tetrapod}$@30 wt% Pt showed the highest mass activity and stability for ORR.

GRAPHICAL ABSTRACT
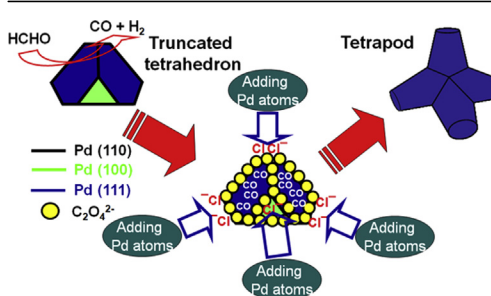
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ABSTRACT

The synthesis, characterization, and application of bimetallic Pd–Pt nanocatalysts with heterogeneous structures are reported. The Pd tetrapod core is demonstrated to enhance the catalytic activity and durability of Pd@Pt nanodendrites for the oxygen reduction reaction (ORR). Special attention is given to the effects of oxalate-ion–formaldehyde during the hydrothermal synthesis of various Pd morphologies at different temperatures. Pd tetrapod synthesis can be delicately achieved without directly using hazardous CO gas. 30 wt% Pt on tetrapodal and truncated-octahedral Pd cores and 50 wt% Pt on tetrapodal Pd cores are prepared and compared against the commercial Pt/C catalyst (E-Tek) for ORR. The $Pd_{tetrapod}$@30 wt% Pt catalyst exhibits the highest ORR activity. Overall, the Pd tetrapod core is a functional morphology which offers high-index facets for the subsequent deposition of Pt(110) nanodendrites, with the bimetallic interaction between two materials allowing for good electron transfer from the Pd core onto the Pt surfaces. Both effects contribute to the increased catalytic activity of $Pd_{tetrapod}$@30 wt% Pt, even under a lower loading of Pt. Furthermore, $Pd_{tetrapod}$@30 wt% Pt has a rather large particle size ($\sim$39.5 nm) which enhances durability and resistance to the agglomeration of Pt.

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1. Introduction

For polymer electrolyte membrane fuel cells (PEMFC), a slow oxygen reduction reaction (ORR) is one of the issues requiring improvement [1,2]. Pt is the most efficient and widely used catalyst known for the ORR. However, Pt suffers from poisoning associated

with electrolytes and the hydroxyl layer, which limits the ORR kinetics and its long-term stability. Factors such as size, morphology, and composition controls of Pt particles have been extensively studied in the past decades in the search for a higher ORR activity, long-term stability and reduced Pt consumption [2–13].

Recent studies have shown that the improved catalytic properties could be attributed to relatively large surface areas and the presence of particularly active facets on Pt nanocrystals supported on metal nanoparticles [14–16]. The seed-mediated growth method has been used in the synthesis of such Pt-based heteronanostructures, because this technique can enable the formation of metallic nanostructures with precisely controlled morphologies and compositions [17–20]. Additionally, the morphology of seeds and corresponding exposed facets have a great influence on the nucleation and growth of the deposited metal and thus determine the structural and catalytic properties of the resultant nanostructures [6]. However, the morphologies of seeds applied thus far have been limited to low-index facets [6,16,19]. For example, Xia and co-workers showed that Pt dendrites on truncated octahedral Pd cores (including Pd(111) and Pd(100) planes) exhibited higher electrocatalytic activities and stabilities toward ORR than that of Pt/C (E-TEK) [16], while the contributions of cores with multi-pod morphologies and/or concave surfaces to inherent ORR activity and durability of Pt-based nanodendrites have not yet been revealed.

Generally speaking, smaller nanocatalysts show higher activities than larger ones, but electrocatalyst durability is directly proportional to the particle size [21]. Recently, a tetrapod morphology of CdTe nanoparticles was synthesized and applied to optoelectronic applications [22]. For the tetrapod morphology, the contact surface area is almost equal to the sum of the surface areas of four small particles with the size of individual branches in a nanotetrapod. From this viewpoint, nanotetrapods exhibit excellent contact surface areas and stepped planes for high activity, as well as a large particle size required for improved durability. As a result, the tetrapod shape can be seen as a functional morphology as a metal core for heteronanostructures of Pt-based nanocrystals. For Pt nanodendrites, Lee et al. showed that nanocatalysts with a particle size of between 15 nm and 30 nm exhibited higher catalytic activities and stabilities than that of Pt/C (E-Tek) [21]. In addition, Pd–Pt heteronanostructures showed superior catalytic activity for ORR [7,15,17,23]. The reaction kinetics of the synthesis of nanocrystals can be controlled by reagent concentration, pH of the precursor solution, temperature, type of reductant, addition of ionic species or a combination of these factors, but complications among these reaction parameters further increases the difficulty in controlling the reaction. Therefore, it is challenging to implement adequate kinetic control to produce nanocrystals with unusual morphologies, including those with high-energy facets and/or a negative curvature on the surface [15,19,24–28]. It is worth noting that $Na_2C_2O_4$ and HCHO are used as the (111)-facet selective agent and reductant in the synthesis of alloyed Pd–Pt nanotetrahedra [29]. Shape-controlled synthesis of Pd nanocrystals (e.g., spheres, tetrahedra and multipods) is also successfully developed in the presence of oleylamine and alkyammonium alkylcarbamate as chelating agents using a Pd^{2+} precursor to control the reaction kinetics [30]. In these two examples, the control over the reduction kinetics by adding facet-selective agents to disturb the growth of seed allows for controlling the shape of noble metal nanocrystals. Thus, it is believed that the combination of selected-facet adsorbates and temperature can be employed to effectively control the facet growth for producing tetrapod nanoparticles.

In this work, Pd nanotetrapods were prepared and used as cores in Pd–Pt multipod dendritic (or flower-like Pd–Pt dendritic) nanocrystals, using a seed-mediated method, while Pd nanotetrapods were synthesized by a hydrothermal method in the presence of HCHO, PVP, and $C_2O_4^{2-}$ ions as the reductant, stabilizer, and efficient facet-selective agent, respectively. It was found that the presence of oxalate ions and formaldehyde along with a suitable temperature are key to the successful formation of Pd(111) nanotetrapods. The dendritic Pt shells were grown directly on tetrapodal Pd cores in the presence of ascorbic acid as a reductant (see Experimental section) with the slow addition of a $PtCl_6^{2-}$ ion precursor. The electrochemical properties of the materials were examined to evaluate the effects of the morphologies of various Pd nanocores (e.g., truncated octahedrons and tetrapods) and shell thickness on their catalytic activity and stability during the ORR. The target of this work was to explore the synthesis of Pd nanotetrapods and highlight the advantages of the tetrapod Pd core compared to catalysts using truncated octahedral Pd cores with flat facets.

2. Experimental

2.1. Synthesis of Pd nanocubes

Pd nanocubes were synthesized by adding K_2PdCl_4 solution into a mixture of ascorbic acid (AA), KBr, and NaCl according to a previously published method [16,31]. In a typical synthesis, aqueous solutions (8.0 ml) containing polyvinylpyrrolidone (PVP) (105 mg), AA (60 mg) and different amounts of KBr (5 mg) and NaCl (185 mg) were placed in a vial preheated to 90 °C in a stirred oil bath for 10 min. Next, an aqueous solution (3.0 mL) containing $KPdCl_4$ (57 mg) was added using a pipette. After the vial had been capped, the reaction was allowed to continue at 90 °C for 3 h. The products were collected by centrifugation, washed several times with deionized (DI) water to remove excess PVP and redispersed in 11 mL of water to form the Pd nanocubes ($\sim$10 nm).

2.2. Synthesis of Pd truncated octahedrons

The procedure for the synthesis of Pd truncated octahedrons, from small Pd nanocubes in the presence of KI, was adapted from the work of Niu et al. [32]. In a typical synthesis of Pd truncated octahedrons, aqueous $KPdCl_4$ solution (9.5 mg/3 mL of DI water) was added into an aqueous solution (8 mL) containing PVP (105 mg), HCHO (100 μL), cubic Pd seeds (1 mL of Pd cube ($\sim$10 nm) solution) and DI water at 60 °C with magnetic stirring (400 rpm). After 3 h of heating, the vial was removed from the oil bath and centrifuged to collect the product, which was washed three times with water and redispersed in DI water (4 mL) [32].

2.3. Synthesis of Pd tetrapods

In a typical synthesis, formaldehyde (0.4 mL) was added into an aqueous solution (10 mL) containing $KPdCl_4$ (12.5 mg), $Na_2C_2O_4$ (100 mg) and PVP (16.6 mg). The pH of the solution was adjusted with 4 drops ($\sim$0.2 mL) of aqueous HCl (1:1); the total volume of the solution was kept at 15 mL. The resulting homogeneous light-yellow solution was transferred to a 25 mL Teflon-line stainless steel autoclave and sealed. The autoclave was then heated at 150 °C (after initial heating from ambient at 8 °C min^{-1}) for 3 h before cooling to room temperature. The black nanoparticles were centrifuged in an acetone–ethanol mixture (15 mL, 1:1 in volume) and washed with ethanol/water several times. The product (average yield >80%) was redispersed in 4 mL of DI water.

2.4. Synthesis of Pd–Pt bimetallic nanocrystals with a dendritic structure

In a typical synthesis, 2 mL of an aqueous suspension of Pd nanocores (truncated octahedrons, tetrapods) and 7 mL of an