



A facile reflux procedure to increase active surface sites form highly active and durable supported palladium@platinum bimetallic nanodendrites



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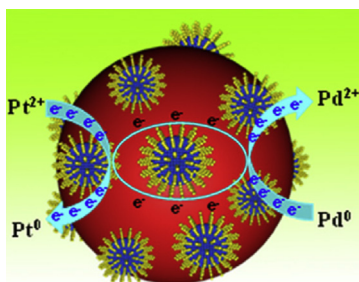
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HIGHLIGHTS

- Pd@Pt bimetallic are synthesized by using different capping agents.
- A facile method to remove these capping agents is reported.
- The structure and morphology can be retained, enhancing the number of active sites.
- The catalysts manifest superior catalytic activity towards the methanol oxidation.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of well-dispersed bimetallic Pd@Pt nanodendrites uniformly supported on XC-72 carbon black are fabricated by using different capping agents. These capping agents are essential for the branched morphology control. However, the surfactant adsorbed on the nanodendrites surface blocks the access of reactant molecules to the active surface sites, and the catalytic activities of these bimetallic nanodendrites are significantly restricted. Herein, a facile reflux procedure to effectively remove the capping agent molecules without significantly affecting their sizes is reported for activating supported nanocatalysts. More significantly, the structure and morphology of the nanodendrites can also be retained, enhancing the numbers of active surface sites, catalytic activity and stability toward methanol and ethanol electro-oxidation reactions. The as-obtained hot water reflux-treated Pd@Pt/C catalyst manifests superior catalytic activity and stability both in terms of surface and mass specific activities, as compared to the untreated catalysts and the commercial Pt/C and Pd/C catalysts. We anticipate that this effective and facile removal method has more general applicability to highly active nanocatalysts prepared with various surfactants, and should lead to improvements in environmental protection and energy production.

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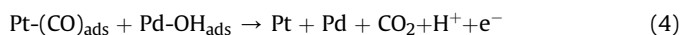
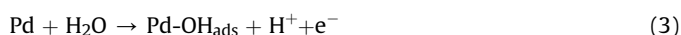
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1. Introduction

Over the past few decades, the ever-increasing environmental problems, such as energy crisis and fuel cells consumption have

simultaneously stimulated intense research on alternative energy storage and conversion devices as sustainable energy materials [1–3]. It is noteworthy that methanol has attracted increasing attention as a fuel in low temperature fuel cells (DMFCs, direct methanol fuel cells) due to its higher safety and energy density [4–6]. However, the electro-oxidation of methanol occurring on the anode side of DMFCs is associated with poor catalytic activity over monometallic Pt catalyst and a resulting decrease in cell efficiency. The oxygen-containing species Pt-(CO)_{ads} adsorbed on the surface of the monometallic Pt only at higher potentials (>0.7 V vs RHE) creates a significant over-potential that limits the applicability for the methanol oxidation reaction (MOR) [7]. The development of low-cost and highly active Pt-based bimetallic or trimetallic catalyst is still urgently needed to overcome this technical obstacle.

Alloying a metal (M) with Pt has become a popular way to Pt-based catalysts with much reduced Pt usage and enhanced Pt mass activity [8]. Depending on the chemical properties of M, Pt-M can be made highly active for either electro-oxidation for MOR or oxygen reduction reaction (ORR) [9]. Among various Pt-M alloys, Pt-Pd bimetallic represents an interesting group of catalysts not only for ORR [10], but also for MOR [11], ethanol [12–18], and ethylene glycol [19]. Alloying of Pt with Pd that can supply the oxygen species at lower potential is one strategy to reduce the poisoning of the Pt with CO and enhance the mass activity towards MOR [7]. This process can be written by the following Equations. (1)–(4).



Pd-Pt bimetallic nanocrystals have attracted significant research attention owing to their high catalytic efficiency in MOR and ORR [20,21]. As a result, the size and shape-controlled synthesis of Pd-Pt bimetallic has recently stimulated tremendous research efforts, and thereby various morphologies have been fabricated. The last decades has witnessed the synthesis of many Pd-Pt bimetallic with various morphologies such as nanocages [22], nanowires [23], nanodendrites [24], nanoclusters [25], nanocubes [26], and nanopolyhedra [27]. Among them, Pd-Pt bimetallic nanodendrites have attracted increasing interest due to its higher catalytic activity in MOR, as compared to other morphologies. Rational design and synthesis of Pd-Pt bimetallic nanodendrites have been reported to exhibit superior electro-catalytic activity and stability due to their distinguished properties, such as porous structures, high specific surface areas and high-index facets, which in general helps to increase the mass and specific catalytic activity. For example, Yamauchi's group designed a Pt on Pd bimetallic nanodendrites via a chemical etching approach [28]. Xia et al. successfully synthesized Pd@Pt bimetallic nanodendrites through a seed mediated method with high catalytic activity for ORR, and the Pd@Pt nanodendrites exhibited superior electro-catalytic activity compared to commercial Pt/C and Pt-black catalysts [29]. Wang's group reported a facile, wet-chemical strategy for the high-yield synthesis of ultralong Pd@Pt bimetallic nanodendrites nanowires, which exhibited high surface area and enhanced electro-catalytic activity towards MOR [30]. However, almost all of these Pd@Pt bimetallic nanodendrites were fabricated by using various surfactants, such as PVP, F127, CTAB, and so on. And these surfactants, which are strongly adsorbed onto the surface of the nanodendrites are essential for the exclusive growth of the dendrites and the

branched morphology control. And the surfactant adsorbed on the surface definitely blocks the access of reactant molecules to the active surface sites, and thus the catalytic activities of these bimetallic nanodendrites are significantly restrained [31]. Catalytic performance strongly relies on having clean surfaces where reactants can bind to surface atoms and undergo MOR or ORR. Obtaining a clean surface free of extraneous species in these catalysts is therefore essential to synthesis active and durable catalysts. Therefore, developing an effective, facile and general method for removal of these surfactants is an urgent topic to be solved.

Here we report on a facile reflux procedure to effectively remove capping agent molecules from supported catalysts without significantly affecting their sizes. More significantly, the structures and the morphologies of these nanodendrites can also be retained, enhancing the numbers of active surface sites, catalytic activity and stability toward methanol and ethanol electro-oxidation. The preparation strategy and reflux procedure are shown in Scheme 1. In the first step, a series of well-dispersed bimetallic Pd@Pt nanodendrites were successfully synthesized by using different surfactants. For the second step, we reported a facile reflux process to effectively remove various surfactant molecules without significantly affecting their sizes and morphologies. The as-obtained hot water reflux-treated Pd@Pt/C catalysts manifest superior catalytic activity and stability both in terms of surface and mass specific activities, as compared to the untreated Pd@Pt/C and commercial Pt/C and Pd/C catalysts. We demonstrate this reflux process for supported Pd@Pt nanodendrites and show their improved application as electro-oxidation catalysts. We anticipate that this effective and facile removal procedure has more general applicability to highly active nanocatalysts prepared with various surfactants, and should lead to improvements in environmental protection and energy production.

2. Experimental section

2.1. Materials

Potassium tetrachloroplatinate (K₂PtCl₄, Aladdin, 98%), potassium tetrachloropalladate (K₂PdCl₄, Aladdin, Pd ≥ 32.6%), polyvinylpyrrolidone (PVP, (C₆H₉NO)_n, Aladdin, 58,000), Pluronic[®] P123 (Sigma-Aldrich), Pluronic[®] F127 (Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB, J&K), ascorbic acid (C₆H₈O₆, J&K), citric acid (C₆H₈O₇·H₂O), methanol (CH₃OH), ethanol (CH₃CH₂OH), Nafion[®] perfluorinated resin solution (Sigma-Aldrich), Pt/C (30% Pt) (Alfa Aesar), Pd/C (30% Pd) (Alfa Aesar), Carbon black (XC-72).

2.2. Preparation of Pd@Pt nanodendrites

Pd@Pt nanodendrites as the starting material were synthesized by a one-step route in an aqueous solution at room temperature with the assistance of surfactants. In a typical synthesis, an aqueous solution (5.0 mL) containing 0.10 mmol K₂PtCl₄, 0.05 mmol K₂PdCl₄ and the surfactants (100 mg of PVP, 60 mg of P123, 50 mg of F127, 55 mg of CTAB, respectively) were placed in a breaker, then 0.23 M citric acid (2.0 mL) and 0.17 M ascorbic acid (3.0 mL) were added into the above mixture. The resulting mixture solution was stirred for 8 h at room temperature. Then the resulting slurry was filtered, washed several times with distilled water and absolute alcohol. The resulting Pd@Pt catalyst was dried at 60 °C in an oven.

2.3. Preparation of Pd@Pt/C catalysts

The Pd@Pt nanodendrites catalysts were supported onto XC-72 carbon blacks with metal loading of 30% by adding carbon blacks

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