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Regular Article

Platinum$_{69}$-cobalt$_{31}$ alloyed nanosheet nanoassemblies as advanced bifunctional electrocatalysts for boosting ethylene glycol oxidation and oxygen reduction

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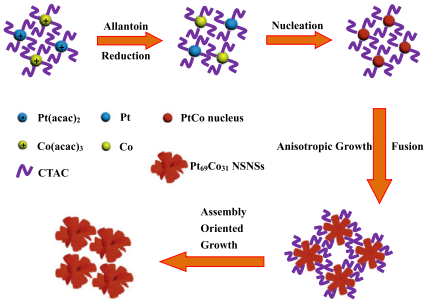
GRAPHICAL ABSTRACT



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ABSTRACT

Pt-based bimetallic nanocrystals are feasible to dramatically improve the catalytic performances in fuel cells via morphology- and composition-engineering. Herein, bimetallic platinum$_{69}$-cobalt$_{31}$ nanosheet nanoassemblies ($Pt_{69}Co_{31}$ NSNSs) were facilely synthesized through a one-pot co-reduction solvothermal strategy in oleylamine (OAm), using cetyltrimethylammonium chloride (CTAC) and allantoin as the directing agents. The current synthesis highly depended on the critical concentrations of Pt and Co precursors, the combined use of allantoin to OAm as the co-reductant, and the use of proper allantoin concentration. The obtained nanocatalyst exhibited largely enhanced electrocatalytic activity and durable ability towards ethylene glycol oxidation reaction (EGOR) and oxygen reduction reaction (ORR) relative to home-made $Pt_{85}Co_{15}$ nanoparticles (NPs), $Pt_{19}Co_{81}$ NPs and Pt black catalysts due to its much larger electrochemically active surface area than the contrasts.

1. Introduction

Nowadays, various clean renewable energy sources attract substantial attention on account of the serious energy shortage and greenhouse gas emission [1]. Particularly, fuel cells have drawn extensive attention owing to their low pollution level, high energy density and enhanced energy-conversion [2]. However, some issues are still remained such as the sluggish kinetics of different fuels on the anode and oxygen reduction on the cathode, which severely restrict their commercial applications [3,4]. In this regard, a lot of efforts have been dedicated recently to explore effective nanocatalysts [5].

Pt nanomaterials are known to be the most promising catalysts for oxygen reduction reaction (ORR) [6] and fuel oxidation (e.g. ethylene glycol oxidation reaction, EGOR) [7]. However, Pt catalyst

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is seriously hindered because of the easy deactivation by toxic carbon monoxide (CO)-like intermediates, high cost and low stability [8]. Inspiringly, these issues can be effectively resolved by alloying Pt with another metal, especially 3d-transition metal to modify the electronic structure of Pt [9]. To this end, the alloyed Pt would have high efficiency and durability due to the ensemble effects of the bimetals [10]. Up to date, a number of Pt-based bimetallic catalysts have been synthesized [11]. Pt-Ag nanoparticles (NPs) had the greatly enhanced catalytic capacity towards ORR [12]. Also, Pt-Au hollow nanospheres exhibited enlarged electrochemically active surface area (ECSA) and superior electrocatalytic characters for EGOR [13].

Meanwhile, the size and morphology of a catalyst are critically associated with the catalytic activity [9]. Thus, a great number of methods have been developed to design and construct Pt-based nanocatalysts with diverse shapes, such as core-shell structures [14], dendrites [15] and wires [16]. Particularly, sheet-like architectures have attracted tremendous attention because it can efficiently maximize the utilization of metal atoms for its specific structure [17]. Accordingly, many strategies have been designed to synthesize Pt-based nanosheets. Schaak and co-workers prepared PtCo nanospheres with hollow structure by a two-step approach [18]. Li's group fabricated Pt-Co nanoparticles by a wet-chemistry method with a N_2 in/outlet, refluxing tube, and a thermal couple [11]. Graphene supported Pt nanosheets were synthesized through a one-step microwave-assisted way [19]. Besides, Pt-Cu nanosheets were prepared by a controllable two-step method [20]. These examples are usually suffered from the time-consuming, seed mediated growth and/or complex procedures [21]. Thus, it is desirable to develop effective and simple strategies to construct novel Pt-based nanocatalysts.

Allantoin as a derivative of purine catabolism contains more amino- and imino-groups, which can fast chelate with the metal precursors and thereby modulate the metallic crystal growth [22]. Herein, a facile one-pot solvothermal strategy was carried out for synthesis of bimetallic $Pt_{69}Co_{31}$ nanosheet nanoassemblies ($Pt_{69}Co_{31}$ NSNSs) in oleylamine (OAm) with the assistance of allantoin (Fig. S1, Supporting Information, SI) and cetyltrimethylammonium chloride (CTAC). The electrocatalytic property of the obtained products were investigated through EGOR and ORR, using homemade $Pt_{85}Co_{15}$ NPs, $Pt_{19}Co_{81}$ NPs and commercial Pt black as the references.

2. Experimental

2.1. Synthesis of $Pt_{69}Co_{31}$ NSNSs

For the typical synthesis of $Pt_{69}Co_{31}$ NSNSs, 0.1600 g of CTAC was added into 20 mL of OAm to obtain the homogeneous suspension under magnetic stirring at 60 °C. Afterwards, 0.0157 g of Pt $(acac)_2$, 0.0143 g of $Co(acac)_3$ and 0.0791 g of allantoin were put into the above suspension under stirring for 40 min, in which the molar ratio of $Pt(acac)_2$ to $Co(acac)_3$ (defined as Pt/Co for simplicity) is 1:1. Then, the mixture was transferred into a Teflon-lined stainless autoclave (25 mL), heated up to 180 °C and reacted for 10 h. Eventually, the products were obtained through centrifugation, and totally washed by ethanol and cyclohexane, followed by drying at 60 °C in a vacuum.

In the contrary experiments, the referenced PtCo products were constructed by adjusting the Pt/Co molar ratios of the two precursors, or modulating the concentrations of allantoin, while the other experimental conditions were kept identical.

More detailed information about *Chemicals*, *Characterization*, and *Electrochemical measurements* were shown in SI.

3. Results and discussion

3.1. Characterization

The transmission electron microscopy (TEM) measurements were firstly employed to investigate the morphological features of the typical sample. Fig. 1A and B display the low- and medium-magnification TEM images, showing the abundant well-defined and well-dispersed flower-like structures assembled by numerous nanosheets with the mean diameter of 20.32 nm (inset in Fig. 1A). Control experiments demonstrate that the well-defined architectures are highly correlated with the Pt/Co molar

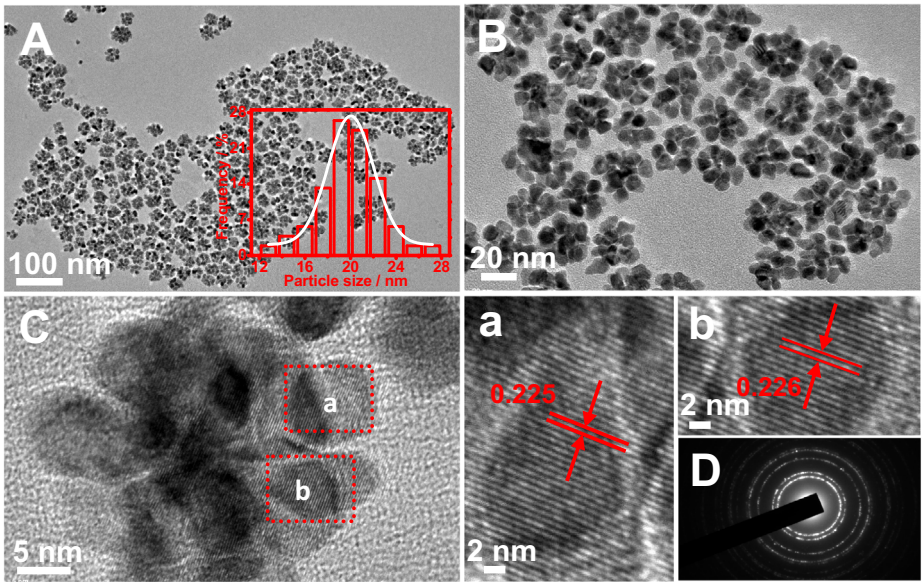

Fig. 1. (A) Low-, (B) medium-, and (C, a and b) high-magnification TEM images of $Pt_{69}Co_{31}$ NSNSs. (D) The corresponding SAED pattern. Inset in (A) shows the size distribution of the nanosheets.