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Full Length Article

Monodispersed porous flowerlike PtAu nanocrystals as effective electrocatalysts for ethanol oxidation

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ABSTRACT

Designing and tuning the bimetallic nanoparticles with desirable morphology and structure can embody them with greatly enhanced electrocatalytic activity and stability towards liquid fuel oxidation. We herein reported a facile one-pot method for the controlled synthesis of monodispersed binary PtAu nanoflowers with abundant exposed surface area. Owing to its fantastic structure, synergistic and electronic effect, such as-prepared PtAu nanoflowers exhibited outstandingly high electrocatalytic activity with the mass activity of 6482 mA mg^{-1} towards ethanol oxidation, which is 28.3 times higher than that of commercial Pt/C (227 mA mg^{-1}). More interesting, the present PtAu nanoflower catalysts are more stable for the ethanol oxidation reaction in the alkaline with lower current density decay and retained a much higher current density after successive CVs of 500 cycles than that of commercial Pt/C. This work may open a new way for maximizing the catalytic performance of electrocatalysts towards ethanol oxidation by synthesizing shape-controlled alloy nanoparticles with more surface active sites to enhance the performances of direct fuel cells reaction, chemical conversion, and beyond.

1. Introduction

Owing to the rapid consumption of traditional fossil fuels and growing energy demand in people's daily life, searching for the novel renewable energy for the replacement of the traditional fossil fuels is urgently needed [1–3]. Direct fuel cells (DFCs) have drawn broad notices in both scientific research and industry field due to its some special characteristics such as high efficiency and cleanness [4,5]. As one of the most significant energy sources in direct fuel cells, ethanol possessed plenty of remarkable advantages such as efficient energy conversion, high energy density, easy storage and transportation but low environmental pollution [6,7]. In addition, many previously reported literatures have revealed that ethanol can be produced from the biomass-related cellulose with high yield, which offered the great promise for the sustainably commercial application of direct ethanol fuel cells (DEFCs) [8,9].

In spite of these superiorities, the lack of efficient catalysts for anode oxidation reaction remains a tough challenge, which need to conquer for the commercial development of DEFCs [10–12]. As for anode catalysts, up till now, it has been generally recognized that Pt is still one of the most effective catalysts for the electrooxidation of ethanol as well as various industrial chemical reactions [13,14]. While both of the limited nature abundant and skyrocketing high costs seriously hinder the large-scale commercial application [15,16]. Therefore, a crucial step in the synthesis of new-generation electrocatalysts will be the development of hybrids, which not only retain the high activity of Pt but also cut down the cost of catalysts [17,18].

Following this guideline, up till now, many strategies have been proposed. Interestingly, one of effective approaches to greatly enhance the electrocatalytic performances is to alloy Pt with some of other less expensive transition metals (Cu, Bi, Pb, Ru) [19–22], owing to their novel alloy, electronic, and synergistic properties [23,24]. Among multitudinous transition metals, Au has been proven to be one of the most efficient metals to serve as catalyst alloy, which can not only form the steady alloy with Pt but also

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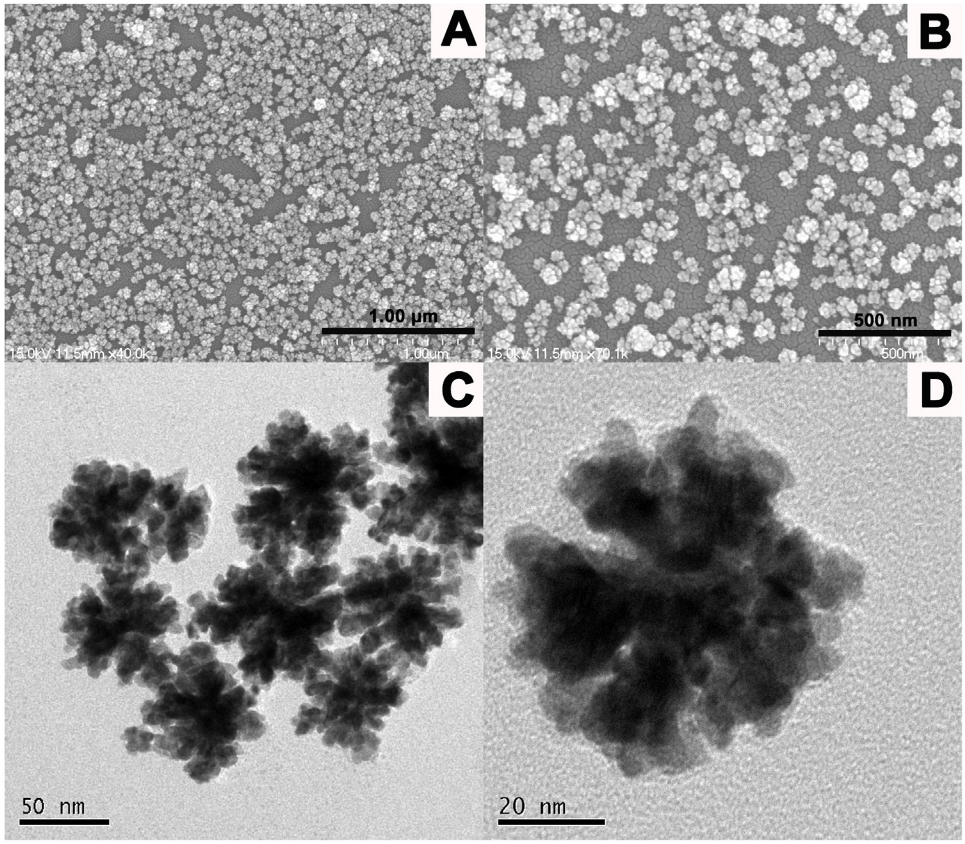

Fig. 1. Representative images of SEM (A and B) and TEM (C and D) with different magnification of flower-like Pt_1Au_1 nanocrystals.

assist in oxidizing small organic molecules [25], showing its great potential application for DEFCs [26,27].

Impressively, another successful method for developing high-performance catalysts with maximized Pt utilization is designing the nanostructure of Pt, which is conductive to improve the surface exposure and electronic effect on the surface of catalysts [28]. In this regard, the morphology and structure of nanocatalysts appeared as additional parameters greatly affect the catalytic activity for the electrooxidation of ethanol. In the last decade, varieties of Pt-based nanocrystals with diverse structures have been successfully synthesized for the application of DEFCs, such as core-shell [29], nanowire [30,31], nanocube [22], dendritic structures [32] and so on. Among them, the flowerlike structures have attracted increasing attentions because of much more increased catalytic active sites in the catalyst surface caused by its unique structure [11,33,34]. Therefore, at this point, if we can combine the benefits of both alloy effects and the unique structural advantage to develop a facile method to engineer binary PtAu flower-like nanocrystals, it will be extremely favorable for the preparation of ideal electrocatalysts towards ethanol oxidation with outstandingly high activity and long-term stability and ultimately greatly boosting the commercialization of direct fuel cells.

Herein, we report our tremendous efforts for demonstrating a facile method for the controlled synthesis of PtAu binary nanoparticles with flower-like structure. A class of monodispersed PtAu nanoflowers with tunable ratio have been produced with high yield via a facile one-pot method. As a consequence, the new-generation PtAu nanoflowers with optimized atomic ratio show extremely high mass activity towards ethanol oxidation, which is 28.3 fold enhancements than that of commercial Pt/C. Besides, they are also more stable than that of the commercial Pt/C, indicating that the as-obtained monodispersed PtAu nanoflowers can be well applied as stable and efficient electrocatalysts for DEFCs and beyond.

2. Experimental section

2.1. Catalysts preparation

The typical wet-chemical method for the preparation of binary PtAu nanoflowers involves of the application of chloroplatinic acid (H_2PtCl_6) and chlorauric acid ($HAuCl_4$) as the metal precursors, polyvinylpyrrolidone (PVP) as surfactant agent, hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and water as reducing agent and solvent, respectively. Briefly, the H_2PtCl_6, $HAuCl_4$, PVP and $N_2H_4{\cdot}H_2O$ in the controlled molar ratio were added into a round bottom flask contained 60 mL water in sequences with rapid stirring. After that, the homogeneous aqueous solution was stirred at room temperature for 1 h. The final products were collected via centrifugation and washed with an ethanol and acetone for three times. The as-obtained product was denoted as Pt_1Au_1, for comparison, the Pt_1Au_3 and Pt_3Au_1 catalysts were also prepared under the same conditions by tuning the amount of $HAuCl_4$.

2.2. Characterization of PtAu nanoflowers

The morphology and structure of the nanocomposites were firstly investigated by scanning electron microscopy (SEM) and energy dispersive X-ray analyzer (EDX) with the S-4700 system (Hitachi High Technologies Corporation, Japan). Low magnification transmission electron microscopy (TEM) was conducted on a HITACHI HT7700 transmission electron microscope at an accelerating voltage of 120 kV. High-resolution transmission electron microscopy (HRTEM) were conducted on a TECNAI-G20 electron