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Folic acid bio-inspired route for facile synthesis of AuPt nanodendrites as enhanced electrocatalysts for methanol and ethanol oxidation reactions

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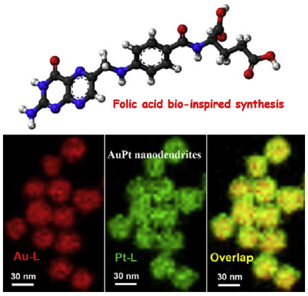
HIGHLIGHTS

- Uniform AuPt NDs are facilely prepared by a simple bio-inspired method.
- Folic acid is used as the structure director and stabilizing agent.
- The alloyed architectures have large electrochemically active surface area.
- The nanocrystals display improved catalytic activity and stability for MOR and EOR.

GRAPHICAL ABSTRACT



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ABSTRACT

Folic acid (FA), as an important biomolecule in cell division and growth, is firstly employed as the structure director and stabilizing agent for controlled synthesis of uniform $Au_{65}Pt_{35}$ nanodendrites (NDs) by a one-pot wet-chemical bio-inspired route at room temperature. No pre-seed, template, organic solvent, polymer, surfactant or complex instrument is involved. The products are mainly characterized by transmission electron microscopy (TEM), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray diffraction (XRD), and X-Ray photoelectron spectroscopy (XPS). The architectures have enlarged electrochemically active surface area (60.6 $m^2\ g_{Pt}^{-1}$), enhanced catalytic activity and durability for methanol and ethanol oxidation in contrast with commercial Pt black and the other AuPt alloys by tuning the molar ratios of Au to Pt (e.g., $Au_{31}Pt_{69}$ and $Au_{82}Pt_{18}$ nanoparticles). This strategy would be applied to fabricate other bimetallic nanocatalysts in fuel cells.

1. Introduction

With the rapid growth of energy demand, direct alcohol fuel cells (DAFCs) have attracted great attention because of their high energy densities, fast reaction kinetics and no pollution [1]. Regarding alcohol oxidation, Pt is still the most efficient catalysts although they suffer from the drawbacks including relative low kinetics, low poisoning tolerance and reserves [2–4].

Alloying Pt with another metal (M = Au, Pd, Ru, etc.) is practically desired to improve the catalytic activity and decrease the usage of Pt [5]. In recent years, several Pt-based bimetallic nanocatalysts have been constructed such as PtPd flowers [6], PtRu particles [7], Pt-Pd tubes [8] and Pt-Au core-shell rods [9], showing

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the enhanced electrocatalytic performances.

As well known, Au owns better electrical conductivity and is cheaper than Pt [10]. Thus, the formation of AuPt alloy would enhance the electrocatalytic performance when compared with single Au and Pt counterparts, thanks to the synergetic effects between Au and Pt which are mainly dominated by bifunctional and electronic effects [11,12]. Specifically, bifunctional effects facilitate water dissociation occurred at more negative potential because of the bimetallic alloy, promoting the removal of the adsorbed carbon oxide (CO_{ad}) to improve the catalyst stability [13]. On the other hand, electronic effects endow the alloyed Pt with higher affinity to alcohol adsorption and easier formation of surface oxides at relatively lower potential for eventual removal of CO_{ad} [14].

Most investigations reveal that the morphology and structure are also crucial to nanocatalysts [15,16]. Recently, branched nanostructures have drowned much attention for their superior catalytic activities, thanks to the existence of more steps, edges, and corners in densities which would provide more active sites accessible for the catalytic reaction [17]. For example, Zhang and co-workers prepared Au—Pt dendritic nanostructures at 65 °C by a two-step seed-mediated successive reduction approach, which exhibited high catalytic performance towards methanol oxidation [18]. In another example, Meng's group synthesized Pd—Ag bimetallic dendrites *via* a galvanic replacement process, which showed higher catalytic activity for the reduction of 4-nitrophenol [15].

Folic acid (FA, Fig. 1) is important for the production and maintenance of new cells, synthesis of DNA and RNA [19]. It plays a significant role in the maintenance of DNA conformation and methylation patterns, which are benefit to prevent cancer and slow aging [19]. FA contains carboxyl, hydroxyl and amino groups, which would adsorb on the nuclei surfaces and control the crystal growth of nanomaterials [20].

In this work, FA was firstly used as the structure director for synthesis of AuPt nanodendrites (NDs) by a one-pot wet-chemical bio-inspired strategy at room temperature. The electrocatalytic performances of the as-prepared nanocatalyst was determined by using methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR) as two model systems.

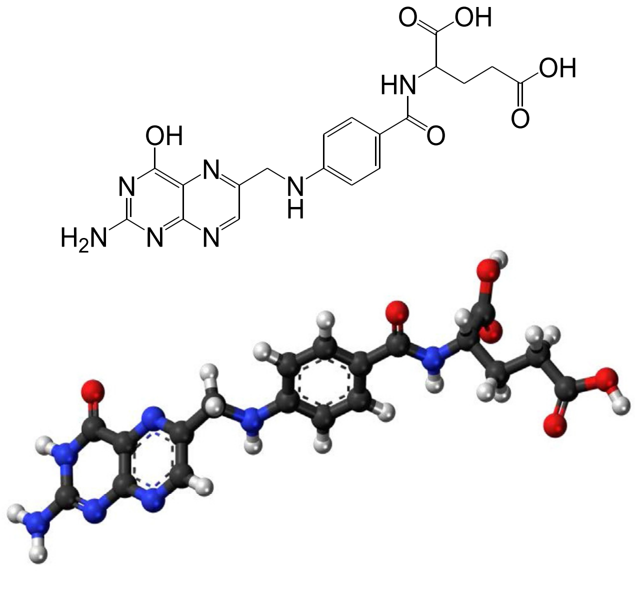

Fig. 1. Chemical structure and ball-and-stick model of folic acid.

2. Experimental

2.1. Synthesis of $Au_{65}Pt_{35}$ NDs

The typical preparation of AuPt NDs was described as below. Firstly, 0.1103 g of FA, 0.5 mL of NaOH (1.0 M), 0.518 mL of H_2PtCl_6, and 0.823 mL of $HAuCl_4$ (i.e., the final molar ratio of $H_2PtCl_6/HAuCl_4$ is 1:1.) were subsequently put into water and stirred for 5 min to obtain a homogeneous suspension with the volume of 10.0 mL. Next, 100 μL of hydrazine solution (16.41 M) was injected into the mixture and reacted for 1 h at room temperature. After thoroughly washing with NaOH solution and ethanol to remove the residue of FA, the final products were collected and dried in vacuum oven at 60 °C, and named as $Au_{65}Pt_{35}$ NDs (the molar ratios of Pt to Au in AuPt NPs are obtained from the XPS analysis).

In control experiments, the other types of AuPt alloys with the molar ratios of H_2PtCl_6 to $HAuCl_4$ of 3:1 and 1:3 are prepared in the same way, which are named as $Au_{31}Pt_{69}$ nanoparticles (NPs) and $Au_{82}Pt_{18}$ NPs, respectively.

The details of the chemicals and apparatus were listed in Supporting Information (SI).

2.2. Electrochemical measurements

All the electrochemical experiments were operated at a standard three-electrode system [16]. For construction of the modified electrode, 1.0 mg of the sample ($Au_{65}Pt_{35}$ NDs) was dispersed into 1.0 mL of water by ultrasonication for 0.5 h. Next, 6 μL of the mixture was covered on the surface of a glassy carbon electrode (GCE), and dried in air naturally. Subsequently, the Nafion solution (4 μL, 0.05 wt%) was dropped onto the electrode surface to seal the deposit. In control experiments, commercial Pt black, $Au_{31}Pt_{69}$ NPs and $Au_{82}Pt_{18}$ NPs catalysts modified electrodes were fabricated similarly.

The electrochemically active surface area (ECSA) was evaluated by measuring the hydrogen adsorption or hydrogen desorption charges from −0.2 to 1.5 V in 0.5 M H_2SO_4 by cyclic voltammetry (CV) based on the literature [21].

The electrocatalytic activity of the catalysts modified electrodes were determined by CV toward MOR and EOR. Also, their stability was examined by chronoamperometry in 1.0 M KOH containing 0.5 M methanol or ethanol by applying the potential of −0.3 V.

3. Results and discussion

3.1. Physical characterizations

Fig. 2A and B show the transmission electron microscopy (TEM) images of the typical sample. Clearly, there are a lot of well-dispersed nanodendrites observed with the narrow size distribution from 30 to 35 nm. Furthermore, their polycrystalline nature is manifested by the selected area electron diffraction (SAED, inset in Fig. 2B).

Fig. 2C displays the high-resolution TEM image of the product, in which there are many clear lattice fringes with the inter-planar distances of 0.229 and 0.232 nm from the marked positions. These values correspond to the (111) crystal planes, in agreement with that of the face-centered cubic (fcc) AuPt alloy [22]. These values are coincidently located between those of pure Au (0.235 nm) and Pt (0.226 nm), as well supported by the carbon nanofiber-supported bimetallic AuPt electrocatalyst [23]. It verifies the alloy nature of the product, which is in good agreement with the result obtained from the SAED pattern.

As shown in Fig. 3, high angle annular dark-field scanning transmission electron microscopy-energy-dispersive X-ray