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Simple synthesis of self-supported hierarchical AuPd alloyed nanowire networks for boosting electrocatalytic activity toward formic acid oxidation

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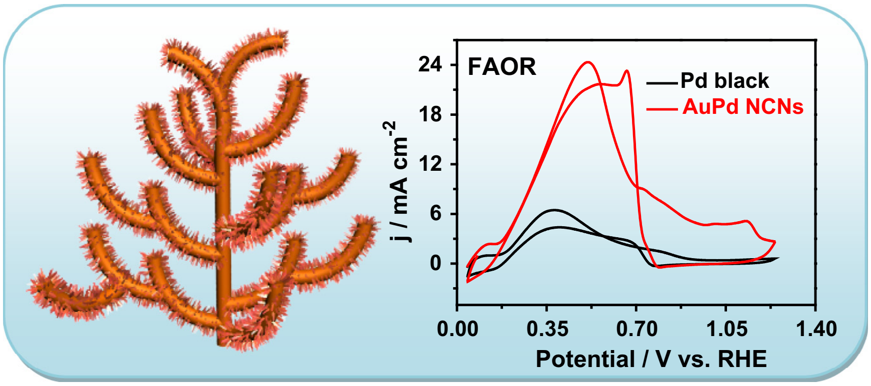
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, self-supported hierarchical AuPd alloyed interconnected nanowire networks (AuPd NCNs) were fabricated by a one-pot co-reduction method. Theophylline was acted as the capping and structure-directing agents. The product was mainly characterized by a series of techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The hierarchical nanostructures had the enlarged electrochemically active surface area (EASA), and the enhanced catalytic activity toward formic acid oxidation reaction (FAOR) and strengthened poisoning tolerance for poisoning CO-like intermediates by cyclic voltammetry and chronoamperometry, which outperformed commercial Pd black catalyst. This strategy supplies a simple and general method for mass preparation of AuPd NCNs with potential applications in fuel cells.

1. Introduction

In recent years, direct liquid fuel cells have been attracted enormous attention owing to their wide applications in industry as clean energy sources [1]. Among the fuel cells, formic acid, alcohols, and hydrazine are the common fuels [2], and their oxidation strongly relies on the anode catalysts [3]. Therefore, substantial efforts are devoted to explore novel catalysts to enhance the correlative catalytic property in fuel cells [4].

Among them, formic acid has wide applications as an environment-friendly and efficient fuel in energy devices

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especially for portable devices, owing to its low toxicity, high power density, safe storage and transportation [3]. However, the sluggish kinetics of formic acid oxidation reaction (FAOR) are the main impediment to influence the energy efficiency [5]. Therefore, significant efforts are continuously made to develop novel anode catalysts in the aforementioned areas [6]. Particularly, Pd-based nanomaterials are commonly used as anode catalysts for FAOR, mainly due to their enhanced catalytic activity and improved durability when compared with other catalysts reported previously [7].

As it is well-known, Pd-based nanocatalysts have widespread applications in energy storage and transformation [8,9] because of their remarkably catalytic ability [10]. To date, many researches have been conducted to maximize the catalytic ability and durability of Pd-based catalysts [11]. Alloying Pd with another metal (PdM, M = Au, Pt, Co) to form bimetallic catalysts is the common strategy [6] for the synergistic effects between the bimetals [12]. Meanwhile, it is feasible to optimize the size and shape of the catalyst with the purpose to enlarge the active area to the maximum degree [13].

Notably, it is reasonable for the combination of Au and Pd to enhance the catalytic performance and strengthen the poisoning tolerance of the resultant catalysts. To date, a variety of approaches were developed to fabricate AuPd nanomaterials accordingly [14]. For example, Dong et al. prepared core-shell Au@Pd nanoparticles by multi-step synthetic method, where core-shell Au@Ag nanoparticles were firstly prepared in organic solvent, followed by the conversion of the pure Ag shells into AgPd alloyed ones via galvanic replacement reaction, followed by the subsequent removal of the Ag component in the saturated NaCl solution [15]. Therefore, it is necessary to develop a simple, green and shape-controlled method to synthesize novel bimetallic AuPd nanocrystals.

Theophylline as one naturally xanthine is widely existed in beverages such as tea and coffee [16]. Recently, it has received great attention in chronic obstructive pulmonary disease and asthma due to its anti-inflammatory activities and antioxidant [17]. Moreover, theophylline contains the positive-charged amino groups to combine multivalent metallic species via electrostatic interactions and the strong chelating ability, which would widely explore especially in preparation of nanomaterials [18].

For fabricating bimetallic alloyed nanostructures, one-pot aqueous method is usually utilized owing to its easier operation and simplicity [19]. In this context, a simple one-pot strategy was designed for construction of self-supported bimetallic hierarchical AuPd interconnected nanowire networks (AuPd NCNs) by using theophylline as the capping and structure-directing agents. The electrocatalytic activity and durability of the prepared AuPd NCNs were examined by using FAOR as the model system.

2. Experimental

2.1. Synthesis of hierarchical AuPd NCNs

For typical preparation of AuPd NCNs, 0.054 g of theophylline was dissolved into 8.98 mL of water after adding the NaOH solution (0.40 mL, 0.50 mM) under stirring at room temperature, accompanied by putting 0.41 mL of $HAuCl_4$ (24.30 mM) and 0.10 mL of H_2PdCl_4 (100 mM) into the above theophylline solution. After homogeneously mixing, 0.10 mL of the hydrazine solution (80%) was rapidly injected into the mixture and then reacted for 1 min. In the end, the precipitate was centrifuged for 5 min at 3000 rpm, and washed sequentially with the freshly-prepared NaOH solution (0.05 mM) and water, followed by drying in vacuum at 60 °C for further characterization, denoted as AuPd NCNs for clarity and simplicity.

More detailed information regarding the Materials, Characterization and Electrochemical measurements was provided in Supporting Information (SI).

3. Results and discussion

3.1. Characterization

Firstly, the morphology of AuPd NCNs was characterized through transmission electron microscopy (TEM) analysis. As revealed by the typical low- and medium-magnification TEM images (Fig. 1A and B), the product possesses many self-supported interconnected nanowire networks with rough surfaces and porous reticular structure. Meanwhile, the width of the main stem is roughly in the range from 4 to 19 nm, with an average size of 12 nm (Fig. S1, SI). Their polycrystalline nature is forcefully manifested by the selected-area electron diffraction (SAED) pattern (inset in Fig. 1B) [20].

High-resolution TEM (HR-TEM) images display the well-defined lattice fringes from the marked locations (Fig. 1C–F). As seen, the interplanar spacing distances are measured to be 0.227 and 0.233 nm (Fig. 1D), along with 0.235 nm and 0.234 nm (Fig. 1F), respectively, which are well matched with the (1 1 1) crystal planes of the face-center cubic (*fcc*) AuPd alloy [21]. Besides, AuPd NCNs have the highly rough surfaces, as powerfully supported by the high density of the atomic steps on the surfaces (Fig. 1D and F). Impressively, the high density of atomic steps with low-coordination strongly demonstrates the formation of AuPd alloyed phase [22]. And the structural defects and high density of low coordinated atomic steps would provide lots of active sites accessible for reactants and ultimately facilitate the subsequent FAOR [23].

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) mappings (Fig. 2) are used to examine the correlative structural features and composition distribution [24]. Fig. 2A displays the correlated HAADF-STEM image. Fig. 2B–D shows Au and Pd elements uniformly dispersed across the entire AuPd NCNs, which manifest the formation of the AuPd alloy, in good coincidence with the analysis from the line-scanning profiles (Fig. 3A). In addition, the co-existence of the bimetals (i.e. Au and Pd) is found from the EDS spectrum (Fig. 3B), and the atomic ratio of Au against Pd is roughly 49.17:50.82 (inset in Fig. 3B).

X-ray diffraction (XRD) analysis was provided to characterize the crystal structures of the typical sample, using standard XRD patterns of bulk Au (JCPDS: 04-0784) and Pd (JCPDS: 46-1043) [25] as the references [26]. There are five representative diffraction peaks appear at 38.85°, 45.78°, 65.23°, 77.95° and 83.45° (Fig. 4), which are well indexed to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of the *fcc* AuPd alloy [21]. It confirms the formation of the alloyed AuPd NCNs again, which is consistent with the previous report [27].

X-ray photoelectron spectroscopy (XPS) analysis was conducted to determine the surface composition and valence state of the typical product [28]. As illustrated by the high-resolution Pd 3d XPS spectrum (Fig. 5A), the diffraction peaks are de-convoluted into two couples of peaks. The peak intensities of Pd^0 (340.87 and 335.54 eV) are much larger than those of Pd^{2+} species (341.12 and 335.92 eV), indicating that Pd^0 is the main species in AuPd NCNs [29,30]. Similarly, Fig. 5B displays two strong diffraction peaks at 87.21 and 83.43 eV in the high-resolution Au 4f XPS region corresponding to the $4f_{7/2}$ and $4f_{5/2}$ orbitals of metallic Au^0, conforming the efficient reduction of the Au precursor to Au^0, as powerfully demonstrated by the early relative reports [30,31]. Notably, the binding energy of Pd 3d in AuPd NCNs has a