



Superior liquid fuel oxidation electrocatalysis enabled by novel one-dimensional AuM (M = Pt, Pd) nanowires

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ABSTRACT

Active and enduring catalysts for the electrooxidation reaction of liquid fuel play a crucial role in affecting the commercial application of direct fuel cells technology. Unfortunately, the electrocatalysts used in direct fuel cells fall far from the expectations and suffer from the issues of both extremely high cost and serious activity degradation. In this work, we herein demonstrate a template free method to successfully synthesize the unique one-dimensional AuM (M = Pt, Pd) nanowires. The alloy and electronic effect between Au and Pt (or Pd), as well as the unique one-dimensional nanowire structure are of vital significance for the electrocatalytic activity enhancements of Pt₁Au₁ and Pd₁Au₁ nanowires towards ethylene glycol and glycerol oxidation with the mass activity of 7.81 and 5.72 A mg_{Pt}⁻¹, 6.55 and 4.52 A mg_{Pd}⁻¹, respectively. Our efforts highlight a split-new channel to maximize catalytic efficiency with noble metal utilization for efficient liquid fuel electrocatalysis and beyond.

1. Introduction

Preeminent energy density and perfect environmental benignity make fuel cells an ideal energy storage and conversion device [1]. And the sustainable and clean energy generated through the typical electrochemical processes, for which the reaction happened between a liquid fuel at the anode and molecular oxygen at the cathode [2,3]. However, one of the major obstructions facing the large-scale commercialization of fuel cell is the requirement of cost-efficient catalysts for the electrooxidation reaction [4]. Till now, Pt and Pd undoubtedly play the crucial roles in the ongoing commercial development of fuel cells for their extremely superior electrocatalytic activity and durability, while both the scarce natural abundance and poor anti-poisoning ability impose major limitations on its role in future electrocatalyst application [5–7]. To this end, engineering the electrocatalysts with less usage of noble metal Pt or Pd but greatly enhanced electrocatalytic activity and superior CO-tolerance has attracted increasing research notices [8,9]. Au, emerged as an interesting catalyst ligand had attracted an increasing research notice due to the fact that Au at the nanoscale could show a battery of mesmerizing features, such as its size-related electronic, optical and magnetic effect [10,11]. In addition, Au was also not prone to be poisoned by CO, therefore, it shed light on the use as a promising component of catalyst hybrids [12–15].

On the other hand, apart from the influence of compositions, the

catalytic performances of electrocatalysts are also morphology-dependent [16,17]. In general, tuning or optimizing the exposed surface active area via regulating the shape of the catalyst is deemed to be an effective approach for improving the electrocatalytic performances. In this respect, many fascinating nanostructures such as core-shell [18,19], dendrite [20], nanowire [21,22], nanocube [23] and some other nanocatalysts with unique shapes [24] have been developed. Due to the fact that the maximized utilization of noble metals and abundant active surface areas available for small organic molecules, all of these electrocatalysts with unique morphologies apparently exhibit excellent electrocatalytic performances towards liquid fuel oxidation [25,26]. Therefore, shape-controlled synthesis of multicomponent metal nanocrystals bounded with abundant exposed active surface areas is of vital significance in the design and synthesis of high-activity catalysts [27]. In view of this, another popular technique for synthesizing typical Pt or Pd-based electrocatalysts with both elevated electrocatalytic activity and durability is to construct the nanocatalysts with desirable morphology and structure [28]. Among multitudinous structures, owing to its inherent anisotropy, larger interfacial area and self-supported properties [29], one-dimensional (1D) nanowires (NWs) can not only enhance charger transfer [30] but also facilitate the binding between reactant and NWs, ultimately lead to the superior catalytic activity and durability [31].

In accordance with this guideline, if we take the advantages of both

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composition and morphology to engineer the PtAu and PdAu inter-metallic phases nanocatalysts with desirable nanostructures, it will be extremely favorable for greatly enhancing the catalytic performances of electrooxidation reaction of liquid fuel [32,33].

Herein, a template free strategy has been reported for engineering a novel class of ultrafine 1D PtAu and PdAu alloy NWs at a milder condition with the assistance of dual capping agents of polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB). Impressively, the formation of these unique 1D alloy NWs may originate from the directional coalescence of the as-produced nanoparticles. Owing to the abundant surface active areas derived from the fascinating 1D NWs structure, as well as the alloy and electronic effects between different metals, both the as-obtained 1D PtAu and PdAu NWs with optimum compositions exhibited unprecedentedly high electrocatalytic performances with the mass activities of 7.81 and 5.72 $\text{A mg}_{\text{Pt}}^{-1}$, 6.55 and 4.52 $\text{A mg}_{\text{Pd}}^{-1}$ towards ethylene glycol (EG) and glycerol oxidation, respectively. In addition, the chronoamperometry (CA) and successive cyclic voltammetry (CV) of 500 cycles have revealed that the attractive 1D PtAu and PdAu NWs possessed the extremely superior long-term stability. We confirmedly believed that this proposed plot may be significant for the fabrication and modification for future metallic catalysts and the as-prepared unique 1D NWs electrocatalysts with outstandingly excellent electrocatalytic performances can be well applied for boosting the development fuel cells.

2. Experimental section

2.1. Preparations of electrocatalysts

In a typical preparation of PtAu nanowires, appropriate amount of PVP and CTAB were added to a 50 mL beaker containing 20 mL secondary distilled (DI) water in sequences with rapid stirring. After complete dissolution, 1.32 mL H_2PtCl_6 (7.7 mM) and 0.42 mL HAuCl_4 (24.3 mM) were added dropwise to above mixture with continue stirring. Subsequently, 4 mL L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 10 mg, 99%) solution was added dropwise to above homogeneous solution serving as reducing agent. After continue reaction for 12 h, the products denoted as Pt_1Au_1 NWs were collected by centrifuging and washing with ethanol and acetone for several times. For the purpose of comparison, Pt_1Au_2 and Pt_2Au_1 were also prepared under the same conditions by tuning the amount of HAuCl_4 . Similarly, the synthesis of PdAu NWs is same as PtAu NWs, for which just substitute the addition of H_2PtCl_6 with H_2PdCl_4 while keep the other reaction conditions the same.

2.2. Physicochemical characterizations

A HITACHI HT7700 transmission electron microscope operating at an acceleration voltage of 120 kV has been employed to firstly analyze the morphology and structure features of the as-prepared products. And then the scanning transmission electron microscopy (STEM) and high-magnification transmission electron microscopy (TEM) were operated on an FEI Tecnai F20 transmission electron microscope at an accelerating voltage of 200 kV were also employed to further characterize their morphological features. The compositions and elemental valences were characterized by X-ray photoelectron spectroscopy (XPS), which was performed on a VG Scientific ESCALab 220XL electron spectrometer using 300 W Al K α radiation. The structure and crystal properties of the samples were collected on an X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K α X-ray source ($\lambda = 1.540598 \text{ \AA}$) at a step scan of 10°min^{-1} from 5° to 90° .

2.3. Electrochemical measurements

In this work, the CHI760E electrochemical workstation fabricated by Chen Hua Instrumental Co., Ltd. (Shanghai, China) was employed to complete all the electrochemical measurements. A standard three-

electrode system including a glassy carbon electrode (GCE, diameter: 3.0 mm), a platinum wire and a saturated calomel electrode (SCE), was employed to conduct the electrochemical measurements. Every time before electrochemical measurement, the GCE need to be carefully polished with alumina slurry on a polishing cloth and then sonicated in ethanol bath for 10 min. For the typical preparation of PtAu (or PdAu) modified electrode, 10 μL of catalyst inks were attached to the surface of pre-polished GCE and dried in the oven at 333.15 K. Therefore, the theoretical mass of Pt loading on the surface of each electrode is 1.95 μg (or 1.06 μg for Pd). Additionally, we also employed the ICP-AES to analyze the content of Pt (or Pd), the results are in agreement with theoretical calculated value. Additionally, we have also added 3 μL of nafion (0.05%) to cover on the surface of catalysts power for further avoiding the dissolution of the catalysts ink. All the CV were operated at the potential range from -0.8 to 0.4 V at a scanning rate of 50 mV/s in both 1 M KOH + 1 M EG and 1 M KOH + 1 M glycerol solutions. Additionally, the CA curves and successive CVs of 500 cycles have also conducted for investigating its long-term durability.

3. Results and discussion

3.1. Characterizations of PtAu and PdAu NWs

As described as above, the designs of AuM (M = Pt, Pd) were conducted at the ambient temperature with the assistance of PVP and CTAB. The morphological features were initially investigated through TEM. The representative TEM images with different magnifications in Fig.1A–C, featuring with an interconnected network structure of Pt_1Au_1 NW bundles [34]. The diameter distribution of this unique 1D NWs in Fig.1D displayed an extremely tiny average diameter of approximately $13.80 \pm 1.75 \text{ nm}$. Similarly, the PdAu nanostructures prepared via the same method also exhibited the apparent structure features with 1D NWs structure in Fig.2A–C, indicating the formation of fascinating 1D PdAu NWs. In addition, the diameter distribution of these PdAu NWs in Fig.2D also showed the narrow size distribution of $14.16 \pm 1.95 \text{ nm}$, which is close to that of PtAu. Impressively, different from some NWs prepared via template method, both the as-prepared PtAu and PdAu NWs in this work were found to be more flexible and willowy, which may benefit for the exposure of more surface active areas [35,36].

For making a detailed morphology comparison of these AuM NWs with different atomic ratios, the representative TEM images of Pt_1Au_2 , Pt_2Au_1 , Pd_1Au_2 and Pd_2Au_1 with different magnifications have also been conducted. As is demonstrated in Fig.S1 and Fig.S2, the another two types of as-obtained PtAu and PdAu nanoparticles with different atomic ratios showed the typical nanowire-like structure as Pt_1Au_1 and Pd_1Au_1 , both of which exhibited porous interconnected structures, further indicating that this approach can be well applied for synthesizing porous 1D PtAu and PdAu NWs with high yield regardless of the change of compositions [37,38].

To the best of our knowledge, both CTAB and PVP are efficient capping agents, which can guide the formation of 1D NWs [30,39]. In this regard, we have made a deep investigation on the effect of molar ratio of CTAB: PVP on the morphology of both PdAu and PtAu nanoparticles. Fig.S3 showed the TEM images of the Pt_1Au_1 prepared by adjusting the CTAB: PVP molar ratios with the other conditions kept unchanged. When only CTAB was used as the surfactant without PVP, the resulting samples contains multi-morphological nanoparticles (Fig. S3A), and some particles have PtAu alloy structures with abundant flower-like structure. However, when PVP was also introduced as another surfactant, the morphologies of as-prepared samples completely changed. When the amount of PVP gradually increases to 2:1 (Fig. S3B), formed extremely few nanowires accompanied by some irregular nanoparticles. As the molar ratio extended to 1:1, the products are mainly composed of nanowires (Fig. S3C). While continually increasing the amount of PVP to 1:2 (Fig. S3D) does not have a positive role in the growth of high-quality NWs and the mixture of nanoparticles and short

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