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One-pot synthesis of platinum–palladium–cobalt alloyed nanoflowers with enhanced electrocatalytic activity for ethylene glycol oxidation

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ABSTRACT

In this work, three-dimensional trimetallic Pt–Pd–Co alloyed nanoflowers are fabricated by a facile one-pot solvothermal strategy, with the assistance of oleylamine as the solvent, surfactant, and reducing agents, along with cetylpyridinium chloride (CPC) as the co-surfactant and shape-directing agents. Their morphology and crystal structure were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning transmission electron microscope (STEM), and X-ray photoelectron spectra (XPS) in details. The respective electrochemically active surface area (ECSA) is estimated to be 32.53 $m^2 g^{-1}$, and current density is 132.91 mA cm^{-2} for the electrooxidation of ethylene glycol (EG). These values are much higher than those of PtPdCo nanoparticles, PtPd nanoparticles, commercial Pt black, and Pd black under the identical conditions, showing the improved catalytic activity of Pt–Pd–Co nanoflowers. The excellent performances are attributed to the specific structure and synergistic interactions of the trimetallic alloy. The as-prepared nanoflowers can serve as a promising electrocatalyst in fuel cells.

1. Introduction

Ethylene glycol (EG) is considered as the most viable alternative to methanol for direct alcohol fuel cells, owing to its low toxicity, high boiling point, high energy density, commercial availability, and low cost [1–4]. For EG oxidation in fuel cells, platinum (Pt) displays enhanced electrocatalytic performance because of its unique reactivity and stability [5,6]. However, Pt has the very high price and is easily poisoned by carbon monoxide (CO) [7].

In the last few decades, many efforts have been focused on overcoming the disadvantages such as the synthesis of Pt-based alloyed catalysts to reduce the cost, and improve the catalytic activity and stability. For example, Pt–Pd and Pt–Au nanocatalysts exhibited higher catalytic activity and better methanol tolerance properties than those of single Pt, owing to their synergistic effects [8–11]. Recently, ternary Pt-based catalysts have been prepared to further improve the catalytic activity and stability, especially alloying with Pd and other transition metals (e.g., Fe, Co, Ni and Cr) [12,13]. Tri-metallic Pt-based catalysts possess improved catalytic activity and better stability [14–16] in contrast to mono- and bi-metallic counterparts, which is mostly attributed to the electronic effects between the metals. According to the density function theory (DFT), the addition of Co or other transition metals induce the down-shift of d-band energy center (ε_d) of Pt, leading to the weaker interactions with adsorbates [17–19].

Oleylamine (OAm) is used not only as a solvent for many organic and inorganic compounds, but also as a surfactant and even a mild reducing agent in the previous work [20,21]. As a result, OAm is extensively used for the fabrication of versatile nanostructures such as spheres [22], flowers [23], polypod-like [24], triangular [25], and nanowires [26]. Park and co-workers synthesized CoO nanocrystals with hexagonal structures with the assistance of OAm [27]. Petridis et al. prepared three-dimensional ferromagnetic CoPt nanopolypods by thermolytic reduction of platinum(II) acetylacetonate ($Pt(acac)_2$) and $Co(CH_3COO)_2$ in OAm at high temperature [24].

Previous studies show that the shape, size, composition, and structure of alloyed nanomaterials are also essential to their catalytic properties [28,29]. Therefore, their size-, shape-, and structure-controlled synthesis are the prerequisite to improve the associated physical and chemical properties [30], especially for porous structures in fuel cells. This is attributed to their enlarged surface area to volume ratios, low density, and more active sites available for absorbed molecules [10,31].

Herein, well-defined Pt–Pd–Co alloyed nanoflowers were prepared by a facile one-pot solvothermal approach at relatively low temperature, without any post heat treatment in reducing gas atmosphere. In the synthesis, OAm is used as the “triple roles” of

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solvent, surfactant, and reducing agents, along with cetylpyridinium chloride (CPC) as the co-surfactant and shape-directing agents. The electrocatalytic performance of the ternary nanoflowers was investigated in some detail, using EG oxidation reaction as a model system.

2. Experimental section

2.1. Chemicals and materials

Oleylamine (OAm, 80%～90%), cetylpyridinium chloride (CPC, 99%), palladium (II) acetylacetonate ($Pd(acac)_2$), platinum(II) acetylacetonate ($Pt(acac)_2$), cobalt (II) acetylacetonate ($Co(acac)_2$), commercial Pt black and Pd black, as well as ethylene glycol were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). All the other chemicals were of analytical grade and used without further purification. All the aqueous solutions were prepared with twice-distilled water in the whole experiments.

2.2. Preparation of Pt–Pd–Co nanoflowers

For typical synthesis of Pt–Pd–Co nanoflowers, 0.1 g CPC was dispersed in 20 mL OAm and ultrasonicated for at least 30 min. Then, $Pd(acac)_2$ (0.0152 g), $Pt(acac)_2$ (0.0197 g), and $Co(acac)_2$ (0.0178 g) were dissolved into the mixture under gentle agitation. After another 30 min of ultrasonication, the mixture was transferred into a 25 mL Teflon-lined autoclave. The autoclave was maintained at 170 °C for 24 h, and then cooled down to room temperature in air. The resulting black precipitates were collected by centrifugation and thoroughly washed with ethanol for several times, and dried at 60 °C in vacuum for further characterization.

In control experiments, PtPdCo nanoparticles were prepared without CPC, while other conditions were kept unchanged. Besides, PtPd nanoparticles were prepared under the similar conditions, except using $Pd(acac)_2$ and $Pt(acac)_2$ as the precursors.

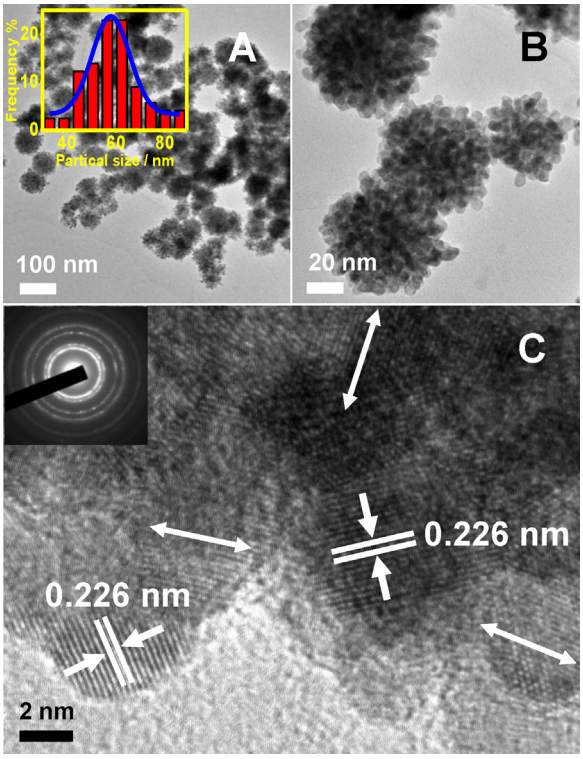

Fig. 1. TEM (A–B) and HRTEM (C) images of Pt–Pd–Co nanoflowers. Insets show the corresponding histogram of particle size distribution and SAED pattern.

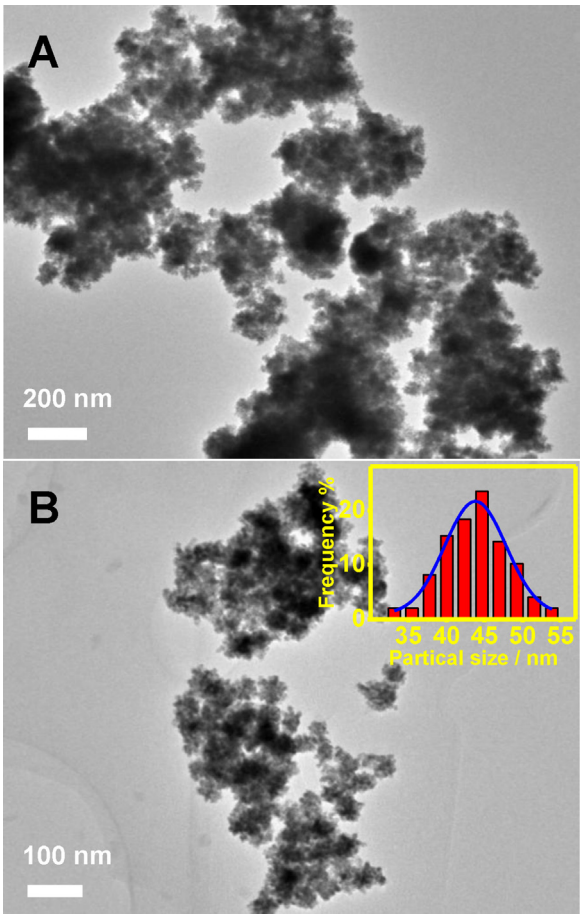

Fig. 2. TEM image of PtPdCo nanoparticles (A) and PtPd nanoparticles (B) obtained in the absence of CPC. Inset in B shows the corresponding histogram of particle size distribution.

2.3. Characterizations

The morphology and crystal structures of the samples were determined by transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) on a JEM-2100F transmission electron microscope operating at an acceleration voltage of 200 kV equipped with selective area electron diffraction (SAED) and energy dispersive X-ray spectrometer (EDS). The elemental mappings were recorded on the scanning transmission electron microscope (STEM) with a high-angle annular dark-field (HAADF) detector (HITACHI S-5500). X-ray diffraction (XRD) analysis was performed on a Philips PW3040/60 diffractometer with Cu Kα radiation source (λ = 0.15418 nm). X-ray photoelectron spectra (XPS) were acquired on a K-Alpha XPS spectrometer (SCIENTIFIC ESCALAB 250) with Al Kα X-ray radiation (1486.6 eV) for excitation.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out at room temperature on a CHI 660D electrochemical workstation (CHI Instruments, Chenhua Co., Shanghai, China) with a three-electrode cell, containing a bare or modified glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

For typical preparation of Pt–Pd–Co nanoflowers modified electrode, 2 mg of the sample was put into 2 mL water and ultrasonicated to form a dark homogeneous suspension.