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Facile synthesis of bimetallic alloyed Pt-Pd nanocubes on reduced graphene oxide with enhanced eletrocatalytic properties

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ABSTRACT

In this work, a one-pot solvothermal method was developed for large-scaled synthesis of well-defined bimetallic alloyed Pt-Pd nanocubes uniformly supported on reduced graphene oxide nanosheets (Pt-Pd nanocubes/RGOs). Herein, poly(vinylpyrrolidone) (PVP) and KI were employed as a capping agent and a structure-directing additive, respectively, and *N*, *N*-dimethylformamide (DMF) is used as a solvent and a reducing agent. The as-prepared Pt-Pd nanocubes/RGOs exhibited the enlarged electrochemically active surface area, enhanced electrocatalytic activity, and improved stability for ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR), compared with commercial Pt-C (10 wt %).

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1. Introduction

In the last decades, Pt-Pd nanostructures have been extensively investigated, owing to their unique properties and wide applications [1–5]. Their catalytic activity mainly depends on their size and morphology [6], and thereby tremendous efforts have been devoted to their size- and shape-controlled synthesis [7–9]. Among them, monodisperse Pt-Pd cubes have received increasing attention for their extraordinary crystalline structure, photoelectric property, and extensive applications [10,11]. Many methods have been developed accordingly [12,13], such as microwave method [3], hydrothermal/solvothermal process [11], and seeded growth approach [14].

Small adsorbate (e.g., halide anions, CO, and amines) assisted strategy is the most common route to prepare Pt-Pd nanocubes [15]. For example, Huang et al. fabricated cubic $Pt_{51}Pd_{49}$ nanocrystals with improved catalytic activity for hydrogenation of nitrobenzene by the control of I^- ions [16]. In another example, Yang and co-workers synthesized Pt-Pd nanocubes by the CO-assisted way [17]. Despite these demonstrations, it is still urgent to develop a facile and efficient synthetic strategy for large-scaled preparation of well-defined small Pt-Pd nonocubes with better dispersity and narrow size distribution demanded in chemistry.

Generally, sub-10 nm nanoparticles display significant enhancement in activity and selectivity, compared with their larger bulk [18]. It is efficient to use a support to immobilize these nanoparticles by controlling their particle size and reducing their dosage [19–21]. And graphene has aroused great interest recently, owing to its intrinsic material properties including large surface area, low cost, good electrical conductivity, and mechanical strength [22–24]. These characters can contribute to the enlarged electrochemically surface area and improved mass transport of a catalyst. For instance, Lu and co-workers synthesized graphene-based PtPd concave nanocubes with enhanced electrocatalytic performance for methanol oxidation [25]. Zheng et al. prepared hollow Ag@Pt core-shell nanospheres supported on reduced graphene oxide nanosheets (RGOs) with enhanced electrocatalytic activity for ethylene glycol oxidation [26].

To date, facile one-pot solvothermal method was developed for synthesis of nanomaterials because of its high purity and yield [11,27]. Herein, a benign and simple route was developed for preparation of sub-10 nm Pt-Pd nanocubes supported on RGOs (donated as Pt-Pd nanocubes/RGOs) under solvothermal conditions, using *N*, *N*-dimethylformamide (DMF) as a reducing agent, KI as the structure-directing agent and poly(vinylpyrrolidone) (PVP) as a capping agent. The electrocatalytic property of Pt-Pd nanocubes/RGOs was examined by using ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR) as model systems.

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2. Experimental section

2.1. Chemicals

Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$), palladium chloride ($PdCl_2$), PVP (MW = 58000), DMF, KI, and commercial Pt-C (10 wt %) were purchased from Shanghai Aladdin Industrial Corporation (Shanghai, China). All the other chemicals were analytical grade and used as received. All aqueous solutions were prepared with twice-distilled water throughout the whole experiments.

2.2. Apparatus

The morphology, composition, and crystal structures of the samples were characterized by transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) on a JEM-2100F transmission electron microscope coupled with an energy-dispersive X-ray spectrometer (EDS, Oxford-1NCA). TEM analysis was carried out at an accelerating voltage of 200 kV, and Cu grids were used as substrates. The crystal structures were performed by X-ray diffraction (XRD) using a Bruker-D8-AXS diffractometer system equipped with Cu Kα radiation (Bruker Co., Germany) at a scan rate of 1° min^{-1} and operating at 40 kV. X-ray photoelectron spectroscopy (XPS) on the K-Alpha XPS spectrometer (ThermoFisher, E. Grinstead, UK) using Al Kα X-ray radiation (1486.6 eV) for excitation and vacuum in the analysis chamber was kept at about 10^{-9} mbar. The binding energy was corrected by means of C 1s peak energy of 284.6 eV. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet NEXUS-670 FT-IR spectrometer in the range of 400 ~ 4000 cm^{-1}. Raman spectra were acquired on a Renishaw Raman system model 1000 spectrometer equipped with a CCD detector. Thermogravimetric analysis (TGA) was performed under a flow of air on a NETZSCH STA 449 C analyzer. The samples were heated from 25 to 800 °C with a heat rate of 10 °C min^{-1}.

2.3. Preparation of Pt-Pd nanocubes/RGOs

Typical synthesis of Pt-Pd nanocubes/RGOs was described as follows. Firstly, graphene oxide nanosheets (GOs) were prepared by the modified Hummer's method [28]. Then, the aqueous solutions of H_2PtCl_6 (2.59 mL, 38.62 mM), $H_2[PdCl_4]$ (1 mL, 100 mM), GOs (1.0 mL, 5 mg mL^{-1}), PVP (0.32 g), KI (0.17 g), and 20 mL DMF were mixed together and stirred for 1 h to obtain a homogeneous suspension at room temperature. Next, the mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave and heated at 130 °C for 5 h. Then, the autoclave was cooled to room temperature naturally. The final black precipitate was collected by centrifugation, thoroughly washed with ethanol and water to remove the residual PVP, and dried at 60 °C in a vacuum for further characterization.

Pt-Pd nanocubes with less Pt/Pd loading supported on RGOs (donated as Pt-Pd_L nanocubes/RGOs) were synthesized by using H_2PtCl_6 (0.74 mL, 38.62 mM) and $H_2[PdCl_4]$ (0.29 mL, 100 mM), while the other conditions were kept unchanged.

2.4. Electrochemical study

All electrochemical experiments were performed on a CHI 660D electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China), and conducted on a conventional three-electrode cell, including a platinum wire as the counter electrode, a saturated calomel electrode (SCE) or Ag/AgCl electrode as the reference electrode, and bare or modified glassy carbon electrode (GCE, 3 mm in diameter) or rotating disk electrode (RDE, 4 mm in diameter) as the working electrode.

For fabrication of Pt-Pd nanocubes/RGOs modified electrode, 2 mg of the sample was put into 1 mL water and dispersed by ultrasonication for 30 min to obtain a homogeneous suspension (2 mg mL^{-1}). Next, 6 and 20 μL of the suspension were homogeneously casted on the clean GCE and RDE, respectively, followed by casting another layer of Nafion (0.05 wt %) on the electrode surface to seal the sample in place and drying in air. Meanwhile, Pt-Pd_L nanocubes/RGOs/GCE and Pt-C/GCE were prepared with the similar procedure. The specific loading of each catalyst was 0.17 mg cm^{-2} on the GCE, and 0.318 mg cm^{-2} on the RDE, respectively.

To test the electrochemically active surface area (ECSA) of Pt-Pd nanocubes/RGOs/GCE, Pt-Pd_L nanocubes/RGOs/GCE and Pt-C/GCE, electrochemical CO-stripping voltammograms were recorded by oxidizing pre-adsorbed CO (CO_{ad}) in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. CO was bubbled through the electrolyte for 30 min to allow complete adsorption of CO onto the deposit. The amount of the CO_{ad} was evaluated by integrating the CO_{ad} stripping peak and correcting for the capacitance of the double electric layer.

The cyclic voltammetric experiments were performed in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. Meanwhile, cyclic voltammetric experiments were conducted to examine the catalytic activity of Pt-Pd nanocubes/RGOs/GCE, Pt-Pd_L nanocubes/RGOs/GCE, and Pt-C/GCE in 1.0 M KOH + 0.5 M ethanol at 50 mV s^{-1}. The chronoamperometric experiments were conducted at an applied potential of –0.2 V in 1.0 M KOH + 0.5 M ethanol. The stability measurement was further carried out by cyclic voltammetry at 50 mV s^{-1}. To test the catalytic properties of Pt-Pd nanocubes/RGOs/RDE, Pt-Pd_L nanocubes/RGOs/RDE and Pt-C/RDE toward ORR, linear sweep voltammetry measurements were conducted in O_2-saturated 0.1 M KOH at a scan rate of 5 mV s^{-1}. All experiments were performed at room temperature, if not stated otherwise.

3. Results and discussion

3.1. Characterization of Pt-Pd nanocubes/RGOs

Fig. 1 displays the representative TEM images of Pt-Pd nanocubes/RGOs at different magnifications. Low magnification TEM images (Fig. 1A, B) show a lot of nanocubes uniformly dispersed on RGOs. Furthermore, the nanocubes feature exhibits good reproducibility even decreasing the concentration of Pt and Pd precursors (Fig. S1, Supporting Information). These are ascribed to the strongly selective adsorption of I^- ions onto PtPd crystal planes triggering their preferential growth on the specific planes [16,25]. HRTEM images reveal their single-crystalline structure, with the particle size below 10 nm (Fig. 1 C, D) [29]. Moreover, the lattice spacings of the adjacent fringes are about 0.196 nm and 0.222 nm for two nanocubes (insets in Fig. 1D), which correspond to the (200) and (111) planes of face-centered cubic (fcc) Pt/Pd, respectively, as strongly confirmed by their associated fast Fourier transform (FFT) patterns (insets in Fig. 1D) [18], indicating the formation of Pt-Pd alloy.

The HAADF-STEM-EDS mapping and EDS line scanning profiles of Pt-Pd nanocubes were performed to determine the composition distribution in Pt-Pd nanocubes. Obviously, Pt and Pd are homogeneously dispersed across a whole nanocube (Fig. 2B-D), further confirming the formation of Pt-Pd alloy [30]. Besides, their EDS line scanning profiles indicate that the atomic ratio of Pt to Pd is around 54:46. This value is close to the theoretical composition of 1:1, as also verified by the corresponding EDS pattern (Fig. 3A). These observations mean the formation of Pt-Pd alloy [31].

The XRD pattern of Pt-Pd nanocubes/RGOs was measured to investigate the crystal structure (Fig. 3B). The representative diffraction peaks at 40.1°, 46.8°, 68.0°, and 81.8° are well indexed to the (111), (200), (220), and (311) planes, revealing the face centered

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