



Preparation of a highly active palladium nanoparticle/polyoxometalate/reduced graphene oxide nanocomposite by a simple photoreduction method and its application to the electrooxidation of ethylene glycol and glycerol



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ABSTRACT

A one-pot phosphotungstic-acid-assisted photoreduction approach was used to fabricate reduced graphene oxide decorated with Pd nanoparticles, with the phosphotungstic acid acting as both photocatalyst and stabilizer. The resulting nanocomposites were tested, and the electrochemical results showed that their electrocatalytic activity towards the electrooxidation of ethylene glycol and glycerol could be tailored by varying the composition of the material. As a result of the increased surface area of the reduced graphene oxide and the catalytic properties of the Pd nanomaterial and phosphotungstic acid, the prepared nanocomposite exhibited better catalytic activity towards the electrooxidation of ethylene glycol and glycerol in alkaline media than commercial Pd/C catalysts.

1. Introduction

Graphene has attracted huge interest in many fields due to its large surface area, unique transparency, high electrical conductivity and great mechanical strength. All these properties make graphene a promising support for nanocatalysts [1,2]. In parallel, Pd nanomaterials have been developed to improve the catalytic activity of anode catalysts because Pd is more abundant than Pt and also has excellent electrocatalytic properties [3]. Increasing attention has therefore been paid to the development of Pd–graphene nanocomposites. Over recent years, many chemical methods have been used to synthesize graphene-supported Pd nanocatalysts, which involve many additional reducing agents [4–6]. Extensive use of reducing agents not only requires complicated procedures, but may also cause environmental pollution. Compared with conventional chemical reduction processes, photochemical reduction provides a facile, environmentally friendly route to the preparation of novel metal nanomaterials and graphene in aqueous solution [7]. However, the strong interactions between the nanoparticles may result in aggregation if no stabilizer is present. Various stabilizers have therefore been developed in order to keep the nanoparticles suspended in solution [8]. In recent years, polyoxometalates (POMs), a special type of metal–oxygen cluster, have been shown to be able to stabilize graphene or metal nanoparticles (NPs) in aqueous

solution [9–11]. In terms of photochemical reduction, POMs can also be used as photocatalysts in the fabrication of graphene or metal NPs owing to their excellent redox properties and the fact that their structure remains unchanged after a multi-electron redox process [12,13]. Furthermore, Keggin-structured POMs also show activity as anode electrocatalysts which could be used to help improve the activity of an individual metal [14]. However, to the best of our knowledge, the preparation of a hybrid material containing Pd and reduced graphene oxide (RGO) by photoreduction with the assistance of POMs has never been reported. The resulting material has excellent activity towards the electrooxidation of ethylene glycol or glycerol in alkaline electrolyte.

In this work, Pd and RGO are simultaneously obtained by a simple and eco-friendly method involving a UV-irradiation process with the assistance of phosphotungstic acid. Phosphotungstic acid, a typical Keggin-type structure with a molecular formula of $H_3PW_{12}O_{40}$ (abbreviated as HPW), serves as both photocatalyst and stabilizer. No organic templates or surfactants are employed during the whole photoreduction process, which avoids the introduction of toxic organic molecules. The resulting nanocomposite is characterized and applied to a glassy carbon electrode (GCE) to investigate its electrocatalytic activity towards ethylene glycol and glycerol in alkaline media.

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2. Experimental section

2.1. Chemicals

All chemicals were of analytical grade and used as received without purification. Ultrapure water with resistivity no less than 18.2 M Ω cm was used throughout the experiments.

2.2. Preparation of Pd/HPW/RGO nanocomposite

Graphene oxide (GO) was prepared from natural graphite powder by acid oxidation using a modified Hummers' method [15].

In a typical photoreduction experiment, 1.5 mL of aqueous GO solution (0.2 mg mL⁻¹) was first mixed with a 1.5 mL mixture of HPW (5 mM) and isopropanol (5 mM), and then 40 μ L of H₂PdCl₄ (56.4 mM) with a mass ratio of GO to Pd of 5:4 was added, followed by ultrasonication at room temperature. Finally, the mixture was allowed to react under UV irradiation for 30 min (UV intensity per unit area is measured to be ca. 109 mW cm⁻²). The reaction product was collected by centrifugation and denoted Pd/HPW/RGO-4. A range of nanocomposites was prepared by changing the mass ratio of GO to Pd to 5:1, 5:3, 5:5 or 5:7, designated Pd/HPW/RGO-1, Pd/HPW/RGO-3, Pd/HPW/RGO-5 or Pd/HPW/RGO-7, respectively. The final compositions of the products were identified by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.3. Characterization

The morphology, structure and elemental composition of the prepared nanomaterials were investigated by transmission electron microscopy (TEM, JEOL JEM-2200FS), energy-dispersive X-ray spectrometry (EDX, JEOL JSM-7610F), TEM/EDX (Tecnai G2 S-Twin F20, FEI), X-ray diffraction (XRD, D/max 2550 V/PC), X-ray photoelectron spectroscopy (XPS, ESCALAB-MKII), and ICP-AES (OPTIMA 3300DV). All electrochemical measurements were carried out using an electrochemical workstation (CHI 660E) in a conventional three-electrode configuration, with a platinum wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and the modified GCE (3 mm in diameter) as working electrode. The working electrode was prepared by casting and drying the as-fabricated catalyst ink on the pre-polished GCE, followed by pipetting and drying with 10 μ L of 0.5 wt% Nafion. An aqueous solution of potassium hydroxide (0.5 M) was used as the supporting electrolyte. Cyclic voltammetry (CV) and chronoamperometric experiments were performed in 0.5 M KOH aqueous solution containing 0.5 M ethylene glycol or glycerol at room temperature. The catalytic activity was normalized by the mass of Pd for all CV curves.

3. Results and discussion

A typical TEM image of the prepared Pd/HPW/RGO-4 nanocomposite is shown in Fig. 1A. Roughly spherical NPs are found to be evenly dispersed on the surface of the prepared nanocomposite, indicating the successful fabrication of metal NPs on RGO with the assistance of HPW. The EDX results support this assumption, as peaks corresponding to C, O, P, Pd and W can be observed on Pd/HPW/RGO-4 (Fig. 1B). We further randomly chose one area to examine by elemental mapping (Fig. 1C–E). W is evenly dispersed on the support, while Pd is mainly observed in the areas corresponding to the bright dots in the TEM image shown in Fig. 1C, confirming the good spatial distribution of the hybrid. The other nanocomposites produced with different GO:Pd ratios showed similar morphology and structure when studied by TEM (data not shown). The TEM results demonstrate the successful combination of Pd, HPW and RGO, which should probably be ascribed to the adsorption of HPW on RGO and the NPs as a stabilizer. The presence of the Pd component is further shown by HRTEM. The well-resolved

lattice fringe of the Pd (111) lattice plane (0.219 nm) can be clearly seen in Fig. 1F, further indicating the successful fabrication of Pd NPs.

XRD was also utilized to determine the chemical composition of the nanocomposite. Fig. 2A depicts the XRD patterns of (a) GO and (b) Pd/HPW/RGO-4. For GO, a characteristic diffraction peak at 10.87 $^\circ$ corresponding to the C (001) plane can be observed. For the Pd/HPW/RGO-4 hybrid, diffraction peaks located at 40.12 $^\circ$, 46.66 $^\circ$, 68.12 $^\circ$, 82.10 $^\circ$ and 86.62 $^\circ$ are associated with the (111), (200), (220), (311) and (222) planes of the face-centered cubic (fcc) Pd structure (JCPDS No. 46-1043), demonstrating the existence of metallic Pd. Furthermore, after the photoreduction process, a characteristic peak for RGO can be observed at 26.61 $^\circ$, while it is hard to see the diffraction peak for GO, suggesting the reduction of GO to RGO after the UV irradiation treatment. XPS was used to evaluate the surface states and further verify the composition of the as-prepared Pd/HPW/RGO-4 nanocomposite. The Pd 3d region of the XPS spectrum shown in Fig. 2B illustrates the co-existence of Pd⁰ and Pd²⁺ species on the sample surface. The binding energy peaks at 335.7 eV and 341.0 eV are indexed to 3d_{5/2} and 3d_{3/2} of Pd⁰ [16], while the peaks appearing at binding energies of 338.4 eV and 343.6 eV are ascribed to Pd²⁺ [17], suggesting that part of the elemental Pd is oxidized to Pd²⁺ on the surface of the Pd/HPW/RGO-4 nanocomposite. In addition, peaks at binding energies of 35.8 eV and 38.2 eV in the W 4f region of the XPS spectrum are ascribed to the spin-orbit split states of W 4f_{7/2} and 4f_{5/2}, respectively (Fig. 2C). Furthermore, four fitting peaks at 284.8 eV (C=C), 286.0 eV (C–O), 287.0 eV (C=O) and 288.5 eV (O–C=O) can be observed in the deconvoluted C 1s XPS spectrum (Fig. 2D). When compared with the C 1s XPS data of GO [13], the intensity ratio of the peaks representing C=C to oxygen-containing functional groups like C–O, C=O and O–C=O is significantly increased. The increase in the C to O ratio from 2.4 for GO to 4.6 for RGO also suggests that GO can be effectively reduced to RGO by the proposed photoreduction approach. The XPS results coupled with the XRD data strongly support the view that Pd/HPW/RGO-4 has been successfully produced using the proposed fabrication method.

Direct alcohol fuel cells have been widely studied in recent decades, and increasing interest is currently focused on using ethylene glycol or glycerol as an alternative fuel, since these chemicals can be produced by renewable, pollution-free and inexpensive methods [18–21]. We therefore applied the as-prepared nanocomposite onto the GCE surface to examine its electrocatalytic performance. In KOH solution, the Pd/HPW/RGO-4 hybrid shows the largest active area among the nanocomposites studied, which is calculated to be 34.5 cm² cm⁻² of geometric electrode area according to previous literature [22]. The catalytic activity of GCEs modified with nanocomposites of different compositions towards the electrooxidation of ethylene glycol in alkaline electrolyte was then examined using CV (see Fig. 3A). Two obvious oxidation peaks can be seen on all CV curves, which are typical of the oxidation of ethylene glycol during the forward and reverse scans [22]. The specific activity of the Pd/HPW/RGO-4 is the largest among the investigated nanocomposites. Moreover, the Pd/HPW/RGO-4 nanocomposite shows enhanced specific activity towards ethylene glycol compared with the commercial catalyst (inset in Fig. 3A), highlighting the possibly significant role played by HPW. As displayed in Fig. 3B, the maximum specific current on Pd/HPW/RGO-4 (415.3 mA mg⁻¹ Pd) is ca. 1.8, 1.3, 2.2, and 3.4 times the corresponding value for Pd/HPW/RGO-1 (237.0 mA mg⁻¹ Pd), Pd/HPW/RGO-3 (310.2 mA mg⁻¹ Pd), Pd/HPW/RGO-5 (186.0 mA mg⁻¹ Pd) and Pd/HPW/RGO-7 (121.1 mA mg⁻¹ Pd), respectively. The activity normalized by the active area on Pd/HPW/RGO-4 (2.1 mA cm⁻²) is also the largest found among the investigated materials. In addition, the catalytic activity per unit total catalyst mass for Pd/HPW/RGO-4 is as high as 136.4 mA mg⁻¹ total Pd, which is better than the results obtained with previously reported Pd-related catalysts [23,24]. Furthermore, chronoamperometric experiments on the Pd/HPW/RGO-4 hybrid showed good stability and catalytic activity towards ethylene glycol electrooxidation after a long-term test (data not shown). Overall, the Pd/

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