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Facile synthesis of PtAu nanoparticles supported on polydopamine reduced and modified graphene oxide as a highly active catalyst for methanol oxidation

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ABSTRACT

In this paper, a facile strategy for the synthesis of PtAu nanoparticles (NPs) with different Pt/Au ratios supported on polydopamine reduced and modified graphene oxide (PtAu/PDA-RGO) is reported. The as-prepared PtAu/PDA-RGO composites were extensively analyzed by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), Raman spectroscopy, energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. It is found that PDA plays an important role in enhancing the dispersion and stability of the catalyst. Moreover, the bimetallic PtAu/PDA-RGO catalysts exhibits higher catalytic activity than the monometallic Pt/PDA-RGO toward methanol oxidation reaction (MOR), with the best performance found for the Pt/Au molar ratio of 3/1. The PtAu(3:1)/PDA-RGO catalyst also shows better catalytic activity for MOR than PtAu(3:1)/RGO and PtAu(3:1)/C catalysts, suggesting that PDA-RGO can be a promising catalyst support for fuel cells. These findings also indicate that the molar ratios of Pt/Au and the catalyst support are the two critical factors to affect the overall performance of the catalyst.

1. Introduction

In recent years, direct methanol fuel cells (DMFCs) as sustainable energy sources have attracted a great deal of interest thanks to their high energy-conversion efficiency, high power density, and environmental benignity in an attempt to relieve the energy and climate crisis [1–4]. Platinum (Pt) is currently the most extensively used catalyst for methanol oxidation because of its unique electrocatalytic activity [5,6]. However, its high cost and low CO poisoning tolerance severely impede the commercialization of DMFCs [7–9]. Hence, there is an urgent need to exploit relatively inexpensive and highly active catalysts for methanol oxidation.

One direction to achieve these goals is to fabricate Pt-based catalysts, by alloying it with transition elements such as Ru, Au, Ni, Pd, Cu and other non-precious metal oxides to decrease Pt loading [10–15]. In these cases, the enhanced electrocatalytic activity and poison tolerance are usually interpreted by bifunctional mechanism or electronic effect [16,17]. The other important direction to enhance the catalytic activity and reduce the amount of catalyst is to develop a suitable supporting material to more effectively disperse the catalyst NPs [18,19]. With unique properties, such as high conductivity (10^3 to 10^4 S m^{-1}), extremely high specific surface area (theoretical value of 2630 m^2 g^{-1}) and superior thermal/chemical stability, graphene has generated a tremendous amount of research interest in recent years [20–23]. These exceptional properties make graphene an attractive support for metal NPs. Up to now, many methods have been developed for the preparation of high-quality graphene, among which the chemical reduction of graphene oxide (GO), such as using reducing agents like hydrazine hydrate and hydroquinone is regarded as an effective approach for the large scale production of RGO [24,25]. However, these reducing agents are highly toxic and even more the excessive reducing agents existed in the system will contaminate the resultant product [26]. Besides, the chemical reduction of GO usually suffers from serious aggregation, or even restack into graphite through van der Waals interactions, which greatly hinders the effective dispersion of the metal NPs depositing onto the RGO surface [27,28]. Therefore, searching for an effective and green

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approach for the reduction of GO in large quantity as well as to improve the stability and dispersity of RGO is highly desirable, which still remains a great challenge.

Recently, Lee et al. [29] have found that PDA, a mimic of the specialized adhesive foot protein Mefp-5 (Mytilus edulis foot protein-5), could be prepared through self-polymerization of dopamine at weak alkaline pH, which is easy to coat on various substrates. Liu et al. [30] have reported that PDA coatings contain abundant positively charged sites because of the nitrogen-containing groups in the structure of PDA, which enables PDA to absorb on the surface of carbon materials through π–π interaction and electrostatic interaction, forming electrostatic repulsion between carbon materials and thus preventing them from aggregating in aqueous solution. Inspired by this, herein, we utilize PDA to disperse graphene, aiming to improving the solubility and/or dispersibility of the graphene. Notably, as the dopamine self-polymerized in the GO suspension, the color of the suspension gradually changes from yellow brown to black, which indicates the GO is simultaneously reduced. The obtained PDA-coated RGO composite is then employed as a matrix for dispersion of PtAu NPs. Several benefits involved in this work are inspiring: (i) GO could be reduced and modified simultaneously by PDA without using reducing agents; (ii) the as-prepared PDA-RGO can form a stable suspension for several months in the absence of any stabilizers and thus re-stacking of the RGO sheets is effectively inhibited; (iii) PDA plays an important role in improving the electrocatalytic activity and stability of the catalyst; and (iv) the PtAu/PDA-RGO composite exhibits high electrocatalytic activity and stability toward MOR.

2. Experimental

2.1. Materials

Graphite powder (Sinopharm Chemicals Reagent Co., Ltd, China) was used as received. $H_2PtCl_6{\bullet}6H_2O$, $HAuCl_4$ and $NaBH_4$ were purchased from Shanghai Chemical Reagent Co. Ltd (Shanghai, China) and used as received without further purification. $NaNO_3$, $KMnO_4$, H_2O_2 (30%), CH_3OH, CH_3CH_2OH, KOH and H_2SO_4 (95%) were all of analytical grade purity. Dopamine hydrochloride (98%) was purchased from Alfa Aesar. Tris(hydroxymethyl) aminomethane hydrochloride (Tris-HCl, 99%), which is used as a buffer agent, was purchased from Sigma–Aldrich. Secondary distilled water was used throughout the whole experiments.

2.2. Preparation of GO

The GO used in this work was synthesized from graphite powder by a modified Hummer's method as described in our previous publications [31,32]. Briefly, 1.0 g graphite powder and 0.5 g $NaNO_3$ were added into 24 mL concentrated H_2SO_4 solution with stirring in an ice bath. Then, 3.0 g $KMnO_4$ was slowly added into the solution under vigorous stirring for 30 min at 20 °C, and then the mixture was stirred for another 30 min at 35 °C. After that, 46 mL of secondary distilled water was added into the above mixture and the temperature was increased to 98 °C and further stirred for 15 min. Finally, 140 mL secondary distilled water and 10 mL 30% H_2O_2 solution was added to terminate the reaction. The obtained GO was filtered and washed repeatedly with 5% HCl until removal of the SO_4^{2-} ions. The purified GO was dried and stored in a desiccator prior to use.

2.3. Preparation of PtAu/PDA-RGO

Firstly, 60 mg of as-prepared GO was dispersed in 80 mL of doubly distilled water with ultrasonication for 2 h to form a homogeneous GO suspension. Then, 40 mg of dopamine hydrochloride was added into the GO suspension, followed by ultrasonication for 30 min to ensure the dopamine hydrochloride was uniformly dispersed in the GO suspension. Subsequently, 40 mL of 12.5 mM Tris-HCl solution (pH = 8.5) was added, and the reaction mixture was stirred at 80 °C for 24 h, where the color of the mixture gradually changed from yellow brown to black. The mixture was then washed with double distilled water for several times to remove unreacted dopamine. Thereafter, 1100 μl H_2PtCl_6 (7.5×10^{-3} mol L^{-1}) and 113 μl $HAuCl_4$ (2.43×10^{-2} mol L^{-1}) with the molar ratio of the Pt and Au precursors was 3:1 was added into 10 ml of the as-prepared black suspension under stirring. Then, a freshly made $NaBH_4$ aqueous solution (0.03 g, 5.0 mL) was slowly added to the mixture with vigorous stirring for 2 h to completely reduce the metal precursors. The products were collected by centrifugation and washed several times with distilled water to remove residual salts and then redispersed in 10 ml distilled water ultrasonically to obtain a uniform catalyst ink. Similarly, PtAu(4:1)/PDA-RGO, PtAu(3:1)/RGO, PtAu(2:1)/PDA-RGO, PtAu(1:1)/PDA-RGO, Pt/PDA-RGO and PtAu(3:1)/C, catalysts were also prepared in the same way.

2.4. Characterization

The morphology and structure of the products were examined by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements on a Tecnai G220 electron microscope operating at an accelerating voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was obtained with an EDAX detector installed on a HITACHI S-3000 N scanning electron microscope operated at 15.0 kV. X-ray diffraction (XRD) patterns of the as-prepared samples were taken using a PANalytical X'Pert-Pro MRD system with Cu Kα radiation (k = 1.54056 Å) operated at 40 kV and 30 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα X-ray radiation as the X-ray source for excitation. The Raman spectra were recorded on a Renishaw inVia plus Raman microscope using a 633 nm argon ion laser.

2.5. Electrochemical measurements

All electrochemical experiments were performed on a CHI 660B electrochemical workstation (Shanghai Chenhua Instrumental Co., Ltd. China) at room temperature. A conventional three-electrode system was used with Pt wire and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. The working electrode was prepared by pipetting a total of 30 μl of catalyst ink onto the surface of a polished glassy carbon electrode (GC, 3 mm in diameter) and dried in air. All solutions were deaerated by a dry nitrogen stream and maintained with a slight overpressure of nitrogen during the entire experiment. All electrochemical experiments were carried out at room temperature.

3. Results and discussion

Fig. 1A shows the digital photos of GO (left) and PDA-RGO (right). It can be seen from Fig. 1A that the as-prepared GO can disperse well in water with the aid of sonication to form a stable yellow brown suspension for several months. As the dopamine self-polymerized in the GO suspension going on, the color of the suspension gradually changed from yellow brown to black, suggesting that the GO was reduced. Meanwhile, the obtained PDA-RGO can also disperse well in water. Raman spectroscopy is a useful tool to monitor the structural changes that occur during the