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Gourd-shaped silver nanoparticle–graphene composite for electrochemical oxidation of glucose

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ABSTRACT

Graphene nanosheets decorated with gourd-shaped Ag nanoparticles (GAg) were prepared from the precursor silver phosphate–graphene oxide nanocomposite (GOAgPO) by original substrate self-generated reduction methods. The material was studied for electrochemical oxidation of glucose in alkaline solution. GAg showed excellent activity at low peak potential. The reason was that the high temperature promoted transformation of GO to graphene, thereby reducing the resistance of the substrate, restructuring from the silver phosphate to gourd-shaped silver and enhancing the interaction between Ag and the substrate. The positive correlation between the scan rates and the anodic currents implied a diffusion-controlled kinetic process even at a high scan rate.

1. Introduction

The electrochemical oxidation of glucose has generated much research interest over the years due to its possibility of medical applications such as blood sugar sensors and biological fuel cells [1–4]. The glucose oxidation process, a chemical process that provides energy for organism, is an important process, especially for humans. The level of glucose concentration is very important to the health of humans, so development of electrochemical glucose oxidation technology in medical applications is necessary besides biological fuel. The electrocatalytic activity depends on the nature of the electrode material such as gold [5–7]. To optimize the activity, gold was fabricated into nanoparticles [8] or composite with other metals [9]. However, gold or even platinum is not suitable as electrocatalysts because the chemisorbed intermediates such as CO will poison the electrode surface besides being expensive [6]. Non-noble metals, such as Co [10], Ni [11], Cu [12], are investigated for cheaper and more anti-poisoned replacements, but their overpotentials are much higher with low activity. Silver, as a relatively cheap noble metal and a highly effective electrode material for electro-oxidation of glucose, has been regarded as a prime candidate for electrode material [13–18]. Substrates always play a vital role in the dispersion and stability of the catalysts, especially metallic nanoparticles. Graphene is a huge open π-electron system with a combination of armchair and zigzag edges that are analogous to cis- and trans-polyacetylenes, respectively. Its structure and properties motivated the development of new materials for electronics, batteries, supercapacitors and so on. Its chemical stability and high surface area give a chance as substrate for metallic nanoparticles in heterogeneous catalysis applications [19,20].

Herein, a new facile and distinctive method via silver phosphate–graphene oxide nanocomposite (GOAgPO) as intermediate was developed to synthesize gourd-shaped silver nanoparticle–graphene composite (GAg) catalyst, which showed excellent activity for glucose oxidation at low peak potential with distinct oxidation current in the anodic scan.

2. Experimental

Reagents: Nafion (5 wt% ethanol solution) was purchased from Alfa Aesar, and diluted to 0.1 wt% with doubly distilled water in use. H_3PO_4 (85%), sodium hydroxide and $AgNO_3$ were obtained from Beijing Chemical Company. All stock solutions used in this work were prepared with deionized water of resistivity no less than 18.2 MΩ cm.

Synthesis of the materials: Graphene oxide was generated from natural flake graphite according to a modified Hummer's method [21]. 340 mg $AgNO_3$, 410 mL 85% H_3PO_4, 1 g sodium dodecyl sulfonate, and 12 g urea were dissolved in 180 ml deionized water. 50 mg graphene oxide was added to the solution and sonicated for 10 min. The solution was then heated for 12 h at 353 K. GOAgPO was separated by filtration and dried in an air oven at 333 K overnight. Following the same process, AgG was obtained by calcining GOAgPO in a tubular furnace under nitrogen

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atmosphere finally. The temperature rose at the rate of 10 K/min till 773 K, and then remained for 2 h.

Characterization: Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2400 diffractometer with Cu-Kα radiation. The morphologies of the materials were observed by scanning electron microscopy (SEM, XL30S-FEG, 5 kV). For TEM analysis, samples were dissolved in ethanol under ultrasonic treatment and then put a drop of the solution was placed on a Cu grid. TEM images were taken with a FEI Tecnai G2 T20.

UV–visible spectroscopy (Cary Varian 50) with a 1 cm quartz cell was used. XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono Al-Kα (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV. Raman spectroscopy was obtained using a Horiba HR800 Raman system with three laser lines and a 632.8 nm line from He–Ne laser.

Preparation of modified GCE: The glassy carbon electrodes (GCEs, 3 mm diameter, Tianjin Aida, Inc.) were polished with α-Al_2O_3 powder (40 nm), rinsed twice by deionized water and ethanol, and then dried at room temperature. 5 mg catalyst was dispersed in 1 ml of 0.1 wt% nafion solution. Then the mixture was dropped on a pre-treated GCE to fabricate a modified GCE. Finally the modified GCEs were dried under infrared light.

Electrochemical measurements: Electrochemical experiments were performed on a CHI660D electrochemical workstation (CHI, Shanghai) using a three-electrode setup at 298 K. GCE or modified GCEs acted as working electrodes. A saturated calomel electrode (SCE) was used as reference electrode, and platinum wire as the counter electrode.

1. Results and discussion

The hybrid nanomaterial GAg was developed by a two-step facile method (Fig. 1A). Firstly, the exfoliated graphene oxide was decorated with Ag_3PO_4 NPs in a hydrothermal reactor, and then the silver phosphate–graphene oxide composite materials were calcined at 773 K under N_2 atmosphere. Although there was no reducing atmosphere like hydrogen, calash-shaped Ag was obtained but not Ag_3PO_4. As shown in Fig. 1D, it was still Ag_3PO_4 obtained after only Ag_3PO_4 calcification at 773 K. In fact, the XPS

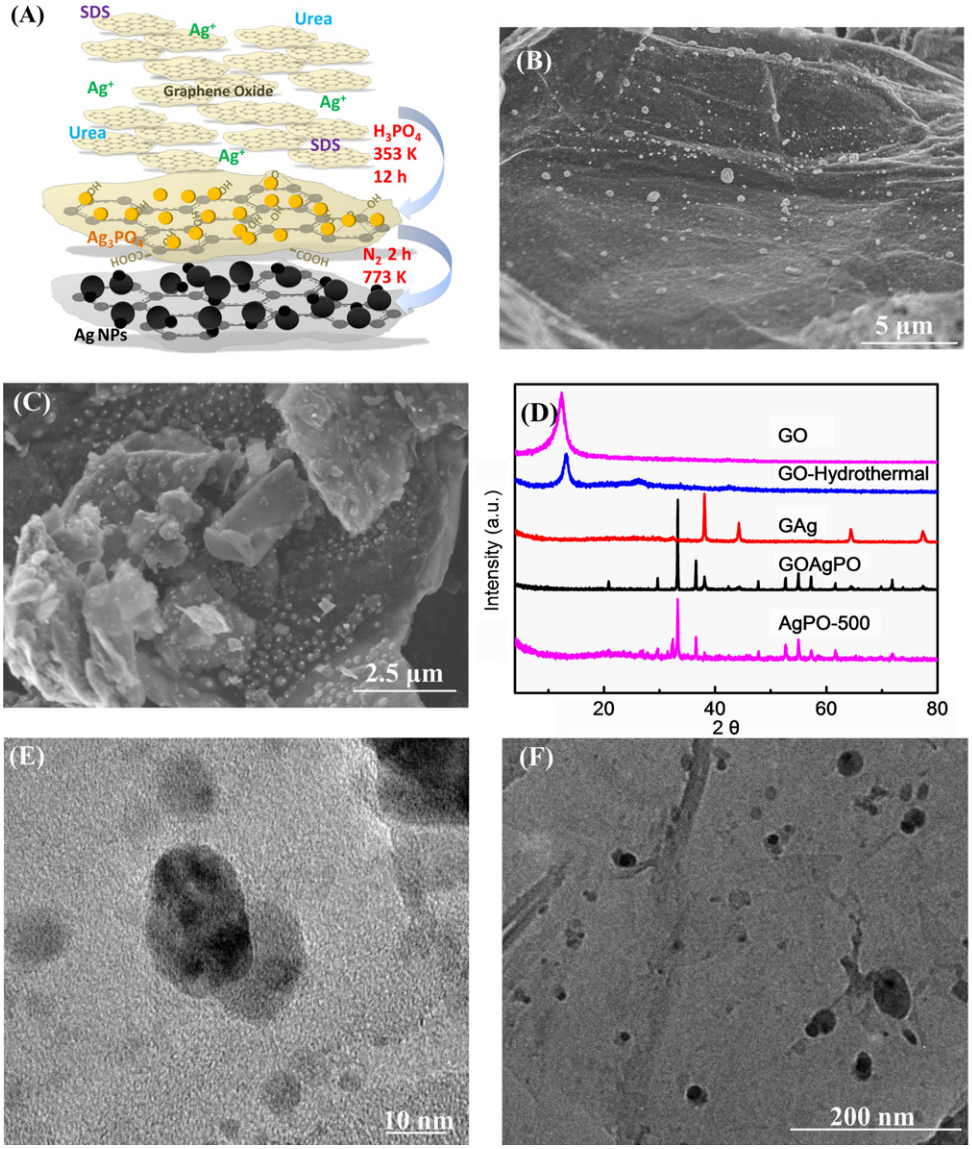

Fig. 1. Scheme of preparation of GOAgPO and GAg (A). SEM images of GOAgPO (B) and GAg (C). XRD patterns of GOAgPO, GAg, GO, GO after hydrothermal treatment (GO-Hydrothermal) and Ag_3PO_4 calcination at 773 K (AgPO-500) (D). TEM images of GOAgPO (E) and GAg (F).