Noble metal-free modified electrode of exfoliated graphitic carbon nitride/ZnO nanosheets for highly efficient hydrogen peroxide sensing

Hailin Tian, Huiqing Fan*, Jiangwei Ma, Longtao Ma, Guangzhi Dong

State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, PR China

ARTICLE INFO

ABSTRACT

Graphitic carbon nitride (g-C_3N_4)/ZnO nanosheets were coated on the surface of fluorine-doped tin oxide (FTO) glass as a noble metal-free g-C_3N_4/ZnO/FTO electrode, which was used for the determination of hydrogen peroxide (H_2O_2). The exfoliated g-C_3N_4 nanosheets were firstly prepared and then ZnO nanosheets were grown on g-C_3N_4 nanosheets by a microwave-assisted hydrothermal synthesis. The g-C_3N_4 nanosheets combined with ZnO nanosheets can greatly improve the adsorption of hydrogen peroxide and increase the conductivity of materials as well. The g-C_3N_4/ZnO nanosheets were characterized by powder X-ray diffraction (XRD), scanning electron microscopic (SEM), transmission electron microscopic (TEM), and X-ray photoelectron spectroscopy (XPS) analysis. Meanwhile, electrochemical measurements of the g-C_3N_4/ZnO/FTO electrode were utilized to investigate the amperometric sensing of hydrogen peroxide. The prepared g-C_3N_4/ZnO/FTO electrode revealed the sensitivity of 540.8 $\mu A\,mM^{-1}\,cm^{-2}$ at $-0.5\,V$ with the linear response range from 0.05 to 14.15 mM, which even was superior to some noble metal-decorated H_2O_2 sensors. Additionally, the g-C_3N_4/ZnO/FTO electrode also showed the reliable operational and environmental stability for electrochemical reduction of H_2O_2.

1. Introduction

Hydrogen peroxide (H_2O_2) is the vital intermediate in chemical and food industries and also involved in our life process. Research on the quantitative detection of H_2O_2 received considerable attention in recent decades [1–5]. Though many noble metal-based H_2O_2 sensors possess good sensitivity and limit of detection (LOD), they are environmentally instable and high cost [6–9]. Therefore, the development of noble metal-free electrodes is significant to produce the practical hydrogen peroxide sensor with high sensitivity and wide linearity range. To date, carbonaceous materials or binary heterostructures of metal oxides and carbon materials, such as NCNTs [10], g-C_3N_4 nanosheets [11], MnO_2/SWCNT-Nf [12], and RGO/ZnO [3], have been prepared for the modified electrode of noble metal-free H_2O_2 sensors. As a fascinating semiconductor material, bulk g-C_3N_4 can be prepared by the polycondensation of various precursors, such as cyanamide [13–15], melamine [16] and other s-triazine heterocyclic compounds [17]. In particular, the exfoliated g-C_3N_4 nanosheets from bulk g-C_3N_4, a material that has not been much looked at from

the perspective of 2D layered structure is in fact an excellent metal-free catalyst for various reactions [18–20]. Zinc oxide (ZnO) is a typical n-type oxide semiconductor with a band gap of 3.37 eV and has great potential applications in the determination of H_2O_2 [21–23]. To the best of our knowledge, there are no reports available for assembling g-C_3N_4 nanosheets and ZnO as the electrocatalyst of H_2O_2 sensors. Predictably, g-C_3N_4/ZnO nanosheets should be a promising electrocatalysis material of noble metal-free H_2O_2 sensors.

Designing the shape and morphology of materials is a key step to extend their applications due to the direct correlations between the morphology and chemical reactivity [24,25]. For the H_2O_2 sensing applications, fascinating ZnO nanostructures with different morphologies, as well as ZnO heterostructures, have been studied widely [3,26]. Hierarchical nanostructures with controllable morphologies not only increase surface area, but more importantly can facilitate the adsorption and mass transfer in catalysis [27–29]. Therefore, g-C_3N_4/ZnO nanosheets, as a novel ZnO-based heterostructures, may effectively improve the electrocatalytic properties for H_2O_2 and elucidate the morphology-controlled properties.

In this work, we report the preparation of g-C_3N_4/ZnO nanosheets at 120 °C for 2 h by a microwave-assisted hydrothermal

synthesis as the modified electrode of noble metal-free H_2O_2 sensors for the first time. The chemical composition and morphology of g-C_3N_4/ZnO nanosheets are characterized by XRD, SEM, TEM, and XPS analysis. The g-C_3N_4/ZnO nanosheets sensor exhibits the high sensitivity and wide linearity range towards H_2O_2, which are attributed to their large surface area and fantastic morphology.

2. Experimental section

2.1. Materials

All raw materials were analytical reagent grade and used without further purification.

2.2. Preparation of g-C_3N_4/ZnO nanosheets

The g-C_3N_4 nanosheets were exfoliated by bulk g-C_3N_4 according to the previous work in our group [30]. Briefly, 2 g melamine and 10 g lithium chloride were mixed by the vigorously mechanical stirrer. Lithium chloride was an exfoliated reagent for g-C_3N_4 nanosheets. The mixed powder was calcined at 380 °C for 2 hours in air at ramp rate 6.7 °C per minute and heated to 550 °C for 4 hours at a same ramp rate. After grinding, the yellow powder of bulk g-C_3N_4/LiCl was obtained. Then, 0.5 g bulk g-C_3N_4/LiCl powder was dispersed in 500 mL deionized water under the magnetic stirrer of 1000 rpm for 24 hours. Finally, the light yellow powder of exfoliated g-C_3N_4 nanosheets was collected from the dispersed suspension by centrifugation at 8000 rpm for 5 minutes.

Then, the exfoliated g-C_3N_4 nanosheets (243 mg) were dispersed in 30 mL deionized water to form a light yellow solution under ultrasonic bath. The weight ratio of g-C_3N_4/ZnO was 1:1, which was an important reason for the morphology of g-C_3N_4/ZnO nanosheets. And 0.1 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.4 M sodium hydroxide (NaOH) were added to the above solution. After stirring for 30 minutes at room temperature, the solution was transferred into a 100 mL Teflon-lined autoclave and maintained at 120 °C for 2 h in the microwave workstation. (MDS-10, Sineo Microwave, Shanghai, China). The obtained precipitate was separated by centrifuging and washed with deionized water and ethanol several times and then dried at 70 °C for 8 h in an oven.

2.3. Characterizations

The morphology of g-C_3N_4/ZnO nanosheets were observed by using field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan), transmission electron microscopy (TEM; Tecnai F30G, FEI, Hillsboro, OR, USA) operating at an accelerating voltage of 200 kV. And the sample was loaded by Cu grid coated with carbon for TEM measurement. The thickness of the 2D material was analyzed by atomic force microscopy (AFM; SPM-9600, Shimadzu, Tokyo, Japan) in air. AFM tip was Si_3N_4 and mica substrate was used for AFM work. The crystal structure of the as-synthesized material was analyzed by using powder X-ray diffraction (XRD; X'pert PRO MPD, Philips, Eindhoven, The Netherlands) with Cu Kα radiation (λ = 1.5406 Å) in the range of 10–80°. Surface chemical element analysis of g-C_3N_4/ZnO nanosheets was carried out by using X-ray photoelectron spectroscopy (XPS; VG ESCALA-B220i-XL, Thermo Scientific, Surrey, UK) with an Al Kα (hv = 1486.6 eV) source at a residual gas pressure below 10^{-8} Pa. Nitrogen adsorption-desorption was performed on a nitrogen adsorption apparatus at 77 K (V-Sorb 2800P, Gold APP Corp., Beijing, China), the sample was degassed at 120 °C for 2 h before measurement. Electrochemical measurements were all operated on a CHI 660E electrochemical analyzer (Chenhua Co., Shanghai, China) with a conventional three-electrode method,

using a Pt plate as the counter electrode and an Ag/AgCl electrode (saturated with KCl) as the reference electrode. The working electrode was fabricated as follows. Briefly, 50 mg of g-C_3N_4/ZnO nanosheets, 30 mg of ethyl cellulose, 20 mg of lauric acid and 350 mg terpilenol were mixed and ground in an agate mortar to form a paste. And then the paste was coated on FTO glass via a doctor blade method, using Scotch tape as the spacer. Subsequently, the coated film was dried in an infrared lamp for 5 minutes and baked at 350 °C for 1 h. The exposed area of the working electrode was 1 × 1 cm. Phosphate buffer solution (PBS, 0.2 M, pH 7.4) was used as the supporting electrolyte, and the electrolyte was stirred by the magnetic stirrer with 100 per minute when the determination of H_2O_2 was performed. The oxygen reduction occurred on the g-C_3N_4/ZnO/FTO electrode may interfere with the response of H_2O_2 reduction. In order to obtain the accurate quantitative determination of H_2O_2, high-purity nitrogen was employed to remove oxygen of the solution (Fig. S1).

3. Results and discussion

The formation process of g-C_3N_4/ZnO nanosheets is illustrated in Fig. 1(a). The exfoliated g-C_3N_4 nanosheets as the substrate can promote the growth of ZnO nanosheets. And the concentration ratio of Zn^{2+} and OH^- ions is 1:4, which is a key parameter to form the hierarchical ZnO nanosheet flowers. The detection of the H_2O_2 sensing is operated on an electrochemical analyzer with a conventional three-electrode method in Fig. 1(b). The catalytic current due to the electrochemical reduction of H_2O_2 was recorded by using cyclic voltammetry and the amperometric current-time response, when H_2O_2 molecules were adsorbed and diffused on the surface of the working electrode. Therefore, as shown in Fig. 1(c), the sensitive detection of H_2O_2 can be widely applied in many fields such as biosensing and chemical sensing applications. The phase composition of g-C_3N_4/ZnO nanosheets is characterized by XRD in Fig. 2. In the case of g-C_3N_4 nanosheets, the strong XRD peak at 27.6° is a characteristic interlayer stacking reflection of conjugated aromatic systems, indexed for graphitic materials as the (002) planes [13]. And an additional peak at 13° can be attributed to an in-planar repeat period of 0.678 nm in the crystal [14]. The hexagonal wurtzite structure of ZnO can be confirmed by the standard card (JCPDS 36-1451). In g-C_3N_4/ZnO nanosheets, all peaks can be assigned to g-C_3N_4 nanosheets and ZnO phase, respectively. And no diffraction peaks from impurities can be detected. The intensity ratio of the broad peak at 13° and (002) peak at 27.6° is decreased due to ZnO reveals the strong peaks in g-C_3N_4/ZnO nanosheets. The position of two peaks has no obvious shift in comparison of g-C_3N_4 nanosheets, indicating that the layered structure of g-C_3N_4 nanosheets is stable during the preparation of g-C_3N_4/ZnO nanosheets. As shown in Fig. 3(a), ZnO nanosheets can be recognized from the exfoliated g-C_3N_4 nanosheets according to color contrast. And the thin ZnO nanosheets are uniformly dispersed on the laminar morphology of g-C_3N_4 nanosheets. In Fig. 3(b), the morphology of g-C_3N_4/ZnO nanosheets was further observed by TEM. The thin nanosheets stack up hierarchical ZnO with flower-like nanostructures. And g-C_3N_4/ZnO nanosheets exhibit the rich inner-channels in the observation of TEM. Compared to g-C_3N_4/ZnO nanosheets, SEM and TEM images of only g-C_3N_4 nanosheets are also given in the supplementary material (Fig. S2). The exfoliated g-C_3N_4 nanosheets are transparent to electron beams, and cross-sectional atomic force microscopy (AFM) image of g-C_3N_4 nanosheets is given in Fig. 3(c). The typical AFM image and thickness analyses reveal g-C_3N_4 nanosheets have a uniform thickness of 4–5 nm, as the plane substrate material, g-C_3N_4 nanosheets are favorable to the growth of ZnO nanosheets in the process of hydrothermal synthesis.