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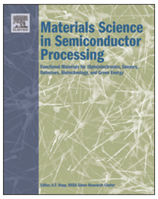

Hierarchical architecture of nanographene-coated rice-like manganese dioxide nanorods/graphene for enhanced electrocatalytic activity toward hydrogen peroxide reduction

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ABSTRACT

Rice-like MnO_x nanorods covered by nanographene (M_xNRS@NG) are prepared via a simple one-step hydrothermal route. After combination with graphene (GS) and calcination, M_xNRS are converted into MnO_2 nanorods (MNRS) and the hierarchical architecture of MNRS@NG/graphene (MNRS@NG/GS) is obtained. In this ternary architecture, GS is an excellent supporting substrate for the electrocatalysis of MNRS, and NG can provide abundant active carbon atoms of edge phase and accelerate the electron transfer between MnO_2 and GS. Electrochemical results demonstrate that the electroreduction of MNRS toward H_2O_2 is significantly enhanced by the assembly of GS and NG. The MNRS@NG/GS modified electrode exhibits excellent performance in H_2O_2 detection over the concentration range of 0.002–4.44 mM, with a high sensitivity (707.9 μA mM^{-1} cm^{-2}) and a low detection limit (0.2 μM).

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1. Introduction

As one of the most representative nanomaterials over the last decade, graphene (GS) has drawn intensive research interests in a wide range of applications such as electronics, catalysis, chemical sensing, and energy conversion/storage devices [1–6]. GS is a zero band gap semiconductor with large specific surface area, extremely high room-temperature electron mobility and quantum Hall effect. Due to these remarkable properties and low environmental impact, GS has become one of the promising candidates for constructing electrochemical sensors [7–11]. Noteworthily, the properties of GS are largely dependent on their geometric characteristics including size, shape and thickness (i.e. the number of graphene layers) of the sp^2 domains [12,13].

The lateral size of GS varies from several nanometers to micrometers, and GS fragments with size range of 1–100 nm can be called nanographene (NG) [14]. It was reported that heterogeneous electron transfer is faster at the edge phase of GS than the basal phase, and the edge structure largely contributes to the electrochemical activity [15–17]. Thus, NG, which has more edges than larger-sized GS, could deliver peculiar electronic and chemical properties due to the edge effects and quantum confinement [18–20], receiving much attention in field-effect transistors, catalysis, bioimaging and biosensing applications [20–22]. For example, in a core–shell structure of reduced nanographene oxide (r-NGOs) coated TiO_2 nanoparticles, the r-NGOs were verified to retard the charge recombination and promote electron transfer on the surface of TiO_2 nanoparticles, resulting enhanced photocatalytic activity of the hybrids [23]. Wu et al. [18] prepared hydrophilic NG as supporting material for tyrosinase biosensor, and obtained improved interface conductivity than carbon nanotube-based biosensor. These results indicate that NG could be an efficient tool to facilitate electron transfer and thus show great potential in electrochemical sensing.

Because of the hydrophobic nature, GS has poor dispersion in aqueous solution and exhibits strong tendency of irreversible agglomeration, which severely limit its application for electrode materials [24]. Once the number of GS layers exceeds 5, only the outer layers could maintain its original properties [25]. To overcome the restacking of GS, numerous 1D and 0D nanomaterials, including nanowires, nanorods and nanoparticles, have been incorporated with it. In sensor fields, the introduced materials are usually catalytic active to achieve high sensor response. Manganese oxides, especially MnO_2, are important electrocatalytic materials that have been vastly studied for the modification of sensor electrodes [26–30]. Compared with noble metals, MnO_2 is highly attractive owing to the low cost, nontoxicity and eco-friendliness.

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Mahmoudian et al. [28] reported reduced graphene oxide/MnO_2 nanotubes composite for non-enzymatic detection of H_2O_2, which can effectively prevent the aggregation of GS and harvest the good catalytic activity of MnO_2.

Here, we report the synthesis and characterization of a novel hybrid of GS and NG-coated rice-like MnO_2 nanorods (MNRS@NG/GS). With NG forming a bridge between GS and MNRS, the electron transfer on the MNRS@NG/GS modified electrode is expected to be promoted to reach high electrocatalytic activity. The modified electrode is implemented as an enzyme-free sensor for the detection of hydrogen peroxide, and shows excellent performance including high sensitivity, low detection limit, good selectivity and long-term stability.

2. Experimental

2.1. Material synthesis

All reagents used were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used in this study. Graphite oxide (GO) sol was synthesized from nature graphite flake (Alfa Aesar) by a modified Hummers' method [31]. In a typical process, graphite flake (2 g) was added to the suspension of 3 mL 98% H_2SO_4, 1 g $K_2S_2O_8$ and 1 g P_2O_5 and reacted at 80 °C for 6 h. The mixture was then diluted with distilled water and filtered, and the filtrate was rinsed and dried in vacuum to obtain pre-oxidated graphite. Next, 2 g pre-oxidated graphite was added to 46 mL 98% H_2SO_4 (containing 6 g $KMnO_4$) in an ice bath under stirring with the temperature below 20 °C. The above mixture was stirred at 35 °C for 2 h and diluted with 920 mL distilled water. After 15 min, a yellow mixture was obtained by treating with 2.8 L distilled water and 5 mL H_2O_2 solution (30 wt%), which was then filtered and washed with 1 L 10% HCl aqueous solution and 1 L deionized water. Finally, the collected precipitate was centrifuged and dispersed in 100 mL distilled water, forming a highly water-soluble GO sol (about 0.02 g mL^{-1}, GS toward sol).

The NG-coated rice-like MnO_x nanorods (M_xNRS@NG) were prepared by a hydrothermal process. 3 mL GO sol was added into 80 mL distilled water in a 250 mL round-bottom flask, and sonicated for 2 h to achieve the highly dispersed solution of graphene oxide sol. Then 0.632 g $KMnO_4$ and 0.148 g NH_4F were added into above solution under stirring. After that, the suspension was sealed in a 100 ml Teflon-lined stainless-steel autoclave and maintained at 180 °C for 48 h. The precipitate was collected by centrifugation followed by washing and drying, and a brown powder (M_xNRS@NG) was yielded. To figure out the role of GO in the formation of M_xNRS@NG, a contrast sample was also prepared using the same hydrothermal conditions without the addition of GO sol, and the product was named MnO_x nanowires (M_xNWS).

To prepare MNRS@NG/GS modified glassy carbon electrode, the as-obtained M_xNRS@NG was dissolved into distilled water (80 mL), and then GO sol (10 ml) was added with ultrasonic treatment for 2 h. The suspension was reduced by hydrazine, and centrifuged, washed several times with distilled water. After a thermal treatment at 600 °C under the atmosphere of nitrogen for 2 h, the products of MNRS@NG/GS were obtained. As a contrast, M_xNRS@NG is heated at 600 °C in the surrounding environment to prepare MNRS, and MNRS/GS was synthesized from MNRS by the same route as MNRS@NG/GS.

2.2. Material characterizations

The morphologies of the as-prepared samples were observed by scanning electron microscope (SEM) (Hitachi S-4800, Japan) and transmission electron microscope (TEM) (JEOL-2100F, Japan) at 200 KV. Elemental analysis was characterized by an energy-dispersive spectroscopy (EDS) in SEM. X-ray diffraction (XRD) was used to confirm the crystal structures of the samples at a Bruker D8 Advanced X-ray diffractometer (Germany).

2.3. Electrochemical measurements

The as-prepared materials were dispersed in distilled water and bath sonicated for 2 h to obtain a homogeneous slurry (1 mg mL^{-1}). Subsequently, 50 μL of slurry was dropped onto the pretreated glassy carbon electrode (GCE, $d=5$ mm) [32,33] and dried in air. At last, the modified GCE was cast with 10 μL Nafion solution (0.5 wt% in ethanol, Sigma-Aldrich) and air-dried. The electrode is named MNRS@NG/GS/GCE.

The electrochemical measurements were performed on a CHI660B electrochemical workstation (CHI, China). A conventional three-electrode system was adopted, with modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the counter electrode. The electrolyte was 0.1 M NaOH solution which had been purged with nitrogen for at least 30 min.

3. Results and discussion

3.1. Morphology and structure analysis

Fig. 1a, b and c displays the SEM and TEM images of M_xNRS@NG. It can be seen from Fig. 1a that a mass of rice-like nanorods are produced after the hydrothermal treatment. As further revealed by TEM in Fig. 1b, these rice-like nanorods exhibit the aspect ratio between 2 and 5, with the range of 80–200 nm in length and 20–50 nm in diameter. Moreover, there are some small transparent fragments located at the periphery of M_xNRS, indicating that the product contains not only MnO_x but also GS. To confirm the presence of GS, a magnified TEM image is presented in Fig. 1c showing the microstructure of the sample. It is obvious that GS fragments with average size of ~30 nm cover on the surface of MnO_x nanorods, which are regarded as NG. Thus, NG-coated MnO_x nanorods (M_xNRS@NG) are fabricated in this study. Fig. 1d displays the SEM image of the material produced by the hydrothermal reaction without GO sol. Instead of nanorods, numerous MnO_x nanowires (M_xNWS) were produced through the decomposition of $KMnO_4$, suggesting that GO sol is the critical factor to control the morphology and size of M_xNRS. The possible mechanism of the formation of M_xNRS@NG is explained as follows: In hydrothermal environment, GO sol can react with $KMnO_4$ to produce MnO_x. The abundant oxygen functional groups at the edges and on the plane of GO can provide nucleation sites for the redox deposition of MnO_x [34]. With the growth of M_xNRS, GO is etched into fragments of nanosized GO (~30 nm), which spontaneously cover onto M_xNRS to form a heterostructure. After then, the nanosized GO is reduced [35] and M_xNRS@NG are ultimately synthesized.

After thermal treatment at 600 °C under the protection of nitrogen, M_xNRS@NG is transformed into MNRS@NG, and MNRS can be prepared by the same route without nitrogen. Fig. 2a displays the SEM image of MNRS@NG, which retain the same shape and morphology as M_xNRS@NG. As seen from the TEM image in insert of Fig. 2a, NG still covers on the nanorods, indicating that calcination in nitrogen does not cause any change in the morphology of M_xNRS@NG. Similarly, MNRS also exhibit rice-like morphology (Fig. 2b). The EDS image in Fig. 2c illustrates that except manganese and oxygen, MNRS@NG contain 10.1 wt% of carbon, which testifies the presence of NG. However, Fig. 2d shows that the carbon content in MNRS is only 0.56 wt%, because most of NG can

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