Preparation of Three-Dimensional Graphene/Bimetallic PtPd Nanoparticle Hybrid and Its Electrocatalysts Application for H$_2$O$_2$

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Abstract—a hybrid material of three-dimensional graphene sheets beaded with bimetallic PtPd nanoparticle was prepared by using a simple process. The three-dimensional graphene/PtPd hybrids exhibited an interconnected microporous framework with PtPd NPs dispersed and encapsulated within the graphene sheet layers. In addition, the three-dimensional graphene/PtPd hybrids show a highly sensitive response to H$_2$O$_2$ reduction and oxidation.

Keywords-Graphene; Dimensional; microporous; Sensitivity;

I.   INTRODUCTION

Graphene (GE) is a flat monolayer of sp^2 carbon atoms tightly packed into a two- dimensional (2-D) honeycomb lattice, which has attracted a great deal of attention due to its remarkable electronic and structural properties. [1] Recently, a lot of efforts have been devoted to the design and controlled fabrication of composites or hybrid materials which integrate graphene oxide (GO) or reduced GO with polymers, nanoparticles, or even nanotubes and fullerenes. [2] With this in mind, GE based nano-hybrid materials are used as a new nanomaterial with different device applications, such as sensor,[3] fuel cell,[4] photocatalysis, [5] supercapacitor devices, [6] lithium-ion batteries, [7] organic photovoltaic (PV) devices, [8] biophysics area [9] etc.

The hybrids of GE with metallic nanomaterials might produced new properties via cooperative interaction btween GE and metal nanoparticles, and promote electron transfer on the metal catalyst. However, the π-π interaction of GE causes the aggregation and stacking emergence, which decreases the electrolyte diffusion, damages the specific surface area and the catalyst performance. [10] Due to the three-dimensional (3D) GE has ideally interconnected porous structure for catalyst loading, this meens 3D GE based nanohybrids might overcome obstacle of aggregation and stacking, and facilitate the mass transfer and maximize the accessibility for reactants to the active catalyst surfaces.This makes them promisingfor the future development of sensors, fuel cells, supercapacitors and lithium-ion batteries. [11] For example, Dong et al. [10] have reported the preparation of a 3D Co$_3$O$_4$/GE electrode using a simple hydrothermal procedure combined with chemical vapor deposition, and found its high electrocatalytic activity for glucose detection. Yuan et al. [11] prepared 3D GE/ PdCu nanoparticles hyrids, which be used in glucose sensor, by a facile one-step hydrothermal strategy.

Hydrogen peroxide (H$_2$O$_2$) is a major reactive oxygen species (ROS) involved in various diseases such as cardiovascular disorders, cancer, and Alzheimer's disease. [12] H$_2$O$_2$ estimation by electrochemical approach is an alternative for biosensors. Platinum is a well-known catalytic material for H$_2$O$_2$ (Hall et al., 1998). However, at the bare macro Pt electrode, the peroxide of oxidation potential is high overpotential, this many electroactive substances, e.g., ascorbic acid (AA), and uric acid (UA), which are usually present in real samples, may be oxidized to give interfering signals. [13] Many efforts have been devoted to improve the analytic performance of Pt sensors for H$_2$O$_2$ detection. The facile access is to fabricate novel Pt based-bimetallic nanomaterials with high catalysis activity. since the addition of the second metal brings about vitally strategic variations in particle size, shape, surface-morphology, composition, chemical and physical properties including the catalytic activity and chemical selectivity of the material as compared to the separate components. [14] Here we describe the preparation and characterization of PtPd bimetallic nanoparticles-decorated 3D GE for electrocatalysts application of H$_2$O$_2$.

II. EXPERIMENTAL

All chemicals and standard solution were purchased from Acros. The starting materials used in the experiments were natural graphite (99 wt. % purity, Oingdao Yingshida Graphite Co. Ltd), NaNO3 (Tianjin Guangfu Chemicals Co., Ltd), H_2SO_4 (98 wt. %, analytical reagent = A. R., Beijing Beihua Chemicals Co., Ltd), H_2O_2 (30 wt. %, A. R., Beijing Beihua Chemicals Co., Ltd), HCl (37 wt. %, A. R., Beijin Beihua Chemicals Co., Ltd), $H_2PtCl_6 \cdot 6H_2O$ (99 .99 wt. %, A. R., Beijing Beihua Chemicals Co., Ltd), $PdCl_2$ (99.99 wt. %, A. R., Beijing Beihua Chemicals Co., Ltd).

A. Synthesis of graphene oxide

GO was prepared using a modified Hummers method from graphite powders. [2] $NaNO_3$ (1.5 g) was mixed with concentrated sulfuric acid (67.5 ml) at room temperature. Then natural graphite (2.0 g) was added to the solution while stirring, this mixture was cooled to 0 ^{o}C in an ice bath, followed by slow addition of 9.0 g $KMnO_4$, and the reaction mixture was allowed to stand for five days at room temperature with stirring. On completion of the reaction, 100 mL of 5 wt. % H_2SO_4 aqueous solution was added to the mixture over about 1 h with stirring for 2h. Then 6 mL of H_2O_2 (30 wt% aqueous solution) was added to the above liquid and the mixture was stirred for 2 h at room temperature. Finally, the resulting suspension was filtered, washed with a mixed aqueous solution of 3 wt. % H_2SO_4/0.5 wt. % H_2O_2 and water, and dried at room temperature for 24 h to obtain GO sheets.

B. Preparation of 3D GE/PtPd nanoparticle hybrids

The following is the typical preparation procedures of 3D GE/PtPd hydrids. 12 mL GO aqueous dispersion (1.5 mg•mL^{-1}) was loaded in a 20 mL glass vial. Then, a certain amount of H_2PtCl_6 and $PdCl_2$ were added. After sonication for 10 min, 100 mg of ascorbic acid was added to glass vial, a homogeneous yellow-brown dispersion was obtained. Successively, the as-prepared dispersion was heated at 90 ^{o}C for 2h to produce the 3D GE/PtPd hydrids. The excess ascorbic acid was further removed by dialysis.

C. Electrochemical investigation

We used a 15 ml of the glass electrochemical cell containing three electrodes: a glassy carbon disk working electrode (3 mm diameter) embedded in Teflon, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Before use, the glassy carbon electrodes were polished with 0.3 μm alumina slurry, washed with the deionized water, then immersed for 2 min in a sonicator bath, and finally washed with the deionized water.

To modify the glassy carbon electrode (GC, 3 mm in diameter) with 3D GE/PtPd hybrids, 4.0 mg of this sample were dispersed in 400 μl deionized water to form a homogenouscatalysts ink by sonication, and then a 2 μl of the catalysts ink was mixed with a 1μL of 0.5% Nafion®117 ethanol solution. The mixture was spread and air-dried on the electrode at room temperature. After water evaporated, a three-electrode setup was configured with CHI 920C inter-faced to a personal computer at room temperature for the electrochemical characterization. The electrolytic solution was bubbled with nitrogen for 20 min before the electrochemical experiment. H_2O_2 redox was investigated by cyclic voltammetry in 0.2 M phosphate buffer solution (PBS, pH 7.4) containing different concentrations of H_2O_2. The modified glassy carbon electrode was scanned from −0.4 V to +0.8 V at the scan rate of 50 mV s−1.

III. RESULTS AND DISCUSSION

A 1.5 mg mL^{-1} GO dispersion containing Pt^{4+}, Pd^{2+}, and ascorbic acid is stable and no precipitation was observed (the inset in Figure 1a, right). After 2 h of chemical reduction at 90 ^{o}C, a columniform of 3D GE/PtPd hybrids was obtained (the inset in Figure 1a, left). According to previous report, the formation of the macroscopic gel is attributed to the regional overlapping and coalescing of flexible reduced GO nanosheets through π-π interactions. Field emission scanning electron microscopy (FE-SEM) was used to determine the microstructure of the 3D GE/PtPd hybrids. The FE-SEM images (Figure 1) show that the hybrids exhibit an interconnected, porous 3D framework with the PtPd nanoparticles uniformly dispersed on both sides of the GE sheets, even encapsulated within the GE layers. The pore sizes of 3D GE are in the range of several micrometers to tens of micrometers. This might be attributed to the residual oxygen functionalities or oxygen defects on GE sheets which make the assembly between the NPs and the GE sheets more efficient. [11]
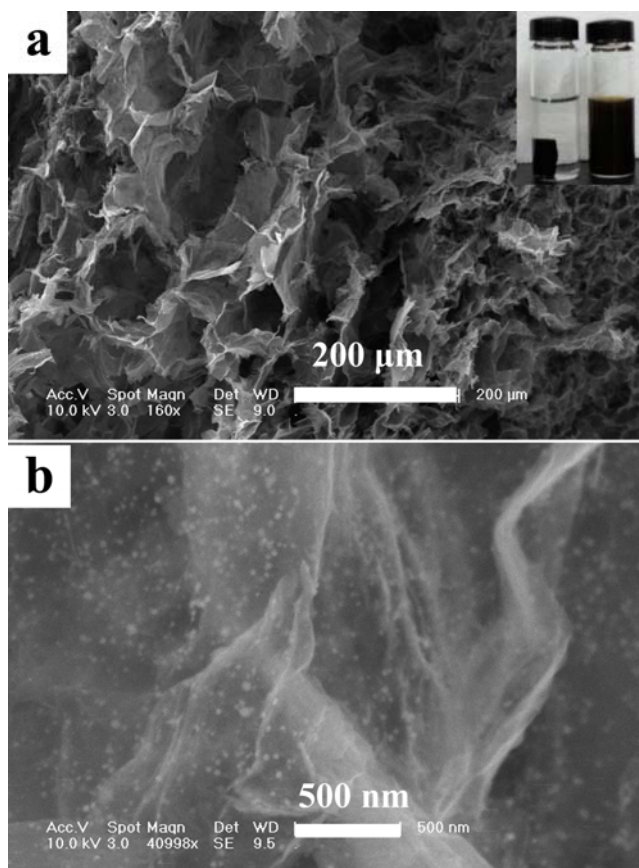
Figure 1 SEM images of the 3D GE/PtPd hybrids having two different magnifications, in which the inset (a) is the photographs of an aqueous mixture of GO (1.5 mg·mL^{-1}), H$_2$PtCl$_6$, PdCl$_2$ and ascorbic acid before (right) and after (left) chemical reduction at 90 ℃ for 2 h.

The electrochemical catalysis toward H$_2$O$_2$ was also investigated by cyclic voltammetry. Figure 2 shows cyclic The voltammetric features of the modified electrodes were similar to bulk Pt electrodes. As shown Figure 2, Platinum hydroxide (Pt-OH) and oxide (Pt-O) formed in voltammograms of the glassy carbon electrode (3D GE/PtPd /GCE) in 0.2 M N2-saturated PBS solution without (black) and (red) with 1.5 mM H$_2$O$_2$. The 3D GE/PtPd /GCE exhibit a good catalytic activity for H$_2$O$_2$. The 0.55V range, the Pt-O was reduced at 0.38 V. Moreover, two pairs of H$_2$O$_2$ oxidation /reduction peaks in the potential range of -0.25 to -0.2 V were clearly discerned in curves Ⅱ, This observation is a clear evidence of electrocatalysis of 3D GE/PtPd, proving that the detection of H$_2$O$_2$ was favored on oxidized PtPd surfaces.
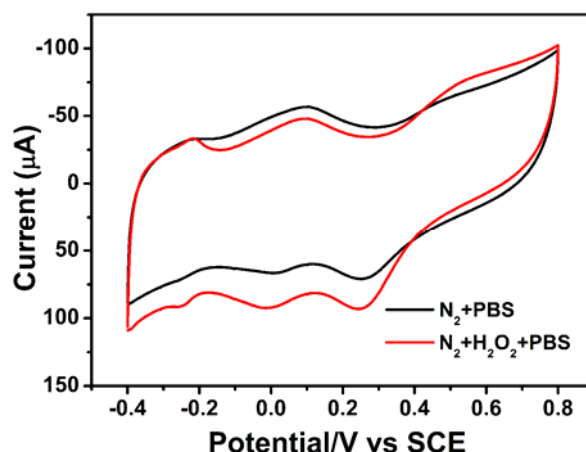

Figure 2. Cyclic voltammograms of the 3D GE/PtPd hybrids in 0.2 M N$_2$- saturated PBS (pH 7.4) solution without (black,) and (red line) with 1.5 mM H$_2$O$_2$.

Figure 3A shows the cyclic voltammograms of the 3D GE/PtPd hybrids modified electrode in various concentrations of H$_2$O$_2$. It was found that the peak current
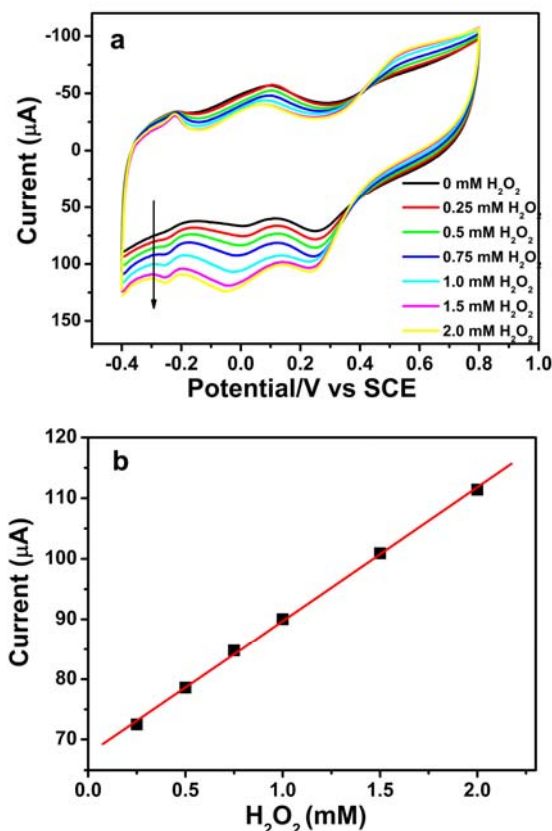

Figure 3. (A) Cyclic voltammetric measurements at the 3D GE/PtPd hybrids /GCE 0.2 M N$_2$ saturated PBS (pH 7.4) solution containing various concentrations of H$_2$O$_2$: 0, 0.25, 0.5, 0.75, 1.0, 1.5, 2.0 mM from up to down. (B) The calibration curve of H$_2$O$_2$ concentration on the modified electrode.

increased with the sequential addition of H$_2$O$_2$, indicating a stable relationship between the reduction current and the H$_2$O$_2$ concentration. As shown of Fig. 3B, a linear response to H$_2$O$_2$ ranging from 0.25 to 2.0mM (R = 0.993) and high sensitivity of 219.6 μA mM^{-1} cm^{-2} could be

observed. In addition, the 3D GE/PtPd hybrids -modified electrode also has good reproducibility.

IV. CONCLUSIONS

We have prepared a 3D microporous GE/PtPd hybrids by a one-step chamecle reduced method. The bimetallic PtPd nanoparticles were excellently dispersed and encapsulated on the 3D framework of GE sheets with high surface area and adequate oxygen functionalities. Moreover, the as-prepared the 3D GE/PtPd hybrids modified electrode exhibits very strong and sensitive responses to H_2O_2.

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