



Short communication

A comparison of nitrogen-doped sonoelectrochemical and chemical graphene nanosheets as hydrogen peroxide sensors

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ABSTRACT

Nitrogen-doped graphene nanosheet (N-SEGN) with pyrrolic nitrogen and 5–9 vacancy defects has been successfully prepared from a hydrothermal reaction of tetra-2-pyridinylpyrazine and sonoelectrochemistry-exfoliated graphene nanosheet, with point defects. Additionally, based on the same reaction using chemically reduced graphene oxide, nitrogen-doped chemically reduced graphene oxide (N-rGO) with graphitic nitrogen was prepared. The N-SEGN and N-rGO were used as a non-enzymatic H₂O₂ sensors. The sensitivity of the N-SEGN was 231.3 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$, much greater than 57.3 $\mu\text{A}\cdot\text{mM}^{-1}\cdot\text{cm}^{-2}$ of N-rGO. The N-SEGN showed their potential for being a H₂O₂ sensor.

1. Introduction

Nitrogen-modified carbon nanomaterials are of increasing importance in electrocatalysis [1] and electrochemical sensors [2]. These catalysts contain nitrogen incorporated into the edge or core structure of carbon materials. Nitrogen primarily exists as pyrrolic and pyridinic N sites located at the edge, while graphitic N directly replaces sp²-bonded C atoms in the core structure of N-doped carbon nanomaterials [3]. The pyrrolic or pyridinic N atom bonded to two C atoms can donate electrons to an aromatic π structure. In the graphitic N case, the N atom bonds with three C atoms. The dependence of N-bonding types on N-containing carbon catalyst activity has recently been demonstrated [4]. The N-doped carbon nanoparticle-embedded carbon nanofibers with predominantly pyrrolic N have higher activity for the hydrogen peroxide reduction reaction (HPRR) [5]. Compared with graphitic N, the active sites for catalyzing the oxygen reduction reaction are carbon atoms with Lewis basicity next to a pyridinic N [1]. The relative order of pyridinic N > pyrrolic N > graphitic N regarding catalytic activity in the oxygen reduction reaction has been demonstrated both experimentally and theoretically [4]. However, the typical synthesis method used to dope N into a carbon structure often results in a mixture of nitrogen species.

Hydrogen peroxide sensing involves a rapidly growing set of methods and techniques with applications in diverse fields such as food additives [6], clinical applications [7], and environmental analyses [8]. Due to the intrinsic activity of enzymatic biosensors, non-enzymatic electrochemical sensors composed of Pt [9] and Au nanomaterials [10] have been recently developed. However, these noble metal catalysts are

expensive, which restricts their commercialization as sensors.

We previously reported a sonoelectrochemical method to prepare graphene nanosheets (SEGN) with more physical defects compared to chemically reduced graphene oxide (rGO) [11]. A graphite working electrode was rapidly intercalated by sodium n-dodecyl sulfate (SDS), and the SEGNs with physical defects were then exfoliated by the combined application of ultrasonic power and fixed potentials. We compared SEGN and rGO as a carbon source for N-doping by tetra-2-pyridinylpyrazine (TPPZ) in a hydrothermal reaction. Nitrogen-doped SEGN (N-SEGN) and nitrogen-doped rGO (N-rGO) were applied as catalysts for HPRR and as non-enzymatic sensors of H₂O₂.

2. Experimental

SEGN was prepared by a modified sonoelectrochemical method from the reported preparation [11] with 20 mL of a 0.1 M SDS aqueous solution as the electrolyte under ultrasonic radiation and an applied potential of 2.9776 V. The power and frequency of the ultrasonic oscillator (Elma, P60H) was 240 W and 37 kHz, respectively. A three-electrode cell consisting of a graphite plate (1 cm × 1 cm × 0.3 cm) working electrode, a Pt counter electrode (1 cm × 1 cm × 0.05 cm), and an Ag/AgCl (3 M KCl) reference electrode was used. The three electrodes were connected to a potentiostat (627C, CH Instrument). The working and counter electrodes were fixed in place using a Teflon spacer with a spacing of approximately 0.5 cm. After 6 h, solutions containing dispersed powders of SEGN were obtained. The rGO was prepared by chemical reduction of graphene oxide powders from Hummers' method [12] as described previously [11]. SEGN and rGO

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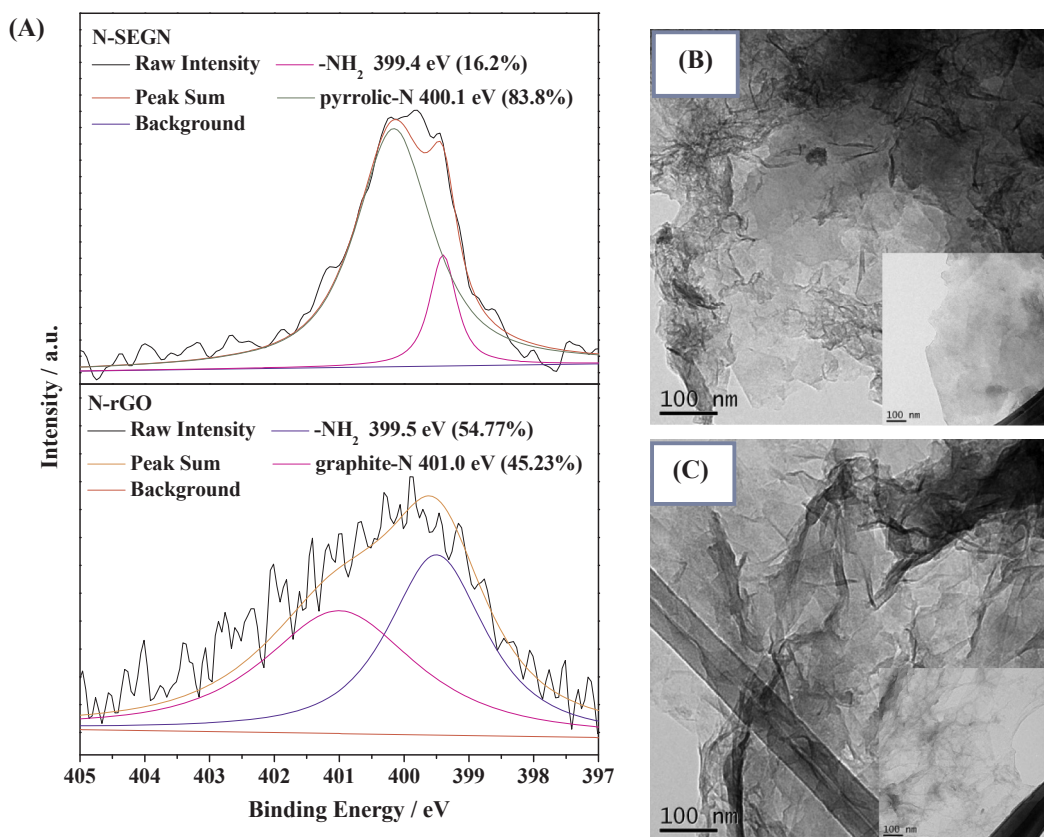


Fig. 1. N 1s XPS spectra (A) and TEM images (B–C) of N-SEGN and N-rGO. The insets of Fig. 1B and C are TEM images of SEGN and rGO, respectively.

were purified as described in the [supplementary material](#).

N-SEGN and N-rGO were synthesized in a hydrothermal reactor. Initially, 10 mg of SEGN powder was added to 10 mL ethanol solution. 10 mg TPPZ was dissolved in a solution of ethanol (1.5 mL), deionized water (1.5 mL), and pure HCl (0.1 mL). Then, the SEGN solution and TPPZ solution were mixed and stirred for 6 h before transfer to a 25 mL Teflon container in an autoclave at 180 °C. After 3 h, a solution containing N-SEGN powder was obtained. The N-SEGN solution was precipitated at 6225 xg and redispersed with ethanol to remove impurities. Purification was repeated, and the obtained powder was precipitated and dried in an oven at 60 °C. N-rGO was prepared by the same method.

The morphology of the SEGN and rGO before and after N-doping was examined by transmission electron microscopy (TEM, JEOL JEM-2100). The defects of N-SEGN as compared with SEGN were observed using spherical-aberration corrected field TEM (80 kV, JEOL JEM-ARM200FTH). X-ray photoelectron spectroscopy (XPS, VersaProbe PHI 5000) was used to characterize the N species in N-SEGN and N-rGO.

The catalytic activity of N-SEGN was compared to that of N-rGO in HPRRs by electrochemical measurements using a catalyst-coated glassy carbon electrode (GCE, 0.07 cm²) and a computer-controlled potentiostat. A catalyst solution containing 1 mg carbon catalyst, 0.8 mL isopropanol, 0.2 mL deionized water, and 5 μ L Nafion (5 wt%) was prepared. The solution was sequentially drop-casted onto the GCE surface and dried to obtain a homogeneous layer in an oven at 60 °C. The loading weight of carbon catalysts was 14 μ g. Measurements were performed in a N₂-saturated 0.01 M phosphate buffered saline (PBS) solution (100 mL, pH = 7.4), with or without 5 mM H₂O₂. A three-electrode cell with the catalyst-covered working, Pt foil counter electrode, and an Ag/AgCl (3 M KCl) reference electrode was used. The sensitivity and interference studies were performed by transient HPRR experiments with a continuously applied potential of -0.4 V (vs. Ag/AgCl) to electrochemically sense H₂O₂. In the interference study, 2 mM

H₂O₂, 0.4 mM ascorbic acid (AA), 0.4 mM uric acid (UA), and 2 mM H₂O₂ was added at 40, 80, 120, and 160 s after triggering the measurement, respectively. Real sample analysis was conducted with varying concentrations of H₂O₂ solutions mixed with milk (1 mL) and added to PBS solution (5 mL, 0.01 M) at a fixed potential of -0.4 V.

3. Results and discussion

XPS was employed to identify the doped-nitrogen sites on N-SEGN and N-rGO after N-doping hydrothermal reactions. The N content in N-SEGN and N-rGO was 2.6% and 3.7%, respectively, from the elemental analyses data obtained by XPS. Interestingly, the type of N-functionalized carbon structures was dependent on the carbon nanomaterials that were chosen for nitrogen doping. Fig. 1A reveals high-resolution narrow scans from the N region of XPS spectra for N-SEGN and N-rGO, which were fit to a mixed Lorentzian-Gaussian function. The large peak in the N-SEGN spectrum was observed at the binding energy (BE) = 400.1 eV and assigned to pyrrolic N [2]. One small peak at 399.4 eV was consistent with an amine bonded at the N-SEGN edge [13]. Most of N sites in the N-SEGN were pyrrolic N with a relative content of 83.8%. However, the N 1s XPS (Fig. 1A) of N-rGO showed the nearly equal presence of amine and graphitic N recorded at BE = 401 eV.

Fig. 1B and C and their insets show TEM images of SEGN and rGO after and before nitrogen doping, respectively. Many folds dominated by C-OH, C=O, and O-C=O groups were observed on the N-rGO (Fig. 1C) compared to the rGO (inset) as identified and confirmed from the C 1s spectrum of XPS in our previous publication [11]. The folds may originate from the compact packing of N-rGO by π - π stacking [14] and covalent bonds due to dehydration of hydroxyl and carboxyl groups under hydrothermal reaction conditions [15]. Compared to SEGN shown in the inset of Fig. 1B, the wrinkles on the N-SEGN (Fig. 1B) prepared by the sonoelectrochemical method formed 3-D-like

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