Covalently bonded reduced graphene oxide/polyaniline composite for electrochemical sensors and capacitors

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A B S T R A C T

Polyaniline grafted reduced graphene oxide (RGO-g-PANI) composites were synthesized via a facile and efficient two-step method. RGO was first surface-modified with 1,3-diaminopropane, which provided reactive NH_2 groups that can polymerize with aniline, and then grafted with polymer chains. The analysis results showed that the surface of the RGO sheets was covered with a smooth thin layer of polyaniline. The as-prepared composites were used to modify the glass carbon electrodes for the chemical detection of hydrogen peroxide in aqueous solutions. The response to H_2O_2 was linear in the range, 0.05 to 14 μM ($R^2 = 0.995$), and the detection limit was 0.37 μM (at an S/N of 3). In addition, the specific capacitance of the obtained composite was as high as 1337 F g^{-1} at a very high current density of 15 A g^{-1}, highlighting its promising applications as an efficient electrode material for supercapacitors.

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1. Introduction

Polyaniline (PANI) has attracted increasing attention for applications in both academia and industry because of its facile synthesis, high environmental stability, and simple acid/base doping/dedoping chemistry, thermal and electrochemical stability, interesting electronic, optical and electro-optical properties [1–5]. Many composites based on PANI have been developed for potential applications, such as anti-corrosive coatings, energy storage and conversion systems, gas sensors, and electrocatalytic devices [6–12]. Moreover, among the conducting polymers, PANI is recognized as the only conducting polymer that is stable in air [13]. For sensor applications, PANI acts as an effective mediator for electron transfer in redox or enzymatic reactions and it can also be used as a suitable matrix for the immobilization of biomolecules [14]. PANI is a sensitive material at around room temperature and is an attractive developmental prospect.

Owing to its conductance, the extent of surface adsorption, large specific surface area, and low Johnson noise [14,15], graphene is considered a promising candidate for the detection of a variety of molecules, such as gases to biomolecules [16–20]. Furthermore, charge transfer between the adsorbed molecules and graphene sheets has been proposed as a cause of the chemical response. It is reported that the molecules adhere on the surface of the graphene sheets, where was experienced charge transfer with graphene as a donor or acceptor, resulting changing the Fermi level, carrier density and electrical resistance of graphene.

To date, many approaches have been used to prepare graphene-based composites, particularly, graphene oxide/PANI or graphene/PANI composites, which exhibit a range of functional properties for many applications, such as batteries, supercapacitors, catalysts, solar cells, and electrochemical sensors [21–26]. Graphene nanosheets when compounded with PANI can enhance not only the electrical conductivity, but also the mechanical strength of the resulting composites. For sensor applications, there have been several studies on the use graphene oxide/PANI composites as an electrocatalyst. Fan et al. [27] prepared a graphene/PANI nanocomposite for the determination of 4-aminophenol (4-AP). This sensor exhibited high performance for the detection of 4-AP with a low detection limit and high sensitivity. Bao et al. [28] reported that graphene oxide/PANI composites exhibit preferable electroactivity even in neutral media and display excellent electrocatalytic activity in the simultaneous determination of ascorbic acid, dopamine and uric acid. In previous studies, GO/PANI and GO/poly(o-phenylenediamine) composites were developed for the determination of H_2O_2 [29,30]. However, most of graphene-based composites, as described above, were prepared via a noncovalent mixing/adsorption route. The preparation of composites with a homogeneous dispersion of individual graphene sheets within the smooth thin polymer layer is often difficult using these methods, resulting in a decrease in the electrocatalytic activity of the resulting composite. Therefore, new methodologies are needed to prepare hybrids with enhanced properties through the synergistic effects between the two components.

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Very recently, covalently-grafted PANI on GO or reduced graphene oxide (RGO) was synthesized by various methods [31–34]. The obtained composites showed high electrical conductivity and high stability, which were necessary for their application as electrode materials for supercapacitors or sensors. However, most of the covalent connections in those composites were based on the functional groups of GO, which could not form a π-conjugated molecular linkages and resulted to limit the overall conductivity of the composite [31]. Therefore, to enhance the overall performance of covalently RGO/PANI composites, the synergistic effect between PANI and RGO is still needed.

In this paper, RGO-g-PANI was synthesized via facile and efficient two-step method. The as-prepared composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmitted electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and ultraviolet–visible spectroscopy (UV–Vis). The RGO-g-PANI composites were used as an electrocatalyst and an active material for the chemical detection of hydrogen peroxide in aqueous solutions and the modified electrode of a supercapacitor, respectively.

2. Experimental

2.1. Materials

Graphite powder (99.995%, Alfa Aesar), was used as received. Aniline (99%, Aldrich) was distilled under reduced pressure prior to use. The other reagents were of analytical grade and used without further purification.

2.2. Synthesis of GO–NH$_2$

Graphene oxide (GO) was synthesized from graphite powder using a modified Hummers method [29]. In typical synthesis of GO–NH$_2$, 0.5 g GO was added to 100 mL anhydrous dimethylformamide, and sonicated for 1 h. Subsequently, N-Hydroxysuccinimide (NHS, 1.71 g) and N-(3-(dimethylamino)propyl)-N′-ethylcarbodiimide hydrochloride (EDC.HCl, 2.88 g) were added to the above suspension at 0 °C and stirred for 2 h under a N$_2$ atmosphere, and 1.9 mL 1,3-diaminopropane was then added and stirred overnight at room temperature. The product was collected and washed several times with water and ethanol, and dried overnight in a vacuum oven at room temperature.

2.3. Synthesis of RGO-g-PANI composite

Typically, GO–NH$_2$ was first dispersed in 10 mL HCl (1 M) and bath-sonicated for approximately 30 min to obtain a homogeneous dispersion (1 mg/mL). This suspension was cooled in an ice bath to 0 °C. Aniline (0.5 mL) was then added to GO–NH$_2$ suspension with continuous stirring, after which, a freshly prepared solution of 1.35 g K$_2$S$_2$O$_8$ in 10 mL water was added slowly while stirring under cool conditions. The reaction was allowed to continue for a further 5 h in an ice bath to ensure proper polymerization. The resulting dark green product was filtered after washing with a HCl solution to remove any unreacted monomer and oxidant. The product was then washed several times with deionized water and hexane followed by drying under vacuum overnight at 45 °C to yield RGO-g-PANI.

2.4. Characterization

The as-prepared products were characterized by SEM (Hitachi, S-4200), TEM (Philips, CM-200) at an acceleration voltage of 200 kV, XRD (PANalytical, X'Pert-PRO MPD) with Cu Kα radiation, and XPS (ULVAC-PHI electron spectrometer, Quantera SXM) using an Al X-ray source. The FT-IR (Nicolet iS10, Thermo Scientific) spectra were recorded over 500–4000 cm^{-1} at a resolution of 16 cm^{-1} within 32 scans

using a diamond ATR attachment. The electrical conductivity was measured by the standard four point probe method at ambient temperature (Advanced Instrument Technology CMT-SR1000N with Jandel Engineering probe). The composites were pressed to tablets and checked five times of the same sample for calculating the average conductivity value. All electrochemical experiments were performed on Autolab PGSTAT302N (Metrohm, Netherlands) in a three-electrode configuration. Platinum foil and a saturated calomel electrode were used as the counter and reference electrodes, respectively.

For sensor applications, the working electrode was made using the same quantity of the samples being coated on carbon paper (1 cm × 1 cm in diameter) in each experiment. Typically, 2 mg of the composite was sonicated in a solution containing 700 μL isopropyl alcohol and 6 μL Nafion (5 wt.%) to form a homogenous dispersion. Approximately 20 μL of the above solution was then drop-cast onto the surface of a bare glassy carbon electrode and dried in an ambient atmosphere for 12 h.

For supercapacitor applications, the working electrode was fabricated by mixing the as-prepared powder (2 mg, 80 wt.%) with 15 wt.% acetylene black and 5 wt.% polytetrafluorene-ethylene (PTFE) binder, and coated onto carbon paper electrodes (1.0 cm × 1.0 cm). The measurements were taken in 1 M Na$_2$SO$_4$ and 1 M H$_2$SO$_4$ aqueous electrolytes at room temperature. The specific capacitance (Cs) of the electrode was calculated using the following equation: C = It / mΔV, where C, I, t, m, and ΔV are the specific capacitance (F g^{-1}), discharging current (A), discharging time (s), mass of active materials (g), and discharging potential range (V), respectively.

3. Results and discussion

3.1. Synthesis of the RGO-g-PANI composites

The surface morphology of the samples was examined by SEM and TEM. Fig. 1 shows SEM images of bare GO, pure PANI and RGO-g-PANI at different magnifications. GO showed thin sheets with distinct edges, wrinkled surfaces and folding (Fig. 1a). A comparison of the composite morphology showed that the pure PANI changed remarkably after composite formation. Pure PANI exhibited dendritic nanofibers with mean diameters of ca. 100 nm and lengths up to the micron size. The low dimensional morphology of PANI was attributed mainly to the chain structure of the PANI molecules (Fig. 1b). The surfaces of the RGO sheets surfaces were clearly covered with PANI layers (Fig. 1c and d). To further characterize the composite morphology more clearly, the pure PANI and RGO-g-PANI composites were examined by TEM (Fig. 2). The RGO-g-PANI composites showed a different morphology from pure PANI due to the thin polymer layers covering the RGO sheets almost completely.

The chemical structural information of pure PANI, bare GO, GO–NH$_2$, and RGO-g-PANI composite was obtained from the FT-IR spectra (Fig. 3a). The spectrum of GO showed representative peaks at 3445 cm^{-1} (O–H), 1721 cm^{-1} (C=O), 1410 cm^{-1} (C–OH), and 1042 cm^{-1} (C–O) [35]. The spectrum of PANI showed usual characteristic stretching vibration bands at 1561 cm^{-1} (C=C, quinoid rings), 1492 cm^{-1} (C=C, benzenoid rings), 1287 cm^{-1} (C–N), and 1083 cm^{-1} (C–H). After the modification of GO with amine and alkyl compounds, several new peaks were observed, indicating the occurrence of a chemical reaction. GO–NH$_2$ exhibited the characteristic symmetric and asymmetric stretching vibrations of methyl and methylene groups at 2867 and 2941 cm^{-1}, respectively, and bending vibration of methylene groups at 1439 cm^{-1}, which confirmed the existence of amine compounds grafted to GO [36]. After polymerization, a new peak was appeared at 791 cm^{-1} (N–H vibration of secondary amine group), which suggests that the polymerization is initiated from the amino group grafted from the RGO sheets. In the FTIR spectrum of the RGO-g-PANI composite was similar to that of PANI, which confirmed that the GO surface was wrapped completely by PANI. There