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

Van Hoa Nguyen, Charmaine Lamiel, Dian Kharismadewi, Van Chinh Tran, Jae-Jin Shim

ARTICLE INFO
Article history:
Received 1 July 2015
Received in revised form 25 September 2015
Accepted 21 October 2015
Available online 22 October 2015

ABSTRACT
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 NH2 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 H2O2 was linear in the range, 0.05 to 14 μM (R2 = 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, highlighting its promising applications as an efficient electrode material for supercapacitors.

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 anticorrosive 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 ble 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 ble in air [13].

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 H2O2 [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.
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 (98%, 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–NH₂

Graphene oxide (GO) was synthesized from graphite powder using a modified Hummers method [29]. In typical synthesis of GO–NH₂, 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’-ethylenediamine hydrochloride (EDC.HCl, 2.88 g) were added to the above suspension at 0 °C and stirred for 2 h under a N₂ 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–NH₂ was first dispersed in 10 mL HCl (1 M) and bathsonicated 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–NH₂ suspension with continuous stirring, after which, a freshly prepared solution of 1.35 g K₂S₂O₈ 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 x 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 NaFON (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 fabricate}
no peak was observed at 1720 cm$^{-1}$ (C=O vibration), indicating the reduction of GO. In addition, compared to the pure PANI, the quinoid band at 1565 cm$^{-1}$ of RGO-g-PANI has lower intensity than the benzenoid band at 1483 cm$^{-1}$, which further confirms that the PANI has been covalently grafted onto the surface of the RGO sheets. The observed IR bands were in good agreement with previously reported results [37,38].

Fig. 4 shows the XPS spectra of GO–NH$_2$ and the RGO-g-PANI composite at the core-level C 1s, N 1s, and O 1s peaks. The C 1s peak of GO could be deconvoluted to four peaks at BEs of 285.5 (C–C), 286.4 (C–OH), 287.5 (C–O–C), 288.5 eV (C=O), and 289.5 (O–C=O), respectively [27] (Fig. 4a). This shows that the original GO–NH$_2$ is partially oxidized and contains hydroxyl, carboxyl and carbonyl groups. The core-level O 1s peaks were observed at 532.8 eV (C=O) and 533.5 eV (C–O) (Fig. 4b). The N 1s peaks in Fig. 4c showed that there are two types of nitrogen bond in the composite structures, pyrrolic and graphitic nitrogen. In the XPS spectrum of the RGO-g-PANI composite, a peak representing nitrogen atoms was also observed, indicating the presence of PANI. The intensity of both C 1s and O 1s peaks decreased in the case of the RGO-g-PANI composite after combination with PANI. The peaks corresponding to C–O–C (287.5 eV) and C–OH (286.4 eV) of graphene oxide disappeared. This was attributed to the increased conjugation and the chemical bonds between the PANI backbone and RGO sheets. The electrical conductivity of RGO-g-PANI was determined by using a four probe resistivity measurement system. The average value was as high as 9.12 S cm$^{-1}$, indicating the good conductive networks in the system based on the covalent bonding between RGO and PANI.
3.2. Electrochemical sensor application

Electrochemical impedance spectroscopy (EIS) is an effective method for measuring the electron-transfer resistance. In general, the EIS curve includes a semicircular part and a linear part. The semicircular part at higher frequencies corresponds to an electron transfer limited process and its diameter is equal to the electron transfer resistance at the electrode surface. The linear part at the lower frequencies corresponds to the diffusion process.

Fig. 5a presents the representative impedance spectrum of the GCE, GCE/PANI and GCE/RGO-g-PANI electrodes in a 0.1 M KCl solution containing 2.5 mM $[\text{Fe(CN)}_6]^{3-}/4^{-}$ with frequencies ranging from $10^5$ to $10^{-1}$ Hz. The bare GCE exhibited an almost straight line that was characteristic of a diffusion limiting step of the electrochemical process. A semicircle curve was observed in the both GCE/PANI electrode and the GCE/RGO-g-PANI electrodes. This indicates that the impedance of the electrodes increased in the presence of RGO and PANI, which hindered the electron transfer of the $[\text{Fe(CN)}_6]^{3-}/4^{-}$. However, in the case of the GCE/PANI, a semicircular radius was found to be larger than that of the GCE/RGO-g-PANI, which indicated high electron transfer resistance to the redox probe. The decreased impedance of the GCE/RGO-g-PANI electrode may be due to the conductivity of the RGO sheets. The high electron transfer of GCE/RGO-g-PANI increases the electrical properties of the redox processes.

Fig. 5b and c shows the cyclic voltammograms of the GCE and the electrodes modified with the pure PANI and RGO-g-PANI composite in the absence and presence of H$_2$O$_2$ in 0.1 M PBS at pH 6.0. In the case of GCE, no anodic or cathodic responses were observed in the presence or absence of H$_2$O$_2$. This suggests that GCE cannot detect H$_2$O$_2$ in the potential measured. For the modified electrode, GCE/PANI did not show a peak in the absence of H$_2$O$_2$ but a small reduction peak was observed in the presence of H$_2$O$_2$. On the other hand, GCE/RGO-g-PANI showed normal redox behavior with a pair of well-defined and quasi-reversible redox peaks in both the presence and absence of a small amount of H$_2$O$_2$. The redox peak currents and reduced oxidation potential increased significantly at the modified electrode, which were attributed to its good electrocatalytic activity. In both cases, the intensity of the GCE/RGO-g-PANI peaks was higher than that of the pure PANI-modified electrode. The net oxidation peak current of H$_2$O$_2$ obtained at GCE/RGO-g-PANI (2.35 mA) was approximately 8 and 7 times higher than those of bare GCE (0.30 mA) and GCE/PANI.

![Fig. 3. FT-IR spectra of (a) pure PANI, (b) bare GO, (c) GO-NH$_2$, and (d) RGO-g-PANI](image)

![Fig. 4. XPS results of the core-levels of C 1s, O 1s and N 1s in the RGO-g-PANI composite.](image)
(0.35 mA), respectively. This shows that the presence of RGO and PANI enhanced considerably the electrochemical activity of the GCE electrode and its ability to detect H$_2$O$_2$. On the other hand, the effects of the scan rate of the potential on the electrocatalytic ability of the RGO-g-PANI modified composite electrode for the detection of H$_2$O$_2$ was also studied. Fig. 5d shows cyclic voltammograms of GCE/RGO-g-PANI in 0.1 M PBS at pH 6.0 in the presence of 10 μM H$_2$O$_2$ at different scan rates. The redox peak currents increased linearly with an increasing scan rate from 10 to 150 mV s$^{-1}$. This suggests that the electrochemical reaction of H$_2$O$_2$ on the RGO-g-PANI film is a surface reaction-limited process.

The sensitivity of the electrode with the modified GCE/RGO-g-PANI composite was examined by varying the H$_2$O$_2$ concentration in 0.1 M PBS pH 6.0 (Fig. 6a). The inset in Fig. 6a showed a linear increase in the peak current with increasing H$_2$O$_2$ concentration. The major cathodic response was extremely sensitive to the H$_2$O$_2$ concentration. The calibration curve plot was linear from 2.0 μM to 14 μM with a correlation coefficient of 0.995. The electrode has a sensitivity of

![Graph1](image1.png)

![Graph2](image2.png)

Fig. 5. (a) Electrochemical impedance spectra of bare glassy carbon electrode (GCE), GCE/PANI and GCE/RGO-g-PANI electrodes in 0.1 M PBS at pH 6.0 containing 2.5 mM [Fe(CN)$_6$]$^{3-/-4-}$; cyclic voltammograms of bare GCE and GCE/PANI and GCE/RGO-g-PANI electrodes in 0.1 M PBS at pH 6.0 in the (b) absence and (c) presence of 10 μM H$_2$O$_2$ at a scan rate of 10 mV s$^{-1}$; (d) cyclic voltammograms of the GCE/RGO-g-PANI composite in 0.1 M PBS at pH 8.0 in the presence of 10 μM H$_2$O$_2$ at different scan rates.

![Graph3](image3.png)

Fig. 6. Amperometric response for GCE/RGO-g-PANI electrode in different concentrations of H$_2$O$_2$ in 0.1 M PBS at pH 6.0 and (b) the effect pH value of voltammetric solution on the current response of GCE/RGO-g-PANI electrode.
10.2μA/M/cm². The detection limit was 0.37μM according to the sensitivity obtained from the calibration curve. Therefore, the RGO-g-PANI modified electrode provided high sensitivity, highlighting the potential applications for fabricating H₂O₂ involved sensors. The pH effect on the GCE/RGO-g-PANI sensor performance was examined in the range, 4–9, by measuring the current response to 15μM H₂O₂ (Fig. 6b). The peak current decreased gradually from pH 4.0 to 9.0 with an increase in pH. In addition, the reproducibility and storage stability of the GCE/RGO-g-PANI electrode were investigated. The reproducibility was carried out using three electrodes prepared under the same conditions. The results showed that the sensor had satisfactory reproducibility with a relative standard deviation of 5.2% for the detection of 50μM H₂O₂. The steady-state response current only decreased by 16% after the electrode was stored at room temperature for 2 weeks.

3.3. Electrochemical capacitor application

To evaluate the electrochemical performance of the RGO-g-PANI composite as an active supercapacitor electrode, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometry (CP) were carried out in a three-electrode system using a SCE as the reference electrode and platinum foil as the counter electrode. At the same scan rate of 2 mV s⁻¹ (Figs. 7a and 8a) in both acidic and neutral electrolyte solutions, the RGO-g-PANI electrode exhibited a much higher current than that of the pure PANI electrode, suggesting that the conducting RGO sheets facilitated electron transport and enhanced the electrochemical utilization of the RGO-g-PANI composite.

The electron conductivity and transport characteristics of the charge carriers within electrodes were compared by EIS. The ideal Nyquist impedance plot was composed of a half semicircle and a line in at the high and low frequency regions, respectively. The high frequency semicircle intercepts the real axis at Rₛ and (Rₛ + Rₘ), where Rₛ means the bulk solution resistance and Rₘ means the charge-transfer resistance, respectively. Rₛ is related to several parts including the electrolyte resistance, the collector/electrode contact resistance and the electrode/electrolyte interface resistance. Figs. 7b and 8b show the impedance curves for pure PANI and RGO-g-PANI electrodes measured in a 1 M H₂SO₄ and 1 M Na₂SO₄ electrolyte solutions, respectively. The RGO-g-PANI electrode exhibited a lower Rₛ of the electrochemical system with an invisible or very small semicircle in the high frequency region and the most vertical line in the low frequency region, which was attributed to the high conductivity and porosity of the present electrode. The improved electrochemical performance was also confirmed by galvanostatic charge–discharge tests performed at different current densities for the RGO-g-PANI electrode (Figs. 7c and 8c) and under the same current density for the comparison to the pure PANI electrode. The CV curves of the RGO-g-PANI electrode in the potential window, 0.0–0.6 V, at various scan rates from 5 to 100 mV s⁻¹ showed an almost rectangular shape at all scan rates (Figs. 7d and 8d), suggesting that the electrode exhibits low resistance and is an ideal supercapacitor [23].

Fig. 9a summarizes the specific capacitances of the pure PANI and RGO-g-PANI electrodes at different current densities, which were calculated from the charge–discharge curves. The results show that grafting with RGO sheets yields enhanced capacitance performance with about 40% (in Na₂SO₄ electrolyte) and 45% (in H₂SO₄ electrolyte) increase in specific capacitance compared to that of the pure PANI electrode (in H₂SO₄ electrolyte). In particular, the RGO-g-PANI electrode showed excellent rate performance, i.e., approximately 73.7% (in Na₂SO₄ electrolyte) and 72.7% (in H₂SO₄ electrolyte) capacitance...
remained, even after applying a very high current rate of 20 A g\(^{-1}\) compared to the low current rate of 2 A g\(^{-1}\). The enhanced capacitance can be attributed to the increased electronic conductivity of the RGO nanosheets. On the other hand, the supercapacitors based on the composite electrode exhibited excellent stability under repeated charging and discharging cycles in H\(_2\)SO\(_4\) electrolyte solution (Fig. 9b). The capacitor retained 80.07% of its initial capacity after being charged and discharged for 5000 cycles at a rate of 5 A g\(^{-1}\), which is comparable to those of RGO/PANI-based supercapacitor electrodes [38–40]. The Coulombic efficiency over ca. 93% during the 5000 charge/discharge cycles clearly shows the electrochemical suitability of the RGO-g-PANI.

4. Conclusions

In this study, a RGO-g-PANI composite was prepared efficiently using a two-step method. SEM and TEM images indicated that the RGO sheets were coated with a polymer layer. The resulting RGO-g-PANI composite showed preferable electroactivity, even in alkaline media and displayed excellent electrocatalytic activity towards the oxidation of hydrogen peroxide, suggesting it to be a promising material for chemical sensors. In addition, the electrode using this composite exhibited high capacitance, such as a specific capacitance of 1337 F g\(^{-1}\) at a very high current density of 15 A g\(^{-1}\), and showed excellent cyclic stability and only an 18.75% decrease in capacitance after 5000 cycles.

Fig. 8. (a) CV curves of pure PANI and RGO-g-PANI composite at a scan rate of 5 V s\(^{-1}\) in 1 M Na\(_2\)SO\(_4\) electrolyte solution; (b) Nyquist plots of pure PANI and RGO-g-PANI composites; (c) galvanostatic discharge curves of pure PANI and RGO-g-PANI composites; (d) CV curves of the RGO-g-PANI composite at different scan rates in 1 M Na\(_2\)SO\(_4\) electrolyte solution.

Fig. 9. (a) Galvanostatic specific capacitance retention of pure PANI and RGO-g-PANI electrodes at different current densities; (b) average specific capacitance retention (red line) versus the cycle number and superior Coulombic efficiency (blue line) of RGO-g-PANI in 1 M H\(_2\)SO\(_4\) electrolyte solution at a current density of 5 A g\(^{-1}\).
Acknowledgment

This study was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2014R1A6A1031189).

References

[27] Y. Li, Y. Ma, S. Guan, F. Ke, H. Xu, Carbon 83 (2014) 79–89.