Optoelectrical and photoluminescence quenching properties of poly (N-vinyl carbazole)-polypyrrole/reduced graphene oxide nanocomposites

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A B S T R A C T
Dodecylbenzenesulfonic acid (DBSA) doped poly(N-vinyl carbazole)/polypyrrole (PNVC-PPy) was decorated on various concentrations of reduced graphene oxide (RGO) by facial in-situ chemical synthesis to produce poly(N-vinyl carbazole)-polypyrrole/reduced graphene oxide (PNVC-PPy/RGO) nanocomposite. Fourier transform infrared spectroscopy (FTIR) confirmed the incorporation of RGO into the PNVC-PPy structure. The thermo-electric properties of PNVC-PPy increased with varying reduced graphene oxide (RGO) contents. Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) analyses showed the formation of PNVC-PPy/RGO nanocomposites with ordered structures. Raman spectroscopy analysis revealed the enhancement of conjugation length of the polymer nanocomposites suggesting enhanced electrical conductivity as measured by four-probe technique. Thermogravimetric analysis (TGA) exhibited significant changes in the thermal stability of the PNVC-PPy/RGO nanocomposites owing to the incorporation of RGO to PNVC-PPy copolymer. The strong π–π interactions between RGO and PNVC-PPy in PNVC-PPy/RGO nanocomposites were observed by the red shifting of the wavelengths in ultraviolet-visible spectroscopy (UV-vis) when RGO was added into the polymer composites. The photoluminescence quenching induced by reduced graphene oxide in (PNVC-PPy/RGO) nanocomposite was attributed to the efficient electron transfer from PNVC-PPy copolymer to RGO.

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1. Introduction

Conducting polymer nanocomposites have emerged as an important area in nanoscience and technology with improved thermal, mechanical, electrical, and gas barrier properties of polymers. This new class of composite materials becomes popular owing to its wide applications in supercapacitors, electronic devices, rechargeable batteries, sensors and solar cells for their unique properties that ordinary composites lack [1–5]. Early investigations on polymer nanocomposites were directed to nanoscale fillers such as silica and clay [6]. However, poor thermal and electrical conductivity of silica-based nanofillers directed investigations into other materials. For instance, nanomaterials prepared from SiC, carbon black, carbon nanotube and expanded graphite were among the candidates with improved properties [7,8].

Graphene is a single-atom-thick layer with a two-dimensional (2-D) honeycomb structure made of sp²-hybridized carbon atoms. Graphene possesses many intriguing properties, such as high thermal and chemical tolerance, high charge carrier mobility [9], large surface area [10], and good mechanical strength [11]. Forming homogeneous dispersions is a major challenge when graphene is used for large-scale production. For instance, to prepare polymer-graphene nanocomposites, one important step is to exfoliate graphene sheets into thin graphitic layers. However, pristine graphene does not disperse in organic and inorganic media, which increases the difficulty of working with pristine graphene. Graphene oxides (GO), the oxidized form of graphene, contain basal planes and edges with various oxygen-bearing functional groups, have attracted much attention [10]. The present use of GO as a precursor is an effective approach to the preparation of dispersible graphene. GO is rich in oxygen-bearing groups (—OH, —COOH, —CHO, epoxy groups); this substance is tuneable...
and readily soluble in solvents thereby enhancing its effectiveness as a nanofiller [12]. Most of the proposed application areas of graphene, such as in organic electrodes, sensors, and organic solar cells, require graphene dispersion in an organic medium. [13]. Thus, a process should be developed to exfoliate and disperse graphene in common organic solvents. To date, researchers have made considerable efforts to develop GO-based nanocomposites for improved solubility and dispersion in organic solvents [14].

One drawback of the graphene oxide is its low conductivity, which is attributed to the covalent character of C—O bonds that disrupts the sp² conjugation of the hexagonal graphene lattice. GO can be partially reduced to conductive graphene-like sheets by removing oxygen-containing groups [15]. To overcome this low conductivity, reduced graphene oxide has been used instead of graphene oxide. Many findings showed that incorporation of RGO remarkably improves the thermal stability of nanocomposites [16,17]. The ease of exfoliation and reduction of GO to graphene in a large-scale makes GO a preferred choice to other expensive fillers such as carbon nanotubes and carbon nanofibres [18].

Despite being a poor electrical conductor, poly (N-vinyl carbazole) (PNVC) is readily soluble in common organic solvents and possesses good thermal stability. Some of the dispersible nanocomposites of PNVC with GO were prepared without further modification of polymer and functionalization of graphene [19]. As for example, Santos et al. prepared a well-dispersed PNVC/GO nanocomposite through solution mixing [20]. This dispersible nanocomposite displays excellent storage stability for up to 30 days in N-methyl pyrrolidone (NMP) and N-cyclohexyl-2-pyrrolidone (CHP) [20]. Solution-processable GO-PNVC has been fabricated by covalently attaching GO to PNVC. The material exhibits good optical and electronic properties and is thus a suitable material for optoelectronic devices [21].

Nanocomposites based on polypyrrole (PPy) and GO have good optical and electrochemical properties [22]. Good thermal stability and enhanced electrical conductivity were observed using reduced graphene oxide (RGO) in polypyrrole/reduced graphene oxide (PPy/RGO) nanocomposite [23,24]. Existing studies reported the use of DBSA as a protonating agent and an emulsifier for the synthesis of polyaniline/reduced graphene oxide (PANI/RGO) nanocomposites [25]. The nanocomposites exhibited enhanced thermal and electrical properties and became dispersible in organic solvents; thus, these nanocomposites are good candidates in several applications, such as functional coatings, electric devices, and sensors [26–29].

To meet the need for optoelectronic applications, polymer nanocomposites need to exhibit high photoluminescence quenching apart from very good thermal and electrical properties. To this end, the present effort has been made to explore the role of reduced graphene oxide in conducting polymer composites to attain high photoluminescence quenching, good thermal characteristics and enhanced electrical properties. We prepared organic solvent dispersible poly(N-vinyl carbazole)-polypyrrole/reduced graphene oxide (PNVC-PPy/RGO) nanocomposites following in-situ chemical oxidative polymerization. This conducting polymer/reduced graphene oxide has not been previously reported.

2. Experimental details

2.1. Materials

Natural flake graphite, N-vinyl carbazole (NVC), pyrrole (Py) and ferric chloride hexa hydrate (oxidant) were purchased from Sigma-Aldrich. Sulfuric acid, hydrochloric acid, ethanol and hydrogen peroxide were purchased from Merck, Germany. Dodecyl benzene sulfonic acid (DBSA, Acros Organics) was used as received, N,N-dimethylformamide (DMF), and acetonitrile were of analytical grade and used without further purification.

2.2. Preparation of PNVC-PPy/RGO nanocomposites

PNVC-PPy/RGO nanocomposites were prepared via in-situ polymerization of pyrrole and NVC in presence of DBSA and FeCl₃·6H₂O with various amount of reduced graphene oxide in acetonitrile. The graphene oxide was prepared from natural graphite flakes by an improved Hummers’ method [30]. The reduced graphene oxide has been synthesized by reducing the graphene oxide at 95°C using hydrazine hydrate as a reducing agent. The preparation scheme of the reduced graphene oxide (RGO) is shown in Fig. 1.

Reduced graphene oxide was varied at 0.1 g, 0.3 g, and 0.5 g in the resulting nanocomposites which were designated as PNVC-PPy/RGO-1, PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3, respectively. First, RGO was dispersed in water by ultrasonication for 20 mins.

![Fig. 1. The preparation scheme of the reduced graphene oxide (RGO).](image-url)
Pyrole (1 M), N-vinyl carbazole (1 M) and dodecyl benzene sulfonic acid (0.01 M) were dissolved in acetonitrile. The resultant solution was added to the dispersion of RGO and ultrasonication was continued for another 30 mins. Ferric chloride hexahydrate solution (3 M) was then added to the mixture of NVC, Py, DBSA and RGO. The polymerization started immediately and the reaction was allowed to continue for 6 h under vigorous stirring. The composite thus obtained was washed several times with the mixture of chloroform, acetonitrile, ethanol and water. Finally, the nanocomposites were dried under vacuum at 65 °C for 24 h.

3. Results and discussion

In this present effort, N-vinyl carbazole (NVC) and pyrole (Py) monomers were polymerized in the presence of DBSA to produce a new solution processable material that possesses both individual properties of PNVC and PPy. Thus, we utilized DBSA as a stearic stabilizer to expand the PPy backbone to enable solvents to diffuse into the inter-molecular spaces created by DBSA. The copolymer was soluble in DMF and exhibited good thermal stability, but its electrical conductivity requires improvement. Therefore, we attempted to form polymer nanocomposites by introducing reduced graphene oxide (RGO) to PNVC-PPy with the aim of improving the electrical conductivity and thermal stability through the π–π* interaction between the polymer and RGO. In the development of polymer/graphene nanocomposite, graphene dispersion is highly important in avoiding particle aggregation [4]. The resulting PNVC-PPy/RGO can disperse thoroughly in DMF to produce a stable radish black solution for at least 2 months (Fig. 2). The solubility of PNVC-PPy/RGO was determined at 2.0 mg mL⁻¹ according to the saturated amount in DMF. The solubility of PNVC-PPy/RGO nanocomposite decreases with the increase in RGO.

The polymerization of NVC and Py with RGO, facilitates the intimate participation of RGO in forming the PNVC-PPy/RGO nanocomposite as shown in the FESEM images (Fig. 3). PNVC-PPy shows a densely packed globular structure with uniformly arranged particles. The PNVC-PPy globules disappeared to show a wrinkled, flaked morphology with globules during in-situ chemical oxidative polymerization with RGO. The image shows an expanded RGO layers in the PNVC-PPy structure owing to the random insertion and deposition of PNVC-PPy during the chemical oxidative polymerization. This effect resulted in a partially disordered solid (PNVC-PPy/RGO) with uneven morphology.

3.1. Raman spectroscopy

Fig. 4 shows the Raman spectra of RGO, PNVC-PPy/RGO-1, PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3. The Raman spectrum of the as-synthesized reduced graphene oxide (RGO) film displays D-band at 1358 cm⁻¹, G-band at 1598 cm⁻¹, and 2D broad peak at 2990 cm⁻¹. The similar band positions for reduced graphene oxide (RGO) have been reported by Li et al. [31]. In the spectrum of PNVC-PPy, the peaks located at 1330 cm⁻¹ and 1580 cm⁻¹ are related to D–bands and G–bands, respectively, while no 2D range peaks have been observed. In the PNVC-PPy/RGO nanocomposite, the 2D peaks at 2750 cm⁻¹ and 2978 cm⁻¹ confirm the presence of RGO in the PNVC-PPy/RGO nanocomposite and these 2D peaks also indicate the multilayer structure of RGO in the composite [32]. The intensity ratio of the D/G band expresses the atomic ratio of sp²/sp³ carbons, which is a measure of the extent of disordered graphite. The intensity ratio of D to G band in the RGO spectrum is calculated to be 1.23, indicating that increased number of sp² domains formed during the chemical reduction process. The Raman spectra for PNVC-PPy/RGO-1, PNVC-PPy/GO-2, PNVC-PPy/GO-3 show that as the amount of RGO increases in the PNVC-PPy/RGO nanocomposite, the D/G band intensity ratio rose as 0.234, 0.318 and 1.03, respectively, indicating the formation of longer conjugation length of the polymer–composite owing to the addition of RGO. Similar observations have been reported for polypyrrole-reduced graphene oxide by Li et al. [31].

3.2. Electrical conductivity

Table 1 shows the electrical d.c. conductivity of PNVC-PPy, PNVC-PPy/RGO-1, PNVC-PPy/RGO-2 and PNVC-PPy/GO-3 measured by four-point probe at room temperature. The PNVC-PPy copolymer attained an electrical d.c. conductivity of 0.08 S/cm. With the incorporation of RGO in the composite, the conductivity of PNVC-PPy/RGO nanocomposite increases three orders of magnitude (30 S/cm). The role of RGO in enhancing the electrical conductivity of the composites is due to the formation of π–π* interaction between RGO and PNVC-PPy as well as enhanced the number of conductive paths for electrical charges. Pathways also include inter-charge transfer between the RGO layers and the PNVC-PPy chains, inter-and intra-charge transfer between the RGO layers, and inter- and intra-charge transfer between the PNVC-PPy chains [29]. The enhanced electrical conductivity derived from the incorporation of RGO into the PNVC-PPy/RGO polymer composite is also linked to the increase in conjugation chain length caused by the presence of RGO as has been observed in the Raman spectra of PNVC-PPy/RGO. Thus, RGO plays the key role in electrical conductivity increase in PNVC-PPy/RGO nanocomposite.

3.3. TGA analysis

The thermal stability of RGO, PNVC-PPy/RGO-1, PNVC-PPy/RGO-2, PNVC-PPy/RGO-3, nanocomposites measured by TGA under N₂ atmosphere are shown in Fig. 5. The initial weight loss of RGO around 2.45% was found between 50 °C and 200 °C and a second mass loss of around 6.36% was observed midway between 250 °C to 400 °C. A third weight loss of 12.43% was found between 450 °C to 800 °C. The small weight loss indicates the thermal stability of the RGO. A considerable enhancement in thermal stability was observed for PNVC-PPy/RGO nanocomposite with the addition of different amount of RGO into the copolymer (PNVC-PPy). Only a mere 4.88 wt%, 5.09 wt%, 2.92 wt% weight loss was observed for PNVC-PPy/RGO-1, PNVC-PPy/RGO-2, PNVC-PPy/RGO-3 nanocomposites, respectively at 200 °C while the weight loss of 6.36 wt% was observed for PNVC-PPy copolymer. It clearly shows the improved thermal stability upon the incorporation of RGO in

Fig. 2. Image of solubility of (a) PNVC-PPy/RGO-3, (b) PNVC-PPy/RGO-2, (c) PNVC-PPy/RGO-1 (d) RGO without presence of PNVC-PPy.
the nanocomposites. After 250–400 °C, a weight loss of 47.87% was found for all the concerned PNVC-PPy. After 450–750 °C, the weight loss for PNVC-PPy was almost 13.4% more than that of RGO-based nanocomposite. All these observations show that the RGO-based PNVC-PPy composite possesses a superior thermal stability to that of PNVC-PPy copolymer.

3.4. FTIR analysis

Fig. 6 shows the FTIR spectra of PNVC-PPy, RGO, PNVC-PPy/GO-1, PNVC-PPy/GO-2, and PNVC-PPy/GO-3 nanocomposites. The FTIR spectrum of RGO shows peaks at 2927 cm⁻¹ and 2851 cm⁻¹ related to the CH₂ asymmetric and symmetric stretching vibrations, respectively. The peaks at 1747 cm⁻¹ and 1438 cm⁻¹ in the RGO spectrum are recognized as the alkoxy groups and C—O stretching vibration of the epoxy group, respectively.

The FTIR spectra exhibit the characteristic peaks of PNVC-PPy at 724 cm⁻¹ (aromatic out of plane C—H bending), 1008 cm⁻¹ (benzene in-plane vibration), 1156 cm⁻¹ (C—O stretching vibrations in C—O—C in epoxide), 1450 cm⁻¹ (ring vibration of NVC moiety), 1590 cm⁻¹ (C=C stretching vibration of tri-substituted pyrrole), 2934 cm⁻¹ (aromatic C—H asymmetric stretching) and 3370 cm⁻¹ (N—H stretching band of Py). This N—H stretching band of pyrrole at 3370 cm⁻¹ shifted to 3413 cm⁻¹ in PNVC-PPy/RGO-1 nanocomposite owing to the C—C stretching of reduced graphene oxide in the latter nanocomposite. With the increase in reduced graphene oxide contents in the composite, this peak further shifted to 3416 cm⁻¹ and 3418 cm⁻¹, for PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3, respectively. These peaks, which are the hallmarks of reduced graphene oxide (RGO), reveal that RGO was effectively incorporated into the PNVC-PPy matrix forming the nanocomposites.

The peak at 2934 cm⁻¹ (aromatic C—H asymmetric stretching) in PNVC-PPy spectrum shifted to 2930 cm⁻¹ in the PNVC-PPy/RGO-1 because of the presence of RGO in the composite. With the increase in the RGO content in the composite, the peak further shifted to 2926 cm⁻¹ and 2920 cm⁻¹, for PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3, respectively. The peaks at 2930 cm⁻¹, 2926 cm⁻¹ and 2920 cm⁻¹ in the FTIR spectra of PNVC-PPy/RGO are due to the overlapping peaks of both RGO and PNVC-PPy as can be evidenced from the individual peaks of RGO and PNVC-PPy. Similar peaks in the above range due to C—H asymmetric stretching vibrations and C—H symmetric stretching vibrations have been reported by others for graphene-based PPy nanocomposites [33,34]. The intensity of these peaks was found to increase with the increase in RGO content in PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3. The peaks at 1451 cm⁻¹ for PNVC-PPy/RGO-1, PNVC-PPy/RGO-2 and PNVC-PPy/RGO-3 emerged from the ring vibration of NVC moiety. Four peaks at 724 cm⁻¹, 726 cm⁻¹, 728 cm⁻¹ and 730 cm⁻¹ derived from PNVC-PPy, PNVC-PPy/RGO-1, PNVC-PPy/RGO-2, PNVC-PPy/RGO-3 respectively, were attributed to 1,3,4-trisubstituted pyrrole ring.

Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Thickness (mm)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVC-PPy</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>PNVC-PPy/RGO-1</td>
<td>0.06</td>
<td>27</td>
</tr>
<tr>
<td>PNVC-PPy/RGO-2</td>
<td>0.06</td>
<td>28</td>
</tr>
<tr>
<td>PNVC-PPy/RGO-3</td>
<td>0.06</td>
<td>30</td>
</tr>
</tbody>
</table>
were observed at $2\theta = 20.02^\circ$, $2\theta = 23.46^\circ$ and $2\theta = 28.15^\circ$, respectively. The intensity of the $2\theta$ peak around $20^\circ$ was observed to increase with the increase in the RGO content in the nanocomposites. It clearly indicates that RGO was incorporated orderly into PNVC-PPy copolymer due to the $\pi-\pi$ stacking of PNVC-PPy with RGO. This kind of mechanism has been demonstrated in the relevant prior works by Zhai et al. [36-40]. The crystalline phases as observed in the XRD of PNVC-PPy/RGO nanocomposites owing to the crystalline nature of RGO are well linked to the conductivity increase, higher thermal stability and enhanced photoluminescence quenching in the prepared conducting polymer nanocomposites.

### 3.6. UV–vis spectroscopy

Fig. 8 shows the UV spectra of PNVC-PPy and composites of PNVC-PPy with various contents of RGO. The absorption peak of the copolymer PNVC-PPy displayed at 290 nm (Fig. 8) corresponds to the $\pi-\pi^*$ electron orbital transition along the backbone of the copolymer’s chain and a shoulder at 350 nm is attributed to the polaronic transition (polaron–$\pi^*$) caused by protonation. For PNVC-PPy/RGO nanocomposite, the color of the dispersion

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**Fig. 5.** TGA analysis (a) PNVC-PPy/RGO-3 (b) PNVC-PPy/RGO-2 (c) PNVC-PPy/RGO-1 (d) PNVC-PPy (e) RGO.

**Fig. 6.** FTIR of (a) PNVC-PPy, (b) RGO, (c) PNVC-PPy/RGO-1, (d) PNVC-PPy/RGO-2, (e) PNVC-PPy/RGO-3.

**Fig. 7.** X-RD spectra of (a) PNVC-PPy, (b) RGO, (c) PNVC-PPy/RGO-1, (d) PNVC-PPy/RGO-2, and (e) PNVC-PPy/RGO-3.

**Fig. 8.** UV spectra of (a) RGO, (b) PNVC-PPy, (c) PNVC-PPy/RGO-1, (d) PNVC-PPy/RGO-2, (e) PNVC-PPy/RGO-3.
changed from pale-brown to black (Fig. 2 inset). The UV bands at 430 nm (2.90 eV), 433 nm (2.88 eV), 436 nm (2.85 eV) were observed for the PNVC-PPy/RGO-1, PNVC-PPy/RGO-2, PNVC-PPy-RGO-3 nanocomposites, respectively, which may be due to an interaction between the PNVC-PPy and RGO in the nanocomposite. This interaction increases the delocalization of electrons along the polymer backbone chain and leads to an increase in the electrical conductivity.

3.7. Photoluminescence (PL) spectra

The photoluminescence quenching of PNVC-PPy/RGO composites was observed by fluorescence spectroscopy. The florescence PL spectra were found quenched with the increase in reduced graphene oxide (RGO) content in PNVC-PPy/RGO (Fig. 9). The quenching difference was high between RGO and PNVC-PPy. The photoluminescence quenching was suppressed remarkably and a blue shift of the emission peak was observed with the increase in RGO content in the PNVC-PPy/RGO nanocomposite relative to that of PNVC-PPy. This photoluminescence quenching confirms the electron transfer at the interface of the composite and suggests the potential of graphene as electron acceptor and light stabilizer for applications in optoelectronic devices. The blue shift of the photoluminescence peak can be explained by the decrease in density of state at the top of the valence band and results in an increase in effective band gaps [28].

4. Conclusion

We wish to report the successful preparation of poly (N-vinyl carbazole)-polypyrrole/reduced graphene oxide by in-situ chemical polymerization in the presence of dodecyl benzene sulfonic acid (DBSA) at various reduced graphene oxide contents. The presence of reduced graphene oxide in the conducting polymer nanocomposites produced high dispersion in common organic solvents, high thermal stability, enhanced photoluminescence quenching, longer conjugation length, high conductivity with ordered structure. The content of RGO in the polymer composites played a significant role in photoluminescence (PL) quenching. High RGO contents resulted in improved PL quenching. The prepared conducting polymer with reduced graphene oxide may afford optoelectronic devices with desirable properties and hence holds promise in such applications.

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References


