

## Short Communication

### Effect of rGO Concentration on the Thermal Stability of PANI/rGO Nanocomposites

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Reduced graphene oxide (rGO) was synthesized from graphite powder employing a modified Hummers method. The (PANI)<sub>1-x</sub>(rGO)<sub>x</sub> composites ( $x = 0, 0.02, 0.04, 0.06, 0.08$ ) were prepared by an in-situ chemical oxidation polymerization of aniline using ammonium peroxydisulfate (APS) as an oxidant in presence of colloidal rGO to improve thermal stability of PANI. The samples were characterized by X-ray diffractometry using  $\text{CuK}\alpha$  ( $\lambda = 1.5407 \text{ \AA}$ ) in order to study the phase and orientation of composites. Raman spectroscopy analysis of PANI/rGO nanocomposites was performed using confocal Raman microscopy. To measure the thermal stability, thermogravimetric analysis was done for PANI and PANI/rGO nanocomposites.

**Keywords:** X-ray spectra, Structure of nanoscale materials, Thermogravimetric analysis.

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## 1. INTRODUCTION

The conducting polymers are another class of materials which are preferred for many technological applications due to their cost effectiveness, simplicity of synthesis and eco-friendliness [1, 2]. The conducting polymers offer low thermal and high electrical conductivity that makes them promising thermoelectric materials [3]. Polyaniline (PANI) is one of such materials offering high electrical to thermal conductivity ratio along with easy preparation and processibility making it useful for modern electronic components and devices [4].

The electrical and thermal properties of reduced graphene oxide (rGO) are better as compared to the graphene and graphene oxide (GO). However, the use of rGO gives us certain advantages in real world applications [5, 6]. The bottleneck of the usage of rGO lies in the form of toxicity and production/processing cost which can be overcome by making use of green methods for reduction and novel techniques for production [7]. The sheet structure with presence of hydroxyl, carboxyl, carbonyl and epoxy functional groups bolsters the uniform distribution in polymer matrix [8]. The better distribution results in the enhanced  $\pi$ - $\pi$  stacking, hydrogen bonding and electrostatic forces between rGO and polymer matrix in a composite material [9].

Among conductive polymers, PANI is considered the most promising material because of its high capacitive characteristics, low cost, and ease of synthesis [10]. In the present work, rGO is prepared by oxidation and subsequent reduction of graphite powder. The PANI/rGO composites were obtained by addition of rGO during an in-situ chemical oxidative polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidizing agent. The obtained nanocomposites carrying

different concentrations of rGO are analyzed by various characterization techniques for finding a favorable composite for modern electronic components and devices.

## 2. EXPERIMENTAL DETAILS

Low temperature (0-5 °C) oxidative polymerization is used to synthesize PANI in a typical reaction with 0.3 M aniline in 1 M HCl solution, 0.3 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and 1 M HCl solution at 0-5 °C [10]. The precipitate is collected, filtered and washed multiple times to remove impurities and finally dried under rotary vacuum to obtain emeraldine base PANI. rGO was synthesized from graphite powder employing modified Hummers method reported elsewhere [9].

The PANI/rGO composite was prepared by an in-situ chemical oxidation polymerization of aniline using APS  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidant in presence of colloidal rGO nanoparticles at 0-5 °C in air. The different contents of PANI/rGO composites were synthesized using 2, 4, 6 and 8 wt. % of rGO with respect to aniline monomer. The structure of PANI, rGO and PANI/rGO nanocomposites is probed with X-ray diffractometry (XRD, Bruker AXS D-8 Advance Diffractometer) using  $\text{CuK}\alpha$  ( $\lambda = 1.5407 \text{ \AA}$ ). Raman spectroscopy analysis of PANI/rGO nanocomposites was carried out using confocal Raman microscopy. Thermogravimetric analysis was done using a Perkin Elmer's STA 6000.

## 3. RESULTS AND DISCUSSION

### 3.1 Structural Characterization

Fig. 1 shows the X-ray diffraction spectra of pure PANI, rGO and PANI/rGO (8 % w/w) nanocomposites. The vertical markers represent the characteristic peak

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position corresponding to the diffraction planes of PANI and rGO. PANI exhibited a completely amorphous nature, while the PANI/rGO (8 % w/w) exhibited diffraction from the lattice planes (002) and (100) of rGO at  $2\theta$  of  $25.47^\circ$  and  $43.02^\circ$ , respectively.

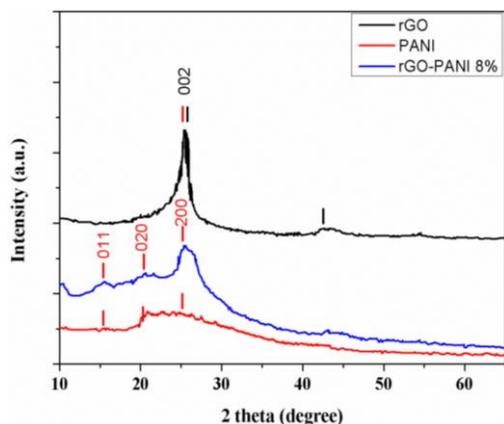


Fig. 1 – X-ray diffraction patterns of rGO, pure PANI and PANI/rGO (8 %) nanocomposite

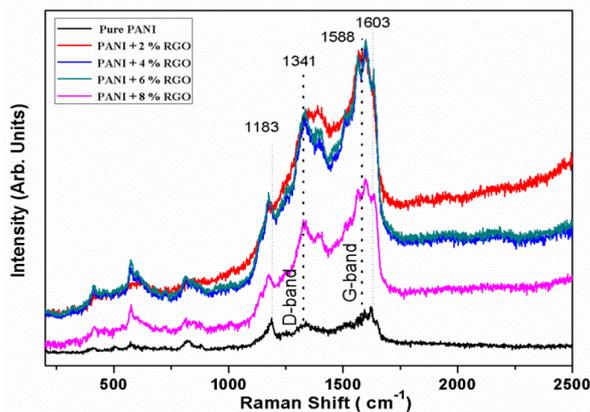


Fig. 2 – Raman spectra of pure PANI and PANI/rGO nanocomposites

Fig. 2 shows the Raman spectra of PANI and PANI/rGO composites, which consist of a prime contribution from the D and G bands indicating the presence of  $sp^2$  hybridized carbon material. The Raman spectrum of PANI exhibits Raman shifts at 572, 1183, 1341, 1588 and  $1603\text{ cm}^{-1}$  which are generally attributed to the high amount of PANI crosslinked segments due to a higher inter-chain interaction, in plane C-H bending of quinoid rings, C-H bending in benzoid ring and delocalized polaron vibrations in the extended polymeric conformation, respectively [11-13].

Further, the increased intensity of D and G bands in composite structure with increased concentration is also evident from the Raman spectra of PANI/rGO composites. The relative increase in the intensity of G band and origin of its shoulder could be attributed to the convolution of G band peak of rGO and contribution of delocalized polaron vibrations in the extended poly

meric conformation. This increase in peak intensity is reported to indicate an increasing number of effective delocalized polarons in the ordered polymeric chain in composite structure [11].

### 3.2 Thermal Properties

Fig. 3 depicts TGA curves for PANI/rGO composites in view of their thermal properties evaluation. It is observed that at almost room temperature in air, the mass loss is initiated for PANI/rGO composites due to removal of water and oxygen-containing groups [14]. On increasing the temperature, mass loss profile increases accordingly for all the studied samples. Near about  $330^\circ\text{C}$ , a transition in weight loss property takes place, i.e. below this temperature, the weight loss property of pure PANI is low and above this temperature, the weight loss property becomes higher in comparison to PANI/rGO composites. It reveals that at such higher temperature molecular main chain segments of pure PANI decomposed more abruptly than PANI/rGO composites. This indicates that rGO improved the thermal stability of the PANI/rGO composites. The outcome of TGA shows that covalent bonds are created between the functional groups of PANI and rGO, improving the thermal stability of the composites [14].

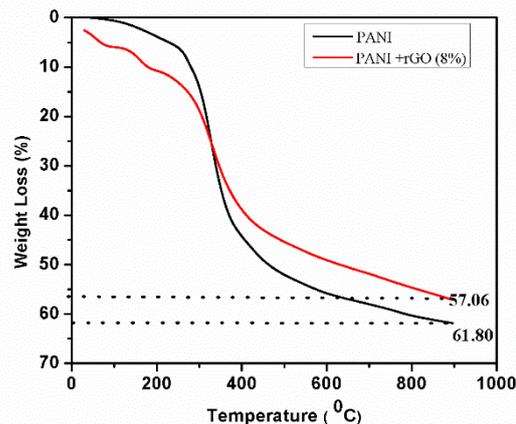


Fig. 3 – TGA spectra of PANI and PANI/rGO nanocomposites

### 4. CONCLUSIONS

In the light of above efficient investigations, the following conclusions are drawn:

- (1) Pure PANI and PANI/rGO nanocomposites are structurally confirmed through XRD and observations. XRD study reveals the amorphous nature of PANI that contains diffraction peaks of rGO consequent to different planes for PANI/rGO nanocomposites.
- (2) The D and G vibration modes of rGO are ascertained through Raman spectra of PANI/rGO nanocomposites.
- (3) TGA analysis reveals that the PANI/rGO nanocomposites offer enhanced thermal stability.

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## Вплив концентрації rGO на теплову стійкість нанокompозитів PANI/rGO

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Відновлений оксид графену (rGO) синтезувався з графітового порошку, використовуючи модифікований метод Хаммерса. Композити (PANI)<sub>1-x</sub>(rGO)<sub>x</sub> (x = 0; 0,02; 0,04; 0,06; 0,08) готували методом хімічної окислювальної полімеризації аніліну in situ, використовуючи пероксидисульфат амонію (APS) як окислювача у присутності колоїдного rGO для підвищення теплової стійкості PANI. Зразки характеризували рентгенівською дифрактометрією з використанням CuK $\alpha$  ( $\lambda = 1,5407 \text{ \AA}$ ) для вивчення фази та орієнтації композитів. Аналіз раманівської спектроскопії нанокompозитів PANI/rGO виконувався за допомогою конфокальної раманівської мікроскопії. Для вимірювання термостабільності проводили термогравіметричний аналіз для нанокompозитів PANI і PANI/rGO.

**Ключові слова:** Рентгенівські спектри, Структура нанорозмірних матеріалів, Термогравіметричний аналіз.