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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 $(PANI)_{1-x}(rGO)_x$ 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 CuKα (λ = 1.5407 Å) 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 **π–π** 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 $(NH_4)_2S_2O_8$ 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 ($(NH_4)_2S_2O_8$) 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 CuKα (λ = 1.5407 Å). 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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ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
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Enhanced Optical and Dielectric Properties of PANI/rGO Nanocomposites for Supercapacitor Application

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The conducting polymer nanocomposites have been extensively used due to manifold applications particularly as a novel supercapacitor material. The present work deals with the fabrication of PANI/rGO nanocomposites and investigating their morphological, optical and dielectric properties. The present paper is focused on the synthesis of $(PANI)_{1-x}(rGO)_x$ nanocomposites (x = 0, 0.02, 0.04, 0.06, 0.08) prepared by an in-situ chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidant in presence of colloidal reduced graphene oxide (rGO) nanoparticles at 0-5 °C in air to improve optical and dielectric constants of PANI for supercapacitor applications. rGO was synthesized from graphite powder employing a modified Hummers method. The morphology of synthesized composite materials was studied by scanning electron microscopy (SEM). FTIR spectroscopy analysis of PANI/rGO nanocomposites was performed using Perkin Elmer FTIR spectroscopy. Dielectric properties of nanocomposites were studied using impedance analyzer and it is observed that incorporation of rGO in PANI improves the dielectric properties. UV-VIS-NIR spectrophotometer was used to study the absorption spectra of the composite samples. The band gap energy (E_g) of the nanocomposites was determined using Tauc's relationship. It has been observed that the increasing the rGO concentration in composites reduces the optical band gap which attributes the enhancement in electron delocalization along the polymer chain. Also, the increment in protons with rGO concentration extends the density of states more into visible region of SEM spectra.

Keywords: Ultraviolet spectra, Structure of nanoscale materials, Dielectric properties of solids and liquids.

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1. INTRODUCTION

The conducting polymers have been employed widely in diverse fields due to their synthesis simplicity, cost effectiveness, and eco-friendliness [1-2]. In conducting polymers, charge carrier transport is originated by interchain and intrachain hopping which can easily be altered by changing the configuration of polymer chain [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]. PANI composites with GO and rGO also present a viable candidate for such applications among which rGO is more preferred due to its higher conductivity and thermal stability as compared to GO and therefore is being advocated as a promising material for modern electronic components and devices like supercapacitors, etc. [5].

The invention of graphene has attracted attention of researchers owing to its superior electronic, optical, mechanical and thermal properties, which can act as a building block for future electronic devices and sensors [6]. The other analogue of this family is reduced graphene oxide (rGO), which is the end result of oxidation of graphite powder and generally obtained by modified Hummer's method followed by action of a reducing agent [7].

Supercapacitor, which is also known as electric double-layer capacitor or ultracapacitor, consists of two electrodes, an electrolyte, and a separator, which isolates the two electrodes electrically as shown in Fig. 1. Supercapacitors are capable to store and transport energy with higher rates along with long life, high power, stretchy packaging, wide thermal range, low maintenance and low weight. The higher speed of charge transport is due to the charge separation mechanism at the interface between the electrode and the electrolyte [8]. Electrode material is the most important component of a supercapacitor. High-surface carbons, noble metal oxides, and conducting polymers are the main families of electrode materials being studied for supercapacitor applications [9].

Conductive polymers have been extensively studied in supercapacitors. Among conductive polymers, PANI is considered the most capable material because of its low cost, ease of synthesis and high capacitive characteristics [10]. However, the relatively poor cycling life restricts its practical applications. Recently, advancement of nanoscale binding technique provides an innovative route to prepare PANI-based nanocomposites with better performance as electrode material [11]. In the present work, PANI/rGO nanocomposite was prepared by an in-situ chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidizing agent.

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