

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 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 (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) 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 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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## 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)<sub>1-x</sub>(rGO)<sub>x</sub> 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. 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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## Optical Properties of *in-situ* Chemically Synthesized PANI-TiO<sub>2</sub> Nanocomposites

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The present manuscript details on the synthesis of (PANI)<sub>1-x</sub>(TiO<sub>2</sub>)<sub>x</sub> nanocomposite ( $x = 0, 0.02, 0.04, 0.06, 0.08, 0.10$ ) using an *in-situ* chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidant in presence of colloidal anatase TiO<sub>2</sub> nanoparticles at 0-5 °C in air. The X-ray diffraction (XRD) of these specimens revealed amorphous nature of polyaniline which did not change with the addition of TiO<sub>2</sub> nanoparticles during polymerization process. The selected area electron diffraction (SAED) pattern obtained from TEM also indicated the amorphous nature of polyaniline. The TiO<sub>2</sub> nanoparticles exhibit diffraction from multiple lattice planes originating from polycrystalline nature of nanoparticles. The SAED pattern corresponding to the nanocomposite displays lattice planes showing inter planar spacing of 3.56 Å resulting from (101) lattice planes of TiO<sub>2</sub> nanoparticles. To study the vibration mode of PANI and PANI-TiO<sub>2</sub> nanocomposites, Raman spectra was observed. Absorption spectra of the nanocomposite samples have been taken using UV-VIS-NIR spectrophotometer (Varian Cary 5000). The band gap energy ( $E_g$ ) of the nanocomposites was determined using Tauc's relationship. As the content of TiO<sub>2</sub> was increased in the polymer matrix, the shift of the optical band gap was observed.

**Keywords:** X-ray spectra, UV-Vis spectra, Structure of nanoscale materials, Dielectric properties of solids and liquids.

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61.46.-W, 77.22.-d

### 1. INTRODUCTION

The nanocomposites have been explored at great lengths in recent past due to their unique properties which were not available in their constituent materials. Conducting polymers are one such class of materials which exhibit unique electrical, optical and chemical properties, but their usage is limited due to their limited thermal stability. These conducting polymers find application in information storage, optical signal processing, batteries, and solar energy conversion [1-2]. Polyaniline (PANI) is one such conducting polymer, which is a candid photosensitizer due to its low band gap,  $\pi$ - $\pi^*$  transition in which the electron can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), high conductivity, good environmental stability, cheap monomer, and ease of preparation [3-5]. In line with other conducting polymers, PANI also suffers from lesser thermal stability which limits its applications. The synthesis of a composite material of PANI with any other component exhibiting superior thermal stability could present a new material with better characteristics for optoelectronic applications [6].

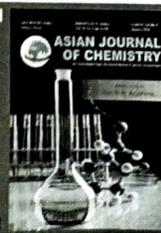
TiO<sub>2</sub> is one such material exhibiting excellent photocatalytic properties along with higher chemical stability, nontoxic and relatively low-price. Titanium (IV) oxide is found in rutile, anatase, brookite three polymorphic forms [7]. Among these forms, rutile and anatase phases are quite popular as a base for the use as pigments, catalysts and in the production of ceramic and

electronic materials. On the other hand, the bottlenecks for TiO<sub>2</sub> usages such as wide band gap (3.2 eV) and low electrical conductance ( $1.1 \times 10^{-5}$ - $3.4 \times 10^{-3}$  Ω/cm) could easily be addressed by mixing it with PANI [8-11]. The anatase TiO<sub>2</sub> is selected in this study which is more efficient as a photocatalyst than rutile form. Further, the clusters of TiO<sub>2</sub> formed during the composite formation can absorb UV energy which makes them suitable for photocatalytic application. The PANI in composite material can be decomposed by oxidation due to the presence of radicals released by irradiation and thus are useful as photocatalyst. Therefore, the contribution of higher conductivity from PANI and higher thermal stability of TiO<sub>2</sub> could complement each other in making new composite material with superior properties [12-14].

### 2. EXPERIMENTAL DETAILS

*In-situ* chemical oxidative polymerization method at lower temperature between 0-5 °C was used for synthesis of PANI, which has been reported earlier [15-16]. The (PANI)<sub>1-x</sub>(TiO<sub>2</sub>)<sub>x</sub> nanocomposite ( $x = 0, 0.02, 0.04, 0.08, 0.10$ ) was prepared by an *in-situ* chemical oxidation polymerization of aniline using ammonium peroxide sulfate (APS) as an oxidant in the presence of an appropriate amount of colloidal TiO<sub>2</sub> nanoparticles at 0-5 °C in air. The obtained powder is washed multiple times and dried in vacuum before the structural, optical and dielectric measurements. The crystallinity of PANI, TiO<sub>2</sub> and PANI-TiO<sub>2</sub> nanocomposites is estimated by X-ray diffractometry (XRD, Bruker AXS D-8

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## Effect of TiO<sub>2</sub> Concentration on Thermal Stability and Dielectric Properties of (PANI)<sub>1-x</sub>(TiO<sub>2</sub>)<sub>x</sub> Nanocomposites

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The current paper deals with investigation of (PANI)<sub>1-x</sub>(TiO<sub>2</sub>)<sub>x</sub> nanocomposites to explore possible material for optoelectronic devices. To investigate the effect of TiO<sub>2</sub> concentration on structural, surface morphology and chemical properties of PANI, samples were characterized by XRD, FTIR, SEM and Raman spectroscopy. The XRD pattern evidence the presence of a blend of anatase and rutile phase of TiO<sub>2</sub> within the PANI matrix which shows amorphous nature of the matrix. FTIR and Raman spectra confirm the formation of PANI/TiO<sub>2</sub> nanocomposites. SEM images show the appearance of lumps into smooth PANI samples with addition of TiO<sub>2</sub> nanoparticles. The thermal and dielectric properties were studied using TGA and Impedance analyzer, respectively. The results showed that the addition of TiO<sub>2</sub> improves the thermal stability, which clearly shows its potential application in optoelectronic devices.

**Keywords:** PANI/TiO<sub>2</sub> nanocomposite, Thermal Stability, Dielectric properties.

### INTRODUCTION

In recent past, the conducting polymers have been employed widely in diverse fields such as chemical and biological sensors, optoelectronic devices (such as solar cell, LEDs, lasers), actuators microelectronic devices and lightweight batteries [1-5]. Polyaniline (PANI) is one of a versatile conducting polymers owing to its unique properties such as high environmental stability, low cost and good electrical conductivity [6-11]. The electrical properties of PANI can be altered by using protonation and/or charge transfer doping [12,13]. Such materials carry utmost importance in integrated electronic circuits such as capacitor and gate oxides. However, the bottleneck of usage of PANI lies in its thermal instability, weak dielectric properties and poor biocompatibility. To eradicate such incompatibility, the nanocomposites incorporating metal oxides could present a better solution due to the higher thermal stability and average conductivity. TiO<sub>2</sub> is one such wide band-gap (3.2 eV) metal oxide with acceptable utility in both optoelectronic and micro-electronic devices applications exhibiting

better mechanical flexibility, thermal and environmental stability [14-18].

Consequently, it is hoped to obtain new materials with complementary behavior between PANI and TiO<sub>2</sub>. The composite structure of PANI and TiO<sub>2</sub> have received much consideration due to dissociation of exciton at the interface of TiO<sub>2</sub> and conjugated polymer [19]. Although there are many studies on PANI/TiO<sub>2</sub> composite structure but most of these reports are still focused on material preparation and morphology characterization, such as size and shape of the oxide particles, degree of dispersion, type of interaction, and interface between the organic and inorganic phase [20,21]. Thermal stability of PANI can be enhanced by introducing TiO<sub>2</sub>. However, addition of TiO<sub>2</sub> decreases the conductivity of nanocomposite [22]. Therefore, the selection of appropriate concentration of TiO<sub>2</sub> must be selected carefully by balancing thermal stability and electrical conductivity. Keeping in mind the expected potential applications of PANI/TiO<sub>2</sub> nanocomposite, thermal and dielectric properties have been discussed in this article with the variation in the concentration of TiO<sub>2</sub> in resulting nanocomposite with PANI.