Synthesis and Characterization of Graphene Oxide, and Reduced Graphene oxide composites with Conducting Polymer

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Abstract - *The synthesis of Graphene oxide (GO) from commercially available graphite powder is demonstrated in this research paper. Via chemical reduction using hydrazine hydrate, the prepared GO is converted to reduced graphene oxide (RGO). Graphene oxide-polyaniline (GO-PANI) and reduced graphene oxide-polyaniline (RGO-PANI) nanocomposites have also been prepared in order to increase the conductivity of GO and RGO. Conducting Polymer-polyaniline was prepared by electrolyte-hydrochloric acid oxidative polymerization and ammonium persulphate was used as an oxidant. The synthesized products were characterized by UV- spectroscopy, Energy-dispersive X-ray spectroscopy (EDXS), Field Emission Scanning Electron Microscope (FESEM) and thermogravimetric analysis (TGA).*

Key Words: Graphene oxide (GO), Reduced Graphene Oxide (RGO), Graphene oxide-polyaniline (GO-PANI), reduced graphene oxide-polyaniline (RGO-PANI)

1. INTRODUCTION

The increasing demand for clean and sustainable energy has driven intensive research efforts toward the development of energy storage and delivery systems. Recent research efforts have been focused on improving the energy density of supercapacitors by exploring novel electrode materials [1]. The tremendous growth in nanotechnology has been occurring because nanomaterials are particularly important in various applications, such as packaging, sensors, and electronic devices [2].

Graphene (G), one of the nanomaterials has become a material of interest for use as nanofillers in enormous composites due to its unique properties, such as high electrical, mechanical and electrochemical properties [2]. These unique features offer great promise for many potential applications. Moreover, certain functionalized graphene-based materials, including functionalized graphene/graphite oxide (GO)/reduced graphene oxide (RGO), exhibit large surface-to-volume ratios. This, together with their superior chemical stability and a broad electrochemical window, renders them as attractive electrode materials for lithium-ion batteries and electrochemical supercapacitor electrodes [3].

Conducting polymers (CPs) can store charges not only in the electrical double layer (EDL) but also through the rapid faradic charge transfer (pseudo capacitance). As a result, the specific capacitance of CP electrodes is higher than that of EDL capacitors based on carbon electrodes [1]. A conducting polymer, doped polyaniline (PANI) is among the most researched materials in these regards due to its cheapness, facile synthesis, presence of functional groups, high environmental stability, tunable conductivity through doping, room temperature operation, thermal and electrochemical stability, and interesting electrical and optical features that are suitable for the mentioned applications [4].

The present study describes methods for the development & characterization of conducting electroactive polymer consisting of GO-PANI & RGO-PANI composites. In this way, important features of PANI would be added to the graphene oxide and reduced graphene oxide composites. Recent researches have revealed this nanocomposite could be a promising material for various applications to make a solar cell, fuel cell, supercapacitor and so many. Is also used in the making of flexible solar cell and textile industries.

- Synthesis of highly fabricated supercapacitor based on GO – PANI and RGO –PANI electrode.
- Characterize the GO-PANI and RGO-PANI with UV-VIS spectroscopy, EDXRs and FESEM.

This route of synthesis has advantages in terms of good yield, short reaction time, neat conditions, and economical.

2. MATERIALS AND METHOD
2.1 Reagent and Chemicals
Graphite powder (Sigma Aldrich), Sulphuric acid (Merck), phosphoric acid (Merck), Potassium permanganate (Rankem), Hydrogen peroxide (Merck), Hydrochloric acid (Rankem), Aniline (Merck), Ammonium persulfate (Sigma Aldrich). All chemicals were used without further purification.

2.2 Experimental
2.2.1 Preparation of Graphene Oxide (GO) solution
GO was synthesized from graphite powder by a modified hummer's method [5]. In a typical synthesis, 1.5 gm of Graphite and 20ml of Phosphoric acid were mixed in 180ml concentrated sulphuric acid in a 100 ml flask, the mixture was stirred for 30 min in the water bath while maintaining vigorous stirring. 9 gm of potassium permanganate was added very slowly to the mixture and the temp was maintained at $\sim35^0 – 40^0C$. The reaction progressed the mixture gradually become pasty and the Colour turned light

brownish. Further 30 ml water was slowly added to the paste with vigorous agitation. The reaction temperature rapidly increases up to 90^0C and the colour changed to yellow. The aqueous suspension was stirred at 90^0C for 24 hrs. Then 10 ml of 30% hydrogen peroxide was added to the mixture for purification the mixture was washed by rinsing and centrifugation (9000 rpm for 30 min) with 12% hydrochloric acid and deionized water (DI) for several times. The product was evaporated and GO was obtained.

2.2.2 Preparation of Reduced GO

(Same procedure was used i.e., Hummer's method for reduced GO, an only reducing agent for the preparation of RGO was hydrazine hydrate) GO was synthesized from graphite powder by a modified hummer's method [5]. In a typical synthesis, 1.5 gm of Graphite and 20ml of H_3PO_4 were mixed in 180 ml concentration sulphuric acid in a 100 ml flask, the mixture was stirred for 30 min in the bath while maintaining vigorous stirring. 9 gm of potassium permanganate was added very slowly to the mixture and the temp was maintained at $\sim 35^0$ – 40^0C. The reaction progressed the mixture gradually become pasty and the colour turned light brownish. Further 30 ml water was slowly added to the paste with vigorous Agitation. The reaction temperature rapidly increases up to 90^0 C and the colour changed to yellow. The aqueous suspension was stirred at 90^0C for 24 hrs. Then 10 ml of 30% hydrogen peroxide was added to the mixture for purification the mixture was washed by rinsing and centrifugation (9000 rpm for 30 min) with 12% hydrochloric acid and deionized water (DI) several times. The product was evaporated and obtained GO. And after that for reduction of GO, hydrazine hydrate was used as a reducing agent. 7 ml hydrazine hydrate added to the solution of GO, stirred continuously and give the temp was set at 40^0-45^0C for 24 hours. The product was washed with ethanol/acetone, filtered and dried [7].

2.2.3 Preparation of Polyaniline solution

Polyaniline nanofibers were prepared by chemical oxidative polymerization of aniline in an acidic solution containing 1.5 M oxalic acid. Polymerization was initiated by dropwise addition of oxidizing agent ammonium persulfate (A.P.S.) to the acidified solution containing the aniline at 0-10^0 C temperature with continuous stirring. After completion of polymerization, the stirring was continued for 36 hours at room temperature. The final product was filtered washed and dried. During filtration, a colorless filtrate was obtained as the conformation of complete polymerization [8, 9].

2.2.4 Synthesis of GO-PANI

In a typical procedure, 0.125 mg of GO powder was added into 50 ml distilled water and ultra-sonicated. Until GO was uniformly dispersed. A certain amount of aniline monomer 0.25 M has then added into the above solution and sonicated for 30 min at room temperature. In another beaker ammonium persulfate, (A.P.S.) 0.1M (1.14gm) was dissolved in 50 ml water. The solution of APS was then added rapidly to the 50 ml of 0.5 M HCl. To form a homogenous mixture of GO and aniline monomer the above solution of ammonium persulfate was added drop by drop solution GO and aniline monomer. The mixture was stirred at suitable temperature and pressure with magnetic stirring. The time was controlled to 4 hours for all samples and then the system was depressurized. The nanocomposite was collected by centrifugation and repetitively washed with water and ethanol several times. This product was dried at 60^0 C for 24 hours under vacuum. [For comparison, the PANI was synthesized chemically in the absence of GO via the similar procedure above] [10].

2.2.5 Synthesis of RGO-PANI

In a typical procedure, 0.125 mg of GO powder was added into 50 ml distilled water and ultra-sonicated. Until GO was uniformly dispersed. A certain amount of aniline monomer 0.25 M has then added into the above solution and sonicated for 30 min at room temperature. In another beaker ammonium persulfate, (A.P.S.) 0.1M (1.14gm) was dissolved in 50 ml water. The solution of APS was then added rapidly to the 50 ml of 0.5 M HCl. To form a homogenous mixture of GO and aniline monomer the above solution of ammonium persulfate was added drop by drop solution GO and aniline monomer. The mixture was stirred at suitable temperature and pressure with magnetic stirring. The time was controlled to 4 hours for all samples and then the system was depressurized. The nanocomposite was collected by centrifugation and repetitively washed with water and ethanol several times. This product was dried at 60^0 C for 24 hours under vacuum. [For comparison, the PANI was synthesized chemically in the absence of GO via the similar procedure above] [10].

2.2.6 UV –VIS Spectroscopy

UV visible spectroscopy is used to confirm the preparation of Graphene Oxide and their composite by confirming the absorption of the final product and their composites. The common solvent use for preparing the sample to be analyzed is either ethyl alcohol or hexane.

2.2.7 Field Emission Scanning electron microscope (FESEM)

FESEM was performed to evaluate the morphology of the synthesized product. FESEM was performed using Hitachi FESEM s-4800 in the characterization lab of North Maharashtra University, Jalgaon.

2.2.8 Energy Dispersive X-Ray Spectroscopy

EDXRs was used to obtain the elemental composition of the synthesized product. The Weight % of the element present in the composition in the material was analyzed.

2.2.9 Thermogravimetric Analysis (TGA)

The Thermogravimetric Analysis (TGA) used for the analysis of the graphene samples. TA Instruments and all the measurements were performed in the air increasing the temperature 5 degrees per minute. The TGA was employed

to obtain an estimation of the mass of the different components in the composite materials.

3. RESULT AND DISCUSSION

3.1 UV –VIS Spectroscopy

UV-Vis spectra of GO, RGO, GO-PANI and RGO -PANI were obtained in ethanol or hexane. All synthesized products show the different absorbance maximum suggest all products are different. Overlain spectra is shown in Figure 1.
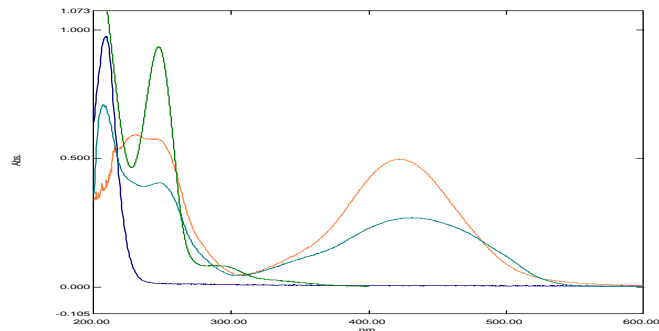

Figure 1: Overlain spectra for GO, RGO, GO-PANI and RGO -PANI

3.2 Field Emission Scanning electron microscope (FESEM)

Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy (SEM), field emission SEM (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nanometers – three to six times better.

The layered structure of the stacked GO sheets can be seen from the FESEM image shown in Figure 2 (A-1). The SEM image Figure 2 (A-4) showed a typical single layer GO sheet with a lateral dimension of several micrometres. As for the GO-PANI composite, a flat and layered structure can be clearly seen from Figure B and C series samples with PANI fibers sandwiched between the GO sheets and on the GO surfaces.
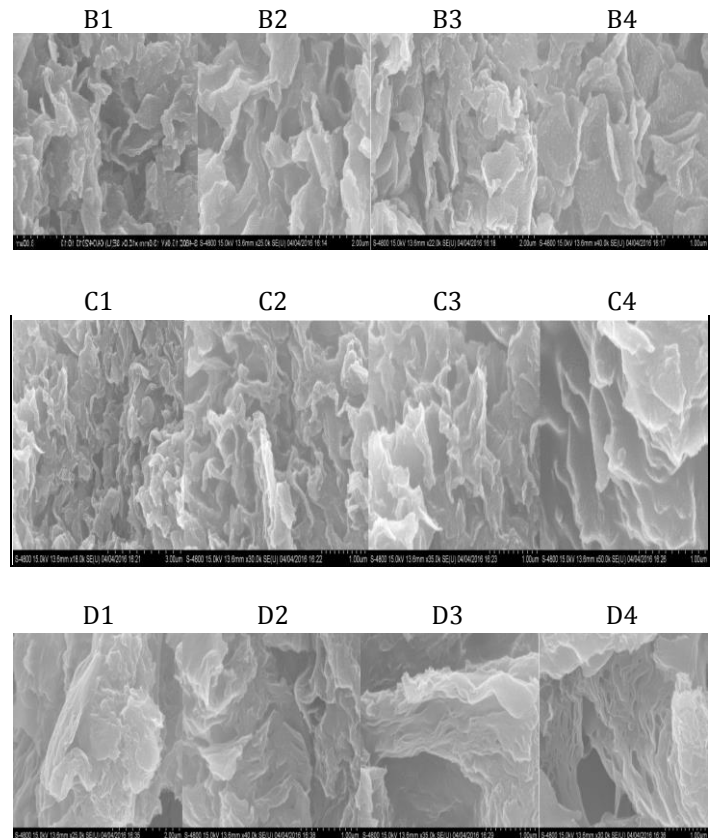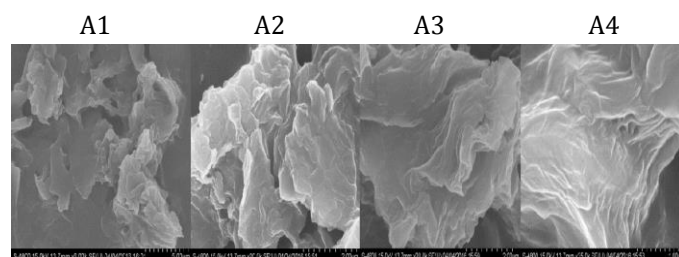

Figure 2: FESEM Image of synthesized products

In addition, the morphology of the conducting polymer can be controlled by varying molarity of PANI. The layered structure of the stacked RGO sheets can be seen from the FESEM image shown in Figure D-1. The SEM image (Figure D-4) showed a typical single layer RGO sheet with a lateral dimension of several micrometres. As for the RGOPANI composite, a flat and layered structure can be clearly seen from Figure E and F series samples with PANI fibers sandwiched between the RGO sheets and on the RGO surfaces.

3.3 Energy Dispersive X-Ray Spectroscopy:

The EDXS data shown in figs reveal the presence of graphene oxide and graphene on the basis weight% of the elements presents in the composition of material.
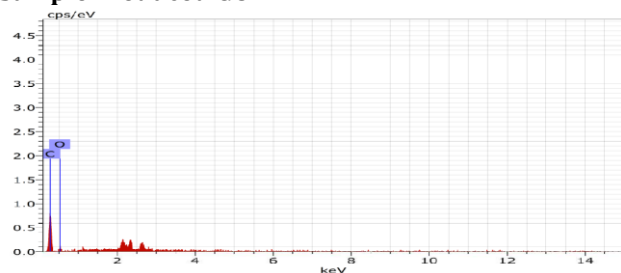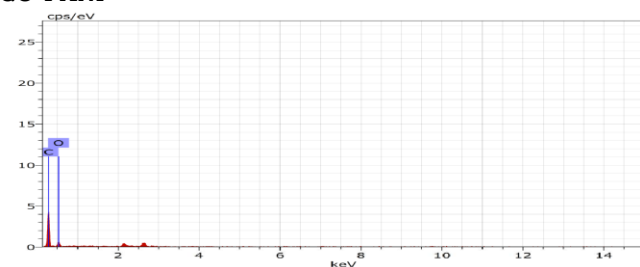
Sample-A pure GO
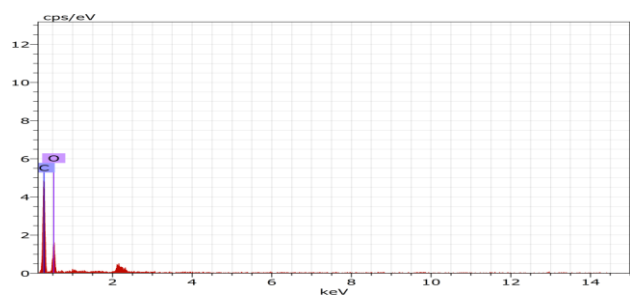
Above graph of GO reveal that wt. % of carbon is 61.22 and Oxygen is 38.78
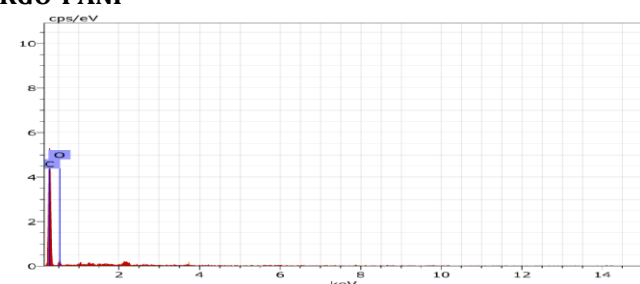
Sample- Reduced GO

In this sample wt. % Carbon is 76.77% and Oxygen is 23.23.

GO-PANI

From the results, it reveals that in this sample the wt. % of Carbon and Oxygen is 74.45 and 25.55 respectively.

RGO-PANI

In this Composition, wt. % Carbon is 86.00 and Oxygen is 14.00.

EDXS techniques can thus confirm the composition of elements of the synthesized product.

3.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the materials showed major weight losses between 150 and 300 °C, which Correspond to CO, CO2, and steam from the most labile functional groups. Between 400 and 750 °C, a slower mass loss was observed and can be attributed to the removal of more stable oxygen functionalities.

Although GO is thermally unstable and starts to lose mass upon heating even below 100 C, the major mass loss occurs at 200 C, presumably due to pyrolysis of the labile oxygen-containing functional groups, yielding CO, CO2, and steam. Hence, the thermal decomposition of GO can be accompanied by a vigorous release of gas, resulting in a rapid thermal expansion of the material. These evident by both a large volume expansion and a larger mass loss (from flying GO debris in the TGA instrument) during a more rapid heating regime. On the other hand, the removal of the thermally labile oxygen functional groups by chemical reduction results in much increased thermal stability for the reduced GO. Apart from a slight mass loss below 100^0 C, which can be attributed to the loss of adsorbed water, no significant mass loss is detected when this material is heated up to 600 C.

4. CONCLUSION

The present study describes methods for the production and characterization of electroactive polymer conducting composites consisting of GO-PANI & RGO-PANI. In this way, essential features of PANI are applied to the composites of graphene oxide and reduced graphene oxide. Recent research has shown that this nanocomposite may be a promising substrate for different solar cell applications.

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BIOGRAPHIES

The author has four years of teaching experience at RC Patel Polytechnic College, Shirpur. She is University Topper at North Maharashtra University, Jalgaon, with gold medal in Physics. She served at DST INSPIRE CAMP as resource person. She has conducted online workshops for Diploma students.