Proceedings of the Technical Sessions, 32 (2016) 55-60
Institute of Physics – Sri Lanka

Synthesis and Characterization of polyaniline/SnO_2/Graphene Nano Composites

M.T.V.P. Jayaweera [1,2], W.L.N.C. Liyanage[2], D.D.N.B Daya[2], S.R.D. Rosa[2], and I.R.M. Kottegoda[1]

[1]*Materials Technology Section, Industrial Technology Institute, Colombo 07, Sri Lanka.*
[2]*Department of Physics, University of Colombo, Colombo 03, Sri Lanka.*

ABSTRACT

Graphene is single layer of sp^2 carbon lattice which has remarkable properties. Lots of research works are being carried out based on graphene because of some special properties. Graphene based composites have also been paid much attraction due to superior performance in various applications. In general, the multifunctional hybrid materials are more capable than those based on pure material. Polyaniline (PANI) is a conducting polymer which is easy to synthesis, low cost and has a good electrical conductivity. Tin oxide (SnO_2) is an n-type semiconductor with a wide band gap of 3.6 eV. As an efficient hybrid material, the present study focuses on preparation of Graphene-SnO_2-Polyaniline (GSP) composite using an efficient one pot synthesis. In this method, Sn (II) Chloride is involving in reducing graphite oxide into graphene oxide while forming SnO_2 in the composite.

The composite was characterized with X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Raman Spectroscopy. In XRD patterns a strong peak observed at $2\theta = 9.66^0$ confirmed that Graphite is completely converted into GO. For GSP sample at $2\theta = 26.7°$, 33.6°, 51.8°, 65.9° confirmed that SnO_2 is formed in the composites. In FTIR analysis peaks at 1294, 1132 and 799 cm^{-1} corresponding to stretching vibrations of C-N, C=N and C-C in the benzenoid ring confirmed that Polyaniline (PANI) is formed in GSP composite. In Raman Spectroscopy the peak at around 1344 cm^{-1} (D band) is related to the defects and disordering in the hexagonal structure, while the 1597 cm^{-1} peak (G band) is due to the vibration of sp^2-bonded carbon atoms in a 2D hexagonal lattice which represent the Graphene indicating successful reduction of GO.

1. INTRODUCTION

In modern day world with increasing demand for renewable energy resources, scientists have great interest in more efficient and high capacitance devices. Great deal of attention is therefore made to synthesize novel composite materials for various applications using immerging materials such as graphene, semiconductors and polymers.

Polyaniline (PANI) is one of the most intensively studied conducting polymers. Its physical, chemical and optical properties such as good electrical conductivity, high environmental stability, low cost, flexibility, light weight and facile fabrication makes it a suitable candidate for a wide range of applications like supercapacitors, sensors, batteries, electromagnetic interference (EMI) shielding and electronic devices[1]. Conducting polymers can be prepared by electrochemical or chemical oxidation of corresponding monomers in various organic solvents and/or in aqueous media[2].

Polyaniline is most often prepared by oxidation of aniline by ammonium peroxodisulfate in acidic aqueous environment. Polyaniline is thermally stable up to 250 °C[2].

Graphene is a single layer of sp^2 carbon lattice which has remarkable properties, such as large specific surface area ($2630\ m^2g^{-1}$), high mobility of the charge carriers ($2 \times 10^5 cm^2V^{-1}s^{-1}$), high chemical stability and high elasticity[3]. Due to these special properties, lots of research works are carried out based on graphene for various applications such as sensors, transistors, nano electronics, super capacitors and some energy storage devices.

Tin oxide (SnO_2) is an n-type semiconductor with a wide band gap of 3.6 eV[4]. The SnO_2 is considered as one of the promising metal oxides for miscellaneous applications due to its high capacitance value, low cost and non-toxicity[5].

As an efficient hybrid material, Graphene-SnO_2-Polyaniline (GSP) composite was synthesized from graphene, SnO_2 and Polyaniline using an efficient one pot synthesis. Due to remarkable properties of these elements the newly synthesized composite(GSP) will be a promising renewable energy storage device like batteries, super capacitors and some application of gas sensors in the future.

2. EXPERIMENTAL

2.1 Synthesis of Graphene/SnO_2/Polyaniline (GSP) nanocomposite

Graphite Oxide (GO) 400 mg was mixed in 150 ml distilled water and 3g $SnCl_2.2H_2O$ (weight ratio of GO: $SnCl_2.2H_2O$ is 1:7.5) added to the solution while solution was stirred. Then the solution was sonicated for 3 h[4]. The solution showed a colour change from light brown to black after sonication for 1h 30min. pH value of the solution was set to 1.5. Initial pH value was observed as 0.88 and by adding few drops of NH_4OH to the solution, final pH value was set to 1.5. Then 3.915 ml of pure Aniline was added to the solution while the solution was in an ice bath. Temperature of the solution when Aniline was adding was 4-6 ^{0}C. Then 9.78 g of $(NH_4)_2S_2O_8$ was added slowly into the solution and stirred for 24 h. The solution quickly turned into black-green colour after adding $(NH_4)_2S_2O_8$. Finally, solution was centrifuged at 3900 rpm for 12 minutes and supernatant was decanted away. Remaining solid material was washed with distilled water for 3 times and after that with Ethanol at last. Then the process was followed by centrifugation at 3900 rpm for 12 minutes and supernatant was decanted away. Solid material obtained was dried for 12 h at 60 ^{0}C.

2.2 Characterization

X-ray diffraction (XRD) characterization was performed on the resulting powder with Regakuultima VI, X-ray Diffractometer using Cu K_α (λ= 1542 Å) radiation to analyze the structure of the sample. Crystallographic information was obtained with the aid of the ICSD data base. Scanning electron microscopic tests (LEO 1420 vp) were carried out to study the formation of PANI-Gn-SnO_2 nano material with maximum enabled instrument resolution. The Fourier Transformed Infrared spectroscopy (FTIR) (Bruker Tensor 27) was carried out to determine formation of the atomic bonds in composites. Raman spectroscopy was carried out using a JOBIN YVON HR800 Confocal Raman system with 632.8 nm diode laser excitation of a 300 lines/mm grating at room temperature.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD) Analysis

XRD is used to verify the formation of lattice structure of the composite. Figure 1(a) shows the XRD patterns of GO. A strong peak observed at $2\theta = 9.66^0$ confirmed that Graphite is completely converted into GO. Fig. 1(b) shows the XRD patterns of GSP. The diffraction peak corresponding to GO is disappeared and new broad peaks are observed for GSP sample at $2\theta = 26.7°$, 33.6°, 51.8°, 65.9° which are attributed to the (1 0 0), (1 0 1), (2 1 1) and (1 1 2) planes of tetragonal rutile SnO_2, indicating the formation of crystalline SnO_2.

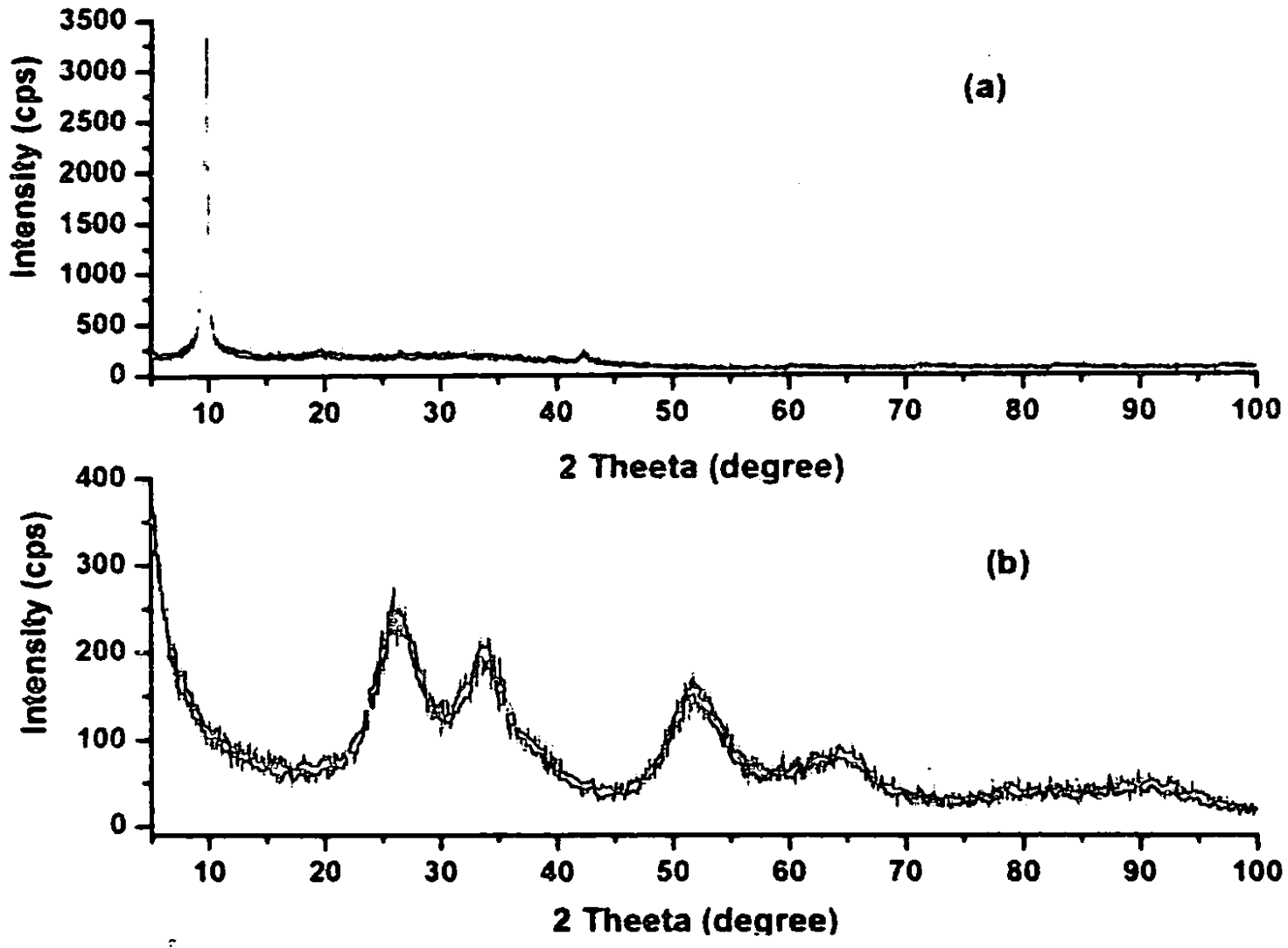

Figure 1: X-ray powder diffraction (XRD) patterns of (a) GO (b) GSP composite

The diffraction peaks of GSP are broad indicating that SnO_2 particles are nanosized [6]. This confirms the oxidation of Sn^{2+} to Sn^{4+} and concurrently reduces the GO to Graphene. The diffraction peak of Graphene and main peak of SnO_2 are at about $2\theta=26°$ and therefore possible to be overlapped due to the low intensity of XRD peak. Therefore the presence of the Graphene was not clearly visible. Thus the presence of graphene and Polyaniline is not clearly asserted by XRD.

3.2 Scanning Electron Microscopy (SEM)

The surface morphology and microstructure of the Graphene/SnO_2/PANI (GSP) sample were investigated by scanning electron microscopy (SEM). Although the presence of Graphene is not clear, the presence of SnO_2 nano particles is clearly visible in the image as a flower like structure. This kind of morphology gives higher surface area which gives possibility to use the composite in applications like supercapacitors, sensors and batteries.

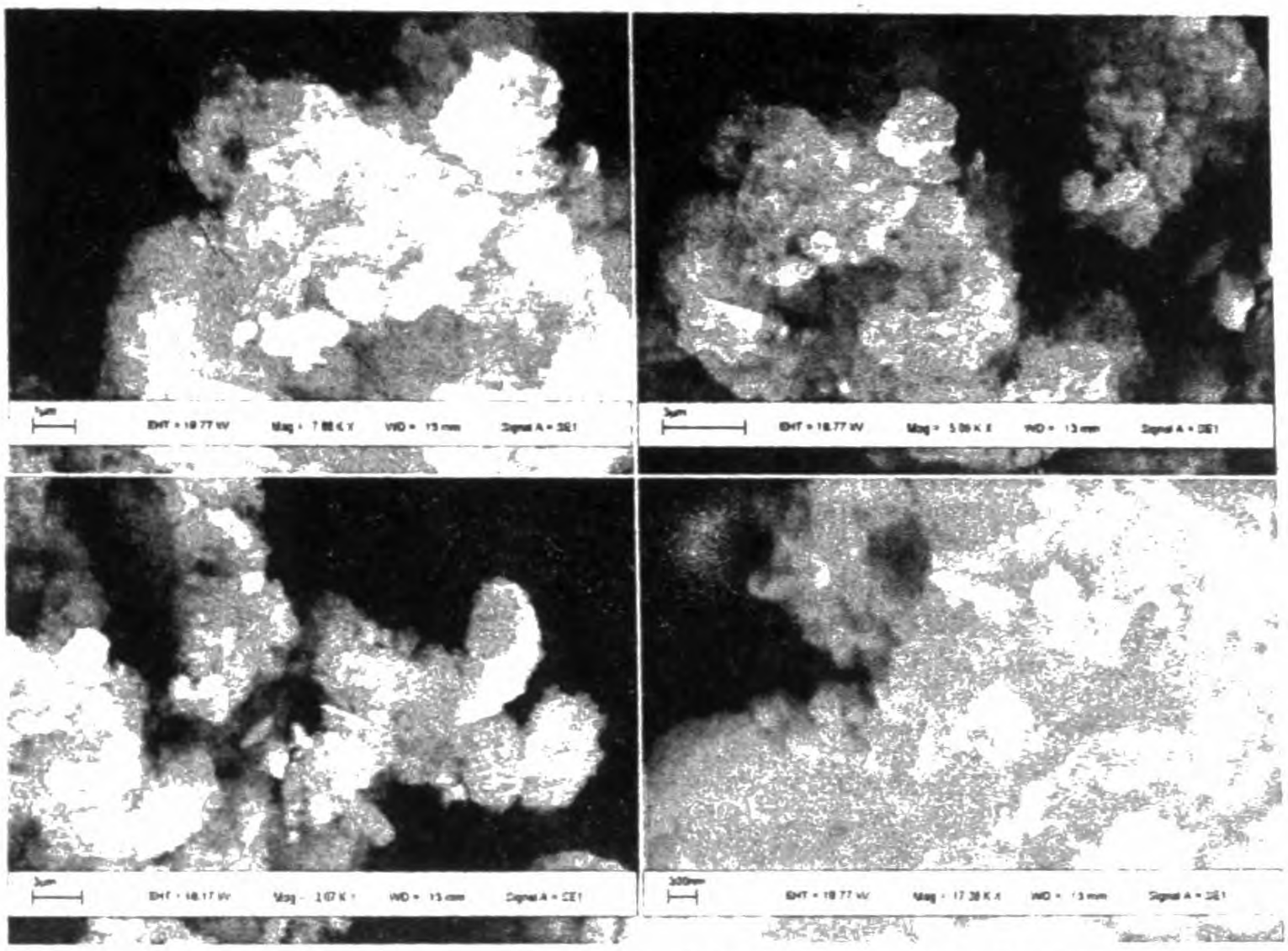

Figure 2: Scanning Electron Microscopy (SEM) images of the GSPcomposite

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

GSP composite is characterized by using FTIR-ATR spectrometer. Although the presence of Graphene and PANI is not detected through XRD, their presence is verified by the FTIR as shown in Figure 3.

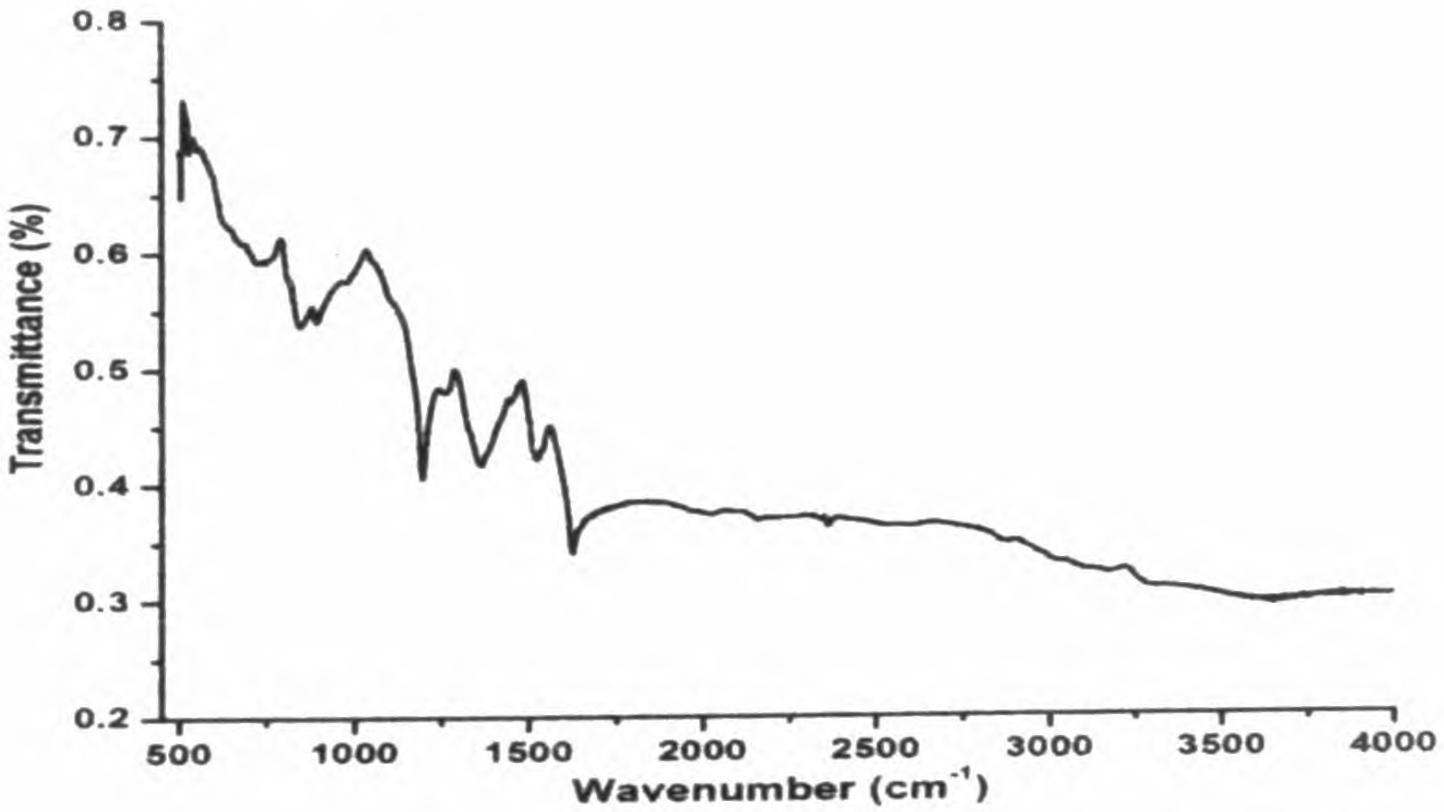

Figure 3: FTIR spectra of the GSPcomposite

Sn^{+2} has reduced GO to Graphene and it is found that sp^2-hybridized C=C peak of reduced Graphene at the band 1556 cm^{-1}in composite and peaks at 1294, 1132 and 799 cm^{-1} correspond to stretching vibrations of C-N, C=N and C-C in the benzenoid ring confirming that Polyaniline (PANI) is formed in GSP composite. At 1242 cm^{-1} sharp peak corresponds to C-O-C stretching indicates that remaining epoxide groups are in reduced Graphene. The peaks present at 515 cm^{-1} and 510 $cm^{-1}$are characteristic vibration modes of Sn-O, which indicates the formation of SnO_2. Therefore, the FTIR results clearly demonstrate the successful formation of SnO_2, PANI and Graphene ternary composite.

3.4 Raman Spectroscopy

Raman spectroscopy is a powerful non-destructive technique to study Graphene and its composites. Raman spectroscopy of GSP composite is shown in Fig. 4. The peak at around 1344 cm^{-1} (D band) is related to the defects and disordering the hexagonal structure, while the 1597 cm^{-1} peak (G band) is due to the vibration of sp^2-bonded carbon atoms in a 2D hexagonal lattice which represent the Graphene indicating the successful reduction of GO. The intensity ratio of the D-band to the G-band (I_D/I_G) generally reflects the degree of graphitization of Graphene and the defect density. The calculated I_D/I_G ratio is 0.96. The relatively high I_D/I_G ratio for GSP composite is contributed by the presence of oxide functional groups on the basal plane and edges. Also this increment of the I_D/I_G ratio is due to the presence of SnO_2 nano size particles on the Graphene sheets. However, both Raman and the FTIR spectra of the composite show formation of Graphene with functionalities rather than pure Graphene. The material can be regarded as reduced Graphene oxide rather than Graphene although for simplicity we refer it as Graphene. Application of the novel GSP composite as supercapacitors is being investigated where preliminary results are promising and would be published separately.

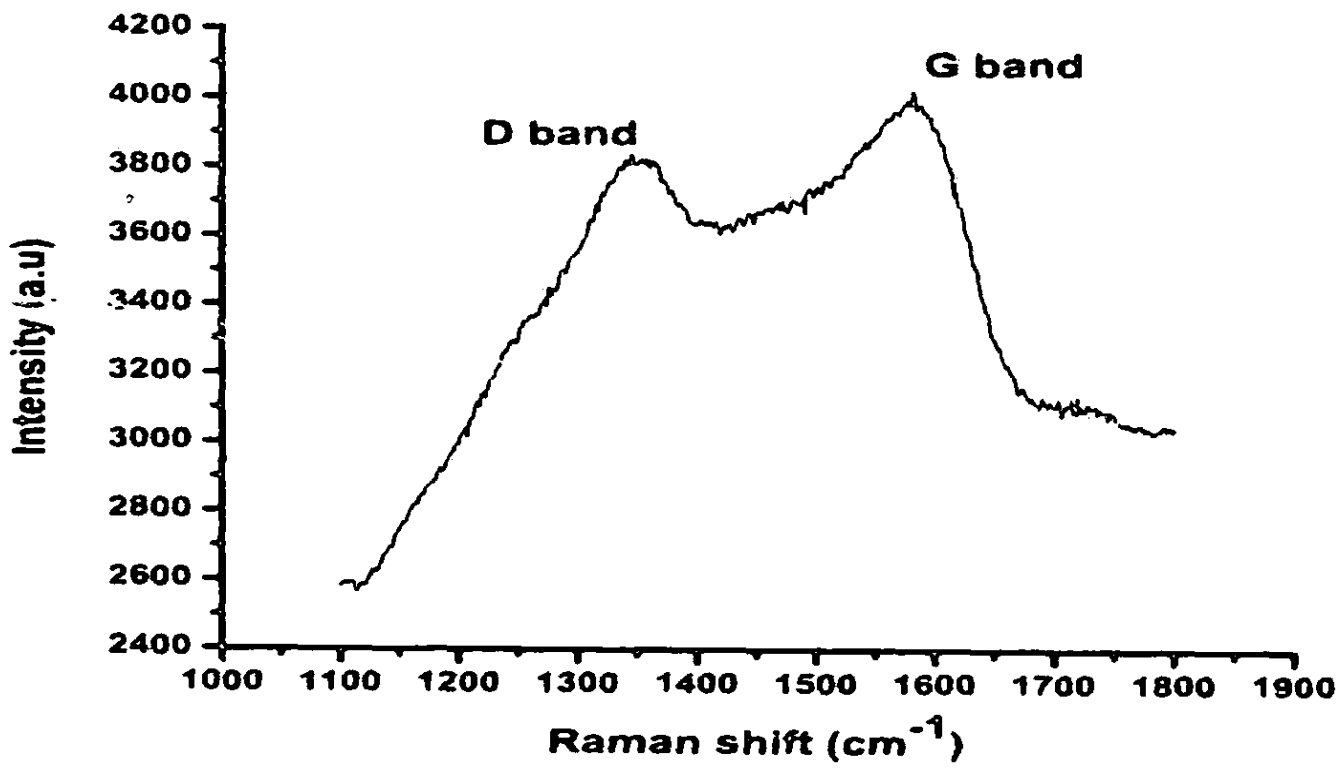

Figure 4: Raman spectra of the GSP

4. CONCLUSIONS

The novel Graphene/SnO_2/Polyaniline composite is successfully prepared using one pot synthesis method and the novel composite would be suitable for various applications such as supercapacitors.

ACKNOWLEDGEMENT

The financial support is provided by NRC Grant (No. 12-022).

REFERENCES

[1] Patil, R.B., et al., *Effect of pH on the properties of chemical bath deposited polyaniline thin film.* Applied Surface Science, 327 (2015) 201-204.

[2] Jaymand, M., *Recent progress in chemical modification of polyaniline.* Progress in Polymer Science, 38(9) (2013) 1287-1306.

[3] Liu, Y.-Z., et al., *A one-pot method for producing ZnO–graphene nanocomposites from graphene oxide for supercapacitors.* Scripta Materialia, 68(5) (2013) 301-304.

[4] Lim, S.P., N.M. Huang, and H.N. Lim, *Solvothermal synthesis of SnO2/graphene nanocomposites for supercapacitor application.* Ceramics International, 39(6) (2013) 6647-6655.

[5] Jin, Y. and M. Jia, *Design and synthesis of nanostructured graphene-SnO2-polyaniline ternary composite and their excellent supercapacitor performance.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 464 (2015) 17-25.

[6] Zhong, C., et al., *SnO2–Graphene Composite Synthesized via an Ultrafast and Environmentally Friendly Microwave Autoclave Method and Its Use as a Superior Anode for Lithium-Ion Batteries.* The Journal of Physical Chemistry C, 115(50) (2011) 25115-25120.