(IJIRSE) International Journal of Innovative Research in Science & Engineering
ISSN (Online) 2347-3207

Structural And Electrical Properties of Poly(o-anisidine)/Graphene Nanocomposite

D. Sangamithirai[1], I. Inigo Valan[1], V. Narayanan[2], A. Stephen[1*]
[1]Department of Nuclear Physics, Guindy Campus, University of Madras, Chennai – 600025, India
[2]Department of Inorganic Chemistry, Guindy Campus, University of Madras, Chennai – 600025, India
Corresponding author – stephen_arum@hotmail.com

Abstract-**A new class of nanocomposite material based on poly(o-anisidine) and graphene (POA/GR) with a molar ratio of 1:1 is synthesized via chemical oxidative polymerization of o-anisidine in the presence of graphene sheets in acidic medium has been reported. The polymer nanocomposite is characterized by FTIR, UV-VIS and Impedance spectroscopy techniques. In FTIR spectra, the presence of vibration bands of the dopant ion and other characteristic bands confirmed the nanocomposite is in conducting emeraldine salt phase. In UV-Vis technique, the peak appearing at 865 nm confirms the formation of emeraldine salt phase of the polymer. The impedance spectroscopic studies show that conductivity increases for POA/GR nanocomposite and reaches a maximum of 3.3 x 10^{-3} S cm^{-1} at room temperature.**

Keywords- conducting polymer, graphene, conductivity.

I. INTRODUCTION

Conducting polymers are attractive materials for a variety of advanced technologies as they possess conjugated π-bonds. Among the conducting polymers, polyaniline (PANI) which is the unique and promising candidate has received a great deal of attention in recent years due to its ease of synthesis, low cost, good environmental stability, high electrical conductivity and wide applications in field- effect transistors, integrated circuits, batteries, electrical or optoelectronic devices and sensors [1]. Nevertheless, the practical use of PANI has been limited due to its insolubility in common organic solvents and infusibility, resulting in poor processability. Efforts have been made to improve the processability of polyaniline by using appropriate functionalized protonic acids or substituted PANI [2]. In the later approach a suitable substituent is attached either at the nitrogen atom or in the phenyl ring of the repeat units. Among the substituted PANI derivatives, poly(o-anisidine) can be easily synthesized either chemically or electrochemically with higher processability and solubility as compared with PANI [3].

The polymers of subsitituted derivatives of aniline exhibit slightly lower conductivity than that of unsubstituted PANI. In order to alleviate this limitation, the combination of PANI with other nanomaterials, such as carbon material might be a good choice. As a new member of carbon nanomaterials, graphene has been proven as an excellent support material due to its high surface area-to-volume ratio, remarkable mechanical stiffness and excellent electrical conductivity which is very beneficial in designing catalysis and sensors [4].Impedance spectroscopy is a very useful technique in solid state electronic system, because it can resolve the conduction components by differentiating between the transport properties of complex systems. This work reports on the synthesis of POA/GR nanocomposite by chemical oxidative polymerization method, where graphene was obtained via a modified Hummers method. The study shows the synthesis and characterization of POA/GR nanocomposite by FTIR, UV-VIS and Impedance spectroscopy techniques.

II. EXPERIMENTAL

A. Materials

The monomer o-anisidine (99%) was distilled under reduced pressure. Ammonium peroxydisulfate (98%), β-napthalenesulphonic acid (70%), graphite (98%), H_2SO_4 (99%), $KMnO_4$ (99%), hydrazine were all of AR grade and used without further purification.

B. Experimental Section

Graphite Oxide (GO) was synthesized through graphite oxidation with sulphuric acid and potassium permanganate (H_2SO_4-$KMnO_4$). Reduction of GO to graphene was achieved via refluxing GO with hydrazine sulphate. The POA/G nanocomposite was chemically synthesized by oxidative polymerization of o-anisidine using ammonium peroxydisulfate $[(NH_4)_2S_2O8]$ under controlled conditions. The o-anisidine to graphene ratio was kept at 1:1 ratio and added in 1M β-napthalenesulphonic acid (β-NSA) solution, where the solution was cooled to 5˚C in an ice bath. Ammonium peroxydisulfate(0.025M) was also dissolved in 200ml of 1M β-NSA solution was precooled to 5˚C. Later, $[(NH_4)_2S_2O_8]$ in 1M β-NSA solution was added slowly in the o-anisidine solution, and the reaction was continued for 48h. The resultant precipitate of the POA/G nanocomposites recovered from the reaction vessel was filtered, and washed using deionized water and acetone as non-solvent to remove any impurities. Further, this precipitate was heated at 60 °C [5] in a temperature-controlled oven. The polymer nanocomposite was characterized by FTIR, Raman and XRD techniques.

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy

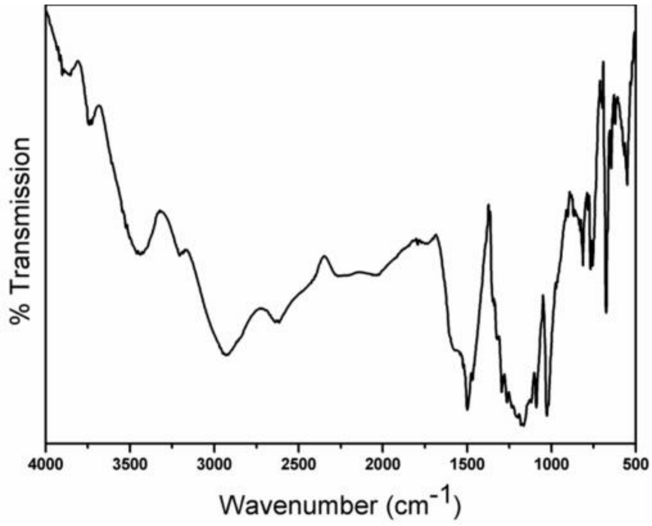

Figure 1. FTIR spectrum of POA/GRnanocomposite

The FTIR spectrum of POA/GR nanocomposite is shown in Figure 1. The characteristic peaks of POA/G composite are observed at about 3722, 3210, 2887-3051, 1505-1571, 1700, 1454, 1303, 1212, 1123, 1027, 825, 750, 665 cm^{-1}. The peaks at 3210 cm^{-1}, 3051 cm^{-1}, 3722 cm^{-1} are attributed to the N-H, C-H, O-H stretching vibration of POA ring. The band at 1454 cm^{-1} is assigned to the C-H bending of $–OCH_3$ group. The bands at 1571 and 1505 cm^{-1} were attributed to the stretching mode of C=C for the quinoid and benzenoid rings [5]. The bands at 1571 cm^{-1} shows that the polymer is composed of amine unit. The band at 1303cm^{-1} is assigned to the emeraldine base structure. The band at 1212 cm^{-1} is assigned to the stretching of secondary aromatic amine. The band at 1027 cm^{-1} corresponds to C-O stretchings of methoxy group. The band at 1123 cm^{-1} is due to SO_3^- group of the β-NSA indicates the efficient doping of POA [6]. The band at 825 cm^{-1} is attributed to the 1,2,4-substitution in the benzenoid rings. The band at 665 cm^{-1} is assigned to C-H out-of-plane ring deformation vibration. The band at 750 cm^{-1} is out-of-plane C-H bending vibration. It should be noted that, the peak due to C=O group within the POA/GR has been downshifted to 1700 cm^{-1}, which is probably due to π-π interactions and hydrogen bonding between graphene and POA rings indicating that the carboxyl groups from graphene acted as efficient dopants in polymerization.

B. UV-Vis Spectroscopy

Figure 2 shows the UV-Vis spectrum of the synthesized POA/GR nanocomposite. The UV-Vis spectrum of POA/GR shows a strong absorption band at 284 nm and a shoulder band around 314 nm. These bands are assigned to the π- π* transition centred on the benzenoid rings (interband transition) [7]. The observed peak at 613 nm is because of n- π* transition from the non-bonding nitrogen lone pair to the conduction band (π*). The peak appearing at 865 nm corresponds to the formation of emeraldine salt phase of the polymer. The peak appearing at 268 nm corresponds to theπ - π* transition of graphene.

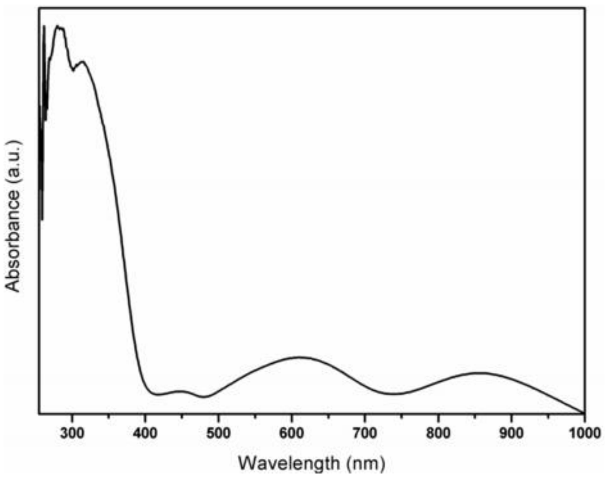

Figure 2. UV-Vis spectrum of POA/GRnanocomposite

C. Impedance Spectroscopy

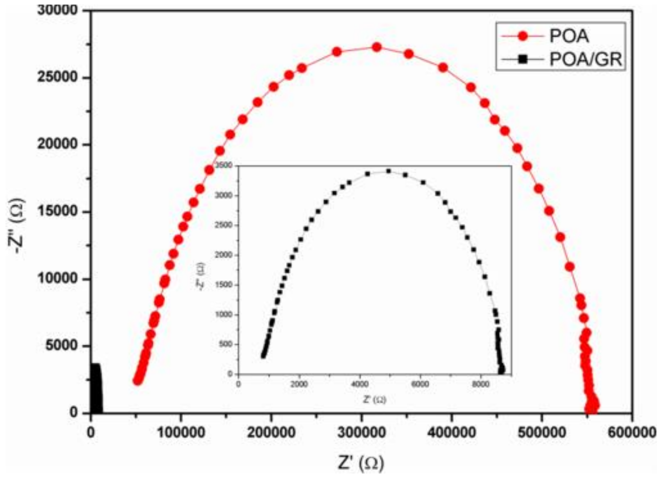

Figure 3. Nyquist plots

Figure 3 shows the typical impedance (Z=Z´+jZ´´) plane plots between real (Z´) and imaginary (Z´´) parts of impedance for POA and the nanocomposite POA/GR. The electrical conductivity of bare POA is found to be 1.28 x 10^{-6} S cm^{-1}. The lower conductivity relative to polyaniline may be explained by an increase of the interchain distance and diluting effect of the charge carriers caused by the presence of bulky methoxy group in the polymer[8]. The substituent present at the ortho position of the benzene ring induces additional deformation along the polymer backbone. This in turn results in a decrease of the degree of conjugation and hence a decrease in conductivity. The value of conductivity is increased to a maximum of 3.3 x 10^{-3} S cm^{-1}at room temperature. It is found that, the real part of impedance of POA/GR nanocomposite shows about tenfold increase as compared with the bare POA. The incorporation of graphene nanosheets in POA reduces the charge trapping centres, thereby leading to a large number of charge participation which increases the conductivity of the composite.

IV. CONCLUSION

In summary, a novel POA/G multifunctional nanocomposite was successfully synthesized by oxidative polymerization of o-anisidine in the presence of graphene nanosheets. In FTIR spectra, the presence of vibration band of the dopant ion and other characteristic bands confirmed that the POA/G nanocomposite is in conducting emeraldine salt phase. The real part of impedance of POA/GR nanocomposite shows a more than tenfold increase as compared with bare POA which increases the sensitivity of the technique.

ACKNOWLEDGEMENT

D.S. thanks DST,New Delhi for the financial support received in the form of INSPIRE fellowship. The authors thank SAIF, IIT, Chenai, India for material characterization.

REFERENCES

[1] Anjali A. Athawale, Milind V. Kulkarni, Polyaniline and its substituted derivatives as sensor for aliphatic alcohols, Sensors and Actuators B 67 2000 173–177

[2] Valter Bavastrello, Victor Erokhin, Sandro Carrara, Francesca Sbrana, Davide Ricci, Claudio Nicolini, Morphology and conductivity in poly(ortho-anisidine)/carbon nanotubes nanocomposite films, Thin Solid Films 468 (2004) 17–22

[3] Dewyani Patila, Pradip Patil, You-Kyong Seo, Young Kyu Hwang, Poly(o-anisidine)–tin oxide nanocomposite: Synthesis, characterization and application to humidity sensing, Sensors and Actuators B148 (2010) 41–48

[4] Sergio H. Domingues,Rodrigo V. Salvatierra, Marcela M. Oliveirab and Aldo J. G. Zarbin, Transparent and conductive thin films of graphene/polyaniline nanocomposites prepared through interfacial polymerization, Chemical Communication, 2011,47, 2592–2594

[5] Satish Bykkam, Venkateswara Rao K., Shilpa Chakra CH. and Tejaswi Thunugunta, synthesis and characterization of graphene oxide and its antimicrobial activity against klebseilla and staphylococcus, International Journal of Advanced Biotechnology and Research, 4(2013), 142-146

[6] Liyuan Zhang, Haiying Wang, Wanting Yu, Zhen Su, Liyuan Chai, Jiehong Lia and Yu Shi, Facile and large-scale synthesis of functional poly(m-phenylenediamine) nanoparticles by Cu2+ - assisted method with superior ability for dye adsorption, Journal of Materials Chemistry, 2012, 22, 18244

[8] Jaidev and S. Ramaprabhu, Poly(p-phenylenediamine)/graphene nanocomposites for supercapacitor Applications, Journal of Materials Chemistry, 22 (2012), 18775

[9] M.V.Kulkarni, A.K.Viswanath, Spectroscopic, thermal and electrical properties of sulphonic acids doped poly(o-anisidine) and their application as humidity sensors, Sensors and Actuators B, 107 (2005) 791