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Transport Properties of Polypyrrole/Graphene Nanocomposites

Prerna R. Modak[1], **Subhash B. Kondawar**[2], **Deoram V. Nandanwar**[2]
[1]Department of Physics, RMG Art, Science and Commerce College, Saoli, Chandrapur, Maharashtra, India
[2]Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur, Maharashtra, India
[3]Department of Physics, Shri Mathuradas Mohata College of Science, Nagpur, Maharashtra, India

ABSTRACT

Graphene, as a new member of carbon allotropes and with its exceptional carrier mobility and ballistic electron transport properties, is prime nanofiller to be employed in nanocomposites for many applications. Polypyrrole is one of the conducting polymers which has attracted a great deal of interest because of its good electrical conductivity, environmental stability, porous nature and easy synthesis. To improve and extend their functions, the fabrication of conducting polymer nanocomposites has attracted a great deal of attention. In this paper we report the study of nanocomposites synthesized by an in-situ chemical oxidative polymerization of aniline monomer with concentration of 1 and 3 wt% functionalized Graphene (GNS) with that of pure polypyrrole (PPy).As prepared nanocomposites were charecterized by SEM and XRD. Nanocomposite shows high electrical conductivity as compared to pure PPy. The transport parameters such as charge localization length, most probable hopping distance and charge hopping energy of PPy/GNS were also studied at 303-353 K.

Keywords: Nanocomposites, Polypyrrole, Graphene, Transport properties

I. INTRODUCTION

Conducting polymers can conduct electricity due to partial oxidation or reduction (i.e., doping), are potential classes of advanced materials. They possess an extended π-conjugation along the polymer backbone and reveal semiconducting behavior [1]. polypyrrole (PPy), is one of the conducting polymers which has attracted a great deal of interest because of its good electrical conductivity, environmental stability, porous nature and easy synthesis. PPy has been used in a various applications, such as batteries, supercapacitors, sensors, and microwave shielding and corrosion protection. These composites offer potentials in EMI shields, electronic packaging, display devices and electrodes [2,3]. The carbon based materials such as graphite, expanded graphite, carbon black, carbon nanotubes and graphene have been explored for various applications. Graphene is originated from graphite [4]. It is a two-dimensional hexagonal lattice [5]; one-atom-thick planar sheet of sp^2 [6]. bonded carbon atoms has emerged as a conductive nanomaterial [7]. The carbon based material graphene and graphene based conducting polymer nanocomposites are found to be more attractive due their exceptional properties like low density, good electrical and mechanical properties, ease to processes and many more. So far, Electrical Conductivity and transport properties of PANI/PVC blends were studied [8]. The transport properties of PANI/CNT and PTH/CNT were also studied [9].

In the present work, PPy/GNS nanocomposites were synthesized by an in-situ chemical oxidative polymerization method with concentration of 3% functionalized Graphene (GNS) as well as pure polypyrrole (PPy).The prepared nanocomposites were characterized by SEM and XRD. The electrical conductivity of the nanocomposites measured using four probe methods. The transport pa-rameters such as charge localization length, most probable hopping distance and charge hopping energy of PPy/GNS were also studied at room temperature 303K **Experimental**

II. MATERIALS AND METHODS

Polypyrrole ammonium persulfate, hydrochloric acid, sulphuric acid and nitric acid, hydrazine monohydrate, potassium permangnate were procured from Merck Ltd., India. Graphene flakes were made available from National Physical Laboratory, New Delhi (India). All chemicals were of AR grade. Pyrrole was distilled under reduced pressure and kept below 4^oC before used for synthesis. De-ionized water was used in all synthesis.

Preparation of PPy/GNS composites: GNS and the functionalization of GNS were conducted in our previously reported work [10] . Graphite oxide (GO) was synthesized from natural purified graphite flakes by the Hammers method, and graphene nanosheets (GNS) were prepared by exfoliation of GO [11,12].The PPy/GNS composites were synthesized by an in-situ polymerization of pyrrole in the presence of GNS. The complete synthesis process is reported in the earlier work [13].

III. RESULTS AND DISCUSSIONS

Morphology: To study the morphology of the composites SEM images were obtained using scanning electron microscope. SEM image of functionalized GNS shows a shiny black nature which confirms the exfoliation of graphene sheets (Fig. 1a). The SEM image of PPy shows granular morphology. The individual granule observed were nearly spherical and has a close packing and high porosity (Fig. 1b) [4]. The PPy/GNS composite shows highly porous morphology (Fig. 1c). The uniform spherical builds up of PPy on top up each other with some pores throughout the GNS. Pyrrole diffused into graphene nanosheets during polymerization and polymerized on the surface of graphene nanosheets layer by layer. In this composite, graphene sheets act as electron acceptors while PPy serves as an electron donor [15,16].

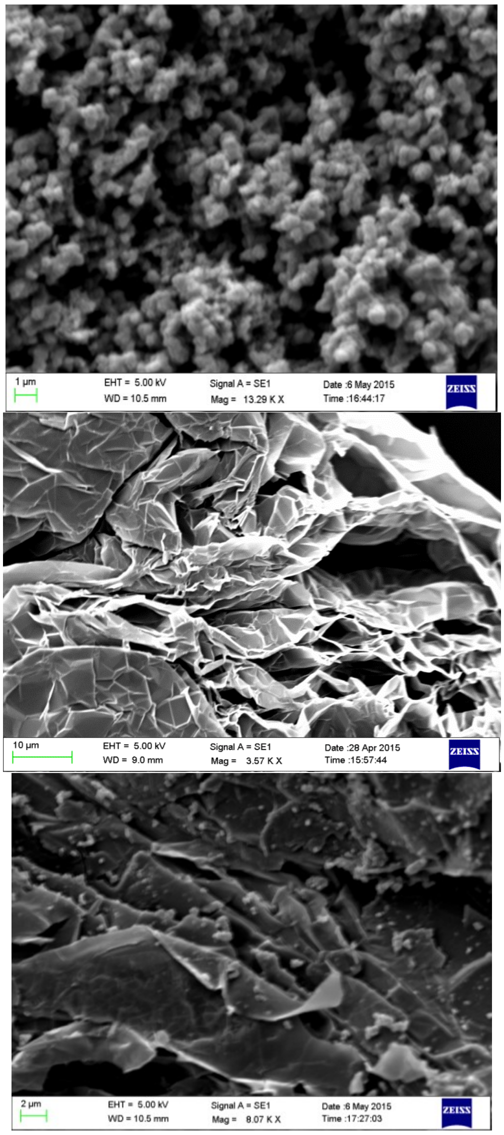

Figure 1. (a) SEM image of pure polypyrrole,(b) functionalized graphene and (c)PPy/GNS nanocomposite

X-ray diffraction: The diffraction pattern of PPy shows a peak at about $2\theta = 12^o$ and a hump around at

2θ = 24º which is typical for conducting amorphous polymer polypyrrole which is already reported. XRD pattern of PPy/1%GNS and PPy/3%GNS nanocomposites are shown in Fig. 2(a) and (b) respectively. The composites show the peaks for both PPy and GNS with some additional Peaks indicating covalent interactions between the phases. Due to this covalent interaction degree of electron delocalization of the conjugated π-system between PPy and GNS suppress. The XRD pattern of PPy/GNS exhibited diffraction peaks at 24.5°, 26° and 42.8º. The diffraction peaks at 24.5° and 42.8º correspond to (002) and (100) planes of graphite like structure while that the peak at 26º corresponds to amorphous PPy. In the PPy/GNS composite, as GNS percentage increased, the broad peak shifted from 2θ ≈ 26º to 24.8º, implying that interaction occurs between GNS and PPy. This feature supports the presence of PPy on graphene sheets.

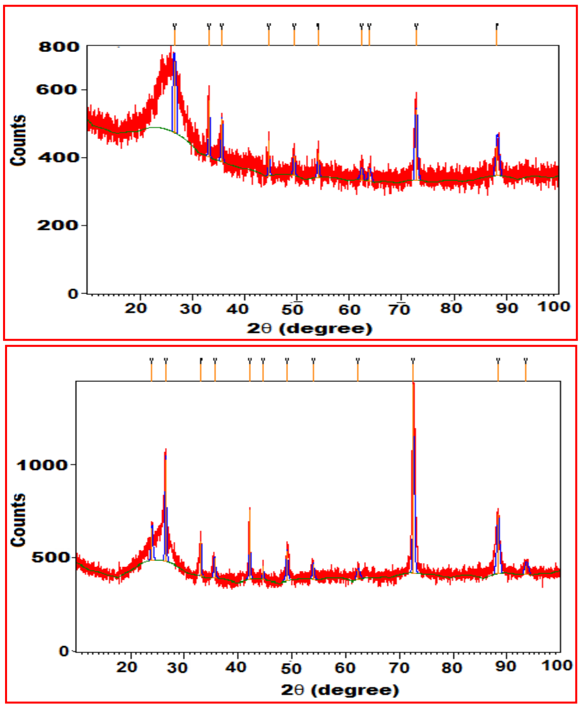

Figure 2: (a) XRD of PPy/1%GNS (b) XRD of PPy/3%GNS.

Electrical conductivity: The intrinsic conductive polypyrrole filled with conductive graphene nanofillers to develop lightweight electrically conductive composite materials. These materials show a non-linear increase of the electrical conductivity as a function of the filler concentration. At certain loading fraction, known as percolation threshold, the fillers forms a network leading to a sudden rise of the electrical conductivity of the composite. The intrinsically high conductivity and aspect ratio of graphene nanofillers make them ideal candidates to achieve this percolated network at low loading fractions [17, 18]. The numerous factors influence the electrical conductivity and the percolation threshold of the composites are concentration of the graphene nanofiller, the presence of functional groups and aspect ratio of graphene sheets, inter-sheet junction, distribution in the matrix, wrinkles and folds in the graphene sheets. The graphene fillers are in direct contact with the polymer matrix for flow of current, the conduction take place via tunnelling between thin polymer layers surrounding the filler particles [19].

We observed that, PPy behaves in the usual activated manner when the temperature increases indicating semiconducting property. It indicates that the conductivity increase with temperature is due to the increase of efficiency of charge transfer. Also the increase in temperature affects the chain alignment of the polymer; this increases the conjugation length and which in turn brings about the increase in conductivity. The increase in temperature will bring the change in molecular arrangement, which make the molecules favourable for electron delocalization [20].

The electrical conductivity of the nanocomposite PPy/GNS were also measured using four probe method, it showed that the electrical conductivity of the nanocomposite increases almost linearly with increase in temperature. The Electrical conductivity is also increases as the weight percent of GNS increases in PPy. The deposition of PPy over the GNS facilitates the electron transfer process between the PPy channels [21]. As shown in Fig. 3, the electrical conductivity for nanocomposite PPy/GNS increases linearly from pure PPy to PPy / 3%GNS, and remains constant for 5% GNS loading at 30ºC, whereas at higher temperature it increases almost linearly the values of electrical conductivity for pure PPy and PPy/GNS composites. It is clear that the highly temperature dependent nature of the nanocomposites at a low graphene content can be related to the dominance of the tunnelling mechanism when the number of graphene sheets are insufficient to allow physical contacts among them. The extent of temperature-dependence became less noticeable when the GNS content increased above the percolation threshold and finally the conductivity remained almost constant when the GNS content was above 3 wt%. At this point, the physical contacts among the fillers are well developed and the "contact" conductivity dominates over the tunnelling mechanism. The slight decrease in conductivity with increasing temperature is an evidence for the prominent role of contact conductivity in these composites.

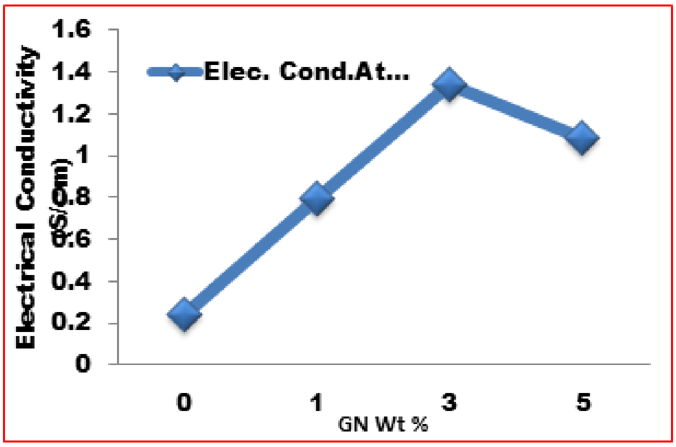

Figure 3: Electrical Conductivity with different weight percent of Graphene in Polypyrrole at 30ºC and 85ºC

Charge Transport:

PPy/GNS interaction could facilitate the charge transfer process between them and influence the charge transport properties of composite [10]. The room temperature conductivity of the nanocomposites along with transport parameters are reported in Table 1. To find transport parameters of the polymer nanocomposites from the data of electrical conductivity, Ziller equation (1) [22], has been used, which describes the inter-chain conductivity where only the neighbour variable range hoping (VRH) of charge is considered.

$$\sigma(T) = \sigma(o)e^{\left(\frac{T_o}{T}\right)^{1/2}} \quad (1)$$

The plot of *log* σ(*T*) versus $T^{1/2}$ was found to be linear for pure PPy and PPy/GNS nanocomposite, hence *To* was determined from the slope of the line. 'T_o' is the characteristic temperature, can be used to calculate the transport parameters such as charge localization length (α^{-1}), most probable hopping distance (*R*) and charge hopping energy (*w*) using equations (2), (3) and (4) respectively,

$$\alpha^{-1} = \frac{8N(Ef)Zk}{T0} \quad (2)$$

$$R = (T_o/T)^{1/2}\,({\alpha^{-1}}/{4}) \quad (3)$$

$$w = ZkT_o/16 \quad (4)$$

In these equations, *Z* is the number of nearest neighbouring chains (˜4), *k* is Boltzmann constant and *N(Ef)* is the density of states per electron volt and is approximately 5×10^{18} eV^{-1}[23]. GNS serve as a "conducting bridge" which connects the PPy conducting domain. Thus functionalized GNS in PPy matrix have better conductivity with enhanced solubility and processability as compared to that of pure PPy.

IV. CONCLUSION

The nanocomposite of PPy/GNS was successfully synthesized by an in-situ chemical oxidative polymerization of aniline. SEM and XRD show the favorable interaction between PPY and GNS also confirm the coating of PPY layer on the GNS surface. The electrical conductivity of nanocomposites was found to be drastically increased as compared to that of pure PPy at room temperature. Incorporation of functionalized GNS into PPY matrix improved the transport properties of the nanocomposite. Transport parameters of PPy/GNS nanocomposite shows that the composite is better electronic material than pure Polypyrrole.

Table 1. Transport Properties of PPy and PPy/GNS composite

Polymers	σ(S/cm) at 303K	T_0(K)	α^{-1} (nm)	R(nm)	w(eV)
PPy	0.242	14.073	0.15	0.255	0.4855
PPy/1%GNS	0.7932	16.874	0.13	0.242	0.5821
PPy/3%GNS	1.34	11.244	0.19	0.289	0.3879
PPy/5%GNS	1.0877	21.812	0.10	0.212	0.7525

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Table 2. Transport Properties of PPy and PPy/GNS composite

Polymers	**σ(S/cm) at 303K**	**T_0(K)**	**α^{-1} (nm)**	**R(nm)**	**w(eV)**
PPy		14073	0.015	0.0255	
PPy/1%GNS		16874	0.013	0.0242	
PPy/3%GNS		11244	0.019	0.0289	
PPy/5%GNS		21812	0.010	0.0212	