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Mdification of poly(3,4-ethylenedioxy thiophene)/poly(4-styrene sulphonate) (PEDOT: PSS)/nanographite nanocomposite through ion beam technique

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ABSTRACT

Ion implantation is a surface treatment process in which the surface of a sample is bombarded with a beam of energetic dopant ions to implant ions into the matrix of the substrate. In the present work, nanocomposites of poly(3,4-ethylenedioxy thiophene) /poly(4-styrene sulphonate) (PEDOT: PSS) and nanographite are prepared and subjected to swift heavy ion implantation using the same ion as that of the filler in the nanocomposites. PEDOT: PSS/ nanographite nanocomposites have been synthesized by solution blending method. The prepared PEDOT: PSS/ nanographite nanocomposite films were irradiated with carbon ions (C ion beam, 50 MeV) in fluence range of 3×10^{10} to 3×10^{12} ions/cm^2. The nanocomposite films were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) before and after C ion implantation and were evaluated for their electrical and sensor properties. SEM and XRD studies clearly depict the homogeneous dispersion of nanograhite in polymer matrix along with densification of the polymer nanocomposite. The implanted nanocomposites exhibit better electrical and sensor properties for the detection of nitroaromatics. Copyright © 2014 VBRI press.

Keywords: Nanographite; ion implantation; SEM; electrical properties.

Sunita Rattan is Professor and Head of Institute, Amity Institute of Applied Sciences, Amity University Uttar Pradesh, Noida. Her major research areas include Nanocomposites, Polymer Grafting and Stimulus Responsive Polymeric Membranes. She has published around 40 research papers in national and international journals and has presented around 70 papers in national and international conferences. She has published 7 books and has supervised a number of students for their PhD programme. She is a life member of number of scientific societies.

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Devesh Kumar Avasthi is Group Leader for materials science and radiation biology at Inter University Accelerator Centre, New Delhi. He implemented elastic recoil detection analysis (ERDA) technique for light element depth profiling. Later a gaseous telescope detector was designed, fabricated and installed to enhance the capabilities of ERDA, which was used for electronic sputtering measurements. The facilities for thin film development and vacuum laboratory were developed to take care of need of accelerator. The most recent developments of his group have been an atom beam sputtering set up for synthesis of nanocomposite thin films, in-situ ERDA, in-situ XRD, in-situ QMA in beam line. His main interest is ion beams for analysis, modification of materials, synthesis and engineering the nanostructures by ion beams. Currently his interest has been creation and modification of nanostructures by ion beams. He had major research projects under 'Intensifying Research in High Priority Area' scheme and currently a project under 'Nano Mission' funded by Department of Science and Technology, Government of India. Dr. Avasthi had several international collaborations with research groups in Munich, Stuttgart, Kiel, Orsay, Padova, Tsukuba and St. Petersburg. He is a member of international committee for the conferences on 'Ion Beam Analysis', 'Swift Heavy Ion in Matter' and "Radiation Effects in Insulators'. He has several conference proceedings as editor and more than four hundred research papers to his credit.

Introduction

Polymer nanocomposites based on conducting nanofillers have been a subject of great interest in the area of thin film device application and fabrication of electronic devices **[1-5]**.The additives can be one-dimensional, such as nanotubes and fibers, two-dimensional, which include layered clay minerals or graphene sheets, or three-dimensional, including spherical particle. In particular, polymers with the incorporation of carbon-based fillers show great potential for electronic device applications, such as organic field emitting displays, photovoltaic cells, highly sensitive sensors, and electromagnetic interference materials **[6-9]**. Further, among the various carbon-based fillers, graphene has attracted intense attention since its isolation by Novoselov et al. in 2004 **[10]**. It has been expected as the promising reinforcement material for polymer nanocomposites that improves electrical, thermal, mechanical, optical properties of polymer matrices, reuniting the laminar properties of layered silicates with the unique characteristics of carbon nanotubes **[11-13]**.

The dispersion of nanographite platlets in a polymer matrix, however, is very challenging in the preparation of these nanocomposites, because the nanographite platlets have a strong tendency to aggregate **[14]**. Many methods have been developed so far to assist dispersion of nanoparticles within the polymer matrix such as high-power ultrasonic mixers, surfactants **[15]**, solution mixing **[16]**, *in situ* polymerization **[17, 18]**, grafting to nanofillers **[19]** or grafting to polymer **[20]** plasma treatment, the functionalization of nanoparticles through covalent and non-covalent interactions with organic molecules, including polymers **[21, 22]**. In spite of the considerable advances, substantial research is still necessary to provide a method for homogeneously dispersed nanographite for full exploitation of potential of the polymer nanographite composites.

The present work relates to a novel method to modify polymer / nanographite nanocomposites through ion implantation technique. A wide variety of materials modification in polymers has been studied by using ion implantation **[23-25]** which offers a promising technique for modifying the materials at electronic and molecular level. Ion implantation has been proven to be a versatile tool for incorporating metal nanoparticles in the polymer matrix to synthesize metal/polymer nanocomposites **[26]**. Ion irradiation has also shown to increase the crystallization in polymers **[27]**.

However no work has been reported on modification of polymer nanocomposites through Swift Heavy Ion implantation using the same ion as that of the filler in the nanocomposites.

In the present work, nanocomposites of PEDOT:PSS/nanographite are irradiated with swift heavy carbon ions. The PEDOT:PSS/nanographite nanocomposites have nanographite as nanofiller. Graphitic nanoplatlets are planar sheets of sp^2- bonded *carbon atoms* derived from the layered structure of graphite. Therefore the polymer nanocomposites are irradiated to further enhance the properties of the nanocomposites. The nanocomposites exhibits enhanced conductivity suitable for electronic/ sensor applications and can be used as chemical vapour sensors.

Experimental

Materials

The natural graphite flake (Asbury carbons Inc.) was used for preparing nanographite. Polymer PEDOT: PSS [poly(3,4-ethylenedioxythiophene)/ poly(4-styrene sulphonate)] in aqueous solution was procured from HC Starck Gmbh, Germany. Other reagents and solvents used were of analytical grade.

Synthesis of nanographite

The nanographite platlets were prepared through intercalation-exfoliation method as reported in literature **[28]**. Natural flake graphite was intercalated via acid intercalation methods and expanded through thermal expansion. The expanded graphite was subjected to ultrasonication to further foliate it into graphite nanoplates.

Preparation of PEDOT: PSS/nanographite composite film

A series of PEDOT:PSS/nanographite nanocomposites were prepared by solution blending technique taking different amounts of PEDOT/PSS and nanographite (v/w) by the method described previously **[29]**. The solution is thoroughly stirred for a 5-6 hours and left as it is over night and then sonicated for 10-12 hours. The films of the PEDOT:PSS/nanographite nanocomposites are poured onto clean glass substrates and dried to evaporate the solvent completely. These polymer/nanographite composite films were used for ion irradiation.

Carbon ion implantation

The prepared nanocomposite polymer film was cut into square pieces of the size of 1 × 1 cm^2 for irradiation. These samples were irradiated by C ion beam (50 M eV) under high vacuum (~10–6 mbar), in fluence range, 3×10^{10} to $3x10^{12}$ ions/cm^2, available from the 15 UD tandem pelletron accelerator at IUAC, New Delhi, India, as per the parameters given in **Table 1**. The energy used for irradiation was determined by utilizing Stopping and Range of Ions in Matter (SRIM) software **[30]**. The energy chosen for irradiation was such that the projected range of the ion beam was less than the thickness of the film so that the ions are implanted in the nanocomposites film (**Table 1**).

Table 1. Energy and fluence used for carbon ion used for irradiation.

Ion (MeV)	Energy	Ion Energy (MeV)	Projected range (µm)	Fluence (ions/cm^2)
Carbon		50	101.35	3×10^{10} to 3×10^{12}

Characterization

Morphological and structural characterization

The morphology of polymer nanocomposites before and after ion beam irradiation was investigated by Leo 435 V P scanning electron microscope (SEM). The thickness of the nanocomposites film was also measured with the help of crossectional images with SEM. SEM images of the films were obtained at 10 to 20,000 times magnifications. The structural studies were carried out by taking X-ray diffraction (XRD) measurements on a Bruker AXS, X-ray diffractometer with Cu-Kα radiation (1.54Å). The measurements were taken out with a scan speed of 1^o/min, covering angles 2θ between 10^o and 40^o.

Electrical measurements and gas sensing experiments

The conductivity of the films was measured by the two point probe technique with a Keithley 6517B electrometer. All the measurements were performed at room temperature. The principle of operation of the chemiresistive sensors is based on the measurement of resistance change associated with the adsorption of analyte by the nanocomposite material. The film was placed in a closed chamber and exposed to the vapors of nitrobenzene. When the electrical resistance of the composite approached its equilibrium value, the sensor was removed from the closed vessel and exposed to air to recover and the change in electrical resistance was recorded.

Results and discussion

Scanning electron microscopy

Ion beam irradiation can easily stimulate chemical reactions in a polymer, causing both structural and chemical changes to the surface of the polymer. The surface morphologies of the samples were observed by SEM. **Fig 1(a)** shows the SEM image of nanocomposite film before irradiation and **Fig. 1(b-d)** shows the SEM image of nanocomposite film after C irradiation at $3x10^{10}$, $3x10^{11}$ and $3x10^{12}$ fluences respectively.

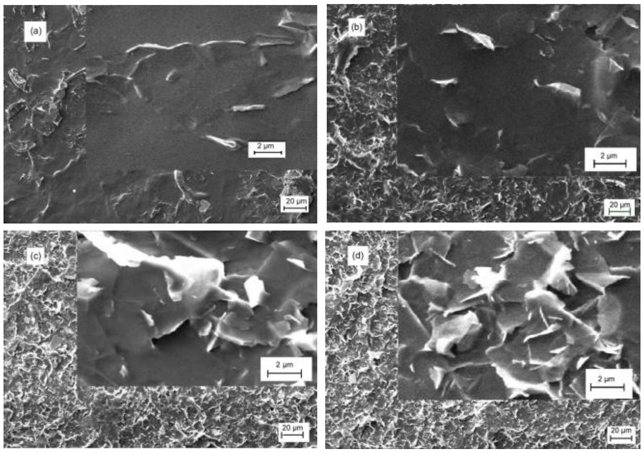

Fig. 1. SEM image of PEDOT:PSS/nanographite composite (a) before Carbon ion irradiation (b) after Carbon ion irradiation at fluence $3x10^{10}$ ions/cm^2 (c) after Carbon ion irradiation at fluence $3x10^{11}$ ions/cm^2 and (d) after Carbon ion irradiation at fluence $3x10^{12}$ ions/cm^2 (Inset in each image shows respective SEM images at higher magnification).

SEM images show significant changes in the morphology of the nanocomposites films before and after irradiation at different fluences. The change in morphology of the nanocomposites films depicts the improved exfoliation of the nanographite platlets and thus their homogenous dispersion within the polymer matrix due to ion beam irradiation. The improved exfoliation of nanographite platlets is further evidenced by the XRD results as discussed in next section. Irradiation of nanocomposites with ionizing radiations creates a cylindrical molten zone, and during which the temperature of the sample is quite high and the viscous polymer can easily diffuse into the gallery of nanofiller to cause more intercalation thus resulting into homogenously distributed nanographite into polymer matrix. It is further evidenced by **Fig. 1(b-d)** that there is sufficient densification of the polymer nanocomposites after the irradiation **[31, 32]** as it is noted that SEM of the irradiated films resemble the lamellar structure of pure graphite shown in **Fig. 2**.

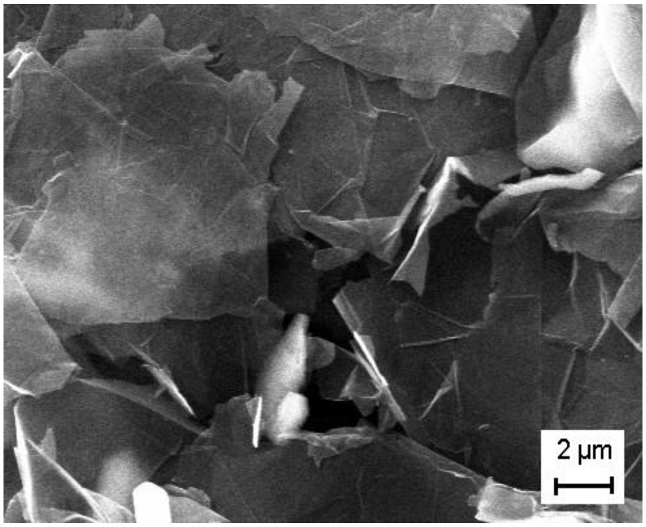

Fig 2. SEM of pure graphite.

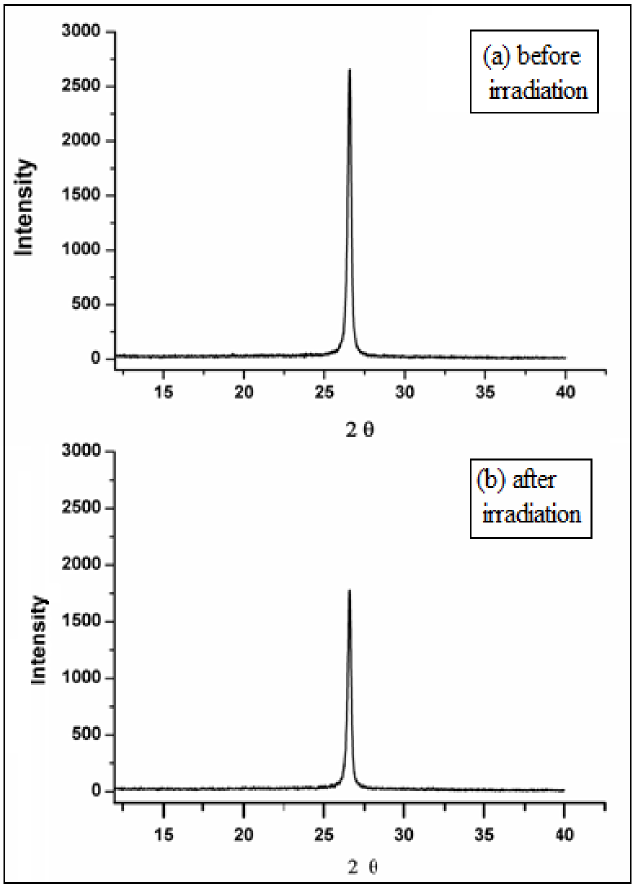

Fig. 3. XRD of PEDOT:PSS/nanographite compositen (a) before carbon ion irradiation (b) after Carbon ion irradiation at fluence $3x10^{12}$ ions/cm^2.

X-ray diffraction

Fig. 3(a) and **(b)** shows the X-ray diffraction curves of PEDOT:PSS/nanographite nanocomposites before and after C Irradiation. The intensity of the peak at 2θ =26.6^0, attributed to 002 plane **[33]** representing the perpendicular direction (*c*-axis) of graphite hexagonal planes, decreases after being irradiated by carbon ions indicating the better exfoliation of nanographite platelets **[34]**.

Table 2. Resistances of the unirradiated and irradiated (carbon ion implanted) PEDOT:PSS/nanographite nanocomposite films.

Composition of PEDOT:PSS / nanographite composite Films	Resistance before Implantation (ohms)	Resistance after Implantation (ohms)	Percentage (%) decrease in resistance after implantation
0.2%	900	600	33.3%
1%	90	20	77.8%

Electrical measurements

The resistances of the unirradiated and irradiated (carbon ion implanted) PEDOT:PSS/ nanographite nanocomposite films of different concentrations are shown in **Table 2**. It is clearly evident from the table that electrical properties of the PEDOT:PSS/nanographite nanocomposites films are greatly enhanced after carbon ion irradiation.

Sensing response of nanocomposites film to nitrobenzene

The response of PEDOT:PSS/nanographite nanocomposites film for vapors of nitrobenzene was measured using conventional resistance measurement methods by placing the sensor inside the gas chamber and exposing to vapors. The sensitivity of the nanocomposites to nitrobenzene vapor was calculated as;

$$S = [(R – Ro)/Ro] \times 100 \%$$

where *R*o and *R* are the original resistance and the maximum resistance of the films upon exposure to the nitrobenzene vapors, respectively.

Fig. 4 (a) and **(b)** shows the response of PEDOT:PSS/nanographite nanocomposites towards nitrobenzene vapours before irradiation and after irradiation with carbon ion respectively. **Table 3** compares the sensitivity and response time of PEDOT:PSS/nanographite nanocomposites toward nitrobenzene vapors before irradiation and after irradiation.

Table 3. Sensitivity of PEDOT:PSS/nanographite nanocomposite for nitrobenzene before and after irradiation.

PEDOT:PSS/ nanographite composite	Response Time (sec)	Ro (ohms)	R (ohms)	(Ro-R)/Ro x100
Before implantation	18	113.61	157.93	39%
After Implantation	15	39.84	70	77.8%

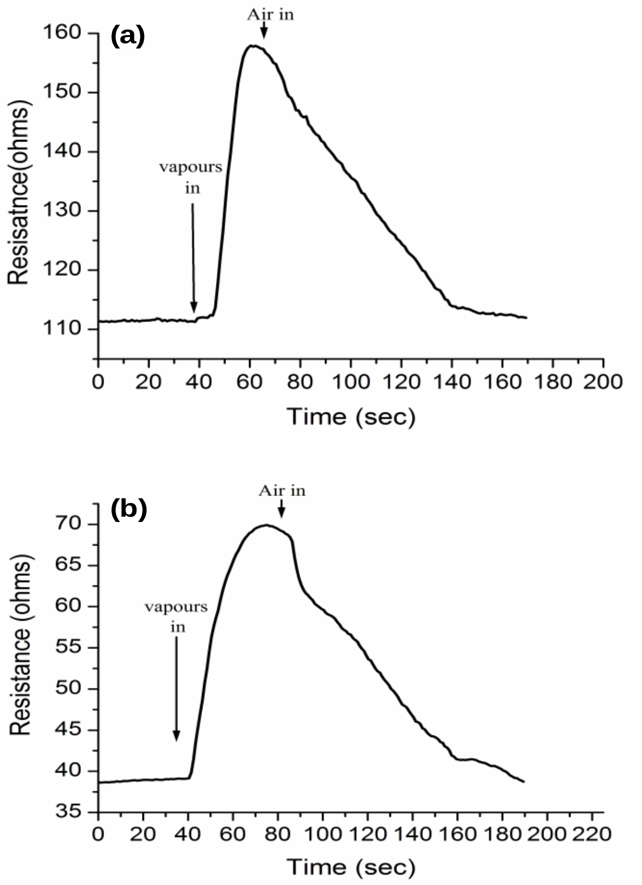

Fig. 4. (a) Sensing Response of PEDOT: PSS/ nanographite nanocomposite to Nitrobenzene Before Irradiation **(b)** Sensing Response of PEDOT:PSS/ nanographite composite to Nitrobenzene After Carbon Ion Irradiation.

Conclusion

Nanocomposites of a conducting polymer (PEDOT: PSS) and nanographite have been synthesized by solution blending technique. The prepared PEDOT:PSS/nanographite nanocomposite films were irradiated with Carbon ion beam (50 MeV) in fluence range of 3×10^{10} to 3×10^{12} ions/cm^2. Ion Irradiation technique proves to be a promising technique to modify polymer nanocomposites for various applications.

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