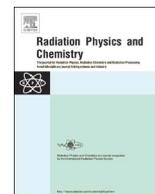




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Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Influence of Oxygen ions irradiation on Polyaniline/Single Walled Carbon Nanotubes nanocomposite

Harshada K. Patil^a, Megha A. Deshmukh^a, Sumedh D. Gaikwad^a, Gajanan A. Bodkhe^a, K. Asokan^b, Mikito Yasuzawa^c, Pankaj Koinkar^d, Mahendara D. Shirsat^{a,*}^a Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, MS 431004, India^b Inter University Accelerator Centre (IUAC), Aruna Asaf Ali Marg, New Delhi 110067, India^c Department of Applied Chemistry, Tokushima University, Tokushima 770-8506, Japan^d Department of Optical Science, Tokushima University, Tokushima 770-8506, Japan

HIGHLIGHTS

- Electrochemical synthesis of Polyaniline/Single Walled Carbon Nanotube nanocomposite.
- Modification of nanocomposite with Swift Heavy Ion Irradiation.
- Irradiation of Oxygen Ion with 100 MeV energy at three different fluences.
- Study of structural, morphological and spectroscopic characteristics before and after irradiation.

ARTICLE INFO

Article history:

Received 2 June 2016

Received in revised form

12 July 2016

Accepted 27 July 2016

Available online 28 July 2016

Keywords:

Nanocomposite

Swift Heavy Ion Irradiation

Atomic Force Microscopy

Fourier transformed infrared spectroscopy

X-Ray Diffraction

ABSTRACT

Influence of Oxygen ions (100 MeV) irradiation on Polyaniline (PANI)/Single Walled Carbon Nanotubes (SWNTs) nanocomposite was studied in the present investigation. PANI/SWNTs nanocomposite was synthesized by electrochemical Cyclic Voltammetry technique. Nanocomposite was exposed under SHI irradiation of Oxygen (100 MeV) ions for three different fluences such as 1×10^{10} ions/cm², 5×10^{10} ions/cm² and 1×10^{11} ions/cm². The SHI irradiated PANI/SWNTs nanocomposite was investigated by using morphological (AFM), structural (XRD) and spectroscopy (FTIR) characterization. AFM study exhibits effects of SHI irradiation on morphology of the nanocomposite and root mean square roughness of the nanocomposite is observed to be decreased as fluence was increased. The FTIR absorption spectrum exhibits formation of new functional sites with the increase in intensity of absorption peaks, due to SHI irradiation. X-Ray Diffraction studies show a gradual decrease in the crystalline nature of the nanocomposite upon irradiation.

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1. Introduction

After the revolutionary discovery and development of electrically conductive polymers (CPs) by Heeger, MacDiarmid and Shirakawa the scientific world has started to look forward these materials with potential applicability. Ease of synthesis, low cost, tunable doping/dedoping properties, modifiable electrical conductivity have proven CPs as challenging, competitive and reliable materials in the development of many application areas (Shirsat et al., 2009, 2008; Kharat et al., 2007; Gade et al., 2006). However, while dealing with the device application, polymer stability is one of the important key factors. Incorporation of carbon nanotubes

(CNTs) in CPs could come up with extraordinary throughputs (Meng et al., 2009; Yao et al., 2010; Spitalskya et al., 2010; Sahoo et al., 2010). In this contest many research groups have investigated efficient role of CNTs exhibiting synergistic properties of CP/CNTs nanocomposite. CP/CNTs nanocomposite exhibits extraordinary properties such as high mechanical strength, electrical conductivity, rheological properties, thermal conductivity, thermal stability (Mohammad Moiruzzaman and Winey, 2006) etc. ultimately resulting in enhanced thermo-electric performance (Zhang and Song, 2009), sensing capability, electrochemical capacitive performance (Xiaolei et al., 2005; An et al., 2004; Nikzad et al., 2012; Waltman and Bargon Can., 1986) etc. of the devices. Electrochemical synthesis is one of the easiest techniques adopted for the synthesis of nanocomposite. The resulting nanocomposite shows good adhesion and electrical contact to the electrode surface. The control over potential/current enables in deciding

* Corresponding author.

E-mail address: mdshirsat@gmail.com (M.D. Shirsat).

thickness, morphology and conductivity of the nanocomposite (Paramo-Garcia et al., 2012).

Swift Heavy Ion (SHI) irradiation plays significant role in tailoring intriguing properties of the nanocomposite. SHI irradiation, due to electronic and nuclear excitations would cause significant changes in the properties of materials which will be important for device applications. Different nanocomposites with various organic inorganic materials such as poly(vinylidene fluoride-hexafluoropropylene) (Kumar et al., 2010), ZnO/PMMA (Sharma et al., 2011), silica-metal (Pivin et al., 2009), ZnO-CuO (Kuriakose et al., 2015), Poly(vinylidene fluorides propylene/layered silicate) (Tiwari et al., 2009), copper/polymethyl methacrylate (Kishore et al., 2013), PPy/SnO₂ (Sarmah and Kumar, 2010) were exposed to SHI irradiation for the investigation of many characteristic properties such as enhanced ionic conductivity, photo-luminescence, photocatalytic activities, piezoelectric β -phase transition etc. There are some reports on Polyaniline, Polyaniline nanofibres irradiated with different ions with various energies O⁷⁺ (90 MeV, 100 MeV, 80 MeV) (Kumar and Banerjee, 2013; Ali et al., 2013a; Chandra et al., 2009), Ni¹²⁺ (120 MeV, 160 MeV) (Hazari et al., 2013; Ali et al., 2013b), C⁵⁺ (40 MeV) (Kumar et al.) at different fluences which results into remarkable structural, conformational and morphological changes. This has ultimately resulted into enhancement in their performance and properties such as conductivity, electrochemical stability, sensitivity, crystallinity, solubility, porosity, density etc. (Ghosh et al., 2013). Sensors based on CPs have been widely studied to achieve lowest explosive levels of hazardous analysts such as various volatile organic compounds, heavy metal ions etc. (Kadam et al., 2010; Srivastava et al., 2006; Rao et al., 2007; Huang et al., 2003). Significant improvement in the sensing capability of the backbone is prominently decided by the surface morphology i.e. roughness of the same (Srivastava et al., 2006). Present investigation deals with the electrochemical synthesis of Polyaniline (PANI)/Single Walled Carbon Nanotubes (SWNTs) nanocomposite. Further, nanocomposite was exposed to SHI irradiation by 100 MeV Oxygen ions with different fluences such as 1×10^{10} ions/cm², 5×10^{10} ions/cm² and 1×10^{11} ions/cm² and influence of SHI irradiation was investigated by using AFM, XRD and FTIR.

2. Experimental details

A single compartment, three cell electrode assembly was used for the synthesis of PANI/SWNTs nanocomposite, using the Cyclic Voltammetry technique. Planar Stainless Steel (SS) substrate ($20 \times 10 \times 0.50$ mm) was used as working electrode, planar platinum ($20 \times 10 \times 0.25$ mm) was used as counter electrode and saturated Ag/AgCl was used as a reference electrode. In electrolyte preparation, COOH functionalized SWNTs (purchased from Nanoshel LLC -Wilmington, DE, USA) were suspended in laboratory grade Sodium dodecyl benzene sulphonate (SDBS). SWNTs suspension, ultra-sonicated for four hours and further after adding to the electrolyte solution (0.1 M aniline monomer and 0.2 M sulfuric acid – H₂SO₄) was kept stirred for twenty minutes. Nanocomposite was synthesized by applying dynamic potential in the range 0.1–1 V. The scan rate during deposition was of 0.1 V/S. A SHI irradiation experiment was carried out at the Inter University Accelerator Center (IUAC), New Delhi, India utilizes 15 UD Tandem Pelletron Accelerator in Material Science beam line under high vacuum (5×10^{-6} Torr). PANI/SWNTs nanocomposites were subjected to 100 MeV Oxygen ion SHI irradiation with fluences 1×10^{10} ions/cm², 5×10^{10} ions/cm² and 1×10^{11} ions/cm². Morphological, structural and spectroscopic investigations were carried out by Atomic Force Microscope (AFM), X-Ray Diffraction (XRD) and Fourier Transformed Infrared Absorption Spectroscopy

(FTIR). Topographic images recorded for surface morphology was obtained from Atomic Force Microscope (AFM) - PARK system - XE7. The Fourier Transformed Infrared Absorption Spectral investigation was carried out using Bruker - Alpha spectrophotometer.

3. Results and discussion

3.1. Synthesis of PANI/SWNTs nanocomposite

Electrochemical synthesis of PANI/SWNTs nanocomposite was carried out using a Cyclic Voltammetry technique. Fig. 1a shows the Voltammogram recorded during synthesis of nanocomposite. Voltammogram exhibits redox current peaks roughly near at 0.2 V and 0.6 V respectively, with the increase in the current intensity at potential region with increase in number of cycles. This indicates electroactive nature of nanocomposite, where aniline is used to solubilize SWNTs via formation of donor-acceptor complex (Wu and Lin, 2006). The formation mechanism of PANI/SWNTs nanocomposite with tubular nanostructure is believed to involve strong interaction between aniline monomer and functionalized SWNTs caused by the presence of π - π^* electron interaction between SWNTs and aniline monomer as well as the hydrogen bond interaction between the carboxyl groups of functionalized SWNTs and the amino groups of aniline monomers. This strong interaction attributes to the fact that the aniline monomer is adsorbed onto the surface of SWNTs which serve as a core and self-assembly template during the formation of the tubular nanostructure (Tarushree and Devendra, Kumar). The wrapping of conducting polymer onto the surface of SWNTs was investigated by AFM, shown in following Fig. 1b (A and B). The line profiles (green-A, red-B) were taken for the determination of the width of the tubular nature of the nanocomposite. It is observed that it is having width ~ 160 nm. The resulting conducting polymer based nanostructure could greatly improve diffusion since it has a much greater surface area (Singh et al., 2010). Therefore, it could be utilized as a sensing platform for determination of different organic/inorganic analyte species.

3.2. Morphological investigations

The surface morphology of PANI/SWNTs nanocomposite was studied by ex situ AFM in non-contact mode. The area of $2 \times 2 \mu\text{m}^2$ was recorded for the topographic surface analysis and considered as the whole nature of the nanocomposite film. Fig. 2 shows the topographic images of pristine and 100 MeV Oxygen ions SHI irradiated PANI/SWNTs nanocomposite. In Fig. 2a–d shows the 2-dimensional (2D) topography of the pristine and SHI irradiated nanocomposite, corresponding Fourier Transformed (FT) images are shown in insets which depicts the obvious presence of a characteristic wavelength, which gets attenuated at 1×10^{10} ions/cm² fluence of the SHI irradiation. Each AFM image was analyzed in terms of surface average roughness i.e. root mean square roughness. The root mean square (RMS) roughness of the nanocomposite were evaluated based on data obtained from the scanned area of nanocomposite film. The observed values of roughness are found to get decrease with an increase in the fluence of SHI irradiation (tabulated in Table 1). The related smoothness is probably due to defect enhanced surface diffusion (Rao et al., 2007). Fig. 2i–iv shows the corresponding 3-dimensional (3D) view and line profile of the same shown in Fig. 3, providing the height dimensions of the pristine and SHI irradiated nanocomposite films. These morphological modifications illustrate the interaction of SHI irradiation with nanocomposite. The high energy ions penetrate deep into the material producing the

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