



Tuning of wettability of PANI-GNP composites using keV energy ions



G.B.V.S. Lakshmi^{a,*}, D.K. Avasthi^b

^a Inter University Accelerator Centre, New Delhi 67, India

^b Amity University, Noida 201313, Uttar Pradesh, India

ARTICLE INFO

Article history:

Received 16 November 2015

Received in revised form 15 February 2016

Accepted 16 February 2016

Available online 24 March 2016

Keywords:

Low energy irradiation

Hydrophilicity/hydrophobicity

SEM

Raman spectroscopy

ABSTRACT

Polyaniline nanofiber composites with various nanomaterials have several applications in electrochemical biosensors. The surface properties of these composites coated electrodes play crucial role in enzyme absorption and analyte detection process. In the present study, Polyaniline-Graphene nanopowder (PANI-GNP) composites were prepared by rapid-mixing polymerization method. The films were prepared on ITO coated glass substrates and irradiated with 42 keV He⁺ ions produced by indigenously fabricated accelerator at IUAC, New Delhi. The films were characterized before and after irradiation by SEM, Raman spectroscopy and contact angle measurements. The as-prepared films show superhydrophilic nature and after irradiation the films show highly hydrophobic nature with water contact angle (135°). The surface morphology was studied by SEM and structural changes were studied by Raman spectra. The surface morphological modifications induced by keV energy ions helps in tuning the wettability at different ion fluences.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Low energy ion beam irradiation has various applications in various fields, particularly in materials science and device technology. Low energy accelerators are now standard tools and their exploitation in engineering materials of all kinds such as electronic, biological, and metallurgical etc. is of interest. Energetic ion beams, when penetrating through the interface of different materials, produce atomic transport across the interface which results in many stable, unstable or even thermodynamically non-equilibrium phase formation around the interface [1,2].

Irradiation induces bond breaking, main chain scission, and creation of unsaturated bonds, intermolecular cross linking, radical formation and loss of volatile fragments in polymers. All these processes are responsible for the modification of chemical, electrical, optical and mechanical properties of polymers [3–8] leading to their applications in different scientific and technological fields viz. microelectronics, sensors, dosimetry, catalysis, light emitting diodes, electromagnetic interference shielding, super capacitors and so on. The effectiveness of these transformations produced in the polymeric materials predominantly depends on the structure and ion beam parameters such as ion energy, linear energy transfer, fluence/dose, mass, charge etc. and the nature of the target material itself [9–11].

When the energy density (obtained by multiplying the fluence with linear energy transfer) is close to or less than 10 eV nm^{-3} , the main changes occurring in the polymer are the formation of new bonds between the chains also known as crosslinking without changing the stoichiometry of the polymer with a slight release of hydrogen [12]. When the fluence increases up to 50 eV nm^{-3} , the polymer like films obtained in which the original molecular structure is overlapped with the amorphous carbon clusters forming three dimensional carbon networks [12]. Further increase in the energy density leads to the formation of graphitic clusters with decreased hydrogen concentration [12,13].

Surface modifications induced by low energy ion beam treatment are used to improve the adhesive properties, wettability, and biocompatibility of polymers [14–19]. The biocompatibility of the polymers depends on the surface morphology, adhesiveness and wettability of the material. Together with a possibility to vary the modification depth through the variation of the ion beam energy, this technique can be used to change the physicochemical properties of the bulk polymer near surface region in a controlled way [20]. The varied surface wettability enhances the biocompatibility as, in tissue regeneration process, the adhesive polymers are required which have to be both hydrophilic and hydrophobic in nature to increase the adhesiveness [21]. Hydrophobic polymers are useful for controlled drug delivery [22]. Various enzymes used in enzymatic biosensors are either hydrophilic or hydrophobic in nature depending on the bonding of the constituting amino acids, which can be adsorbed on the particular counter substrates, where

* Corresponding author at: Materials Science Group, IUAC, New Delhi, India.

E-mail address: lakshmigbvs@gmail.com (G.B.V.S. Lakshmi).

both hydrophilic and hydrophobic surfaces are required to improve the biocompatibility and hence the sensitivity. In physical biosensors, the biological gases have to be monitored for which the gas permissible hydrophobic membranes are required [23].

The combination of surface analysis and electrochemical methods proved to be very useful in the field of ion bombardment of conducting polymers. Surface analysis revealed two major effects: in general the ion beams produce a modified polymer surface with a memory effect compared to the pristine polymer. In no way a vast degradation or carbonization occurs with the applied conditions. However, a distinct dependence of modified surface structure on the chemical nature of the impinging reactive ions was observed. This modified structure is independent of the initial redox state of the polymer [24]. A few percent of hydrogen and nitrogen atoms in polyaniline matrix were removed from the chains of polymer films and are sputtered from the surface under ion bombardment [25].

The contact angle of the polymer composites can be altered by various methods. The wettability can be altered by creating surface roughness [26], which can be altered by various methods as plasma polymerization/etching, template based extrusion, solidification, etc. [27]. But chemical process cannot be used to tune up to particular thickness of the film or a part of the material. Ion beam method is advantageous compared with these plasma treatment and other methods as we can choose a well-defined ion fluence and a lateral space resolution that is important for a thin film texturing. The modification depth near the surface can be varied by varying ion species and energy [28].

In the present study, PANI-GNP composites were synthesized by rapid mixing polymerization method and characterized by SEM, RAMAN spectroscopy and contact angle measurements to measure the change in wettability of the composites. Tuning of wettability will open new doors to use the polymer composites in various biosensor applications. The engineering of the contact angle of the PANI-GNP composites is demonstrated using low energy ion irradiation with light mass He^+ ions are chosen to minimize the damage to polymers.

2. Experimental

2.1. Materials

Aniline monomer (Merck), Ammonium peroxydisulphate (APS from Merck), HCl, Graphene nanopowder (Graphene supermarket), ITO coated glass substrates, Alcohol and de-ionized water.

2.2. Synthesis of PANI-GNP composite

Polyaniline graphene nanopowder composites were synthesized by rapid mixing polymerization method. The aniline monomer was dissolved in HCl solution and APS was dissolved in deionized water. Graphene nanopowder solution was added to the monomer solution and ultrasonicated for 15 min. Then the APS solution was added and mixed rapidly for 30 min and kept undisturbed at room temperature for 24 h. The prepared powders were filtered, washed thoroughly with DI water and alcohol repeatedly until the filtrate was colorless. The dark green color powder was collected and dried in oven at 80 °C until the uniform weight was obtained. The dried powders were dispersed in DI water and 100 μL solution was drop cast on to ITO coated glass substrates in $1 \times 1 \text{ cm}^{-2}$ area. The electrodes were dried by keeping them in fridge overnight. The films were irradiated with 42 keV He^+ ions produced from indigenously fabricated portable accelerator at IUAC, New Delhi at three different fluences as 10^{14} , 10^{15} and 10^{16} ions cm^{-2} . The nuclear and electronic energy loss

of He^+ ions in PANI-GNP composites estimated by SRIM/TRIM software are plotted in Fig. 1.

2.3. Characterization

The composite powders prepared were characterized by micro-Raman spectroscopy (Renishaw in via Raman microscope with Ar ion laser; power: 0.5 mW; excitation: 514.5 nm; exposure time: 10 s); Field emission Scanning electron microscopy (FESEM; MIRA II LMH (TESCAN) for 15 keV and 25 keV electron beam), and wettability properties of water droplet on samples (Contact Angle: KRUSS DSA-10 contact angle measuring system). All the measurements were conducted before and after irradiation.

3. Results and discussion

The pre and post irradiated composite films were characterized by micro-Raman spectroscopy and the spectra recorded between the wavenumber ranges 1200–3200 cm^{-1} are shown in Fig. 2. In the pristine film, the characteristic bands of polyaniline at 1240 cm^{-1} represents $-\text{C}-\text{N}$ stretching mode, 1260 cm^{-1} represents $-\text{C}-\text{H}$ bending in benzenoid ring (B), 1360, 1400 and 1565 cm^{-1} corresponds to $\text{C}-\text{H}$ bending in quinoid ring (Q), $\text{C}=\text{N}$ and $\text{C}=\text{C}$ stretching, respectively. The characteristic bands of GNP at 1580 cm^{-1} (Graphene band) was merged with 1565 cm^{-1} and resulted in broadening. The 1355 cm^{-1} (D band) was merged with quinoid ring band of PANI. Therefore the D band and G band were not visible separately. This is due to the fact that, when the composites were prepared by in-situ polymerization method, and the GNP particles were uniformly coated with PANI chains [29].

After irradiation, Raman measurements at different fluences show the intensity change in various vibration bands. Particularly, the bands at 1300–1400 cm^{-1} in pristine samples merged together to form a broad band in irradiated samples which implies that the irradiation effects the Q-PANI band and D band of graphene and the Q-G merged band ($\sim 1565 \text{ cm}^{-1}$) intensity also increases after irradiation. However, there is no drastic change in the band position which reveals that, the polymer composite was not decomposed or lost the original composition after irradiation.

SEM studies show the surface morphological changes in the composite films shown in Fig. 3. The pristine film show the nanofibrous structure of PANI combined with the PANI coated GNP. With fluence the nanofibrous structure slowly disappears and formation

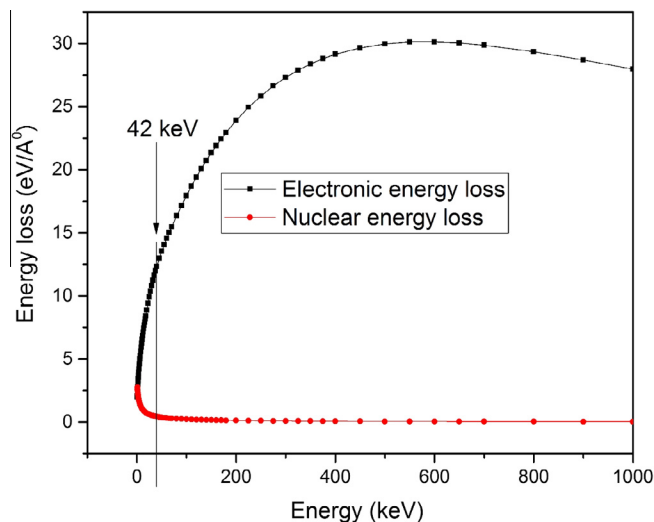


Fig. 1. Ion beam energy vs energy loss of He ions in PANI-GNP composites.

Download English Version:

<https://daneshyari.com/en/article/1679744>

Download Persian Version:

<https://daneshyari.com/article/1679744>

[Daneshyari.com](https://daneshyari.com)