



Engineering polypyrrole nanotubes by 100 MeV Si⁹⁺ ion beam irradiation: Enhancement of antioxidant activity



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ABSTRACT

In this work, the effect of 100 MeV Si⁹⁺ ion beam with four different fluences on antioxidant and structural properties of polypyrrole nanotubes has been investigated. Polypyrrole nanotubes have been synthesized by reactive self degrade template method. Fragmentation of the polypyrrole nanotubes at higher fluence is revealed from the high resolution transmission electron micrograph (HRTEM) and X-ray diffraction (XRD) results. The decrease in characteristics band of polypyrrole in Fourier transmission of infrared spectra (FTIR) spectra suggests the main chain scission of polypyrrole during irradiation. The free radical scavenging activity of pristine and irradiated samples are evaluated by using α , α -diphenyl- β -picrylhydrazyl (DPPH) assay. The decline of the UV–visible absorbance at 516 nm suggests the neutralization of DPPH free radicals through the reaction with polypyrrole. Significant increase in antioxidant activity of polypyrrole nanotubes is observed with increase in ion fluence.

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1. Introduction

Conducting polymers have been extensively studied because of their extra ordinary optical and electronic properties, which arise due to the bond conjugation and structural disorder in the system [1]. These polymers display variety in their morphology due to their partial amorphous as well as crystalline nature [2]. Nano and bulk form of conducting polymers have been used to sensors, actuators, batteries, diodes and electromagnetic interference shielding applications [3–5]. Recently a range of biomedical applications of conducting polymers are being considered such as artificial muscles, controlled drug release, stimulation of nerve regeneration and as antioxidant materials [6]. It is well recognized that the cells damaged by the free radicals lead to various diseases such as cancer, cardiovascular disease and aging etc. [7]. In addition the deterioration of foodstuff, oils and polymers is also caused by the free radicals. Lipid peroxidations, oxidative damage of DNA, oxidative stress are also the results of free radical reaction [8]. To prevent the presumed deleterious effects of free radicals in human body and also to protect oils and polymers against deterioration, there is increasing interest in antioxidant materials, since antioxidant is capable of neutralizing the free radicals. Conducting polymers like polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene) have been reported as an effective free radical scavenger, which motivates the use these materials in food packaging and also in biomedical applications [9]. The redox active property of conducting polymers is beneficial for scavenging of free

radical. C. F. Hsu et al. reported the antioxidant activity of conducting polypyrrole powders by varying the oxidation levels of polypyrrole using ammonium persulfate (APS) as oxidant [10]. Sample having APS to pyrrole ratio of 0.25 shows the highest radical scavenging property. Radical scavenging activity is found to decrease with increase in APS to pyrrole ratio and is possibly due to over oxidation of polypyrrole. M. R. Gizdavic-Nikolaidis et al. [11] synthesized copolymer of aniline and 2-aminobenzoic acid or 2-aminosulfonic acid by microwave assisted chemical polymerization method. These copolymers show excellent antioxidant activity.

The use of ion beam irradiation is getting high impetus for physical and chemical modifications of the polymers. Research has focused on the interaction between swift heavy ion (SHI) and polymers because of good controllability and high penetration depth of the ion beam. On their way SHI lose their energy by electronic interaction with the target material leading to a continuous trail of excited and ionized target atoms along their ion path. A broad range of kinetic energies is carried out by these ejected electrons and induced the secondary ionization process. The primary phenomena take place within a cylindrical zone of few nanometers while the secondary processes spread out up to a micrometer from the track core [12]. The effects of these process leads to some irreversible changes like main chain scission cross linking, emission of atoms, molecules and radicals formation. These processes are responsible for polymer structural modification and fundamental property changes. There are only few reports describing the swift heavy ion conducting polymer interaction, even if this technique is generally used for material modification [13]. A. Kaur et al. [13] reported the effects of 100 MeV Ag⁸⁺ ion beam over electrical and morphological properties of polypyrrole films. R. C. Ramola et al.

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[14] studied the effects of 50 MeV Li^{3+} and 90 MeV C^{6+} ion beam over the structural and electrical properties of polypyrrole film. The crystallinity of polypyrrole film increases with increase in ion fluence of Li^{3+} ion beam up to 10^{13} ion/cm² beyond which the amorphicity increases. On the other hand the crystallinity of polypyrrole decreases continuously with increase in ion fluence upon C^{6+} ion beam irradiation. Electrical conductivity also shows the similar trend as that of crystallinity in the case of sample irradiated with of Li^{3+} ion beam while no significant change is observed over the sample irradiated with C^{6+} ion beam.

In the present investigation we report the enhancement of antioxidant activity of polypyrrole nanotubes synthesized by the reactive self degrade method by irradiating with 100 MeV Si^{9+} ion beam. The effects of ion beam over structural and thermal properties of polypyrrole nanotubes have been investigated.

2. Experimental

2.1. Reactants

Pyrrole 98% pure purchased from Aldrich Chemical and distilled under vacuum before use. Ferric chloride (FeCl_3) from Merck, Methyl orange (MO) from Sisco Research Laboratory (SRL) and Cetyl trimethylammonium bromide (CTAB) from Himedia were used as received.

2.2. Procedure: Synthesis of polypyrrole nanotubes

In typical experiment, on the addition of 0.243 g (1.5 mmol) of FeCl_3 in 30 mL of 5 mM MO deionized water solution a flocculent precipitate was observed. Afterwards 2 mM CTAB and 105 μL (1.5 mmol) pyrrole were added successively and stirred at room temperature for 24 h. CTAB was used to control the average diameter of the nanotubes nearly at 100 nm. CTAB partially solubilized the MO- FeCl_3 template which in turn reduces the nanotubes diameter [15]. The black color polypyrrole precipitate was washed with deionized water and ethanol for several times until the filtrate became colorless and neutral. Subsequently, the residue was vacuum dried for 48 h to obtain polypyrrole nanotubes.

2.3. Instrumentation

To perform the structural characterization XRD and HRTEM studies were carried out. X-ray diffractogram were recorded by using D8 X-ray diffractometer model Bruker AXS, Germany. The HRTEM micrographs were recorded at accelerating voltage of 200 kV with HRTEM model JEOL JSM 6390 LV. For HRTEM experiment samples were prepared by placing a drop of solution of the synthesized polypyrrole nanotubes on a copper grid, following solvent evaporation in ambient air at room temperature. Thermogravimetric analysis (TGA) of the polymers was performed on a Perkin Elmer, model STA 6000 thermal analyzer with a heating rate of 30 °C min⁻¹ and a dynamic nitrogen flow of 20 ml min⁻¹ to minimize mass increase due to oxidation. FTIR studies were accomplished in transmission mode using a Nicolet Impact 410 spectrometer. For FTIR measurement polypyrrole powders were disperse in thin transparent KBr disk pellets. The antioxidant activity and UV-vis spectra was recorded using Perkin Elmer spectrophotometer model LS55.

The SHI beam of 100 MeV Si^{9+} was used for irradiation purpose at four different fluences of 5×10^{10} , 1×10^{11} , 5×10^{11} and 1×10^{12} ion/cm². Irradiation of polypyrrole nanotubes was carried out in Materials Science Chamber of Inter University Accelerator Centre (IUAC), New Delhi (India) under 10^{-6} – 10^{-7} Torr vacuum. Synthesized nanotubes were dispersed uniformly in 2% PVA solution and cast in thin film form (thickness ~ 40 μm) for irradiation purpose. The samples were loaded into a four sided ladder which could be rotated and moved up and down to bring a particular sample in front of the ion beam. The beam current was kept at a low value of 0.6 pA (particle-

nanoAmpere) to prevent the sample burning during irradiation. Particle-nanoAmpere (pA) is defined as number of particles per nanoAmpere of beam current ($1 \text{ pA} = (10^{-9}\text{C/s})/1.6 \times 10^{-19}\text{C} = 6.25 \times 10^9$ particles/s).

2.4. DPPH assay

The DPPH assay for radical scavenging activity has been performed according the methodology of Serpen et al. [16]. 0.6 mg of each test samples was added to 3 ml of 100 μM DPPH solution in methanol. The mixture was vortexed for 30 s and left for 15 min in dark. The absorbance of DPPH free radical at 516 nm was measured using UV-vis spectrophotometer. These experiments were conducted twice for reproducibility. The scavenging efficiency of DPPH free radical was calculated using the following formula,

$$\% \text{ DPPH Scavenging} = [1 - A_S/A_B] \times 100 \quad (1)$$

where, A_S is the absorbance of DPPH with sample and A_B is the absorbance of DPPH without sample.

3. Results and discussion

3.1. HRTEM analysis

The morphology of the pristine as well as irradiated samples is characterized by HRTEM (Fig. 1). The average diameter of the polypyrrole nanotubes is found to be ~100 nm. Fragmentation of the nanotubes has been observed during irradiation (Fig. 1b and c). The fragmentation increases as the irradiation fluence increases. During the passes of swift heavy ion through the target material highly ionized zone of cations, anions, free radicals, chemical species is created along the ion track within a time interval of 10^{-12} s. As the carrier charge mobility in conducting polymer is very less and of the order of 10^{-2} cm⁻² V⁻¹ S⁻¹, the charge neutrality cannot be re-established within the time scale of 10^{-12} s [17]. As a result of which shock waves are generated within the target material due to the electrostatic repulsion of the charge carriers. These shock waves lead to the fragmentation of polypyrrole nanotubes which can be seen in HRTEM micrographs [18].

3.2. X-ray diffraction analysis

Fig. 2 presents the wide angle XRD pattern of the pristine and radiated polypyrrole nanotubes. The peak centered at $2\theta = 20^\circ$ is the most prominent peak and is due to π - π interaction of polypyrrole chains which shows the semi-crystalline nature of conducting polypyrrole [19]. The semi-crystallinity of the conducting polymer arises because of systematic alignment of the polymer chains or by the formation of single and multiple helices, for at least part of their length. As fluence increases there is decline in the peak intensity with slight broadening of the reflection peak indicating a decrease in crystallinity of polypyrrole nanotubes. This may be attributed to the decrease in local ordering of the polymer chain due to main chain scission of polypyrrole nanotubes during irradiation. This change has been analyzed quantitatively in terms of domain length (L) and strain (ϵ) with different ion fluences and has been presented in Table 1. The line broadening in the XRD patterns at different fluence has been analyzed by using single-line approximation method using Voigt function so as to separate the contribution of crystallite size and the strain components [20]. The method involves the extraction and analysis of Gaussian (β_G) and Lorentzian (β_L) component of integral breadth of single Bragg peak corrected for instrumental broadening. The crystallite size is

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