Synthesis, swift heavy ion irradiation and characterization of conducting polymer based nanostructured materials for biomedical and sensor applications

Abstract

The path-breaking discovery of high conductivity in polyacetylene in 1977 by A. J. Heeger, A. G. MacDiarmid and H. Shirakawa opened up a whole new field of research, which won them the Noble prize in the year 2000. Since then the field of conducting polymers has undergone tremendous developments and a wide range of commercial applications have evolved. Conducting polymers have found applications in different areas such as microelectronics, sensors, electrodes for batteries and supercapacitors, EMI shielding etc. Conducting polymers are also being considered for a range of biomedical applications including the development of artificial muscles, controlled drug release and the stimulation of nerve regeneration. Recently, one dimensional (1D) nanostructures such as nanofibers, nanowires, nanorods, nanobelts, and nanotubes have attracted considerable attention of the scientific community owing to their unique applications in mesoscopic physics and fabrication of nanoscale devices. 1D nanostructures are ideal systems for investigating the dependence of electrical, thermal and mechanical properties on quantum confinement and dimensionality. 1D conducting polymer nanostructures deserve a special mention mainly because they combine the advantages of organic conductors with low dimensionality. Among the family of $\pi$-conjugated polymers, polyaniline is especially attractive and have been investigated by several research groups worldwide mainly because of its unique properties like good environmental stability, solubility and simple acid/ base doping/ dedoping chemistry, making it a promising material for a wide range of applications. Polyaniline nanostructures have been synthesized by using templates such as surfactants, micelles or seeds. One-dimensional (1D) polyaniline nanostructures including nanorods, nanotubes and nanofibers, have also been studied as these nanostructured materials are expected to perform better wherever there is an interaction between the material and the surrounding environment. 1D Polyaniline nanostructures have been used in different
applications and it has been observed that in most cases the performance is far better than their bulk counterpart.

Swift heavy ion (SHI) irradiation of polymers can induce irreversible changes in their macroscopic properties such as chemical, electronic, electrical, morphological, tribological and optical properties due to events such as electronic excitation, ionization, chains scission and cross-links as well as mass losses associated with the ion-polymer interaction. SHI irradiation has also been used to modify polymers for biomedical applications. SHI (energy > 1 MeV/u) irradiation deposits the energy in the material in the near surface region mainly due to the electronic excitation. The extent of damage formation and property modification depends strongly on energy, mass and charge state of the ion, its fluence and target density. The impinging ions do not get implanted in the material due to their large range typically a few tens of µm. Ionization trail produced by SHI causes bond cleavages producing free radicals, which are responsible for most of the chemical transformations in polymers such as chain scission, cross linking, generation of active sites, double and triple bond formation, emission of atoms, molecules and molecular fragments.

The present thesis is a description of a number of experiments in the dynamic research field of conducting polymer based nanostructured materials, in general, and polyaniline based nanostructured materials, in particular. We have synthesized polyaniline nanofibers doped with two different types of dopants viz., HCl and camphorsulfonic acid (CSA) using interfacial polymerization and polyaniline nanofiber reinforced polyvinyl alcohol nanocomposites using in-situ rapid-mixing polymerization techniques. The polyaniline based nanostructured materials have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infra red spectroscopy (FTIR), micro-Raman spectroscopy (µRS), ultraviolet visible (UV-Vis) absorption spectroscopy. The conductivity relaxations and charge transport mechanism in these materials have been investigated using dielectric spectroscopy and ac conductivity studies. SHI irradiation of the polyaniline based nanostructured materials have been carried out with 90 MeV oxygen ions (O^{7+}) at different fluences viz., 3×10^{10}, 1×10^{11}, 3×10^{11} and 1×10^{12}
ions/cm² with a view of studying the ion irradiation effects on the physicochemical properties of the nanostructured materials and to utilize the modifications in some specific application areas.

The thesis contains eight chapters, each of which is again divided into several sections and sub-sections. **Chapter 1** begins with an overview of the exciting and emerging field of conducting polymers with an emphasis on conducting polymer based nanostructured materials. Thereafter the potential applications of conducting polymer nanostructures in the field of biomedical science and sensor technology have been reviewed. The chapter also includes literature related to swift heavy ion irradiation induced modifications of conducting polymers. At the end of the chapter, scope of the thesis along with the statement of the thesis problem and the major objectives of the present work has been spelt out.

The mechanisms of formation of polyaniline by chemical polymerization and polyaniline nanofibers by interfacial and rapid mixing polymerization techniques have been discussed in **Chapter-2**. The theoretical framework developed to account for the charge transport mechanisms and relaxations in conducting polymers and conducting polymer based nanostructured materials have been reviewed in this Chapter. Theories developed for explaining ion-solid interactions have also been discussed in brief.

The materials and methods used for the synthesis and characterization of polyaniline nanofibers and polyaniline nanofibers reinforced PVA nanocomposites have been discussed in **Chapter 3**. Principles of various characterizations techniques like XRD, SEM, TEM, FTIR, UV-Vis spectroscopy, micro-Raman spectroscopy (μRS), ac conductivity, dielectric spectroscopy and the biochemical assays used for the study of biological activity of the polyaniline based nanostructured materials have been explained. Fabrication of piezoelectric sensors based on the polyaniline based nanostructured materials and the characterization of the sensors for studying different parameters such as sensitivity, response time and linearity have also been discussed.

**Chapter-4** describes the synthesis of PANi nanofibers using interfacial polymerization and the analysis of the variations in the physico-chemical
properties of PANi nanofibers upon SHI irradiation by different characterization techniques. TEM results show that the size of PANi nanofibers decrease with the increase in irradiation fluence, which has been attributed to the fragmentation of PANi nanofibers in the core of amorphized tracks caused by SHI irradiation. XRD studies reveal a decrease in the domain length and an increase in the strain upon SHI irradiation. The increase in d-spacing corresponding to the (100) reflection of PANi nanofibers with increasing irradiation fluence has been attributed to the increase in the tilt angle of the chains with respect to the (a, b) basal plane of PANi. Decrease in the integral intensity upon SHI irradiation indicates amorphization of the material. Micro-Raman (μR) studies confirm amorphization of the PANi nanofibers and also show that the PANi nanofibers get de-doped upon SHI irradiation. μR spectroscopy also reveals a benzenoid to quinoid transition in the PANi chain upon SHI irradiation. Charge transport and relaxation mechanisms in the pristine and irradiated PANi nanofibers have been analysed and are presented in this chapter.

Chapter-5 deals with the synthesis of polyaniline nanofiber reinforced PVA nanocomposites using rapid mixing polymerization technique and the effects of 90 MeV O\(^{7+}\) ion irradiations on the physico-chemical properties of the nanocomposites. The pristine polyaniline nanofiber reinforced PVA nanocomposites as well as the irradiated samples have been thoroughly characterized and the interpretations of the results are incorporated in this chapter. Modifications in the domain length, strain, normalized integral intensity and the overall degree of crystallinity of the PANi nanofiber reinforced nanocomposites upon SHI irradiation have been investigated using X-ray diffraction technique. FTIR analysis reveals significant variations in the chemical structure of the PANi nanofibers upon SHI irradiation. PALS study shows that the positron lifetimes \(\tau_1\) and \(\tau_2\) decrease sharply from the pristine material to that for irradiated sample with fluence of \(3 \times 10^{10}\) ions/cm\(^2\) but saturates thereafter. The effect of 90 MeV O\(^{7+}\) ion irradiation upon the charge transport and the relaxation mechanisms in the nanocomposite films studied using dielectric spectroscopy and ac conductivity measurements indicate that the conductivity of the PANi nanofiber reinforced PVA nanocomposites enhance upon SHI irradiation.
The applications of polyaniline based nanostructured materials as potential antioxidants have been investigated and the results are presented in **Chapter-6**. It has been observed that polyaniline nanofibers have much better antioxidant activity and biocompatibility as compared to their bulk counterpart. This chapter also focuses on the SHI irradiation induced variations in the antioxidant activity and biocompatibility of the PANi based nanostructured materials. It has been observed that antioxidant activity and the haemolysis prevention efficiency of the PANi based nanostructured materials increases upon SHI irradiation.

**Chapter 7** embodies the fabrication methodology of piezoelectric sensors based on PANi nanofiber reinforced PVA nanocomposites for sensing hazardous chemicals viz., free radicals and hydrochloric acid. This chapter focuses on the interpretation of the experimental results acquired while studying the sensing properties of PANi nanofiber reinforced PVA nanocomposite coated quartz crystal resonators for a class of chemical analytes using a quartz crystal microbalance (QCM). Different parameters such as response time, sensitivity and linearity of the sensors have been determined and incorporated in this chapter. The mechanism of sensing of the analytes by the PANi nanofiber reinforced PVA nanocomposites have also been investigated using different characterization techniques.

**Chapter-8** summarizes the major conclusions drawn from the work contained in this thesis. The low dimensionality of the PANi based nanostructured materials leads to significant improvement in their physico-chemical properties as compared to those of their bulk counterparts and makes them promising materials for biomedical and sensor applications investigated and discussed in the present thesis. At the end of this chapter, the future scope of research in the field of conducting polymer based nanostructured materials has been briefly mentioned.