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Surface functionalization effects on structural, conformational, and optical properties of polyaniline nanofibers

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ABSTRACT

Polyaniline nanofibers have been synthesized by dilute polymerization technique and functionalized with glutaraldehyde under acidic condition. The effects of surface functionalization of polyaniline nanofibers on their structural, conformational, and optical properties have been investigated using transmission electron microscopy (TEM), X-ray diffraction, UV–visible, infrared, and fluorescence spectroscopy. TEM and UV–vis spectroscopy results depict that fiber diameter is decreased from 35.66 to 31.04 nm on functionalization. XRD analysis suggests increased doping of surface functionalized polyaniline nanofibers (SF-PNFs) than that of the pristine polyaniline nanofibers (PNFs). Evolution of fluorescence peak at 452 nm in the fluorescence spectra and disappearance of absorption peak at 630 nm in the absorption spectra of surface functionalized polyaniline nanofibers (SF-PNFs) can be explained on the basis of the dynamic block co-polymeric structure of polyaniline (PAni). Study of optical properties shows that surface functionalization of polyaniline nanofibers (PNFs) brings about a partial transition of emeraldine base (EB) into emeraldine salt (ES) form of polyaniline. This is confirmed from the FTIR analysis, which depicts rearrangement in the polyaniline chain due to oxidation at the amine sites of benzenoid rings and reduction at the imine sites of quinoid rings after functionalization with glutaraldehyde due to its higher reactivity towards amine group. The possible mechanisms of functionalization of polyaniline nanofibers depending on different chemical structures of glutaraldehyde under acidic condition have been discussed in detail.

1. Introduction

Nanostructures viz., nanofibers, nanotubes, nanoparticles, nanowires, etc. of conducting polymers have generated immense excitement in the scientific community because of their potential in the forefront areas of modern science and technology. The last two decades have witnessed tremendous development in the field of conducting polymer nanostructures. There are three main strategies that are generally used for obtaining conducting polymer nanostructures: (a) Template-assisted synthesis, (b) molecular template-assisted synthesis, and (c) template-less synthesis [1]. Among the illustrative group of these polymeric nanomaterials, one dimensional (1D) nanostructures of Polyaniline (PAni) viz., nanofibers, nanotubes, nanowires of PAni deserve a special mention because of the versatility and potential of these materials. Polyaniline (PAni) is not only unique in its molecular structure and doping mechanisms but also has unique optical, electrical, and magnetic properties, which have been used in several applications. Highly conducting ES form of PAni is controlled by two completely different processes: protonic acid doping [2] and oxidative doping [3], while other conductive polymers are affected by their oxidation state alone, resulting in it holding a special position in the field of conducting polymers. PAni nanofibers have shown applications in the field of chemical [4,5] and biosensors [4–8], actuators [9–11], microelectronics [4,18], biomedical sciences [14,16], tissue engineering [14,15], solar cells [4,16,17], supercapacitors [12,13], etc.

Surface functionalization of nanomaterials has been an extensively employed technique for tailoring the properties of nanomaterials with a view to optimize their functions for certain specific applications. Several properties of nanomaterials such as their biocompatibility, catalytic properties, chemical reactivity and specificity, toxicity, etc. can be modulated by functionalizing their surface. Surface functionalized nanomaterials have immense importance in the field of biomedical sciences for applications such as in controlled release [4,14], targeted drug delivery [4,14], biosensors [4–8], nerve regeneration, and tissue engineering scaffolds [14,15], etc.

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Surface functionalization of conducting polymer-based nanomaterials has been reported by several research groups [14,19] working primarily in the field of analyte specific biosensors and other biomedical applications. Surface functionalized conducting polymer-based nanomaterials provide a suitable media for immobilization of enzymes and lead to the fabrication of highly specific biosensors. Surface functionalization of the conducting polymer-based nanomaterials provides a way to retain the enzyme activity after immobilization, which, otherwise is very unstable and may be lost by minute changes in conditions rendering the device inactive. As such research in this field is primarily focussed at studying the effect of surface functionalization upon the activity of the immobilized enzymes and development of efficient biosensors thereof. However, the effects of surface functionalization upon the structural, optical, and conformational properties of the conducting polymer-based nanomaterials have not been explicitly investigated and only a handful of reports are available concerning the variations in certain specific properties of Polyaniline bulk after surface functionalization [20,21]. The variations in the optical properties of the conducting polymers upon surface functionalization with agents such as glutaraldehyde have not been reported at all. The present paper is aimed at making a novel attempt to study the effects of surface functionalization of PAni nanofibers with glutaraldehyde at molecular level on their structural and conformational properties in general and optical properties (fluorescence) in particular, which has not been investigated before. In most of the earlier reports concerning the surface functionalization of conducting polymers with glutaraldehyde, the probability of existence of glutaraldehyde in different structural forms depending upon the acidic/basic conditions of the polymer solution has not been explicitly described. The authors have, therefore, made an attempt to reveal the possible reaction mechanisms of glutaraldehyde with PAni nanofibers taking into consideration the different structural forms of glutaraldehyde under acidic conditions based on vibrational spectra analysis. This is an important aspect of research in the field of fluorescent biosensors and can help in developing of new avenues in allied fields.

2. Experimental details

Aniline (p.a. Merck) was distilled under reduced pressure before use. Ammonium peroxydisulfate (p.a. Merck) and Hydrochloric acid (Rankem) were used without further purification. Deionized water (12 MΩ cm) used for the synthesis was obtained from a Milli-Q system. A total of 25% solution of glutaraldehyde (p.a. Merck) was diluted to 1% using Milli-Q water. All other chemicals and reagents were of analytical grade and used as received.

2.1. Synthesis of PAni nanofibers by dilute polymerization

Polyaniline nanofibers were synthesized using the method described by Chiou [22]. A solution of 1 M HCl (dopant acid) was prepared and the monomer aniline was dissolved in a small portion of that solution. Ammonium peroxydisulfate (oxidizing agent) was dissolved in the remaining portion of the dopant acid solution. The monomer solution was then carefully transferred to the solution of APS. The reaction was allowed to take place in a magnetic stirrer at a very slow stirring rate at room temperature for about 24 h till the whole mixture became dark green. The whole mixture was then filtered and washed with deionized water until the filtrate became colorless. The initial concentration of aniline in the reaction mixture was kept at 8 mM and the molar ratio of the monomer to the oxidant was maintained at 2:1.

2.2. Surface functionalization of PAni nanofibers

Surface functionalization of the PAni nanofibers was accomplished by treating the purified PAni nanofibers with 1% glutaraldehyde solution for a period of 24 h. Subsequently, the surface functionalized PAni nanofibers (SF-PNFs) were washed with deionized water to remove the excess glutaraldehyde. The reason for choosing glutaraldehyde as a surface functionalization agent was its high reactivity towards the amine group [23,24] and as such it has been often used as a cross-linking agent. The molecular form of glutaraldehyde in aqueous solution enables it to cross-link two materials having active amine groups [23,24]. Thus, it was expected that the SF-PNFs would be highly reactive towards other chemical species having active amine groups such as amino acids and enzymes. Also, it has been reported earlier that glutaraldehyde is the most effective cross-linking agent [25] due to its commercial availability and low cost in addition to high reactivity.

2.3. Analytical techniques

The structural, morphological and conformational characterizations of the pristine and surface functionalized polyaniline nanofibers were accomplished using transmission electron microscopy, X-ray diffraction, and FTIR spectroscopy. Transmission electron microscopy was accomplished using a JEOL JEM 200 CX transmission electron microscope (TEM) installed at SAIF, NEHU, and Shillong. X-ray diffraction studies of the nanofibers were carried out using Miniflex X-ray diffractometer (Rigaku Corporation, Japan) in 2θ continuous scanning mode. FTIR spectra of the nanofibers were acquired using a Perkin Elmer spectrum 100 FTIR spectrometer. The optical properties of the pristine and surface functionalized polyaniline nanofibers were investigated employing UV–visible absorption and fluorescence spectroscopy.

3. Results and discussions

3.1. Structural characterization

Fig. 1a and b show the transmission electron micrographs of the pristine and SF-PNFs synthesized by dilute polymerization technique. The average diameter of the pristine PAni nanofibers have been found to be 35.66 nm while that of the SF-PNFs has been determined to be 31.04 nm indicating that there is almost no secondary overgrowth and that surface functionalization of the polyaniline nanofibers using glutaraldehyde does not have any appreciable influence upon the morphology of the nanofibers besides a slight decrease in the diameter. The appearance of only two low intensity diffused rings in the SAED pattern [Fig. 1 (b) inset] of the SF-PNFs c indicates that the SF-PNFs are in amorphous/semi-crystalline phase.

The X-ray diffraction patterns of the pristine and SF-PNFs are shown in the Fig. 2. Two major reflection peaks are observed for both the samples at $2\theta = 19^{o}$ and 25^{o}. In general, the ES form of PAni exists in two crystalline forms ES-I and ES-II depending upon the method adopted for synthesis. The ES-I form is generally considered to have a pseudo-orthorhombic semi-crystalline structure with the unit cell having lattice parameters; $a = 4.3$ Å, $b = 5.9$ Å, $c = 9.6$ Å, and a volume of 24.5 $Å^3$ [26]. The major reflections for the ES-I crystalline structure of PAni are observed at $2\theta = 15.5$, 20, 25.5, 27.6, and 30.2^{o}, which are ascribed to the (0 1 0), (1 0 0), {(1 1 0)}, {(1 1 1)}, (0 2 0) planes, respectively [26].

The two major peaks observed in the X-ray pattern of the pristine PNFs and the SF-PNFs can, therefore, be ascribed to the (1 0 0) and (1 1 0) reflections. The existence of only two X-ray reflection peaks for the pristine and the SF-PNFs, depicts that the alignment