

Fabrication and Characterization of Conducting Copolymer Nanorods

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Introduction

Conducting polymers have attracted considerable attentions due to their increasing applications in numerous fields, such as batteries, chemical sensors, electrochromic devices, light emitting diodes, etc. [1–4]. Polyaniline (PANI) is a kind of electrically conducting polymers with many features that could be exploited in various applications [5,6]. Furthermore, it is unique in the family of the conducting polymers due to its simple preparation and reversible doping/de-doping properties based on acid/base reactions [7]. But the main disadvantages of polyaniline are its poor solubility and poor processability both in melt and solution due to its stiffness of the backbone which limited its further extensive applications in many areas. A major breakthrough in this field was the copolymerization of aniline and ramificate aniline [8,9]. The self-doped polyaniline has several advantages, including better solubility as well as redox activity and conductivity over a wider pH range. A great deal of comonomers involved $-\text{SO}_3\text{H}$, $-\text{COOH}$ groups, etc., have been used in the preparation of self-doped polyaniline [10,11].

Recently years much attention has been paid to the synthesis and characterization of copolymers of aniline and its derivatives. As one of the influential derivatives of PANI, poly(*p*-phenylenediamine) (PpPD) has been widely synthesized by electropolymerization and chemical oxidative polymerization [12]. The PpPD has demonstrated a great potentiality for use as electrochromic display materials, humidity sensors, electrode-modified materials, pH response, and protection against metal corrosion and so on [12]. Among the conducting copolymers, poly(aniline-co-*p*-phenylenediamine) has attracted much attention due to its film forming, electronic and electrochromic properties [13]. More recently, synthesis of conducting polymer nanostructures have been increased considerable attention. A wide variety of methodologies have been used to prepare conducting polymer nanostructures [14–17]. In this article we prepared conducting copolymer, poly(aniline-co-*p*-phenylenediamine) nanorods without any external template.

Experimental section

Materials

Aniline and *p*-phenylenediamine were obtained from Aldrich. Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) and all other organic solvents were of analytical grade and used without further purification.

Preparation of conducting copolymer nanorods

In a typical experiment, monomers, aniline (0.01 M) and *p*-phenylenediamine (0.01 M) were dissolved in 0.1 M HCl and the resulting pre-cooled solution was added to the above dispersion with constant stirring. The contents were then kept in an ice bath and stirred continuously. Finally, acidic aqueous solution of potassium persulfate (0.01 M) was added drop by drop over a period of 30 minutes with constant stirring to initiate the polymerization. The reaction was continued for 24 hr at room temperature, in order to ensure the complete polymerization. Initially the reaction was carried out at 0°C for 5 hr and then continued up to 24 hr at room-temperature. The reaction was terminated by pouring the reaction mixture into acetone, whereupon the copolymer nanorods were precipitated out. The resulting product was thoroughly washed with deionized water to remove the impurities such as unreacted monomers and oxidant, and finally washed with acetone. The product was dried in a vacuum oven at 40°C for 24 hr.

Characterization

Microscopic images of the copolymer nanorods were obtained by a Hitachi S-4200 field emission scanning electron microscope (FE-SEM). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were performed on a TA instruments (SDT Q600 analyzer) from 30 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere. UV-visible spectrum of the diluted copolymer dispersion in the 200-900 nm range was obtained using an Agilent 8453 UV-visible spectrophotometer. FT-IR characterization was performed using an Excalibur Series FTS 3000 (BioRad) spectrometer. The XRD pattern was collected on a powder X-ray diffractometer (PANalytical, X'Pert-PRO MPD) with Cu K α radiation. Room temperature conductivity of the pressed pellet was measured by a standard four-point probe apparatus (Keithley model 196 system digital multimeter).

Results and Discussion

The representative field emission scanning electron microscopic (FE-SEM) images of copolymer nanostructure obtained via oxidative polymerization is composed of nanorods having an average diameter of 80-100 nm (Fig. 1). The length of the nanorods ranges up to micrometer. FE-SEM analysis reveals that nanorods obtained are varying in size as shown in Fig. 1.

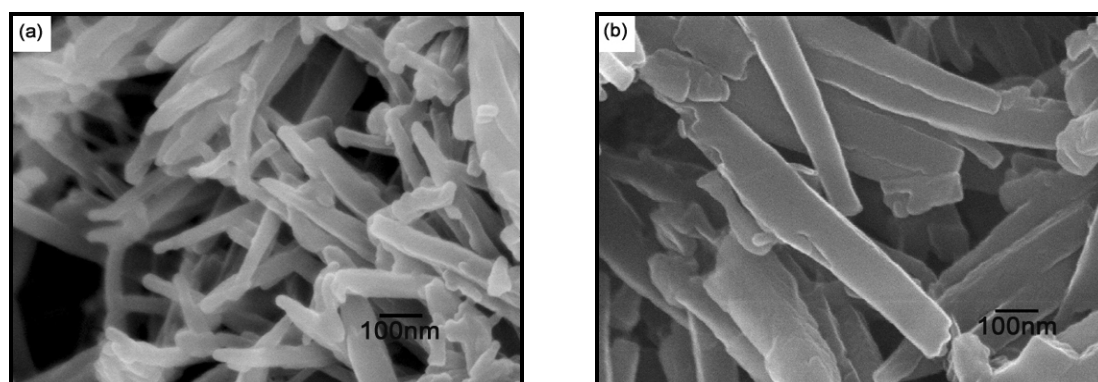


Fig. 2. FE-SEM images of copolymer nanorods (a) low and (b) high magnification

Typical FT-IR spectrum of the copolymer is shown in Fig. 2. The bands centered at 3450 cm^{-1} is attributed to the characteristic N-H stretching vibration of the secondary amine groups of copolymer [13]. A peak at 2925 cm^{-1} is assigned to the C-H stretching vibration that arises from the aromatic rings. The peaks at 1602 cm^{-1} and 1493 cm^{-1} are assigned to C=C stretching vibration of quinoid and benzenoid rings, respectively. The peak at 1245 cm^{-1} is attributed to the C-N stretching vibration of secondary amine. The appearance of these IR bands should verify the formation of copolymer.

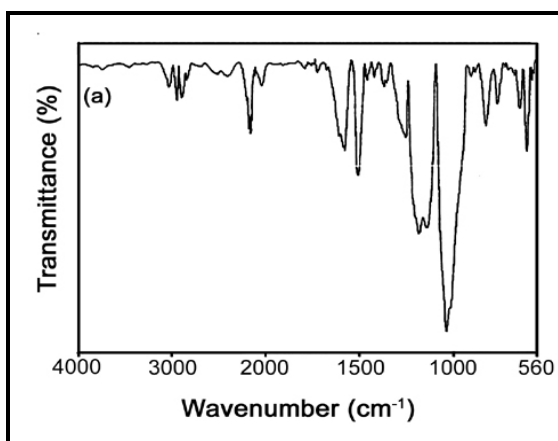


Fig. 2. FT-IR spectrum of copolymer nanorods.

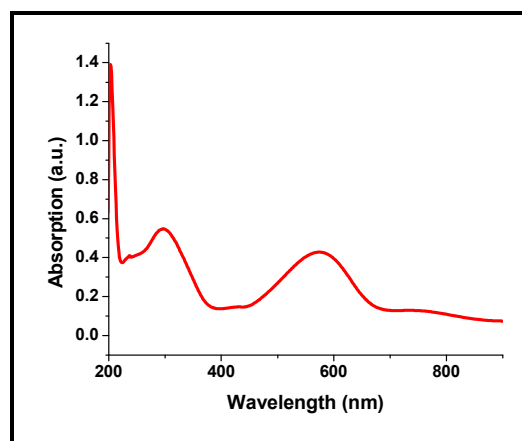


Fig. 3. UV-vis spectrum of copolymer nanorods in DMSO.

UV-visible spectrum of the copolymer nanorods in DMSO is shown in Fig. 3. The copolymer exhibits two major absorption bands. The first absorption band in the region of around 300 nm is assigned to the π - π^* transition of the benzenoid ring of the copolymer. It is related to the extent of conjugation between the phenyl rings along the copolymer chain. The second absorption band at around 600 nm is due to the electronic transition of quinoid imine structures might be assigned to polyaniline segments [13].

To further confirm the crystal structure of the copolymer nanostructure, the sample has been subjected to X-ray diffraction (XRD) analysis at 30°C. Figure 4 shows the XRD pattern of the resultant copolymer nanorods. The broad diffraction peaks centered at $2\theta=18.2^\circ$ and 25.3° are observed in the sample obtained from oxidative polymerization. This indicates that the resulting copolymer is highly crystallinity. The latter diffraction peaks at $2\theta=25.3^\circ$ implies that the phenyl rings are densely packed giving rise to a planar conformation and, thus, to an extensive interchain π - π^* orbitals overlap.

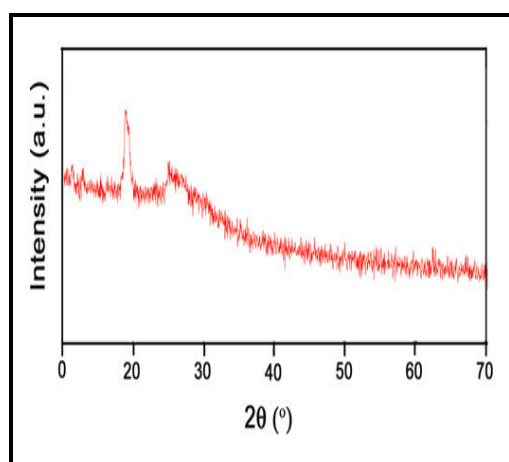


Fig. 4. XRD spectrum of copolymer nanorods.

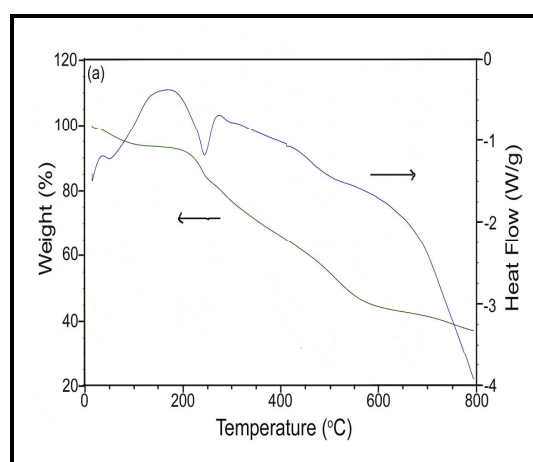


Fig. 5. TGA-DSC curves of copolymer nanorods

TGA and DSC curves of the copolymer nanorods in nitrogen are shown in Fig. 5. The as prepared copolymer exhibits a three-step weight loss. The first weight loss step in the TGA curve between 50–140°C corresponds to the loss of moisture, volatilization of the solvent and adsorbed HCl. The second

step between 170–260°C is due to the loss of dopant and the concurrent evolution of CO₂. The third step occurring between 420–600°C corresponds to the final degradation of the copolymer. DSC curve of the copolymer exhibits two-step degradation. The first endothermic peak in the DSC curve correlates to the loss of adsorbed HCl and moisture in the TG study. The second endothermic peak between 230–270°C can be attributed to the morphological changes and disruption of inter and intramolecular hydrogen bonding.

Conclusions

In conclusion, we demonstrated a novel route to synthesize poly(aniline-co-*p*-phenylenediamine) nanorods at room temperature. The synthesis is easily scalable and reproducible. FE-SEM analysis indicates the formation of one-dimensional nanorods with average diameter of 80-100 nm. The highly conducting and thermally more stable copolymer nanorods may provide potential applications such as nanodevices, chemical sensors or actuators, and many more.

Acknowledgements

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