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Large scale synthesis of polyaniline nanowires and their characterization

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Abstract Polyaniline nanowires were synthesized using chemical technique. Pores in anodic alumina membrane were used as templates. Surface morphology was studied using field emission scanning electron microscopy. Structural analysis was done using X-ray diffraction and Fourier transform infrared spectroscopy. Collective I–V behaviour of polyaniline nanowires observed was nonlinear.

1 Introduction

Conjugated polymer nanostructures have attracted a lot of curiosity because of their unique electrochemical and electronic properties relative to inorganic electronic materials. Excellent reviews are available on the applications of conducting polymer nanostructures [1]. Conducting polymer nanowires and nanotubes have been proposed as nanoresistors, diodes, and field-effect transistors [2, 3], field emission displays [4] and ultrafast electrochromics [5, 6] based on conducting polymer nanowires have been demonstrated.

Conducting polymer nanowires made by chemical reproduction of porous anodic aluminum oxide template can be grown with accurate control over their length and diameter and then incorporated into electronic circuits by dielectrophoretic assembly [7]. It is significant to understand the charge transport in conducting polymer nanowires because the charge transport mechanisms can have vital consequences in terms of their use as sensor applications [8, 9].

Polyaniline (PANI) is one of the most extensively examined conducting polymers due to its advantageous electrical and optical properties, as well as exceptional environmental steadiness. Because of having large surface area polyaniline nanostructures have recently received a large amount of curiosity for the fabrication of biosensors, gas sensors, actuators, drug delivery systems etc. [10–12]. In this paper, we reported the chemical synthesis of polyaniline nanowires and their systematic analyses through morphological, structural and electrical characterization.

2 Experimental details

Aniline, ammonium persulphate and hydrochloric acid (HCl) were employed in the experiment were of pure analytical grade. AAM with pore diameter of 200 nm was purchased from Whatman International Ltd. SEM micrograph of AAM used as template for the synthesis of polyaniline nanowires is shown in Fig. 1a.

AAM was used as a dividing wall in a two-compartment cell. In the first compartment, an aqueous polyanilne solution (0.4 M) + 0.1 M HCl was added and allowed to diffuse through the membrane during 10 min prior to the introduction of the oxidant reagent ammonium persulphate (0.4 M) + 0.1 M HCl in the second compartment. The monomer and the oxidant reagent diffuse toward each other through the pores of the membrane and react to yield the polymer. The polymerization process was continued for 1 h to obtain nanowires. We take low concentration of the reactants to better control the process and also increase the polymerization time to produce well-aligned polyaniline nanowires.

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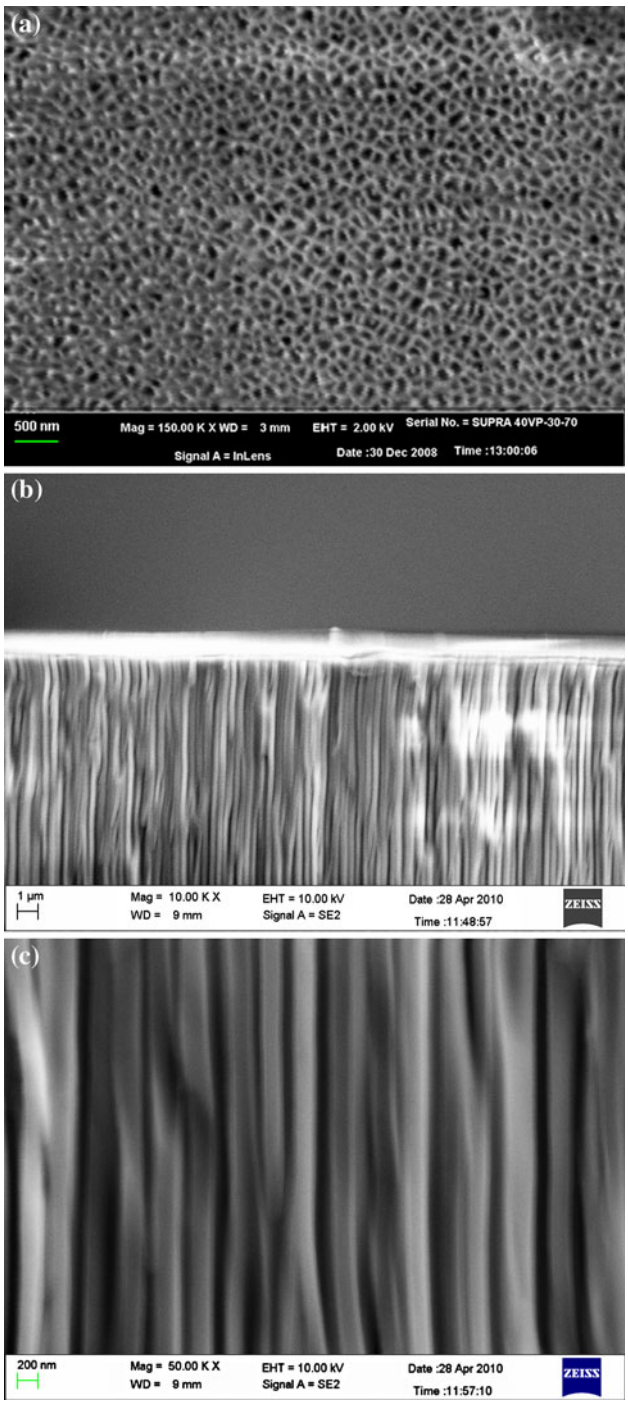

Fig. 1 **a** SEM micrograph of AAM. **b**, **c** SEM micrograph of Polyaniline nanowires

The structural and morphological properties were studied with XRD (PANalytical X'Perto Pro X-ray diffraction machine using copper characteristic wavelength = 1.54 Å) and FESEM (Zeiss). Infrared spectroscopy (IR) measurements were done on a Cary Varian FT-IR spectrometer. Electrical characteristics were studied by Keithley 2602 source meter.

3 Results and discussion

The confined growth of nanowires, within the template pores leads to the formation of quite uniform and ordered high quality nanowires. Generally polyaniline exists in three well-defined oxidation states: leuoemeraldine, emeraldine and pernigraniline. All nitrogen atoms are amines in leucoemeraldine state, whereas in pernigraniline state all nitrogen atoms are imines. The most conducting state is emeraldine in which the amine/imine ratio is about 1. During the chemical synthesis the colour of the polyaniline emebedded membraqne looks greenish which turns into dark blue after complete synthesis. This dark blue color also confirms the emeraldine base [13].

For the FESEM characterization AAM containing the polyaniline nanowires was dissolved in 1 M NaOH solution. It takes a long time to completely dissolve the AAM. Then it was washed with ethyl alcohol several times. Then a single drop was put the stub for FESEM. Figure 1b, c shows the SEM micrograph of the polyaniline nanowires. It clearly shows that the diameter of the wires is same as that of the pores in the host template.

Figure 2 represents the FTIR spectrum of polyaniline nanowires. 790 cm^{-1} peak corresponds to para substituted aromatic rings. 930 cm^{-1} peak assigned to C–H out of plane vibration. The 1,140 cm^{-1} corresponds to C–H in plane deformation suggests the electron like band [14]. This peak also confirms the characteristic peak of protonated state. 1,160 cm^{-1} corresponds to C–N bending mode. 1,304 cm^{-1} assigned to C–N stretching vibration. 1,401 cm^{-1} corresponds to N–H bending formation. FTIR spectrum reveals that the chemically synthesized polyaniline nanowires exist in the conducting emeraldine form. Figure 3 shows the XRD spectrum of polyaniline embedded AAM. A broad peak is observed whose centre is around $2\theta = 21.2°$ and was attributed to the periodicity paralleled to the PANI chains, showing amorphous nature of polyaniline [15].

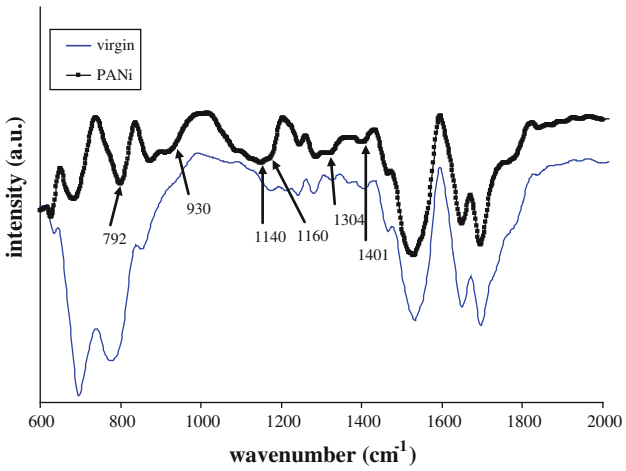

Fig. 2 FTIR spectrum of Polyaniline nanowires

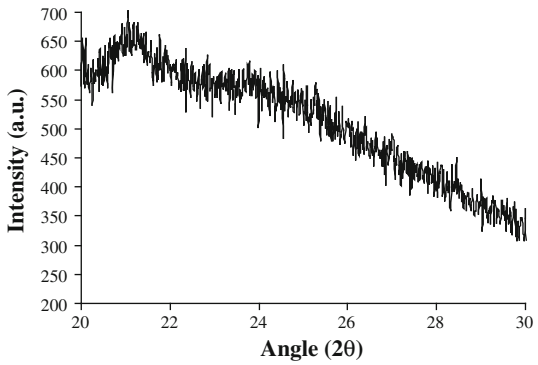

Fig. 3 XRD spectrum of Polyaniline nanowires

I–V characteristics of the Polyaniline nanocylinders were measured by leaving the conducting nanocylinders in the pores of the insulating template membrane. Silver paste and fine copper wires were used to contact the sample. Philips Keithley 2602 source meter was used for current and voltage measurements. We also examined that the solvent in the silver paste does not affect the conductivity of the polyaniline nanowires as done previously [16].

Figure 4 depicts the collective I–V behaviour of polyaniline nanowires embedded in AAM. We studied the collective I–V behaviour from three different positions on the sample. We put the silver paste in then form of circle having diameter 4 mm on the sample for first study. Then we found the nonlinear I–V behaviour of polyaniline wires as shown in Fig. 4 represented by blue curve. Then we repeat the same procedure for other two measurements and found the similar behaviour as represented by red and brown curves in Fig. 4. The conductivity of conducting polymers also depends on morphology. So one dimensional nanowires shows higher conductivity than two dimensional thin films. Cai and Martin

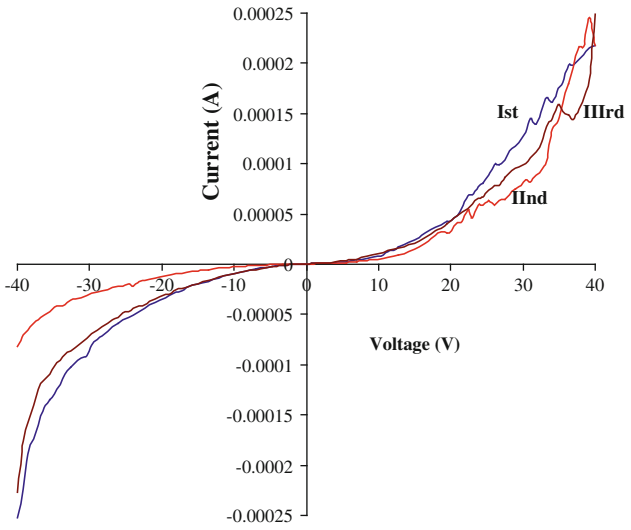

Fig. 4 I–V behaviour of Polyaniline nanowires

[17, 18] suggested that the enhanced conductivity in the smaller diameter nanowires was due to the presence of a highly-ordered layer of conjugated polymer along the pore wall. Consequently deposited layers were less subject to the ordering control of the pore walls. This recommends that the smaller diameter nanowires have a larger proportion of ordered polymer than the larger diameter nanowires. These conducting polymer nanowires can be promising candidates for nano-electronics devices.

4 Conclusions

We have successfully measured the electrical conductivity of individual Polyaniline nanowires synthesized by the template method. This result confirms that the synthesis in the confined space of the template channels can induce alignment of Polyaniline molecular chains, as well as the enhancement of the electrical conductivity of the nanowires. These nanowires can play important role as interconnects as well as device components in the field of nano-electronics.

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