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Fractal like charge transport in polyaniline nanostructures

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ABSTRACT

The structural and electrical properties of camphorsulfonic acid (CSA) doped nanotubes, and hydrochloric acid (HCl) doped nanofibers and nanoparticles of polyaniline have been studied as a function of doping level. The crystallinity increases with doping for all the nanostructures. Electrical transport measurements in the temperature range of 5–300 K show an increase in conductivity with doping for the nanostructures. All the nanostructures exhibit metal to insulator (MIT) transition below 40 K. The metallic behavior is ascribed to the electron–electron interaction effects. In the insulating regime of the nanotubes conduction follows the Mott quasi-1D variable range hopping model, whereas the conduction in the nanofibers and nanoparticles occur by variable range hopping of charge carriers among superlocalized states without and with Coulomb interaction, respectively. The smaller dopant size in case of HCl makes the polymer fractal resulting in superlocalization of electronic wave-functions. The confined morphology of the nanoparticles results in effective Coulomb interaction dominating the intersite hopping.

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1. Introduction

Conducting polymers (CPs) such as doped polyacetylene (PA), polypyrrole (PPy), poly (3, 4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) have been studied extensively for the past four decades due to their promising technological applications [1]. The quest to understand the charge transport mechanisms in CPs has led to intensive investigations on their electrical properties. It is generally believed that disorder-induced localization acts as the principal factor in determining the transport properties of conducting polymers. The common factors for disorder in these materials are partial crystallinity, inhomogeneous doping and synthesis processes. Increasing doping reduces the disorder in conducting polymers thereby increasing the conductivity which may lead to metal–insulator transition (MIT). The nature of disorder, homogenous or inhomogeneous, is the determining factor in the charge transport mechanism. The homogeneous disorder induced MIT can be explained by the localization–interaction model for transport in disordered metals [2] on the metallic side. On the insulating side of MIT, the charge transport can be understood in terms of variable range hopping among randomly localized states. In case of inhomogeneous disorder, however, the polymer consists of small crystalline domains surrounded by amorphous domains and the MIT is better described in terms of percolation between metallic islands (i.e. crystalline domains) [3,4]. In recent years the progress in processing of conducting polymers has substantially improved the material quality by reducing the extent of disorder with a corresponding increase in electrical conductivity. The extent of disorder is reduced in such a way that the correlation length (on the metallic side) or the localization length (on the insulating side), which characterizes the extent of electronic wave functions, becomes greater than the crystalline coherence length. In such a case the disorder can be regarded as homogeneous since there is substantial overlapping of wave functions of the delocalized states [5].

Polyaniline is unique among the conducting polymers for its easy synthesis and doping/dedoping mechanisms, low cost, good environmental stability and high electrical conductivity [6]. In recent years, along with the progress in processing of CPs, the nanostructuring of these materials in the form of nanotubes, nanofibers, nanoparticles, nanospheres etc. which provide large surface area and enhanced charge transport rate, has shown a remarkable development in this field opening up huge opportunities for applications in electronic nanodevices, biomedical technologies etc. [7,8]. There are several reports on electrical transport properties in single nanotube and nanofiber as well as in pressed pellet form showing a metallic behavior and MIT at very low temperature [9–11]. However, there are a few studies investigating the doping level dependence on these properties. Since the quantum size effect and the intrinsic disorder are important factors in these low-dimensional materials, the doping concentration variation could be an effective tool to understand the charge transport mechanism in these otherwise poorly understood systems. We report here for the first time, a comparative study of the electrical conduction of different polyaniline nanostructures

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viz. nanotubes, nanofibers and nanoparticles doped with varying acids to understand the nature of electrical transport and MIT transition as well as to examine their possible correlation with structural ordering, morphology and dopant type.

2. Experimental

2.1. Materials

Aniline monomers were purchased from Merck and distilled under reduced pressure. Sodium dodecyl sulfate (SDS, Merck) was used to form spherical micelles. Hydrochloric acid (HCl, Merck) and camphor sulfonic acid (CSA, Aldrich) were used as doping agents. Carbon tetrachloride (CCl_4) was used as the organic solvent for interfacial polymerization. Ammonium persulfate (APS, Merck) as oxidant was used to initiate the polymerization. Methanol (Merck) and acetone (Merck) were used to wash the obtained nanostructures. All reagents were used as received without any further purification.

2.2. Synthesis

Polyaniline (PANI) nanotubes were synthesized by in-situ doping polymerization of aniline in the presence of CSA. In the self-assembly process aniline–CSA salt complexes form tubular micelles that act as soft templates in the formation of PANI nanotubes [9,10,12]. The micelles are formed due to the hydrophobicity of aniline and hydrophilicity of $–SO_3H$ group of CSA [13]. Since CSA acts as a functional dopant, the micelles need not be removed after polymerization. In a typical synthesis procedure, aniline monomer and CSA were mixed in double distilled (DD) water with stirring. On the other hand, APS was also dissolved in DD water and both the solutions were cooled to about 5 °C. Subsequently, the APS solution was added slowly into the aniline-CSA salt solution. Once all APS was added, the mixture was mechanically stirred for 15 h. The precipitate was then washed with DD water, methanol and acetone several times, and finally dried at room temperature in a dynamic vacuum for 24 h. Four different samples of nanotubes were synthesized with 0.002 M (NT 1), 0.01 M (NT 2), 0.02 M (NT 3) and 0.04 M (NT 4) concentrations of CSA.

PANI nanofibers were synthesized using the interfacial polymerization technique given by Huang et al. [14]. Aniline monomer was dissolved in CCl_4 while APS was dissolved in DD water with HCl in it. The APS solution was carefully transferred over the aniline solution forming an interface between the two layers. After 2–3 mins, green polyaniline forms at the interface and quickly diffuses into the aqueous phase owing to its hydrophilicity. After 24 h, the entire aqueous phase is completely filled with dark green polyaniline and the organic phase is red orange. Polyaniline is collected and washed several times with DD water, methanol and acetone. Three different samples of nanofibers were synthesized with 0.02 M (NF 1), 0.04 M (NF 2) and 0.06 M (NF 3) concentrations of HCl.

PANI nanoparticles were prepared using the soft-template method [15]. Aqueous micellar dispersion was prepared by dissolving SDS in DD water with slow stirring. Then aniline was added to the solution. Subsequently, APS was dissolved in HCl solution which was prepared by dissolving HCl in DD water to form the aqueous phase. The aqueous solution was then added drop wise to the micellar solution and allowed to polymerize with mechanical stirring for about 15 h. The green precipitate formed was filtered and washed with DD water and methanol several times to remove the unreacted chemicals, aniline monomer and SDS. Three different samples of PANI nanoparticles were prepared using 0.02 M (NP 1), 0.04 M (NP 2) and 0.06 M (NP 3) HCl concentration. For all the nanostructures, aniline concentration (0.04 M) was kept the same.

2.3. Experimental techniques

The samples have been characterized by high resolution transmission electron microscope; model JEOL JEM-2100, 200 kV. The X-ray diffraction measurements were carried out using Bruker D8 Advance diffractometer with monochromatic CuK_α radiation ($\lambda = 1.5418$ Å). The dried powders of PANI nanostructures were pelletized for the electrical measurements. The dc conductivity was measured on rectangular shapes (~$3.2 \times 2.5 \times 2.1$ mm^3) cut from the disk shaped pellets in the temperature range of 5–300 K by the standard four-probe method. Electrical contacts were made using highly conducting silver paste. Lakeshore temperature controller 340, Keithley source meter 2400 and Keithley digital voltmeter 180 were used for the measurement.

3. Results and discussion

3.1. Morphological studies

HRTEM studies have been carried out to confirm the formation of PANI nanostructures. Fig. 1(a) shows the high resolution TEM image of entangled nanotubes. The inner and outer surfaces of the tubes are observed to be quite rough. The average inner and outer diameter of the tubes is 47 nm and 100 nm, respectively. The length of the nanotubes is about a few micrometers. Fig. 1(b) shows the high magnification HRTEM image of the inner and outer walls of a nanotube. Fig. 2(a) shows the HRTEM image of dispersed nanofibers with diameters ranging from 5 to 10 nm and Fig. 2(b) shows the

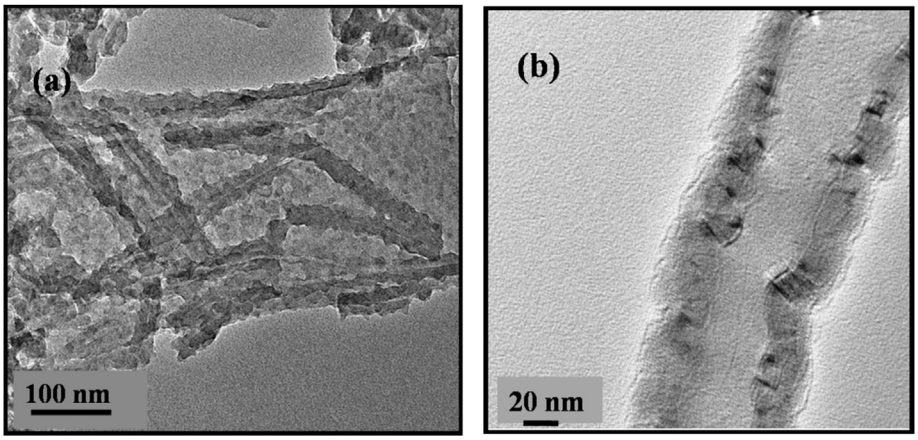

Fig. 1. (a) A representative HRTEM image of entangled polyaniline nanotubes and (b) HRTEM image of the two walls of a nanotube.

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