

Charge transport and ammonia sensing response in poly (aniline-co-1-amino-2-naphthol-4-sulphonic acid)

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The paper reports the synthesis of tubes of poly (aniline-co-1-amino-2-naphthol-4-sulphonic acid) using para toluene sulphonic acid as a dopant. The copolymers have the conductivity of the order of 0.348 S/cm to 0.198 S/cm depending on the ratio of the co-monomers present in the feed ratio. The morphology of the copolymers was studied by scanning electron microscope. Electrical conduction have been studied in the temperature range from 300 K to 30 K. Charge transport has been attributed as tunnelling in the range 30 K to 70 K. Above 70 K, charge transport is represented by Mott's three-dimensional variable hopping. The copolymer has been found to be a better ammonia vapour sensing material and can be used for detection for varying concentration.

Keywords: Conducting polymer, Polyaniline, Copolymer, Nanotubes, Scanning electron microscopy, Charge transport

Conducting polymers have become very popular in the field of material science due to its promising and novel electrical properties such as energy storage devices^{1,2}, gas sensors³⁻⁵, anticorrosive material⁶⁻⁸, EMI shielding⁹⁻¹¹, electrostatic charge dissipation¹²⁻¹⁴, OLED and flexible display devices^{15,16}, active electrode materials in batteries^{17,18}. Among so many conducting polymers polyaniline, polypyrrole, polythiophenes, polyphenyl vinylenes, poly-p-phenylene etc. have drawn a considerable attention because electrical conductivity of it, can be changed into desirable wide range by different doping process for different applications. Besides being highly disordered/amorphous it also contains structural and electronic defects. Conducting polymers essentially have π -electron conjugation in its backbone by dint of which, it acquire unique electroactive properties.

In conducting polymers, the main aspects for conduction mechanism are charge generation and transport. In polyacetylene, mobile charge carrying species are called soliton. The non-degenerate ground states inhibit the existence of solitons in other conducting polymers¹⁹. In such type of polymers, charge carriers are bound to polymer chains in the form of polarons and/or bipolarons²⁰. Polarons are

formed at lower doping levels and it gets combined for forming bipolarons at higher doping concentrations. Many studies have been made for the term second factor, charge transport²¹⁻³¹. The absence of pre defined valence and conduction band edges in the forbidden gap which makes possibility of conduction mechanism in these semiconducting materials^{21,22}. In terms of explaining the charge transport, Kivelson²³ proposed a model which predicts that charge transport occurs by hopping between neutral and charged soliton states at isoenergetic levels. It has been modified for materials having interpolyronic hopping conduction with non degenerate ground state. Mott's variable range hopping^{21,22} (VRH) and fluctuation induced tunnelling²⁵ (FIT) are another one. In FIT model for granular systems, it has been predicted that tiny conducting domains formed during the doping participation in the delocalization of charge carriers by tunnelling among the conducting islands. Here in this intergrain tunnelling distance with grain energy, both determines the conductance and temperature dependence among these grains. In this model, $T^{1/2}$ versus conductivity for a wide range of temperature while crossing to $T^{1/4}$ for low temperatures has been predicted. Mott's variable range hopping^{21,22} (VRH) model is more successful in explaining the charge transport in conducting polymers.

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Polyaniline is a unique member of conducting polymers on the basis of its easy synthesis, environmental stability, simple non-redox doping by protonic acids, and the reversible control of the electrical conductivity by chemical doping and undoping along with its extensive use as sensor material for toxic gases and hazardous vapours. Nano structures of the polyaniline are of great current interest because they combine the properties of low dimensional organic conductors with the area of high surface materials. Hence for sensing studies as well as charge transport studies, 5:5 copolymer has been selected. In the present paper, by using para toluene sulphonic acid as a dopant, we have made the tubes of polyaniline by copolymerizing aniline and (1-amino, 2-naphthol, 4-sulphonic acid). Ammonia gas sensor can be used as a variety of applications as for the safety of medical diagnostic apparatus, environmental, and chemical plant instrumentation^{35,36}.

Experimental Procedure

Materials

Aniline (Loba Chemie), 1-amino-2-naphthol-4-sulphonic acid (Hi Media Laboratories, Mumbai), Ammonium peroxydisulphate (Merck), para toluene sulphonic acid (Aldrich), and. Liq NH₃ (30%, Loba Chemie) were used as chemicals for the synthesis of copolymers. Dimethylsulphoxide (DMSO) (Merck) was used as a solvent. Aqueous solutions were prepared from the double distilled water having specific resistivity of 1 MΩ-cm.

Experimental set-up

The doped polyaniline and its copolymers with 1-amino 2-naphthol, 4-sulphonic acid have been prepared by chemical oxidative polymerisation. The concentration of aniline and 1-amino-2-naphthol-4-sulphonic acid was 0.1 mol and that of PTSA was 1.0 mol. For the copolymer, aniline and 1-amino-2-naphthol-4-sulphonic acid have been mixed in the different molar ratio (AN: ANSA:: 4:1 and AN: ANSA:: 1:1) Polymerization was initiated by the drop wise addition of ammonium peroxydisulphate (0.1 mol). The polymerization was carried out at a temperature of 0 to -3°C for a period of 4-6 h. The synthesized copolymer has been filtered and washed with distilled water to remove oxidant and oligomers. The copolymer has been collected by filtration and followed by drying under vacuum oven at 50°C.

Measurements

The UV-visible spectra of the samples (using DMSO as solvent) have been recorded using Shimadzu UV-1601 spectrophotometer. NICOLET 5700 FTIR spectrophotometer has been used for the structural characterization of polymers. Spectra are recorded in KBr pellets in the range of 400-4000 cm⁻¹. Morphology is observed using SEM (Leo 440). For the conductivity measurements, pellets are prepared and the resistivities are measured by four-point probe technique using (Keithley 220 Programmable Current Source and 181 Nanovoltmeter). Low temperature conductivity has been measured with the help of 6221DC current source of Keithley and 331 Lake Shore temperature controller connected through a PC.

Results and Discussion

Sensing response

Intrinsically conductive polymers have the advantages of morphology and structural properties which are critical for the sensitivity and selectivity of gas sensors. These properties are sensitive to polymerization parameters such as the type of the counter ions, supporting electrolyte, and their concentration and polymerization temperature. By exposing the gases, conducting polymers show significant difference in changing conductivity due to the charge mobility and the amount of charge doping in the film. Electron donation or withdrawal by the analyte vapours leads to conductivity changes in the sensor film. In the present work, we observed that copolymers, formed by copolymerising aniline and 1-amino-2-naphthol-4sulphonic acid in the presence of p-toluene sulphonic acid yields a copolymer which can be used effectively for the detection of ammonia vapours. A structure of monomers and copolymer is given in Fig. 1. Conductivity of the copolymer film changes on exposing to different concentrations of ammonia. It has been observed that the value of conductivity changes from 0.34 S/cm to 10⁻⁷ S/cm when the copolymer is exposed to different NH₃ concentration varying from 10⁻⁴ M to 1.0 M. When copolymer (1:1) was exposed to 1.0 M NH₃, value of conductivity is obtained as 1.56 × 10⁻⁷ S/cm. However, on exposing to 10⁻¹ M NH₃ concentration, the value of conductivity was found to be 1.027 × 10⁻⁵ S/cm whereas on exposing copolymer to 10⁻² M NH₃ concentration, the value of conductivity changes to 4.576 × 10⁻³ S/cm. On exposing copolymer to 10⁻³ M NH₃ concentration, the value of conductivity is

obtained as 1.144×10^{-2} S/cm and on exposing to 10^{-4} M NH_3 concentration, conductivity is 4.719×10^{-2} S/cm. Graph between \ln (concentration) and \ln (conductivity) has been shown in Fig. 2. Hence, it was found that the conductivity of the copolymer changes on treating the polymer to different concentrations of aqueous ammonia and hence the copolymer may be used as an effective ammonia gas sensor.

Conductivity measurement and charge transport

The temperature dependent conductivity (σ_{dc}) of the copolymer is measured in the temperature range 70-300 K. For PTSA doped polyaniline, its

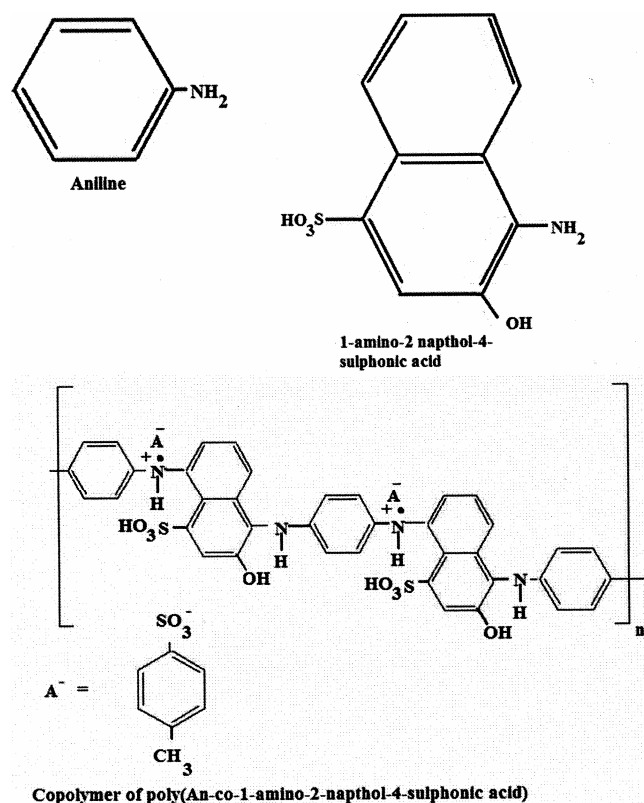


Fig. 1—Structures of aniline, 1-amino-2-naphthol-4-sulphonic acid and copolymer of poly (An-co-1-amino-2-naphthol-4-sulphonic acid)

copolymer with 1-amino-2-naphthol-4-sulphonic acid and different undoped samples of copolymer, room temperature conductivity have been specified in Table 1. It is found 1.74 S/cm for PANI-PTSA, 0.34815 S/cm for 4:1 and 0.19898 S/cm for 1:1 copolymers. It shows the semiconducting behaviour and found to be decreased with temperature (Fig. 3a). Several models have been used to explain the conductivity behaviour in the polymers. According to Arrhenius model, conductivity variation follows the relation

$$\sigma(T) = \sigma_c \exp[-(E_F - E_C)/k_B] \quad \dots (1)$$

where E_F is the Fermi energy, E_C is the mobility edge and σ_c is the conductivity at the mobility edge. In σ_{dc} versus $1000(T^{-1})$ plot (Fig. 3b), shows that the Arrhenius model is not fully applicable for explaining the conductivity mechanism as in case of normal semiconductors.

A mechanism proposed to explain the dc conductivity in disordered and amorphous materials is

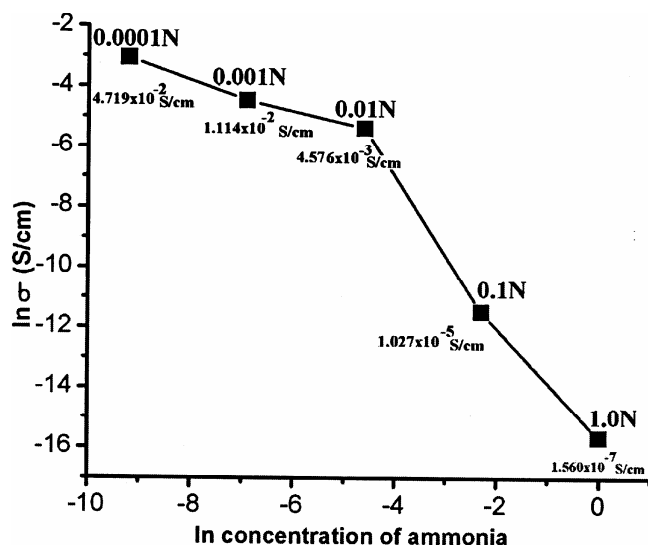


Fig. 2—Log Conductivity of the copolymer with respect to log of ammonia concentration

Table 1—UV-vis spectroscopy and room temperature conductivity

Sample name	I st absorption band (nm)	II nd absorption band (nm)	III rd absorption band (nm)	Room temperature conductivity (Scm ⁻¹)
PANI PTSA	359	442	847	1.74
Copolymer 1:1	355	452	878	0.19898
1.0N	323	622	--	1.560×10^{-7}
0.1N	332	625	--	1.027×10^{-5}
0.01N	343	627	--	4.576×10^{-3}
0.001N	345	448	637	1.144×10^{-2}
0.0001N	349	450	782	4.719×10^{-2}

Mott's variable-range hopping^{21,22}. The mechanism is based on the idea that carriers tend to hope larger distances to sites which lies energetically closer rather than to their nearest neighbours. According to this model, the dc conductivity with temperature is correlated by

$$\sigma_H = \sigma_0 \exp [-(T_0/T)^n] \quad \dots (2)$$

Here, T_0 corresponds to the Mott's characteristic temperature, σ_0 is the conductivity at $T = \infty$ and n is the dimensionality factor and is given by, $n = 1/1+r$. For 1-D, 2-D, 3-D systems value for r are 1, 2, 3 respectively. The temperature for which Eq (2) holds good, activation energy is given by

$$E_A = -\delta \ln \sigma_H / \delta(1/k_B T) \quad \dots (3)$$

Here, E_A is the activation energy and k_B is the Boltzmann constant. From Eqs (2) and (3) value of activation energy can be given as –

$$E_A = nk_B T_0 (T_0/T)^{n-1} \quad \dots (4)$$

From above equation, we note that plot of $\ln E_A$ with $\ln T$ must be a straight line with the slope giving $-(n-1)$. E_A at different temperatures can be estimated from $\log \sigma_H$ versus $1000/T$ plots.

Eqs (2) and (4) give the slope T_0 from the plots of $\log \sigma_H$ versus $T^{-1/4}$ as given by

$$T_0 = \lambda \alpha^3 / \{k_B N(E_F)\} \quad \dots (5)$$

Here, T_0 is the Mott's characteristic temperature and λ is dimensional constant²⁴ and $\lambda \sim (18.1)$. $N(E_F)$ is the density of state at Fermi level and $(\alpha = 1/r_p)$ is the coefficient of exponential decay of the localized states associated in the hopping process, r_p is the polaron radius.

Conductivity σ_0 at $T = \infty$ is given by

$$\sigma_0 = e^2 R^2 \nu N(E_F) \quad \dots (6)$$

Here, $R = [9 / \{8\pi \alpha k_B T N(E_F)\}]^{1/4}$. It is the average hopping distance between two sites and ν is the phonon frequency ($\sim 10^{13}$ Hz).

W , the average hopping energy is given by evaluating R and $N(E_F)$ with the help of following relation

$$W = 3/4\pi R^3 N(E_F) \quad \dots (7)$$

Mott's characteristic temperature may be estimated with the slope of $\ln \sigma_H$ versus $T^{-1/4}$. $N(E_F)$ may be obtained due to the assumption that the wave function

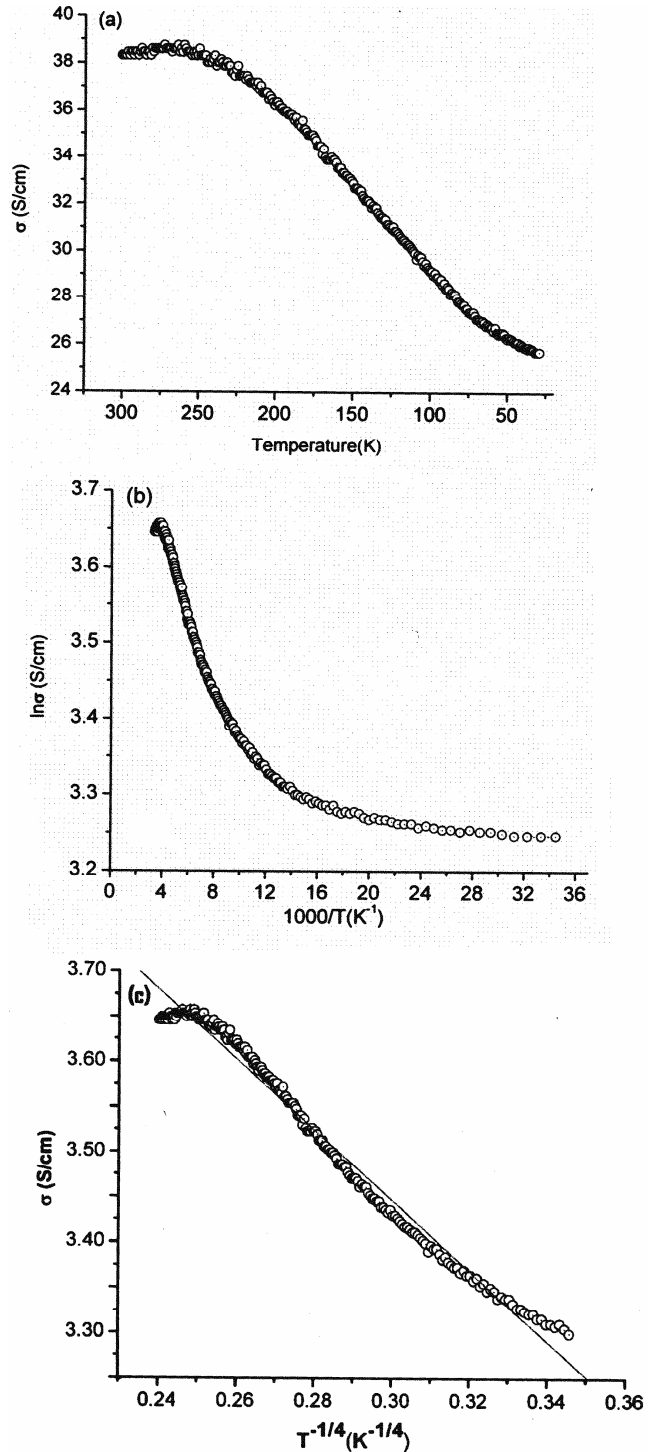


Fig. 3–Temperature dependence of conductivity (a) σ versus temperature, (b) $\ln \sigma$ versus $1000/T$ and (c) $\ln \sigma$ versus $T^{-1/4}$

localization length α is independent of conductivity and temperature. It is observed that the conductivity data fits for the 3D-VRH model with $r = 3$ having the linearity factor of 0.99198 (Fig. 3c) for copolymer but