

SYNTHESIS, CHARACTERIZATION AND ENHANCED ELECTRICAL PROPERTIES OF CTAB-DIRECTED POLYANILINE NANOPARTICLES

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Abstract Inverse microemulsion system of cetyltrimethylammonium bromide (CTAB) molecules is utilized for virtually monodispersed and controlled growth of HCl polyaniline (PANI) nanoparticles at room temperature (*ca.* 300 K). The templated electroconductive polymer reveals lamellar crystalline structure under X-ray diffraction signifying marked sub-chain alignment of the polymerized nanoparticles. The nanostructured polymer has spherically symmetric morphology in a size range of 2.0 nm to 6.0 nm under electron microscope examination. Gel permeation chromatography gives polydispersity index of 1.02 for nanostructured polymer in agreement with the size monodispersity transpired by electron microscopy. The d.c. electrical conductivity σ_{dc} of PANI at room temperature is 10.11 S/cm whereas the variation of conductivity with temperature in the range 227–303 K reveals that the conducting mechanism can be considered as three-dimensional variable-range-hopping (3D-VRH). UV-Vis spectrum indicates two broad absorption bands due to polaron formation that contributes to enhanced electrical conductivity of the polymer. The fundamental absorption edge in the polymer is formed by direct allowed transitions to the extent that the optical band gap value was found to be 2.35 eV. The crystalline nanostructure and homogeneous doping attained in the cationic template of amphiphile are argued as contributing factors to the enhanced conductivity of the polymer.

Keywords: Polyaniline; Nanostructured; Band gap energy; Electrical conductivity.

INTRODUCTION

Polymers that conduct electric currents without the addition of conductive (inorganic) substances are known as “intrinsically conductive polymers” (ICP). Conducting polymers is a prospective class of new materials that combine solubility, processibility and flexibility of plastics with electrical and optical properties of metals and semiconductors. The discovery of conducting polymers opened up many new possibilities for devices combining unique optical, electrical and mechanical properties^[1, 2]. On the top of that, nanostructured conducting polymers combine the advantages of being organic conductors and low dimensional systems and, therefore, should yield many interesting physicochemical properties and useful applications. They are of particular interest because their properties differ significantly from properties of the same conducting polymers with macroscopic dimensions^[3, 4]. Nanostructured polyaniline (PANI) is one such promising conducting material for applications in optoelectronic and microelectronic devices as well as electromagnetic interference shielding and corrosion protection. Conducting PANI nanoparticles, nanotubes or nanofibres are important polymers for many applications because they are processable in conducting form and, in addition, are both thermally and environmentally stable. On that account, morphological and electrical conductivity studies of this conducting polymer are one of the most important research areas^[5–7]. Notwithstanding, since the constituents units of a

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conducting polymer are different from those of conventional three-dimensional (3D) semiconductors or metals, so their doping is also at variance with them. The dopants in conducting polymers are positioned interstitially between polymer chains, i.e. here electroconductivity depends on the structure of the polymer chain while in conventional 3D semiconductors the dopants are substituted into constituent elements. The emeraldine salt of PANI is obtained by adding protons to the insulating emeraldine base or aniline monomer through treatment with an acid^[8–11]. A number of methods have been used for the synthesis of this conducting polymer both in the microscopic and nanoscopic dimensions; nevertheless, an effective and simple technique for the preparation of nanostructured materials is surfactant templating. In this technique, the desired material is synthesized in the environment of template provided by a surfactant or another material organized on nanometer size structure. The template is dissolved afterwards that leaves the desired material in the form of nanostructure corresponding to the shape of the template. It is believed that the nanostructure formation mechanisms as well as the template properties are crucial in determining the properties of the nanostructured materials and their molecular structure. A microemulsion (μ E) is one such highly recommended template for the preparation of nanostructures^[12, 13]. Thermodynamically stable and isotropic transparent solution of two immiscible liquids (*i.e.* an oil and water) stabilized by an amphiphile constitutes the so-called microemulsion. In fact, a microemulsion (μ E) is classified into three types namely w/o (oil continuous), o/w (water continuous) and bicontinuous microemulsion. The droplets of μ E solution are nano-sized reactors that can be utilized as polymerization media for making nanostructured particles. In this article, the inverse (w/o) μ E microemulsion template of cetyltrimethylammonium bromide (CTAB) has been utilized in the direct single-step and accelerated synthesis of nanostructured PANI (alternately referred to as templated polymer) that eliminates the post-processing steps of ordinary synthesis techniques. This work is specifically focused on the contribution of CTAB inverse micelles to the formation of stable dispersions at room temperature. The consequent morphological changes, semiconducting parameters and charge transport properties of the templated polymer nanoparticles have been thoroughly dealt with in this paper.

EXPERIMENTAL

Formulation of Inverse Microemulsions and Synthesis of PANI

Two different samples of HCl-doped PANI were prepared; bulk PANI sample was prepared according to Ref. [14] and the second sample was prepared by μ E technique. Aniline hydrochloride ($\text{C}_6\text{H}_5\text{NH}_2\text{-HCl}$) was used as a monomer, *i.e.* hydrochloric acid (HCl) in equimolar proportion to aniline as a solid aniline salt. In the inverse μ E procedure for the preparation of nanostructured PANI, four components namely CTAB, 1-butanol, aniline hydrochloride (aq.) and *n*-octane, were used. The CTAB concentration in the μ E was 14.18 wt% making the aqueous phase/surfactant ratio as 1/2. On the other hand, the *n*-octane and co-surfactant (1-butanol) ratio was kept at 4.43 wt%. The aqueous phase was prepared by dissolving separately each 0.2 mol/L of aniline-hydrochloride and 0.25 mol/L of oxidant ammonium peroxydisulfate (APS), *i.e.* $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, in 50 mL of deionised water. Reaction started at room temperature in approximately 5 min after the addition of APS to the μ E and was complete in 10 min. To contrast bulk and nanostructured PANI, the reactants of both bulk as well as μ E polymerisation process were kept for 24 h. The greenish precipitate of the polymers was collected by centrifugation, washed with ethanol and deionised water. The liquids were evaporated at room temperature and the polymer was vacuum dried at 333 K for 24 h.

Characterization

The morphology and size of the nanostructured templated polymer were examined with a Philips C12 transmission electron microscope (TEM). Nanostructured polymer powder was dispersed in deionised water wherefrom it was deposited on carbon-supported copper grids. The molecular weight of the bulk and nanostructured polymers was measured by size exclusion chromatography technique, the so-called gel permeation chromatograph (GPC) system (Breeze Brand). The instrument was calibrated using monodispersed polystyrene standards and, using the 410 channel in GPC, dilute polymer solutions were passed at room

temperature (*ca.* 300 K) through a tubular column packed with polymeric gel beads. In the GPC analysis aqueous method was utilised and 50.0 μL volume was injected for a run time of 30.0 min in each case. For the bulk PANI, the elution volume was measured as 12.907 mL and the retention time as 12.907 min, whereas for the nanostructured PANI the elution volume turned out to be 15.631 mL with a retention time of 15.631 min. The electronic absorption spectra of the PANI samples were obtained on a Lambda 25 Perkin-Elmer UV-Vis spectrophotometer. The sample holder was 1.0 cm quartz cuvette and the spectrum was recorded from 300 nm to 1000 nm. Wide angle X-ray diffraction (XRD) studies of the polymer samples were performed on a Philips X-ray diffractometer. The radiation source for XRD was CuK_{α} ($\lambda = 0.1542$ nm). To measure the electrical conductivity of our nanostructured polymer, the samples were first pressed at a pressure of 2.0 ton/cm² to devise circular discs of 1/2 mm thickness and 11.0 mm diameter. The four-point probe method and Janis closed-cycle refrigerator system (CCS-100) were used for measuring d.c. electrical conductivity $\sigma_{\text{dc}}(T)$ at room and low temperatures. Voltage and current were noted by four-point probe method connected to a programmable current source and sensitive digital voltmeter (Jandel Universal, England). For better electrical contact, four thin gold wires (0.05 mm thick and 99% pure gold) were attached in parallel on the sample surface by graphite glue (Acheson Electrodag 502). After ensuring reproducibility of the room temperature conductivity value, the temperature-dependent conductivities were registered in a temperature controlled chamber from 303 K to 227 K.

RESULTS AND DISCUSSION

Electron Microscopy and Size Exclusion Chromatography

A typical micrograph of nanostructured particles of electroconductive PANI examined under TEM is displayed in Fig. 1. The templated polymer has a narrow size distribution — in the size range of 2.0 nm to 6.0 nm — and is almost monodispersed and, in addition, intrinsically conducting being transpired by the intense black-green colour of the polymer nanoparticles^[15]. The HCl-doped nanostructured polymer bears a charged backbone and at the same time, being nanostructured, offers large surface area, therefore, an extended reaction time (approx 24 h) may result in flocculation and aggregation of the particles due to either electrostatic forces or van der Waals force or even both^[16, 17]. This is why some sparsely aggregated nanoparticles of PANI can be perceived in the TEM micrograph. Despite the fact that the morphology of PANI depends on several constraints during preparation, the micrograph of Fig. 1 reveals that the inverse microemulsion template of CTAB specifically helps in the preparation of globular and nanostructured particles of this polymer at ambient temperature. Against this scenario, without a template the polymer chains favour an unorganized and cross-linked structure. These comments are consistent with the observations of Qiu *et al.*^[18] and Antonietti *et al.*^[19]. Whereas Athawale *et al.*^[20] comment that the templated PANI is a short chain polymer that organizes itself in regular mesodomain structure for energy-entropy reasons. We remark arguably that the superb nano-sized inverse micelles of CTAB amphiphile ($\approx 3\text{--}5$ nm) in the presence of water and saturated hydrocarbon (*n*-octane) provide a set motif to the genesis of nanostructured and crystalline microstructure of the polymer. The surfactant CTAB appears to play an important role in the synthetic pathway^[21, 22]. Possibly, upon addition of aniline monomer to the inverse microemulsion system of this amphiphile, some of the aniline hydrochloride is adsorbed and wedged into the arranged CTAB molecules. The remaining aniline hydrochloride is in solution and a dynamic equilibrium is set up between them. The surfactant is adsorbed and arranged regularly in the shape of spherical micelles all around the nucleating and emerging PANI surfaces. When APS was added, a heavy clump precipitate instantly appeared presumably due to electrical neutralization between the quaternary ammonium cation of the CTAB and $\text{S}_2\text{O}_8^{2-}$ of APS. The surfactant is therefore deactivated and some of aniline hydrochloride prepared as PANI becomes encapsulated during precipitation. The resulting polymer nanoparticles are then stabilized by regeneration of the surfactant CTAB. This bears a profound effect on the morphology as well as structure of PANI like soft matter. The molecular weights as well as dispersion of bulk and templated polymers were identified with the help of gel permeation chromatography (GPC). Low molecular weight polymer (*i.e.* nanostructured PANI) took longer time whereas high molecular weight species (*i.e.* bulk PANI) reached to the

exit of the column in shorter time. GPC provided the entire molecular weight distribution from which any of the moments of molecular weight and common polydispersity indices could be calculated. The associated polydispersity index (PDI) was determined then with the standard recipe described as^[23]

$$\text{PDI} = \frac{M_w}{M_n} \quad (1)$$

From GPC measurements on templated polymer, we got $M_w = 12203$ and $M_n = 11970$. The PDI from Eq. (1) for the nanostructured polymer turns out to be 1.02. This is a clear signature on the monodispersity of templated nanostructured polymer. For bulk polymer, PDI happened to be 1.5 ($M_w = 390114$ and $M_n = 263818$), which is an indication of polydispersed bulk polymer.

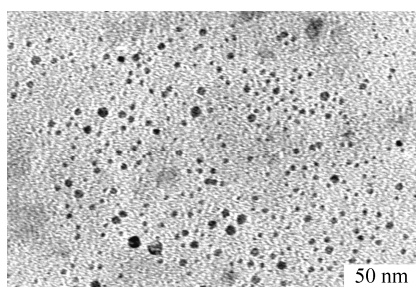


Fig. 1 TEM of nanostructured PANI doped with HCl synthesized at room temperature (*ca.* 300 K) in the inverse microemulsion of CTAB

These data next helped in calculating the size of templated nanostructured polymer (assumed spherical) by using the relation^[24]

$$d_{\text{sph}} = 0.1469 \left(\frac{M_w}{\rho} \right)^{1/3} \quad (2)$$

Employing 1.329 g/cm^3 as the density ρ of PANI in Eq. (2), we got particle size of 3.07 nm for the templated nanostructured polymer. These calculations correspond pretty much with our electron microscopy measurements (cf. Table 1).

Table 1. Size, polydispersity (PDI), resistance (R) and room temperature (*ca.* 300 K) d.c. conductivity (σ_{dc}) of HCl doped nanostructured and bulk polymer measured with TEM, GPC and 4-probe technique

Polymer sample	Size (nm) TEM	Size (nm) GPC	PDI	R (Ω)	σ_{dc} (S/cm)	Band gap (eV)
Bulk (amorphous)	10	9.76	1.5	1.0	2.21	–
Templated (crystalline)	3.5	3.07	1.02	0.909	10.11	2.35

Note: $R = \frac{\Delta V}{\Delta I}$ refers to the resistance of bulk or nanostructured PANI doped with HCl obtained from the straight-line part of the V - I characteristic curves of either of them.

UV-Vis Absorption Spectroscopy

The UV-Vis spectra of the bulk and nanostructured polymers are shown in Fig. 2. In literature reports on PANI, the electronic absorption spectra of PANI base show a band around 320–330 nm and another band around 620–650 nm. These peaks are assigned, respectively, to the excitation of the amine and imine segments of the polymer chain. We noticed in the corresponding spectrum of acidic PANI (*i.e.*, PANI doped with HCl) two new absorption bands centred on 450 nm and 851 nm that are related, respectively, to doping level and formation of polaron. The two characteristic peaks/bands noticed in absorption spectrum of the nanostructured PANI indicate only pure emeraldine salt (ES) formed in the system without the formation of emeraldine base (EB) or

leucoemeraldine base (LEB) of this polymer^[25, 26]. The extended free carrier tail is representative of the delocalized polaron band and conducting form of the polymer. The absorption windows in nanostructured PANI are broad with a doping degree (N^+/N) of approximately 38% in contrast to non-homogeneous and apparently higher level of doping of the bulk polymer. Such phenomena are attributed to the smaller particle size and greater number of charges on the polymer backbone that then transforms the compact coil like structure of polymer to an expanded or linear structure^[27–29]. The optical band gap energy of the nanostructured PANI was obtained by the following equation

$$\alpha(h\nu) = B(h\nu - E_g)^m \quad (3)$$

In Eq. (3), B is an energy-independent constant, E_g is the optical band gap whereas m represents the nature of the transition^[30–32]. Herein the energy $h\nu$ of the photon is related to the wavelength λ of UV-Vis radiation by the following relation

$$h\nu = \frac{1.24}{\lambda(\mu\text{m})} \text{ eV} \quad (4)$$

Assuming direct band gap transition for the doped PANI, m was assigned a value of 1/2. To evaluate a precise value for the optical band gap, we plotted $(\alpha h\nu)^2$ versus energy $E(h\nu)$ (cf. Fig. 3). The optical band gap was determined by extrapolating the linear portion of the plot to $(\alpha h\nu)^2 = 0$ and was found to be 2.35 eV. This band gap energy of the nanostructured PANI is considerably smaller than the value 4.28 eV reported for bulk PANI^[32]. It seems that in addition to the size quantization, the doped nanostructured PANI imparts symmetry to the valence and conduction bands and expanded the width of localized levels that reduced the band gap^[33–35]. Consequently, this augmented the density of states at the Fermi level as has been discussed later.

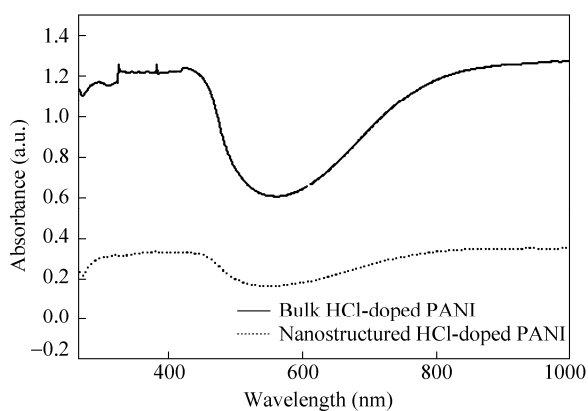


Fig. 2 UV-Vis absorption spectra of bulk and nanostructured PANI doped with HCl
Reaction time for both samples was 24 h.

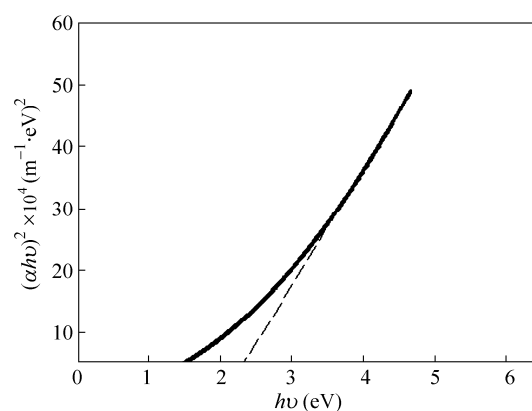


Fig. 3 Plot of $(\alpha h\nu)^2$ versus $h\nu$ for nanostructured PANI doped with HCl and prepared in the inverse microemulsion of CTAB

X-ray Profiles

X-ray scattering spectra of template HCl doped and bulk polymer samples are plotted in Fig. 4. It is evident from these profiles that the bulk polymer has broad spectral peak around 25° and, in addition, a shoulder at 21° . Such scattering profiles point to unstructured and amorphous nature of the polymer or, at the most, a short range order. The templated polymer in contrast exhibits decidedly crystalline structure between 5° and 60° although it still marginally maintains the broad peak between 20° and 30° that will render the polymer partially amorphous. It is interesting to note the marked crystalline features of the nanostructured polymer as against the bulk polymer prepared under similar temperature and pressure conditions in the inverse microemulsion of CTAB. Sharp

peaks, having different relative intensities, are observed at 7.8° , 17.7° , 24° , 26.5° , 30.8° , 33.4° , 36° , 41° , 45° , 48.5° and 56° hinting at the presence of rigid chain and ordered crystalline nanostructure^[36, 37].

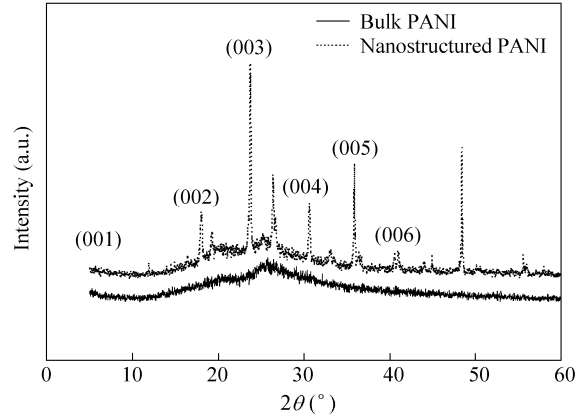


Fig. 4 X-ray diffractograms of bulk and nanostructured PANI doped with HCl
The reaction time for both the samples was kept up 24 h.

It is evident that the nanoscale dimensions help in straightening up the polymer chains followed by their alignment with respect to one another that bestows higher crystallinity upon the material. The X-ray profiles of our HCl-doped nanostructured PANI tally fairly well with the X-ray diffractograms of Han *et al.*^[38] and Goel *et al.*^[39] for their nanostructured systems. The peak at 17.7° , indexed as (002), that is rarely observed in PANI, is conspicuous in our case thereby making the overall ratios of the d-spacing almost 1:(1/2):(1/3):(1/4) corresponding to the values 1.132, 0.502, 0.37, 0.29 nm respectively for 7.8° , 17.7° , 24° , 30.8° etc Bragg reflections on a periodic layer spacing.

Temperature and Size-dependent Electrical Conductivity of Nanostructured PANI

The follow up of Arrhenius behavior is regarded as a good approximation to band theory, so we probed to the highest possible degree the electrical conductivity of our nanostructured polymer sample. In literature the Arrhenius relation for electrical conductivity of PANI-based semiconducting materials is described as^[40]

$$\sigma = \sigma_0 \exp(-E/kT) \quad (5)$$

In Eq. (5), k refers to Boltzmann constant ($= 8.63 \times 10^{-5}$ eV/K), T designates Kelvin temperature, and the pre-exponential factor σ_0 represents the high temperature limit of conductivity, *i.e.* σ at $T = \infty$ and E is the activation energy required to cause an Avogadro's number of holes and/or electrons to move. This is the extra energy needed to cause movement of holes and/ or electrons within the material. A representative plot of Eq. (5) in which $\ln \sigma$ is plotted versus $1/T$, is depicted in Fig. 5. It is noted that the electrical conductivity of PANI increases exponentially with decreasing temperature since decrease in thermal energy cools down lattice vibrations that enhance free movement of the charge carriers. Here the exponential character of temperature dependence of conductivity implies that the doped PANI represents an organic semiconductor and that its electrical conductivity most likely occurs through thermal activation^[41].

In the investigated temperature range, *i.e.*, 303 K to 227 K, the variation trend of logarithmic electrical conductivity versus reciprocal temperature exhibits a variation curve that can be split into two regions of interest (region I and region II). We are of the view that, depending on the temperature range, two different types of conduction or charge transport mechanisms occur in the doped nanostructured PANI. In the high temperature zone (region I), the electrical conductivity is thermally activated that obeys Arrhenius formula (5), meaning that the conduction is due to thermal excitation of charge carriers between 303.03 K and 265 K. Nevertheless, in the low temperature regime, *i.e.* between 265 K and 227.3 K (region II), deviation from the Arrhenius equation is

observed as in this window conductivity increases slowly. The activation energy of conductivity, E_I and E_{II} calculated from the slope is given in Table 2 and it varies from 125 meV for region I to 45 meV in region II. These values are comparable to those for poly(*N*-ethyl aniline) (78 meV) and polyaniline-tetrafluoroborate (82 meV)^[42]. The smaller value of activation energy for region II than that of region I indicates a probable interchain and intrachain conduction mechanism of the charge carriers. When the charge along the polymer chain is interrupted by defects or imperfections, it should hop to the nearest neighbor chains. Nonetheless, an increase in the interchain order can contribute to increased conductivity of the system. Intrachain charge transport occurs along the polymer backbone and requires less energy than interchain charge transport that involves the hopping of the charge to neighboring chains.

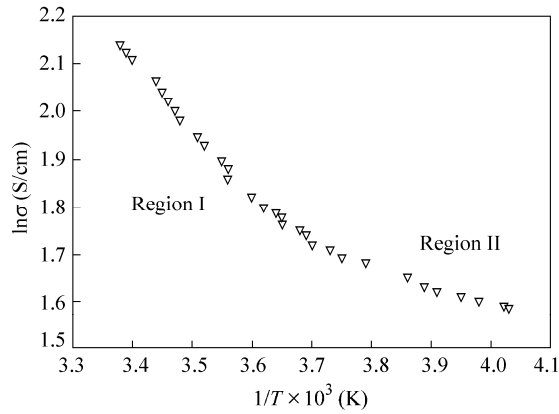


Fig. 5 Plot of logarithmic conductivity ($\ln\sigma$) versus reciprocal temperature ($1/T$) for nanostructured PANI doped with HCl and prepared in the inverse microemulsion of CTAB

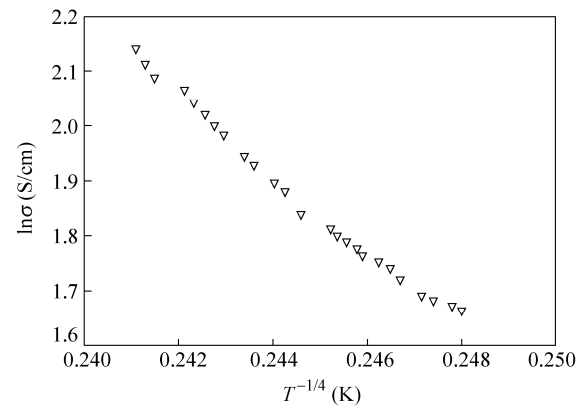


Fig. 6 Plot of $\ln\sigma$ versus $T^{-1/4}$ in a temperature range of 303 K to 227 K for nanostructured PANI doped with HCl and prepared in the inverse microemulsion of CTAB

Table 2. Pre-exponential factor (σ_0), activation energies E_I & E_{II} , T_0 , density of states $N(E_F)$, hopping length R_{hop} and hopping energy W_{hop} for HCl-doped nanostructured PANI

Conductivity parameters	σ_0 (S/cm)	$T_0 \times 10^{-3}$ (K)	$N(E_F) \times 10^{-23}$ ($\text{eV}^{-1}\text{cm}^{-3}$)	R_{hop} (nm)	W_{hop} (meV)	E (meV)
—	—	9.274	7.41	0.265	15	—
Region I	16946.3	—	—	—	—	125
Region II	355.11	—	—	—	—	43

The pre-exponential factor (σ_0) is another reliable indicator, Proposed by Mott and Davis, for pin-pointing conduction mechanism in a polymer system^[43]. According to these authors, σ_0 for conduction in the extended states is of the order of 10^4 S/cm whereas a smaller value of σ_0 indicates conduction by hopping in the localized states. The calculated values of σ_0 for region I and II are 16946.3 and 355.11 S/cm respectively (refer to Table 2). Thus, the computed value of σ_0 suggests the possibility of conduction by extended states in region I, *i.e.* at or above the mobility edge in the entire sample such that the electrons are excited to the mobility edge by phonons, and the conduction behavior is described by thermally activated behavior of the form expressed by Arrhenius relation (5). For region II, the value 355.11 S/cm is much smaller than 10^4 S/cm and, hence, conduction by localized states is dominant in region II as has been suggested by Heeger *et al.*^[44]. The room temperature electrical conductivity σ_{dc} of our HCl-doped nanostructured PANI from the linear part of the plot was found to be 10.11 S/cm. This value is noticeably higher than that of PANI prepared by Yan *et al.* (9.11×10^{-4} S/cm)^[45], Devendrappa *et al.* (5.3×10^{-4} S/cm)^[46] and Palaniappan (7.5×10^{-2} S/cm)^[47]. The d.c. conductivity σ_{dc} value for our nanostructured polymer is still higher than that of Teoh *et al.* (52×10^{-3} S/cm)^[48] for their nanofibres of PANI- Al_2O_3 as well as Ameen *et al.* (11.89×10^{-9} S/cm)^[49]. It is discernable that our

nanostructured PANI sample yield σ_{dc} which is many orders-of-magnitude enhanced. Whilst different factors can alter the conductivity of PANI, we understand that the stark distinction in d.c. electrical conductivity of our sample is attributable to the monodispersity and crystalline structure, but, above all, one cannot gainsay the significant role played by the nano-sized dimensions of our polymer in the hopping process during interchain charge transport. This assertion of ours is in conformity with the comments of Abraham *et al.*^[50].

To ascertain whether the hop is to the nearest state in space above the Fermi level or to a potentially farther state closer in energy for the sake of lower phonon energy, technically named as variable range hopping (VRH) conduction, we resort to Fig. 6 and fit Eqs. (6) to (9) to this figure as described in the forthcoming lines^[51, 52].

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^\gamma \right] \quad (6)$$

$$T_0 = 16 \sqrt[3]{kL^3 N(E_F)} \quad (7)$$

$$R_{hop} = (3/8) \left(\frac{T}{T_0} \right)^{1/4} L \quad (8)$$

$$W_{hop} = (1/4) kT \left(\frac{T_0}{T} \right)^{1/4} \quad (9)$$

As can be judged from Fig. 6, the logarithmic conductivity is approximately linear on $T^{-1/4}$ scale that signifies obeisance of Eq. (6). This way temperature dependence of conductivity is a hallmark of Mott variable-range hopping in three dimensions (3D-VRH)^[53]. The worked out average exponent γ is 1/4 which is expected for Mott VRH with an exponential energy dependence of the hopping conductivity. In the 3D-VRH model, Eq. (6) can be expressed as

$$\sigma = \sigma_0 \exp \left(- \frac{T_0}{T} \right)^{1/4} \quad (10)$$

Therefore, predominantly three dimensional (3D) charge transport occurs in nanostructured PANI adopting variable range hopping process of electrons. In the same vein, the reports of Elamin *et al.*^[51] for this polymer doped with either H_3PO_4 or tartaric acid support semiconductor behavior and VRH mechanism. In their experimental results for nanofibres of the same polymer doped with hydrochloric acid, Li *et al.*^[54] as well have proposed 3D-VRH model. In the present research work, the pellet consists of PANI globular particles (cf. Fig. 1) in which the array of chains will be random. Therefore, charge carriers can hop between chains, between globular particles and/or between chain and globular particle in the PANI pellet thereby adopting the three-dimensional variable range hopping (3D-VRH). In Eq. (6), T_0 is Mott's characteristic temperature associated with the degree of localization of the electronic wave function and can be obtained from the slope of Fig. 6. It is observed that T_0 for nanostructured PANI-HCl is comparable to PANI with chloride ion (3.98×10^3) and trichloroacetate ion (2.52×10^4)^[55, 56]. For 3-D hopping transport T_0 is given by Eq. (7), in which L is the localization length and $N(E_F)$ is the density of states at Fermi level.

One may notice from Eq. (7) that T_0 and L have reciprocal relationship; the degree of disorder of the polymer material precisely diminishes with reducing T_0 and a concomitant rise in electrical conductivity is perceived (cf. Fig. 6). Taking the localization length for the PANI monomer unit as 0.3 nm, $N(E_F)$ values were calculated in the light of charge transport as originating from this conducting polymer. Remarkably higher values were found for the density of states at Fermi level of nanostructured polymer (cf. Table 2) and hence the transition rate will be correspondingly large. The increase of density of states with concomitant decrease of hopping distance and hopping energy means higher polaron mobility^[56]. Statement Eq. (8) is used for average

hopping distance R_{hop} between two sites on (or between) a polymer chain/chains. It is worthy of note that at room temperature the average hopping distance for the nanostructured sample is about 0.265 nm which is even less than the size of a monomer unit. The estimated energy for charge hopping, calculated from Eq. (9), is in the range of 15 meV. The significantly small values of charge hopping distance R_{hop} and hopping energy W_{hop} directly point to the straightened conformation of the polymer chains, ordered crystalline structure and accelerated motion of the charge carriers as we have already asserted. Furthermore, it can be noted that the values of $N(E_F)$ and T_0 increase with elevation in conductivity of PANI probably on account of the availability of more holes but at the same time R_{hop} and W_{hop} have a converse tendency. These trends are intelligible and can be attributed to the upsurge in conductivity thanks to the nanostructured dimensions of our sample. These findings are in agreement with the observations of Pelster *et al.*^[57]. Besides, our research findings correspond well with the behavior noted by Gupta *et al.*^[58] in substituted derivatives and different dopants of PANI. Recently, it has been reported that the electrical conductivity of this polymer is largely affected by the chain alignment due to polymer stretching and the accompanied crystallinity^[59]. When the polymer chains adopt a fixed conformation in tandem with an ordered structure, enhanced chain-chain interactions take place that in turn contribute to facile transport of the charge carriers and pronounced σ_{dc} of the nanostructured polymer.

CONCLUSIONS

Stable inverse microemulsion system of CTAB molecules can be employed at room temperature in the direct single-step synthesis of monodispersed and controlled growth of HCl doped PANI nanoparticles.

The nanostructured polymer obtained from this template has spherically symmetric morphology in size range of 2.0 nm to 6.0 nm.

The electrical conductivity σ_{dc} indicated at room temperature an enhanced value of 10.11 S/cm attributable to the crystalline nanostructure of the polymer achieved in the cationic template of amphiphile.

The fundamental absorption edge in the polymer is formed by the direct allowed transitions, and the optical band gap value was found to be 2.35 eV.

The electrical conductivity of the nanostructured polymer follows Arrhenius relation $\sigma = \sigma_0 \exp(-E/kT)$ such that Mott's 3D-VRH conduction mechanism is obeyed to the extent that polaron acts as charge carrier hopping from state to state in the polymer sample.

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