

DC conductivity studies of doped polyaniline tungsten oxide nanocomposites

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Camphor sulfonic acid (CSA) doped polyaniline (PANI) and tungsten oxide (WO₃) composites (PANI/CSA/WO₃) have been prepared by *in situ* deposition technique by placing different wt% of fine grade nano powder of WO₃(PANI/CSA/WO₃ -10, -20, -30, -40 and -50%) during polymerization of polyaniline. The polymerization of aniline is carried by using ammonium peroxydisulfate as oxidizing agent. The composites are characterized by various physical methods such as Fourier transform infrared spectra (FTIR), X-ray diffractogram (XRD), thermo-gravimetric analysis (TGA), scanning electron micrograph (SEM) and transmission electron micrographs (TEM). The FTIR spectral data shows the homogeneous distribution of WO₃ nano particles in PANI/CSA polymer matrix. The TGA reveals that PANI interacted strongly with the WO₃-SO₃H, enhancing the thermal stability of polyaniline. The SEM images indicate that increase of WO₃ wt% in PANI/CSA/WO₃ composites, enhances the compactness of the matrix. The TEM image clearly shows the size distribution of WO₃ nanoparticles formed during the reaction and ranges from 150 to 200 nm. The temperature dependent DC conductivity of PANI/CSA/WO₃ composites is studied in the temperature range 308-433 K. The results of PANI/CSA/WO₃ indicate strong interaction of PANI/CSA with WO₃ in the composites. The study of DC conductivity shows an evidence for the transport properties of the composites. Due to the positive temperature coefficient of resistance of WO₃, these composites can signify in development of new materials in temperature dependent applications.

Keywords: Doped polyaniline, Tungsten oxide, DC conductivity, Positive temperature coefficient

Polyaniline (PANI) is a typical conducting polymer well-known for its mechanical flexibility, environmental stability and controllable conductivity with acid/base modification (doping/undoping). It has potential applications as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, sensors, etc.¹⁻⁶ There is an increasing demand for polymeric materials such as PANI, whose electrical conductivity can be tailored for a given application and which have attractively combined mechanical and other properties. Thus, they have served as an impetus for many studies on conductive blends to obtain a wide range of conductivities, which is controllable given the conducting polymers varied weight fractions for various potential applications.^{7,8} Thus, by blending PANI with other polymers or fillers, we can obtain new materials possessing improved processability, flexibility and controllable conductivity⁹⁻¹². In recent years, tungsten trioxide has been employed in the production of electrochromic windows, or smart windows. These windows are electrically switchable glass that change

light transmission properties with an applied voltage¹³. This allows the user to tint their windows, changing the amount of heat or light passing through. Another new use for tungsten is in Dense Inert Metal Explosives, the first notable use of these devices was in Israel-Gaza conflict¹⁴. Although the distinct property of PANI-metal oxide (MO) is well-known, the interaction between PANI and MO is difficult to establish. To achieve processability in this aspect, surfactants such as camphor sulphonic acid (CSA), dodecyl benzene sulphonic acid (DBSA), and naphthalene sulphonic acid (NSA) are used, serving as a template for PANI. The important property of PANI synthesized in the presence of these surfactants is its solubility in organic solvent directly from the oxidized state. However, the synthetic method, which requires a relatively large dopant such as DBSA and NSA, reduces the PANI chains interaction. In this study, the PANI/CSA/WO₃ nanocomposite powders were synthesized by *in situ* deposition from the oxidative polymerization of aniline in the presence of tungsten oxide. This research is aimed to synthesize PANI/CSA/WO₃ composite in the presence of camphor sulphonic acid to improve morphological, thermal and

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electrical properties of PANI/CSA/metal oxide composites. A possible mechanism for the conductivity of synthesized doped polyaniline tungsten oxide composite was investigated. Ammonium peroxydisulfate (APS) was utilized as an oxidant in the presence of different mole percentages of WO_3 with an ultrafine grade powder. The thermal properties of the PANI/CSA and PANI/CSA- WO_3 composite powder were compared with those of pure PANI powder and characterized by FTIR, XRD, TGA, SEM, and TEM analysis.

Experimental Procedure

All chemicals used for the synthesis of PANI/CSA- WO_3 and its composites were purchased from Sigma-Aldrich and used without further purification. All solutions were prepared using deionized water. A weighed amount of WO_3 powder was dispersed in 200 mL distilled water, after which 2.0 mL of aniline was injected into this suspension and the suspension was stirred magnetically for 2 h. Afterward, 0.1 M of APS $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ was slowly added to the mixture with constant stirring, and the reaction was performed for about 5 h at 0°C . The precipitated composite was filtered and rinsed with 1 M HCl and distilled water. The composites are abbreviated as PANI/CSA and

PANI/CSA- WO_3 varied weight percentage of WO_3 powder used in the polymerization reaction. The resulting precipitate was filtered and washed thoroughly with deionized water and acetone. It was then dried under vacuum for 24 h in order to achieve a constant weight. Infrared spectra of the polymer and nanocomposite samples palletized with KBr were performed utilizing an FTIR spectrometer (Perkin-Elmer Model 1600) and KBr (polymer: KBr = 1: 20) at a resolution of 2 cm^{-1} from 4000 to 400 cm^{-1} . The XRD patterns were obtained utilizing a Philips Diffractometer (PW 1710) with Cu-K α ($k = 1.5406\text{ \AA}$) radiation. The powder morphology was investigated by utilizing SEM (Philips XL-30 ESEM) and TEM (JOEL, JEM-2010), the thermal properties were obtained by thermogravimetric analysis (TGA) (Perkin Elmer model TGA 7) in the range of $25\text{--}808^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The DC electric measurements for the obtained composite films were performed within the temperature range $300\text{--}500\text{ K}$ using the two-probe technique, with a Keithly 224 constant current source and a Keithly 617 digital electrometer.

Results and Discussion

FTIR Spectra of PANI/CSA/ WO_3

Figure 1 shows the FTIR spectra of PANI/CSA, WO_3 and PANI/CSA/ WO_3 -50. The FTIR spectra of

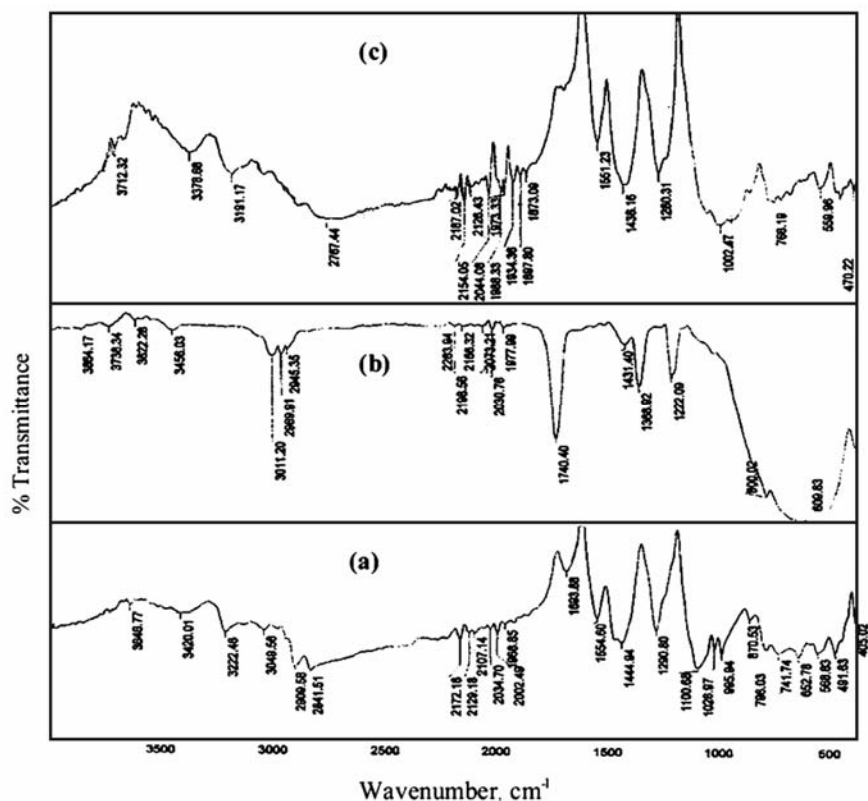


Fig. 1 — The IR spectra of (a) PANI/CSA, (b) Pure WO_3 and (c) PANI/CSA/ WO_3 -50

PANI are similar to those reported in earlier studies¹⁶. The main characteristic absorption bands of pure PANI are observed at 1550 cm^{-1} (C=C stretching of the quinoid ring), 1469 cm^{-1} (C=C stretching of the benzenoid ring), 1243 and 1296 cm^{-1} (C-N stretching), and 797 cm^{-1} (C-H stretching). The presence of absorption bands at 797 cm^{-1} is related to the para-substituted aromatic rings¹⁷. The characteristic peak at 1550 cm^{-1} shows a slight shift from PANI/CSA to PANI/CSA/ WO_3 -50 composite, where in pure WO_3 it does not exist. Those at 1243 cm^{-1} and 1296 cm^{-1} remain unchanged in PANI/CSA/ WO_3 -50 composite. Whereas those at 1459 cm^{-1} and 797 cm^{-1} show slight broadening in PANI/CSA compared to PANI/CSA/ WO_3 -50. The WO_3 characteristic peaks at 1103 cm^{-1} and 452 cm^{-1} are likewise observed in both the spectrum PANI/CSA/ WO_3 -50 nanocomposites. The characteristic peaks from the PANI/CSA around 1300 cm^{-1} , 1486 cm^{-1} and 1560 cm^{-1} , which correspond to the stretching modes of the C-N and C=N bonds, reveal the presence of leucoemeraldine and pernigraniline components. These peaks are shifted to 1303 cm^{-1} , 1492 cm^{-1} and 1568 cm^{-1} in PANI/CSA/ WO_3 -50 composite. The above results show a small shift of peak value to a higher wavelength by the value of $3\text{--}5\text{ cm}^{-1}$. This increase in the peak band indicates that there is a decrease in conjugation length both in PANI/CSA as well as PANI/CSA/ WO_3 -50, which suggests that there exists an interaction between the polyaniline and nanocrystalline WO_3 . It proves the formation of the PANI/CSA/ WO_3 composites.

X-ray diffraction

Figure 2 shows the XRD patterns of the PAN/CSA, WO_3 and PANI/CSA/ WO_3 -50% respectively. The XRD patterns of WO_3 (Figure 2b) match well to the previously reported¹⁷ monoclinic structure, and the strong intensity of the diffraction peaks indicates a highly crystalline structure. The diffraction peaks (2θ) at 23.1° , 23.6° , 24.4° , 26.6° , 28.9° , 33.3° , 34.2° , and 36.2° are assigned as the (002), (020), (200), (120), (112), (022), (202), and (212) planes of the monoclinic WO_3 , respectively. Diffraction of PANI/CSA have a broad peak at about $2\theta = 25.92^\circ$, which is a characteristic peak^{18,19} of PANI/CSA. The crystallinity of the formed composites was followed with X-ray diffraction (XRD) as a function of weight percent of inorganic component. The diffraction pattern of PANI/CSA/ WO_3 nanocomposite shows a peak at about $2\theta = 26.89^\circ$ indicates the presence of WO_3 particles in the conducting polyaniline.

Surface Morphology

Figure 3 shows the SEM images of pure PANI/CSA, WO_3 and PANI/CSA/ WO_3 -50 with variation of the concentration of WO_3 is analyzed for morphological studies. The composites of PANI/CSA relatively have a uniform surface with the agglomeration of PANI/CSA structures that are clearly visible. However, with the addition of WO_3 , the distributions of tungsten oxide particles are clearly visible in the composites. In PANI/CSA/ WO_3 -50, the micrograph demonstrates the dispersion of WO_3 nanoparticles. Therefore, the formation of PANI/CSA nanocomposites may be the result of free PANI particles adsorbed on the surface of the WO_3 nanoparticles, which grow together as the polymerization proceeds. Thus, it may be suggested that the concentration of WO_3 has a positive effect on morphology of PANI/CSA composites. Both pure PANI/CSA and their composites are observed to exhibit particulate structures with a fairly uniform size distribution. The pure PANI/CSA particles are observed to be relatively loosely packed as compared to the composites.

TEM

Figure 4 shows typical low-magnification TEM images of the WO_3 and PANI/CSA/ WO_3 composites. The spherical WO_3 nanoparticles are well distributed and stabilized by the conducting polyaniline. The corresponding histogram of the size distribution of the oxide nanoparticles indicates a broad distribution ranging from 150 nm to 200 nm of the oxide nanoparticles formed during the reaction. The WO_3 are coated with PANI/CSA matrix with a small fraction of the coated particles adhered to the matrix surface.

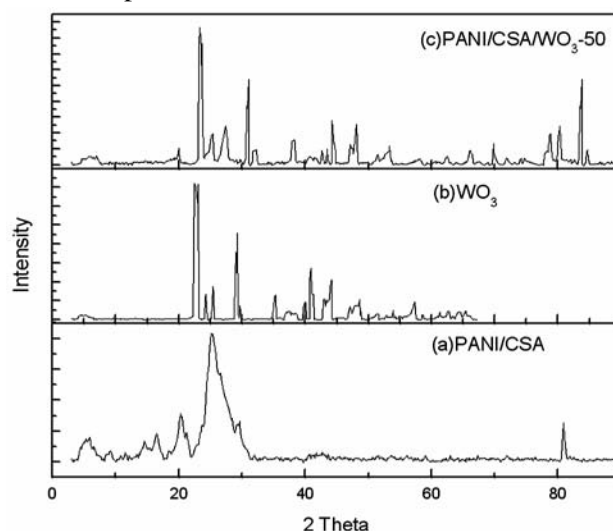
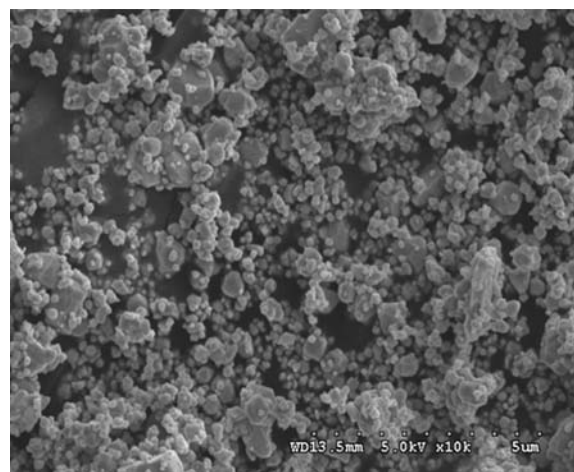
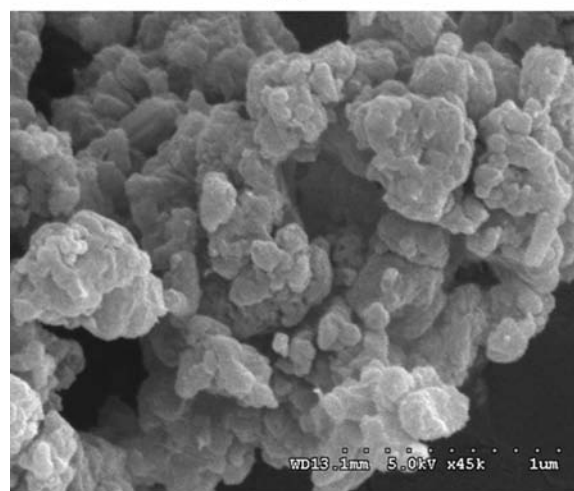


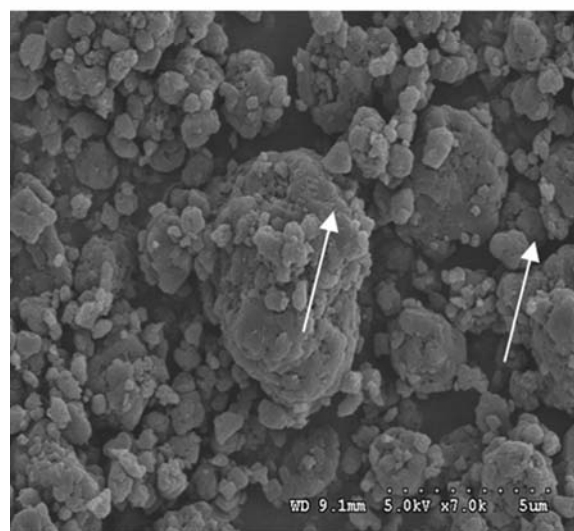
Fig. 2 — XRD Spectra of (a) PANI/CSA, (b) Pure WO_3 and (c) PANI/CSA/ WO_3 -50



(a)

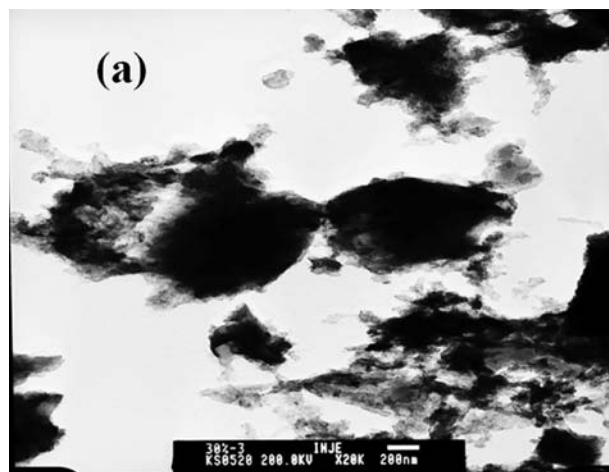


(b)

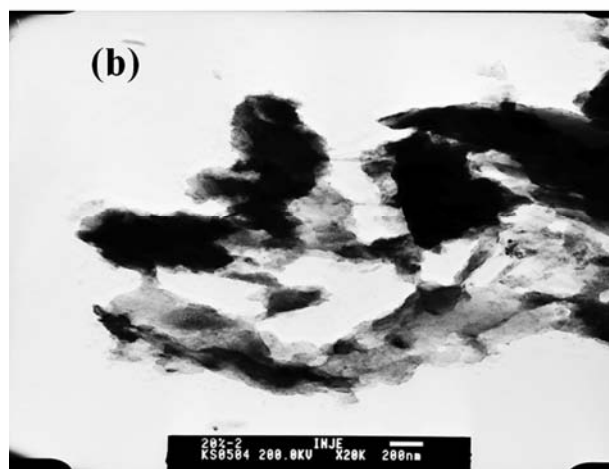


(c)

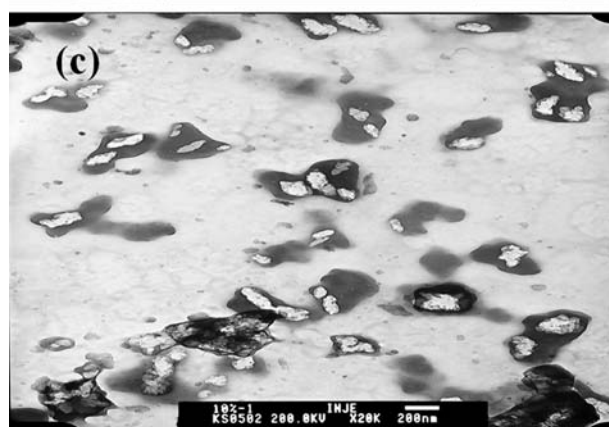
Fig. 3 — SEM images of (a) Pure PANI/CSA, (b) Pure WO_3 and (c) PANI/CSA/ WO_3 -50



(a)



(b)



(c)

Fig. 4 — TEM images of (a) PANI/CSA, (b) PANI/CSA/ WO_3 -10 and (c) PANI/CSA/ WO_3 -50, all at 200 nm

Thermo gravimetric analysis

Further evidence of the presence of conducting PANI was confirmed by TGA analysis (Fig. 5). The content of camphor sulfonic acid and PANI are estimated from the gravimetric analysis of varied percentage of WO_3 oxide (30% and 50%), respectively. As shown in Fig. 5, the camphor

sulfonic acid and PANI start to decompose at 300°C. The decomposition rate of the polymer when combined with WO₃ is found to be very different from the decomposition rate of the bulk polymer. The bulk PANI emeraldine salt (PANI/DS) decomposes between 200 and 700°C and the polymer composite decomposes slowly from 300 to 600°C (Fig. 5). This result implies that PANI interacted strongly with the surface WO₃-SO₃H, enhancing the thermal stability of conducting polyaniline.

DC electrical properties

To investigate the charge transport mechanism in the PANI/CSA-WO₃ composites, electrical conductivity dependence on temperature is studied for all compositions. Figure 6 shows the variation of electrical resistance with temperature for PANI/CSA/WO₃-10, PANI/CSA/WO₃-20, PANI/CSA/WO₃-30, PANI/CSA/WO₃-40 and PANI/CSA/WO₃-50. The electrical resistance decreases exponentially with temperature which is similar to semiconducting behaviour and it rises with the increase in the content of WO₃. The temperature coefficient of resistivity (TCR) was determined from the variation of electrical resistivity with temperature using the following relation²⁰.

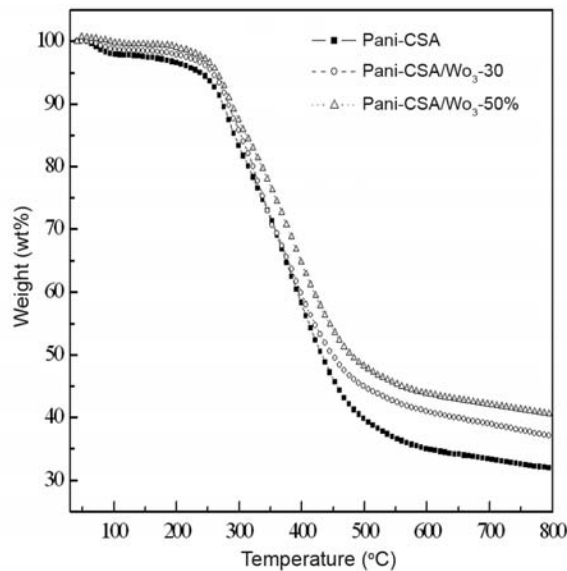


Fig. 5 — TGA curves for the (a) PANI/CSA, (b) PANI/CSA/WO₃-10 and (c) PANI/CSA-50

$$\text{TCR} = 1/\rho(T_1)[\Delta\rho/\Delta T] \quad \dots (1)$$

where $\Delta\rho = \rho(T_1) - \rho(T_2)$, and $\Delta T = T_2 - T_1$.

Table 1 shows the calculated TCR values for different composites. They have negative values and decrease with temperature as the content of WO₃ increases. The increase of conductivity with increasing temperature indicates the composites' semiconducting behavior. The results of conductivity in the composites suggest that WO₃ yields a positive influence on the conducting properties of PANI/CSA composite, which is triggered by the mobility of WO₃ counter ions at a higher temperature. The molecular dispersion of WO₃ in the solution results in a micro-gel state, which moulds the particles in a continuous electron path generating an increased number of active sites for the charge transfer through the interface inside the electrode; this is achieved through constant contact with the PANI/CSA matrix. The WO₃ molecular chain is flat and ribbon like, and its conformation is stabilized by the formation of an intra molecular hydrogen bond in the solution. As a result, the PANI/CSA-WO₃ composite macromolecules display very rigid and extended patterns. These form a continuous electron path by charge transfer at the interface between the electrodes^{17,21-23}. The formation of a chain structure containing PANI/CSA particles

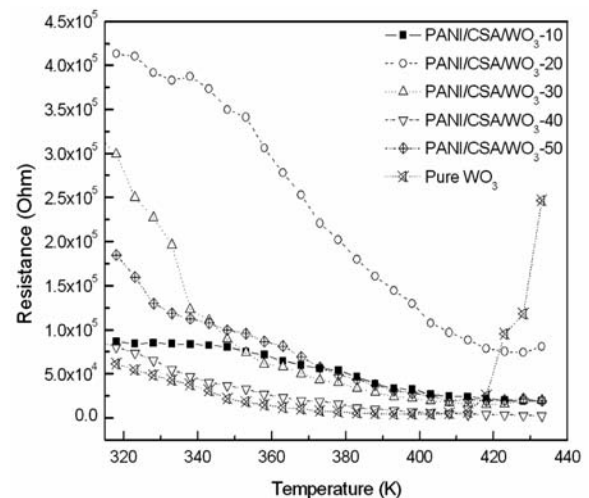


Fig. 6 — Temperature-dependence of electrical resistance of PANI/CSA/WO₃-10, -20, -30, -40 and -50 composites

Table 1 — Calculated values of the temperature coefficients of resistivity (TCR) of PANI/CSA/WO₃-10, -20, -30, -40, -50 and Pure WO₃

Temp. range (K)	Temperature coefficient of resistivity (TCR)					
	PANI/CSA/WO ₃ -10	PANI/CSA/WO ₃ -20	PANI/CSA/WO ₃ -30	PANI/CSA/WO ₃ -40	PANI/CSA/WO ₃ -50	Pure WO ₃
320-350	-0.0041	-0.0005	-0.0201	-0.0207	-0.0161	-0.023
350-400	-0.0113	-0.0136	-0.0148	-0.0158	-0.0148	-0.0153
400-433	-0.012	-0.0075	-0.0059	-0.0187	-0.006	57.55

aligned in the form of interspersed chains with regions²⁴⁻³⁴ results in the increased conductivity properties of the crystalline-like polymer. WO₃ oxide particle shows positive temperature coefficients after 400-433 K.

Figure 7 shows the relation between the logarithmic DC conductivity versus temperature of composites with different wt% of WO₃. The results show a common trend that as the temperature increases the conductivity of all the PANI/CSA/WO₃ composites increases. This is evident from the graphs. But the composites fail in demonstrating the decrease in conductivity as temperature increases, as, it is happening in pure WO₃ (which show decrease in conductivity). This trend not occurring in the PANI/CSA/WO₃ composites may be attributed to two phenomena. First one is the wt% of WO₃ in composites might needs to be more (more than 50 wt% of WO₃). The second reason might be that the phenomena of decrease in conductivity as temperature increases might be occurring at temperature beyond the 440 K. This higher temperature is a limiting point, as this temperature lies beyond the melting temperature of the PANI/CSA which is evident from Table 2. At higher temperatures, the negative

temperature coefficients of PANI/CSA/WO₃ composite starts decreasing. In a typical example of PANI/CSA/WO₃-50 composite¹⁷, the negative temperature coefficient has the minimum value of -0.006, which is minimum among all the composites in the temperature range of 400-433 K. This phenomenon may be caused due to the mobility of counter ions of WO₃ at higher temperature. This is attributed to the modification of bulk morphology of PANI/CSA by WO₃.

Figure 8 shows the relationship between the logarithmic of conductivity versus temperature inverse for PANI/CSA/WO₃-10, PANI/CSA/WO₃-20, PANI/CSA/WO₃-30, PANI/CSA/WO₃-40 and PANI/CSA/WO₃-50, which is exactly a reverse of Fig. 7. The conductivity behavior depending on temperature can be ascribed by two mechanisms for electrical conduction in the composites. The reason for the increase in the conductivity is attributed to the thermal energy at higher temperature to excite electrons to the conduction band (thermal process). Such behavior can be expressed by the Arrhenius equation.²⁶

$$\sigma = \sigma_0 \exp(E_a/k_B T) \quad \dots (2)$$

Table 2 — Calculated values of the activation energies of PANI/CSA/WO₃-10, -20, -30, -40, -50 and Pure WO₃

Temp (K)	Activation energy E_a (kcal/mol) 10^3					
	PANI/CSA/WO ₃ -10	PANI/CSA/WO ₃ -20	PANI/CSA/WO ₃ -30	PANI/CSA/WO ₃ -40	PANI/CSA/WO ₃ -50	Pure WO ₃
320-350	3.0638	3.0427	2.7244	2.8462	2.9246	2.7390
350-400	2.1507	2.1118	2.0289	1.9624	2.0365	1.955
400-433	4.1059	4.1701	3.6625	3.9571	3.6110	6.6796

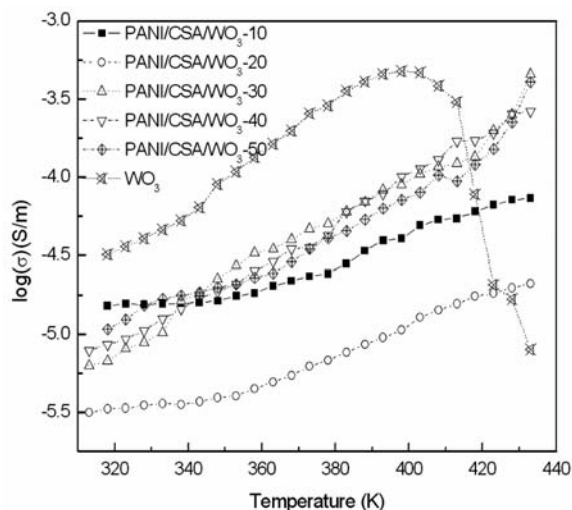


Fig. 7 — Temperature-dependent DC electrical conductivity of PANI/CSA/WO₃-10, -20, -30, -40 and -50 composites

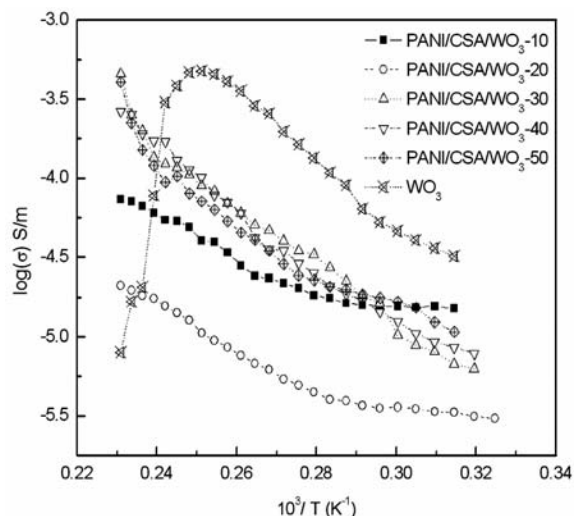


Fig. 8 — Inverse of temperature dependence of logarithmic conductivity for PANI/CSA/WO₃-10, -20, -30, -40 and -50 composites

where σ is the DC conductivity, σ_0 is constant for a material and k_B is the Boltzmann constant, T is absolute temperature, and E_a is the activation energy.

The other mechanism takes place in the low-temperature region, i.e., around 320-350 K and is attributed to the hopping process, in which the excited electrons in this region lose their ability of transition to the conduction band with lowering temperature. Thus, the electron attempts to find a state of similar energy by tunnelling beyond its nearest neighbours to hop into more distant sites. This hopping leads to a greater selection of possible energy levels of electrons. The behavior of DC conductivity in this region is called variable range hopping (σ_v), which is expressed in Mott's theory²⁶⁻²⁸ as follows:

$$\sigma_v = \sigma_0/T^{1/2} \exp(-AT^{1/4}) \quad \dots (3)$$

where A is Arrhenius constant. The values of E_a was determined from the slopes of the fitted lines as in Fig. 8 (best fit of Arrhenius curves), and they are indicated in Table 2 at different temperature ranges. These values show the dependence of the thermal rate process of electron transport within these temperature ranges. The difference in the values of the apparent activation energy (Table 2) for the three temperature ranges show different electrical mechanisms that are taking place in the bulk of these composites.

Figure 9 presents the relation of $\log(\sigma_v) \times (T^{1/2})$ versus $T^{1/4}$ for different composites. The graphs show linear and nonlinear variation with $T^{1/4}$. This can be attributed to the fact that the PANI/CSA/ WO_3 with

different wt% of WO_3 , composites does not show complete negative TCR in all the composites. Some of the composites have the influence dominated by negative TCR and the positive TCR cannot be ruled out in a smaller percentages. Which are responsible for non-linear variations of the graphs, of course from the previous discussion (Fig. 7) it is clear that the negative TCR dominates in the composites. The linear relation within the temperature range supports the assumed mechanism. This observation is consistent with Mott's variable range hopping process.²⁴⁻²⁶ Overall the dependence on temperature of the dc electrical conductivity of the composites is similar to semiconducting behavior with negative TCR. The electrical conductivity of these composites increases with temperature in all these composites as the WO_3 concentration is increased, and this exhibits a thermal electron process (high-temperature region) and a hopping process (low-temperature region). The apparent activation energy shows a pronounced effect with the increase in the content of WO_3 with temperature. The synthesized composites are thermally more conducting than PANI and have a stable DC conductivity which changes with temperature.

Conclusion

PANI/CSA- WO_3 composites were synthesized by the chemical method using aniline in an aqueous media containing well dispersed WO_3 . The DC conductivity was studied within the temperature range of 320-433 K. The increase in conductivity suggests that the WO_3 acts as a suitable material for making PANI/CSA composites. The method described here may be useful for developing new applications of these nano-composites in molecular electronics and other fields. The results of PANI/CSA/ WO_3 indicate some kind of interaction of PANI/CSA with WO_3 in the composites. The study of DC conductivity shows an evidence for the transport properties of the composites. Due to the positive temperature coefficient of resistance of WO_3 , these composites can signify in development of new materials in temperature dependent applications.

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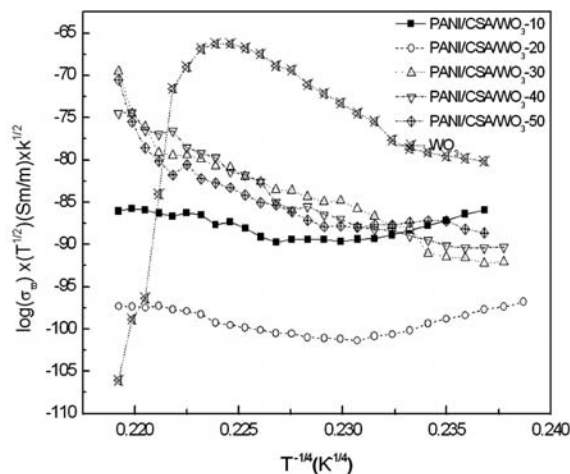


Fig. 9 — Plot of $\log(\sigma_v) \times (T^{1/2})$ as a function of $T^{1/4}$ for PANI/CSA/ WO_3 -10, -20, -30, -40 and -50 composites

References

- 1 Bhadra J & Sarkar D, *Mater Lett*, 63 (2009) 69.
- 2 Rahy A & Yang D Y, *Mater Lett*, 62 (2008) 4311.
- 3 Wu T M, Lin Y W & Liao C S, *Carbon*, 43(4) (2005) 734.
- 4 Sainz R, Benito A M, Martinez M T, Galindo J F, Sotres J, Bari A M, Coraze, Chauvet O & Maser W K, *Adv Mater*, 17(3) (2005) 278.
- 5 Wei Z X, Wan M X, Lin T & Dai L M, *Adv Mater*, 15(2) (2003) 136.
- 6 Baibarac M, Baltog I, Lefrant S, Mevellec J Y & Chauvet O, *Chem Mater*, 15(1) (2003) 4149.
- 7 Omastova M, Kosina S, Pionteck J, Janke A & Pavlinec, *Synth Met*, 81 (1996) 49.
- 8 Ikkala O T, Laakso J, Vakiparta K, Virtanen E, Ruohonen H, Jarvinen H, Taka T & Passiniemi, *Synth Met*, 69 (1995) 97.
- 9 Das B, Kumar S, Chakraborty S, Chakraborty D & Gangopadhyay S, *J Appl Polym Sci*, 69(5) (1998) 841.
- 10 Ghosh M, Barman A, De S K & Chatterjee S K, *Solid State Commun*, 103(11) (1997) 629.
- 11 Carmichael R S, *Handbook of Physical Properties of Rocks*, vol. 1 (CRC Press, Florida), 1982.
- 12 Khasim Syed, Raghavendra S C, Revanasiddappa M, Sajjan K C, Lakshmi Mohana, & Faisal Muhammad, *Bull Mater Sci*, 34 (7) (2011) 1557-1561.
- 13 Lee W J, *J Electron Mater*, 29 (2000) 183.
- 14 *Dense Inert Metal Explosive (DIME)* http://en.wikipedia.org/wiki/Dense_Inert_Metal_Explosive.
- 15 Basavaraja C, Veeranagouda Y, Lee K, Pierson R & Huh D S, *J Polym Sci A: Polym Phys*, 47 (2009) 36-45.
- 16 Basavaraja C, Kim D G, Kim W J, Kim J H & Huh D S, *Bull Korean Chem Soc*, 32(3) (2011) 927-933.
- 17 Wang G, Ji Y, Huang X, Yang X, Gouma P I & Dudley M, *J Phys Chem B*, 110,(2006), 23777-23782.
- 18 Wan M & Li J, *J Polym Sci*, A36(1998) 2799,
- 19 Wan M, Li M, Li J & Liu Z, *J App. Polym Sci*, 53 (1994) 131.
- 20 Basavaraja C, Pierson R, Vishnuvardhan T K & Huh D S, *Eur Poly J*, 44 (2008) 1556.
- 21 Ayse G Y & Gok A, *Synth Met*, 157(4-5) (2007) 235.
- 22 Basavaraja C, Pierson R & Huh D S, *J Appl Poly Sci*, 108 (2008) 1070.
- 23 Kurt I D, Skjak-Braek G & Olav S, *Int J Biol Macromolecules*, 21 (1997) 47.
- 24 Feng X, Liu Y, Lu C, Hou W & Zhu J, *J Nanotechnology*, 17 (2006) 3578.
- 25 Ayse G Y & Gok A, *Synth Met*, 157(4-5) (2007) 235.
- 26 Mott N F & Davis E A, *Electronic Processes in Non-Crystalline Materials*, (Oxford:Clarendon Press, Oxford), 1979.
- 27 Holland E R, Pomfret S J, Adams P N & Monakan A P, *J Phys: Condens Matter*, 8 (1996) 2991.
- 28 Joo J, Long S M, Pouget J P, Oh E J, MacDiarmid A G & Epstein A, *J Phys Rev B*, 57 (1998) 9567.
- 29 Kaiser A K, *Rep Progr Phys*, 64,(2004) 1.
- 30 Hauser J J & Kimerling L C, *Phys Rev B*, 11(10) (1975) 4043.
- 31 Efros A L & Shlovskii B I, *J Phys C*, 8(4) (1975) 49.
- 32 Sheng & Philos P, *Mag A*, 65(3) (1992) 357.
- 33 Zuppiroli L, Bussac M N, Paschen S, Chauvet O & Forro, *Phys Rev B*, 50(8) (1994) 5196.
- 34 Basavaraja C, Veeranagouda Y, Kyoung Lee, Pierson R, Revanasiddappa M & Do Sung Huh, *Bull Korean Chem Soc*, 29(12 1) (2008) 1-4.