



Generation of gold–PEDOT nanostructures at an interface between two immiscible solvents

S. Harish, J. Mathiyarasu^{*}, K.L.N. Phani

Central Electrochemical Research Institute, Karaikudi 630006, Tamilnadu, India

ARTICLE INFO

Article history:

Received 3 February 2009

Received in revised form 28 May 2009

Accepted 29 May 2009

Available online 6 June 2009

Keywords:

A. Composites

A. Nanostructures

B. Chemical synthesis

C. Electron microscopy

D. Microstructure

ABSTRACT

Gold–poly(3,4-)ethylenedioxythiophene (Au–PEDOT) composite with variant morphology was synthesized through interfacial polymerization at room temperature in the absence of a template, phase transfer catalyst or surfactant. A systematic variation of the relative concentration of the reactants yields morphologies typical of nanorods of diameter approximately 20–30 nm and length of few 0.5–1 μm . Transmission electron microscopy reveals the structure of the nanowire to be the one in which the core is Au and the outer shell is made of PEDOT. Oligomer formation, speculated during the interfacial reaction was confirmed by the analysis of the organic phase using ultraviolet–visible (UV–vis) and nuclear magnetic resonance (NMR) spectroscopy techniques.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

In the recent years, conducting polymer nanocomposites have received a great deal of attention due to their unique physical and chemical properties and potential applications such as catalysis, nanoelectronic devices, magnetic devices, sensors and biomaterial separation membranes [1–7]. Myriad methods have been developed and reported for the synthesis of nanocomposite materials. The widely used template techniques, such as organic templates [8], ionic surfactants [9–10], hard template [11], polyelectrolytes [12], seeding [5], etc. are commonly employed in the synthesis of nanostructured polymer composites, but such techniques have the disadvantages of having subsequent removal of the templates to obtain the nanostructure. Techniques that avoid the use of a template are primarily electrochemical based [13,14] and electron beam lithography or electrospinning techniques [15–17]. These non-templating techniques have been of interest for a number of years, with their own merits and demerits [18]. Interfacial polymerization (IP), though a classical technique initially applied for the synthesis of condensation polymers, has not emerged as the one that belongs to the class of non-templating techniques. IP has traditionally been performed using a organic phase–chloroform, toluene, benzene, dichloromethane, etc. and an aqueous phase.

Synthesis of various nanomaterials has been reported using this technique [19–28].

Several researchers have addressed the synthesis of nanostructured conducting polymer materials [29,30] and recently, Lu et al. [31] have reported the synthesis of Au–PEDOT nanocables. Apart from conductivity analysis of the nanocables, they reported that some products arising from the oxidation of EDOT by HAuCl_4 dissolve in the aqueous medium initially to finally get accumulated at the interface. Though the chemical nature of this substance was conjectured to be an oligomer of EDOT, detailed analysis was not reported. In the present study, the reaction between EDOT in organic phase and HAuCl_4 in the aqueous phase not only leads to the formation of Au–PEDOT nanostructures at the interface but also enrichment of the organic phase with oligomer-like species, when the organic phase is dichloromethane. Chemical analysis of this organic-soluble species showed evidence for the formation of neutral EDOT oligomers. However when the organic phase is toluene, only the interfacial product is formed with the organic phase unaffected. In what follows, we present the results of the work involving the interfacial reaction between the reactants in dichloromethane or toluene in the organic phase and the aqueous phase.

In this work, we present our results on the synthesis of Au–PEDOT by a one-step interfacial reaction between EDOT and HAuCl_4 in dichloromethane/water biphasic system and characterization of the interfacial product. In addition, interestingly, species arising out of the oxidation of EDOT are also formed in the organic phase, when the latter is dichloromethane.

^{*} Corresponding author. Tel.: +91 4565 227550; fax: +91 4565 227779.
E-mail address: al_mathi@yahoo.com (J. Mathiyarasu).

2. Materials and methods

2.1. Synthesis of Au–PEDOT

All chemicals were of analytical grade and used as received from Sigma–Aldrich. One pot biphasic reaction was carried out in a 30-ml cylindrical glass container. About 10 mM of EDOT was dissolved in 10 ml of dichloromethane or toluene and equal concentration (10 mM) of HAuCl_4 was dissolved in 10 ml of water. In a typical synthesis, above solutions were transferred to the reaction vessel one by one carefully. The course of the reaction was followed as a function of time at regular time intervals. The product formed at the interface and the oligomers in the organic phase were collected with respect to time. Interfacial product PEDOT and oligomers in the organic phase was subjected to various characterizations like transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–vis and NMR. The effect of reductant concentration on the formation of Au–PEDOT was studied by increasing the concentration of EDOT to 20 mM and 30 mM, whereas the concentration of HAuCl_4 (10 mM) was kept constant.

2.2. Microscopy and spectral experiments

SEM examination was made using Hitachi FE-SEM (Model S4700) with an acceleration voltage of 10 kV in normal mode and analysis done by placing the sample on the copper grid coated with carbon tape. TEM analysis was made by placing a drop of sample dispersed in acetone onto a copper grid coated with carbon film (400 meshes) and dried in vacuum. TEM images were collected from Philips CM200 microscope working at 200 kV. XRD patterns were recorded on a PANalytical diffractometer Model PW3040/60 X'pert PRO operating with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) generated at 40 kV and 20 mA. Scans were done at 3° min^{-1} for 2θ values between 20° and 90° . For infrared and Raman spectroscopic measurements, a Thermo-Electron Corporation make FT-Raman module (InGaAs detector and Nd:YVO₄ laser operating at 1064 nm) coupled with a Nexus 670 model FT-IR spectrometer (DTGS detector) was used. NMR spectra were recorded in 400 MHz Bruker NMR Spectrometer with CDCl_3 . Ultraviolet–visible (UV–vis) absorption spectra of the oligomer in dichloromethane were collected on a Cary 500 scan UV–vis–NIR spectrophotometer with incident light normal to the 1-cm path length quartz cell. Spectra were collected in the wavelength range of 200–800 nm.

3. Results and discussion

3.1. Synthesis

Aqueous/organic biphasic interface is formed with EDOT in the organic phase and auric chloride in the aqueous phase. A range of organic solvents can be used in the formation of biphasic systems. By choosing a denser organic solvent, it is possible to have the aqueous phase over the organic phase. In a typical synthesis, EDOT is dissolved in dichloromethane and auric chloride in the aqueous phase in equal concentration (10 mM). Equal volume of the aqueous phase is carefully transferred to the organic phase in one-pot to form the aqueous/organic interface. In a short period of time, blue colouration occurs at the interface, due to the formation of PEDOT and the colour intensity increases with respect to time. As the reaction proceeds, the colour of the organic phase also gradually changes from colourless to light blue and then becomes dark blue. The blue colouration occurs throughout the organic phase indicating accumulation of some species arising from the oxidation of EDOT. Also, the invariance of the colour at the interface and in the organic phase indicates completion of the

reaction because all the monomer would have been converted to the polymer at the interface or oligomers in the organic phase. Similar observations have also been reported for polyaniline by Kaner and co-workers [32]. Formation of the interfacial product without any change in the colour of the bulk organic phase points to the fact that only the solid polymer is formed in this case. That some of the products or by-products are soluble in the organic phase leads us to speculate that these are of oligomeric nature. It

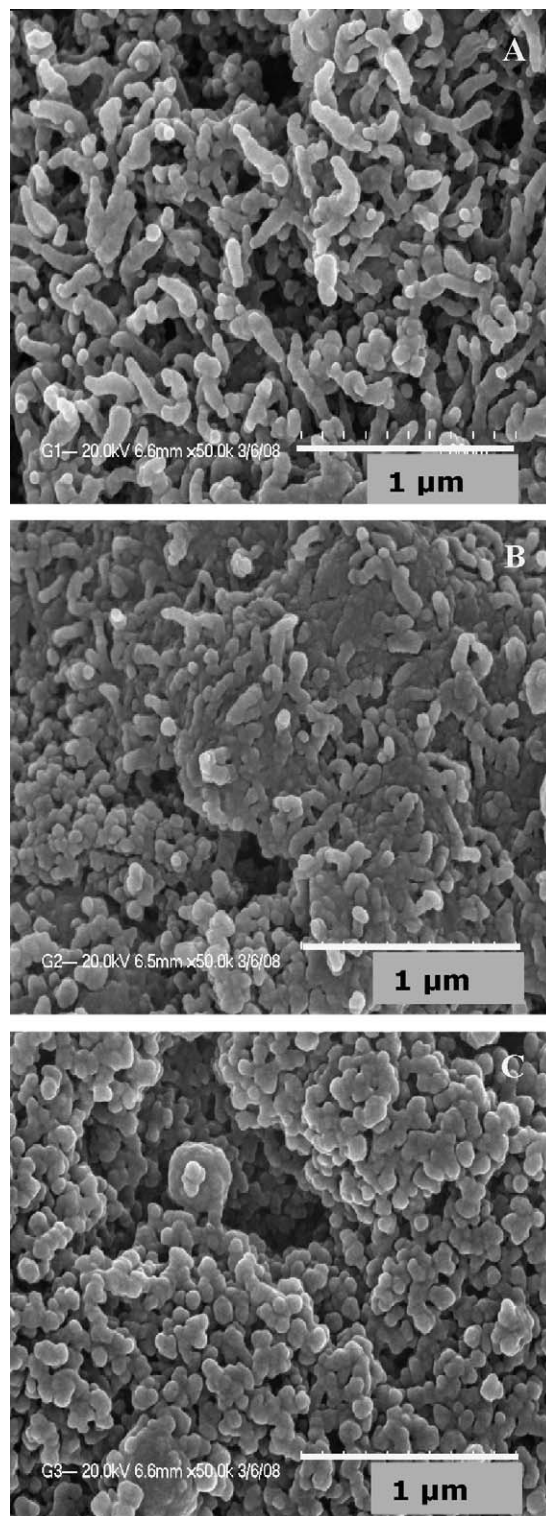


Fig. 1. SEM pictures of Au–PEDOT powder (scale bar of 1 μm); concentration ratio of EDOT and HAuCl_4 : (A) 1:1, (B) 2:1, and (C) 3:1.

may be appropriate to recall from evidence in literature that such by-products soluble in organic media can be oligomeric in nature [33,34].

3.2. Characterization of interfacial product

Fig. 1 shows the FE-SEM images of the interfacial product formed during the course of interfacial polymerization reaction. The images in Fig. 1 show that the nanostructures of Au–PEDOT become denser as the ratio of EDOT:H_{AuCl}₄ increases. Fig. 1A particularly shows that the product, i.e., nano Au–PEDOT has a

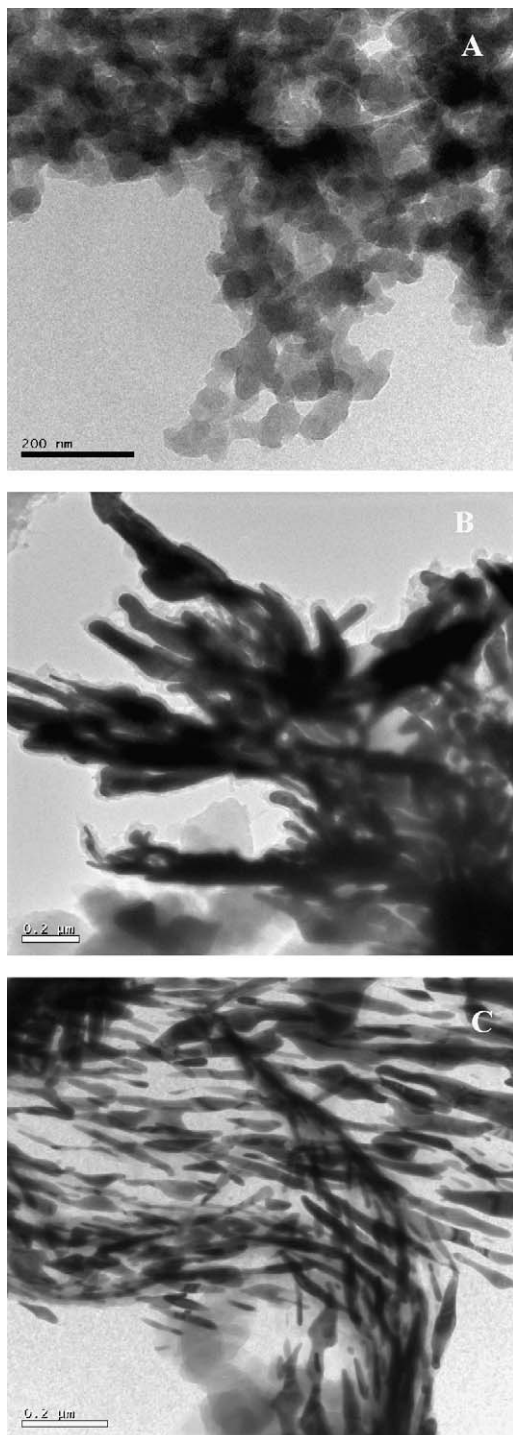


Fig. 2. TEM picture of Au–PEDOT powder (scale bar of 200 nm) (A) 1:1, (B) 2:1, and (C) 3:1 concentration ratio of EDOT and H_{AuCl}₄.

head and tail and this is understandable considering the “drag” of aqueous H_{AuCl}₄ into the organic phase. As small amounts of H_{AuCl}₄ are sufficient to effect oxidation and polymerization of EDOT, higher amounts only lead to more and more EDOT undergoing oxidative polymerization. As can be seen, the diameter/shape of the nanostructures are affected by the reductant concentration, i.e., EDOT. With an increase in the [EDOT]/[Au] ratio from 1:1 to 2:1 and 3:1, a remarkable influence on the morphology of the obtained Au–PEDOT products is observed. At a high concentration of EDOT, we believe that the aggregation of PEDOT results in simple nanoparticle fusion or growth, leading to larger gold–PEDOT nanocomposites; while at low concentration, there may not be sufficient polymer to stabilize the NPs.

The formation of gold nanoparticles was confirmed by TEM. The TEM images show that an increase in the concentration of the reductant (i.e., EDOT) leads to a network structure of rod- or fibrillar shapes. EDOT:Au (1:1) ratio yields a network-like structure within which AuNPs are entrapped. The dark spots in the images show Au embedded in the polymer matrix. Reaction at a ratio of EDOT:Au = 2:1 leads to the formation of nanostructured rods with diameter ranging from 20 to 30 nm; the rod length varying from 0.5 to 1 μm. Further increase in the EDOT content, i.e., 3:1 ratio, the number of fibrils formed increases with the resultant nanofibers of 10–20 nm diameter and several micrometers of length (Fig. 2C).

In Fig. 3A, the image of a single nanofiber is shown at higher magnification, which reveals the polymer shell and Au core in the

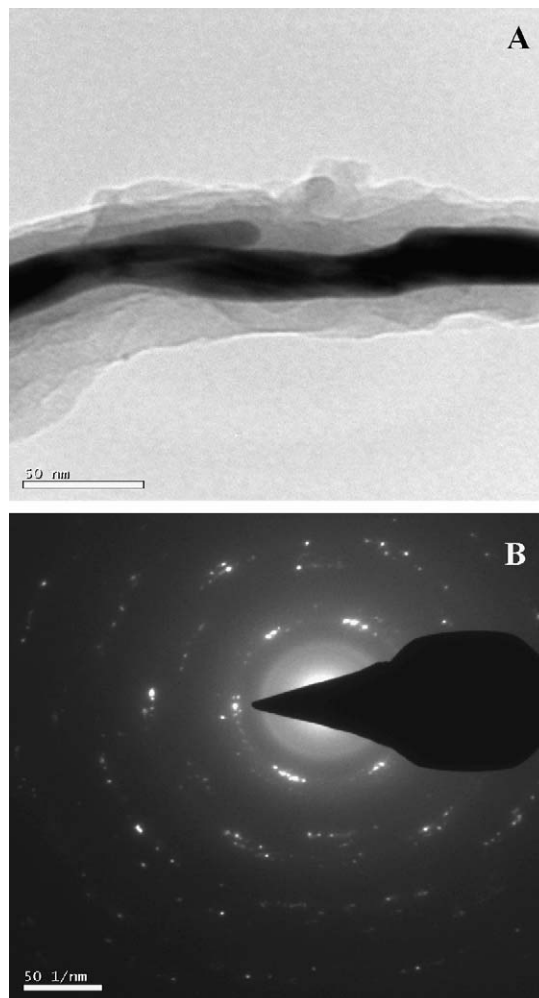


Fig. 3. (A) TEM picture of single nanofiber of Au–PEDOT formed in EDOT/Au (3:1 ratio) (scale bar of 50 nm) and (B) SAED pattern of Au–PEDOT powder.

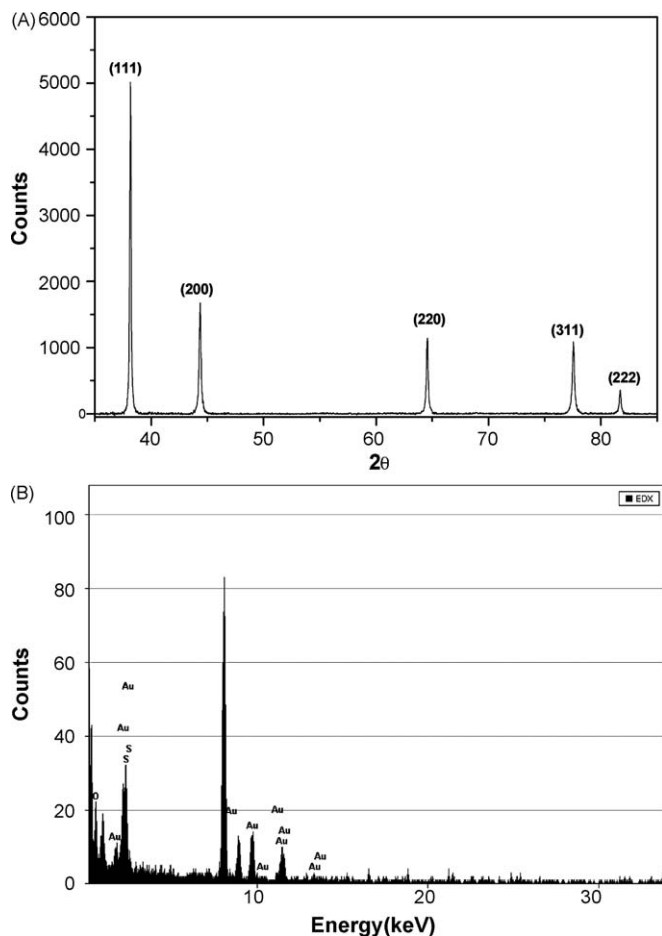


Fig. 4. (A) XRD pattern of Au-PEDOT powder and (B) energy dispersive analysis of Au-PEDOT composite.

fiber of diameter ranging from 8 to 10 nm. Upon focussing on the nanofiber for selected area electron diffraction (SAED) (Fig. 3B), the polycrystalline nature of the Au nanostructures becomes evident. Further, X-ray diffraction analysis of Au-PEDOT (Fig. 4A) also confirms the polycrystalline nature of Au with intense peaks at $2\theta = 38.17^\circ, 44.37^\circ, 64.56^\circ, 77.56^\circ$ and 81.71° corresponding to reflections: (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) of *fcc* phase of Au. The energy dispersive X-ray analysis of Au-PEDOT (Fig. 4B) shows the presence of Au, S and O.

Fig. 5 shows the FT-IR spectra of the Au-PEDOT film and EDOT monomer respectively. It is clear that the strongly intense band to the C-H bending mode (in-plane and out-of-plane) at 891 cm^{-1} and the band at 1186 cm^{-1} disappear in the polymer spectrum in comparison with that of the monomer, demonstrating the coupling

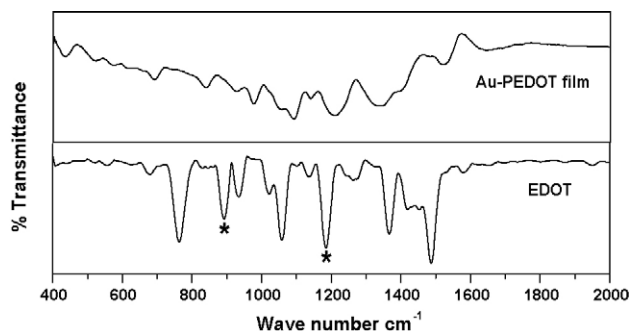


Fig. 5. FT-IR spectra of EDOT monomer and Au-PEDOT nanocomposite.

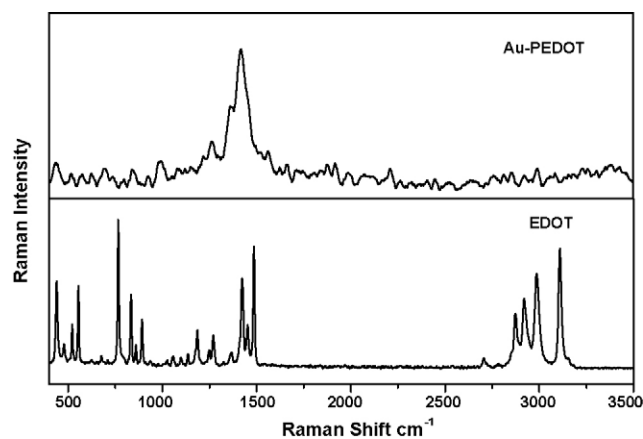


Fig. 6. FT-Raman spectra of EDOT monomer and Au-PEDOT nanocomposite.

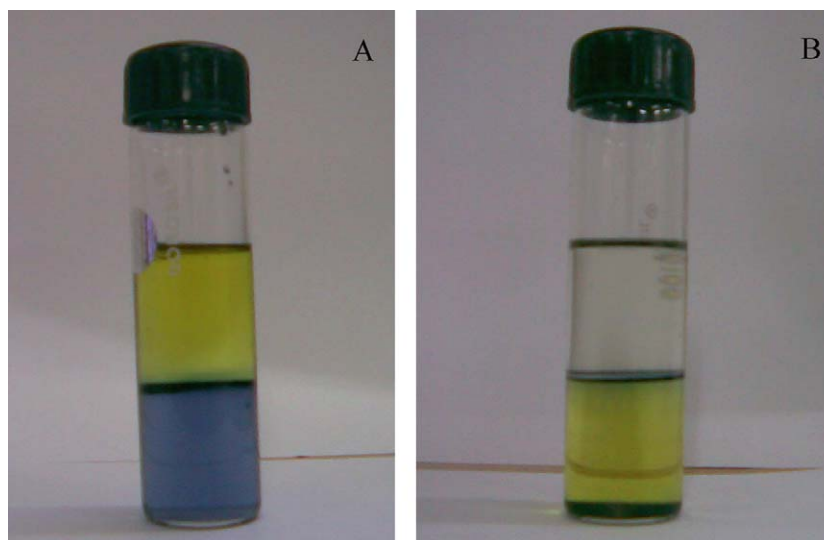
of EDOT at α, α' position. Vibrations at $1520, 1335\text{ cm}^{-1}$ are attributed to the stretching modes of C=C and C-C bonds in the quinoidal structure of thiophene ring. The vibration modes of the C-S bond in the thiophene ring can be seen at $978, 840$ and 692 cm^{-1} . The bands at $1207, 1091\text{ cm}^{-1}$ and 927 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group, and its deformation respectively [35,36].

The FT-Raman spectrum of Au-PEDOT nanocomposite and EDOT monomer are presented in Fig. 6. As expected the EDOT monomer shows strong bands at $1485, 1424, 1185, 891, 834,$ and 763 cm^{-1} . In the Raman spectrum of Au-PEDOT, the strong peak at 1420 cm^{-1} is attributed to the symmetric stretching vibration of $C_{\alpha}=C_{\beta}$ and weak peak at 1512 cm^{-1} for asymmetric stretching vibration of $C_{\alpha}=C_{\beta}$. Other weak peaks observed at $1361, 1262, 1085, 994, 700$ are due to $C_{\beta}=C_{\beta}$ stretching, C-C inner ring stretching, C-O-C deformation and symmetric C-S-C deformation, respectively. This spectral information confirms that PEDOT in the Au-PEDOT is in the highly doped state [37–39].

3.3. Characterization of organic phase-soluble species

Au-PEDOT formation takes place during the redox reaction between the Au^{3+} and EDOT. This reaction will occur only at the interface between the two phases. Dual solubility (organic and aqueous) behaviour of EDOT will be more helpful for partial diffusion to the aqueous phase and after equilibration EDOT in the interfacial region undergoes a redox reaction with Au^{3+} , resulting in the formation of Au-PEDOT. The Au-PEDOT formation increases as time increases and subsequently oligomer formation will occur when a polar organic solvent is employed. Completely soluble oligomer forms only in the organic medium because solubility of EDOT is poor in aqueous medium compared to that in the organic medium [40]. In addition, the oligomers do not form if we employ a non-polar solvent like toluene. This can be reasoned on the basis of the dielectric constant of the medium because mix-up at the interface depends upon the dielectric constant of the solvent. It is well known that if the dielectric constant is high for the solvent then the mix up at the interface will be more and vice versa [41].

Formation of by-products soluble in organic phase can be seen easily by a colour change because the oxidized form of EDOT exhibits blue colour [42]. Hence, in a typical synthesis carried out (as given in Section 2) using dichloromethane whose dielectric constant and solubility in water (g/100 g) are given as 9.08 and 1.32, respectively. It is observed that in a short period of time blue coloured PEDOT is formed at the interface and PEDOT formation increases with respect to time. As the reaction proceeds, the colour of the organic phase also gradually changes to light blue to become dark-blue coloured finally. The blue coloured products remain in



Photograph 1. Biphasic systems showing the colour change in dichloromethane while no colour changes occur in Toluene. (A: dichloromethane/water system; B: toluene/water system).

the organic phase showing the formation of some kind of oligomeric species in the organic phase and also confirms the completion of the reaction because all the monomers would have been converted either to a polymer at the interface or oligomers in the organic phase. Similar experiment was carried out using toluene whose dielectric constant and solubility in water (g/100 g) are given as 2.38 and 0.08, respectively. Since the miscibility or solubility of toluene in water is extremely small, the mix-up of the two phases at the interface is not expected. It is interesting to note that when toluene is employed, there is only the formation of interfacial product and the colour of the organic phase remains unchanged indicating that oligomers are not formed (Photograph 1). As suggested above, the oligomer forms only in the high dielectric solvent and does not form in the low dielectric solvent. This effect can be reasoned as follows: in high dielectric solvents, mix-up at the interface is more and so interfacial reaction extends to the formation of oligomers in the organic phase.

Monomer (EDOT) contains two different proton environments, one in the aromatic ring and the other in the ethylene bridge. Hence NMR spectra of EDOT (Fig. 7) shows two peaks at 4.2 and 6.4 which are due to the ethylene bridge protons and aromatic protons respectively. The peak values are referred from Bruker table. By integrating the area under the peak, the number of protons can be calculated which works out to be in the ratio of 2:1. It matches the

calculation of the protons in EDOT, i.e., four protons in the ethylene bridge and two protons in the aromatic ring. Oligomer/polymer formation takes place by coupling at the α,α' positions in the monomer. In the oligomer, protons are present only in the ethylene bridge and no protons in the aromatic ring. Hence, NMR spectra for the oligomers show a single peak at 5.3. The environment experienced by the protons in the ethylene bridge in the monomer and oligomer is different. In oligomers, protons are in a more deshielded environment than monomer. Hence, the peak in the oligomer shifts to the lower field when compared to the monomer. The NMR spectra confirm the oligomeric nature of the products soluble in the organic phase.

The UV-visible spectra of the EDOT oligomers in CH_2Cl_2 (Fig. 8) show two absorption peaks at 571 and 617 nm indicating that there are two different species present in the organic phase [43]. In addition, the broadness of the peak around ~ 600 nm suggests a $\pi-\pi^*$ transition and the absence of the free tail in the higher wavelength shows that the species are in the neutral state [38,44]. It is reported that neutral polymers/oligomers are soluble in the organic solvents [45]. With an objective of exploring further on this important finding, we are generating different organic-soluble species in a range of solvents (organic phase), characterizing the chain length and other issues using in situ spectral studies.

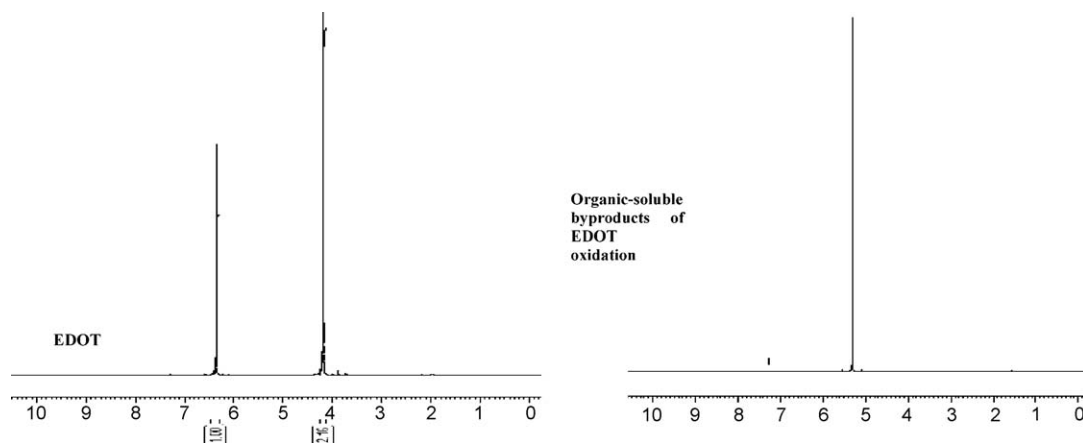


Fig. 7. NMR spectra of EDOT and EDOT oligomers in $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$.

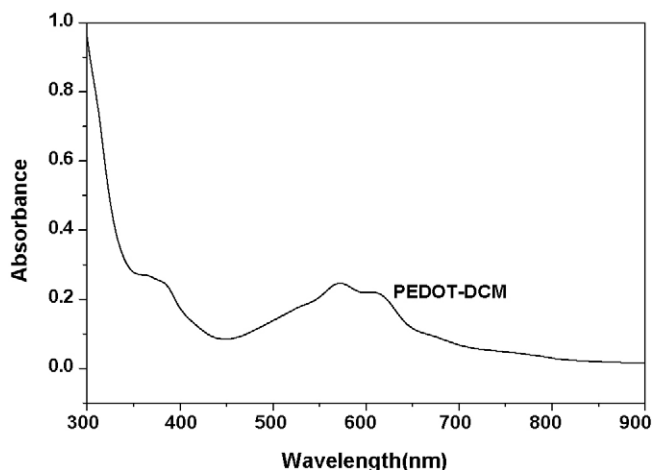


Fig. 8. UV-vis spectrum of EDOT oligomer in CH_2Cl_2 .

4. Conclusion

In summary, we reported here the generation of various morphologies of Au-PEDOT nanocomposite at an interface between aqueous and organic phases. The effect of EDOT: Au ratio on the morphology is discussed using the microscopic and XRD data. The Au-PEDOT nanocomposite was characterized by Raman spectroscopy to be in highly oxidized state. While the formation of AuNPs embedded in PEDOT matrix is observed to be straightforward, a byproduct of HAuCl_4 -EDOT reaction appears to form in the organic phase (dichloromethane) of relatively higher dielectric constant. Formation of such a species is not observed when the organic phase is toluene, a low dielectric solvent. The dichloromethane-soluble species was characterized using UV-vis spectroscopy and proton NMR technique. The latter suggests that the byproducts are short chain neutral oligomers of EDOT.

Acknowledgement

S.H. thanks CSIR, New Delhi, for the award of Research Internship.

References

- [1] C.R. Martin, *Acc. Chem. Res.* 28 (1995) 61.
- [2] J.C. Hulthen, C.R. Martin, *J. Mater. Chem.* 7 (1997) 1075.

- [3] A.N. Aleshin, *Adv. Mater.* 18 (2006) 17.
- [4] R. Xiao, S.I. Cho, R. Liu, S.B. Lee, *J. Am. Chem. Soc.* 129 (2007) 4483.
- [5] X. Zhang, S.K. Manohar, *J. Am. Chem. Soc.* 127 (2005) 14156.
- [6] S. Ko, J. Jang, *Angew. Chem. Int. Ed.* 45 (2006) 7564.
- [7] M. Steinhart, Z. Jia, A.K. Schaper, R.B. Wehrspohn, U. Gösele, J.H. Wendorff, *Adv. Mater.* 15 (2003) 706.
- [8] W. Zhong, J. Deng, Y. Yang, W. Yang, *Macromol. Rapid Commun.* 26 (2005) 395.
- [9] Z. Wei, Z. Zhang, M. Wan, *Langmuir* 18 (2002) 917.
- [10] M.G. Han, S.H. Foulger, *Small* 10 (2006) 1164.
- [11] M. Ikegame, K. Tajima, T. Aida, *Angew. Chem. Int. Ed.* 42 (2003) 2154.
- [12] K. Müller, M.-K. Park, M. Klapper, W. Knoll, K. Müllen, *Macromol. Chem. Phys.* 208 (2007) 1394.
- [13] M. Fujii, S. Abe, H. Ihori, *Synth. Met.* 152 (2005) 41.
- [14] M. Woodson, J. Liu, *J. Am. Chem. Soc.* 128 (2006) 3760.
- [15] D.H. Reneker, I. Chun, *Nanotechnology* 7 (1996) 216.
- [16] I.D. Norris, M.M. Shaker, F.K. Ko, A.G. MacDiarmid, *Synth. Met.* 114 (2000) 109.
- [17] X. Zhang, A.G. MacDiarmid, S.K. Manohar, *Chem. Commun.* (2005) 5328.
- [18] M. Wan, *Adv. Mater.* 20 (2008) 2926.
- [19] U. Sree, Y. Yamamoto, B. Deore, H. Shiigi, T. Nagaoka, *Synth. Met.* 131 (2002) 161.
- [20] M. Nakata, Y. Shiraishi, M. Taga, H. Kise, *Makromol. Chem.* 193 (1992) 765.
- [21] J. Huang, R.B. Kaner, *J. Am. Chem. Soc.* 126 (2004) 851.
- [22] J. Jang, J. Bae, E. Park, *Adv. Mater.* 18 (2006) 354.
- [23] N. Nuraje, K. Su, N.-L. Yang, H. Matsui, *ACS Nano* 2 (2008) 502.
- [24] J.M. Pringle, O. Ngamna, C. Lynam, G.G. Wallace, M. Forsyth, D.R. MacFarlane, *Macromolecules* 40 (2007) 2702.
- [25] X. Feng, H. Huang, Q. Ye, J.J. Zhu, W. Hou, *J. Phys. Chem. C* 111 (2007) 8463.
- [26] D.D. Sawall, R.M. Villahermosa, R.A. Liepeles, A.R. Hopkins, *Chem. Mater.* 16 (2004) 1606.
- [27] R. Knake, A.W. Fahmi, S.A.M. Tofail, J. Clohessy, M. Mihov, V.J. Cunnane, *Langmuir* 21 (2005) 1001.
- [28] C.R.K. Rao, D.C. Trivedi, *Synth. Met.* 157 (2007) 432.
- [29] B.C. Sih, M.O. Wolf, *Chem. Commun.* (2005) 3375.
- [30] R. Gangopadhyay, A. De, *Chem. Mater.* 12 (2000) 608.
- [31] G. Lu, C. Li, J. Shen, Z. Chen, G. Shi, *J. Phys. Chem. C* 111 (2007) 5926.
- [32] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, *J. Am. Chem. Soc.* 125 (2003) 314.
- [33] J. Heinze, in: H. Lund, O. Hammerich (Eds.), *Organic Electrochemistry*, 4th ed., Dekker, New York, 2001.
- [34] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, *Adv. Mater.* 12 (2000) 481.
- [35] X. Li, Y. Li, Y. Tan, C. Yang, Y. Li, *J. Phys. Chem. B* 108 (2004) 5192.
- [36] C. Kvarnström, H. Neugebauer, S. Blomquist, H.J. Ahonen, J. Kankare, A. Ivaska, *Electrochim. Acta* 44 (1999) 2739.
- [37] N. Sakmeche, S. Aeiyaich, J.-J. Aaron, M. Jouini, J.C. Lacroix, P.-C. Lacaze, *Langmuir* 15 (1999) 2566.
- [38] S. Garreau, G. Louarn, S. Lefrant, J.P. Buisson, G. Froyer, *Synth. Met.* 101 (1999) 312.
- [39] W.W. Chiu, J. Travaš-Sejdić, R.P. Cooney, G.A. Bowmaker, *J. Raman Spectrosc.* 37 (2006) 1354.
- [40] S.S. Kumar, C. Sivakumar, J. Mathiyarasu, K.L.N. Phani, *Langmuir* 23 (2007) 3401.
- [41] A.L. Horvath, *Halogenated Hydrocarbons: Solubility-Miscibility with Water*, CRC Press, 1982.
- [42] M.G. Han, S.H. Foulger, *Chem. Commun.* (2004) 2154.
- [43] F. Tran-Van, S. Garreau, G. Louarn, G. Froyer, C. Chevrot, *J. Mater. Chem.* 11 (2001) 1378.
- [44] S. Garreau, G. Louarn, J.P. Buisson, G. Froyer, S. Lefrant, *Macromolecules* 32 (1999) 6807.
- [45] M. Sato, S. Tanaka, K. Kaeriyama, *J. Chem. Soc., Chem. Commun.* (1986) 873.