

Synthesis of poly(2,5-dimethoxyaniline)-SnO₂ nanocomposites and their structural, optical and electrochemical properties

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Nanocomposites have gained much importance in different fields, commercially and technologically, due to the possibilities in tuning the properties. In the present work, poly(2,5-dimethoxyaniline)/tin oxide (PDMA/SnO₂) nanocomposites were synthesized in the presence of sulphuric acid solution by the chemical oxidative polymerization of 2,5-dimethoxyaniline using potassium peroxodisulfate as the oxidant. The prepared samples were characterized by using X-ray diffraction (XRD), infrared spectroscopy (FT-IR), UV-Vis spectroscopy and scanning electron microscope (SEM). The result reveals that prepared composite is crystalline in nature along with improved stability. We report the structural and morphological properties, and electrochemical behaviour of PDMA/SnO₂ nanocomposite. Given the importance of the optical properties of SnO₂, also describe the optical absorbance and photoluminescence of PDMA/SnO₂ nanocomposite materials.

Keywords: Poly(2,5-dimethoxyaniline), SnO₂, nanocomposite, SEM, photoluminescence.

Introduction

In recent years, conducting polymers have been dominating the research area of advanced materials due to their applications in many technological areas such as sensors, batteries, energy storage system, molecular devices and smart windows^{1,2}. Poly(2,5-dimethoxyaniline) (PDMA) is a polyaniline (PANI) derivative which contains the methoxy (-OCH₃) groups substituted at *o*- and *m*-position with respect to nitrogen atoms. It can be easily polymerised and switched from leucoemeraldine or emeraldine to be more oxidized than PANI at a low potential³. The electron donating methoxy group in the aromatic ring can provide a suitable environment for binding with metal or metal oxide through the amine groups in PDMA^{4,5}.

Among the semiconducting nanoparticles of SnO₂ have a large wide direct band gap ($E_g = 3.6$ eV). It is thoroughly investigated for their applied aspect such as in the thin films resistor, gas sensing, photo catalyst and antireflecting coating in solar cells⁶⁻⁸. Conducting polymer-metal oxide composites have attracted interest due to their tuneable properties, which are different from those of pure conducting polymer and metal oxides or metals⁹. A large number of studies

on the optical properties of tin oxide and its alloys incorporated into polymeric matrices have been published during the last five years¹⁰⁻¹² but very few reports have been published on the composite formation of tin oxide/poly(2,5-dimethoxyaniline) PDMA/SnO₂. We thus investigated the possibility of using tin oxide deposited in PDMA. The introduction of tin oxide can strongly influence the electronic and chemical properties of the conducting polymer because of the close interaction between the conducting polymer and metal.

The aim of this work was to preparation PDMA/SnO₂ nanocomposite and studies the enhanced optical properties of this composite. Scanning electron microscope (SEM), Fourier transform infrared spectra (FTIR), X-ray diffraction (XRD), UV-Vis spectroscopy (UV-Vis) and photoluminescence (PL) were used as in the investigation.

Experimental

Materials:

Sn^{IV} chloride, sodium hydroxide, 2,5-dimethoxyaniline (DMA, 98%) was obtained from Aldrich Chemical Co. and used without further purification. The AR grade chemicals,

potassium peroxydisulfate (Merck) and sulfuric acid were used.

Synthesis of tin dioxide nanoparticles:

In this work, extremely fine tin oxide nanocrystals were synthesized through the controlled co-precipitation method. Analytical reagent of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ and NaOH were used as precursor. 0.1 M of Sn^{IV} chloride was added to a flask fitted with a reflux condenser. The above solution was refluxed for about 2 h and then allowed to cool naturally. Aqueous sodium hydroxide (20%) was added drop wise to the solution with constant stirring until a pH value of 10 was reached. All the colloidal suspensions were collected by centrifuge (at 5000 rpm), and settled matter was washed several times with deionized water to remove as much chlorides, hydroxides as possible then it is subjected to calcine in a muffle furnace at 500°C for 4 h.

Synthesis of PDMA/ SnO_2 nanocomposite:

The 2,5-dimethoxyaniline (98%) (DMA) was purchased from Aldrich was dissolved in sulphuric acid (0.125 M) and it is kept stored in ice-freezer water bath below -20°C . Polymerizations were performed only at below -20°C of DMA by the drop wise addition of potassium peroxydisulfate as an oxidant. At the same time tin oxide crystals were incorporate into the above solution, which undergo just initiation polymerization in the presence of SnO_2 nanocrystals. As prepared PDMA- SnO_2 nanocomposites is allowed to settled down for sufficient hour and the solvent of the respective colloidal solution removed by using rotatory evaporator.

Results and discussion

FT-IR analysis:

The FT-IR spectra of PDMA, SnO_2 nanoparticle and PDMA/ SnO_2 nanocomposite are shown in Fig. 1. The FT-IR spectrum PDMA (Fig. 1a) shows main characteristics bands of PDMA, which are assigned as follows¹³.

A broad and weak band at approximately 3436 cm^{-1} is due to the N-H stretching mode, the C=N and C=C stretching modes for the quinoid (Q) and benzoid (B) rings occur at 1608 and 1502 cm^{-1} , bands at 1213 and 1010 cm^{-1} are assigned to the presence of *o*-methoxy group in PDMA, a band at 1112 cm^{-1} attributed to the plane bending vibration of C-H, which is formed during protonation, and a band at 806 cm^{-1} indicates the *ortho*-substitued benzene ring. The FTIR spectrum of the SnO_2 nanoparticles (Fig. 1b) exhibits a broad

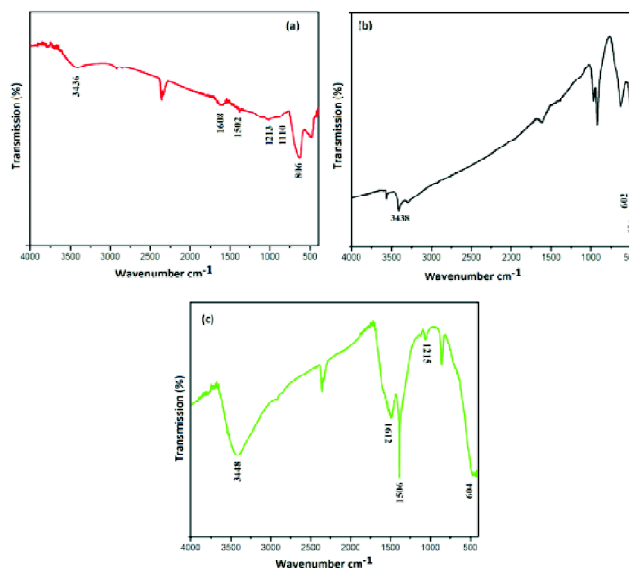


Fig. 1. FTIR spectra of (a) PDMA, (b) SnO_2 and (c) PDMA/ SnO_2 .

band centered at 602 cm^{-1} characteristic of Sn-O vibration and other at 454 cm^{-1} due to Sn-OH vibration¹⁴. In addition, a weak band at 3460 cm^{-1} is observed which is attributed to the OH-stretching vibrations. In FT-IR spectra of PDMA/ SnO_2 nanocomposite (Fig. 1c) are exhibits the main bands corresponding to pure PDMA and a characteristic doublet around at 600 cm^{-1} due to SnO_2 . However, the incorporation of SnO_2 nanoparticles results into the shift of FT-IR bands of PDMA to higher wave number. This indicates that there is some interaction between PDMA and SnO_2 nanoparticles. Thus, the FT-IR spectroscopy result confirms that the PDMA/ SnO_2 nanocomposite has been found formed during chemical polymerization of PDMA in the presence of SnO_2 nanoparticles.

XRD analysis:

The XRD patterns of PDMA, SnO_2 and PDMA/ SnO_2 nanocomposite are shown in Fig. 2.

The XRD pattern of PDMA (Fig. 2a) indicates the broad diffraction peaks at 2θ values of 20.90° and 25.24° , which are attributed to amorphous nature of PDMA. The XRD pattern of SnO_2 nanoparticles (Fig. 2b) indicates the prominent diffraction peaks at 2θ values of 26.72° , 34.30° , 53.70° , 56.64° , 66.63° , and 73.02° corresponding to the (110), (101), (211), (310), (112) and (202) which are attributed to the rutile structure of SnO_2 (JCPDS data card 41-1445)¹⁵. The XRD pattern of the PDMA/ SnO_2 nanocomposite (Fig. 2c) is almost similar to that observed for SnO_2 and additionally two

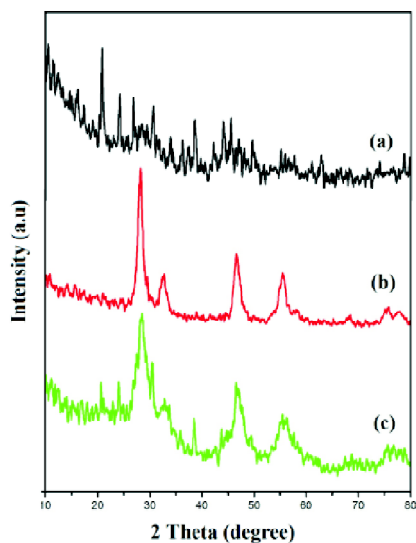


Fig. 2. XRD patterns of (a) PDMA, (b) SnO₂ and (c) PDMA/SnO₂.

broad peaks appeared at 20.90° and 25.24°. This indicates that the crystalline structure of SnO₂ is preserved in the nanocomposite even though it was dispersed in reaction mixture during polymerization process. Moreover, the intensities of the diffraction peaks for the nanocomposite are weaker than those for the pure SnO₂ nanoparticles. This suggests that there is a kind of interaction between PDMA and SnO₂ nanoparticles, which resulted in the reduced intensities of diffraction peaks of SnO₂ nanoparticles in the nanocomposite.

Surface morphology:

The surface morphological nanostructures of SnO₂ nanoparticles and PDMA/SnO₂ nanocomposite were investigated by High resolution scanning electron microscopy. Fig. 3a showed that SnO₂ particles are smooth surface and plate like structure observed. Thus, the SnO₂ nanoparticles were added into the PDMA matrix (Fig. 3b).

It can immediately absorbed onto the PDMA matrix surface, support materials of PDMA nanocomposites plate like structure agglomerated form; the SnO₂ nanoparticles were uniformly distributed on the inside interlayer and growth process occurred on the metal ions Sn⁴⁺ combined to several hydroxyl and nitrogen sites in PDMA chains respectively¹⁶. It is clearly observed that SnO₂ nanoparticle is well incorporated into the PDMA matrix, which also supports the FTIR and XRD results.

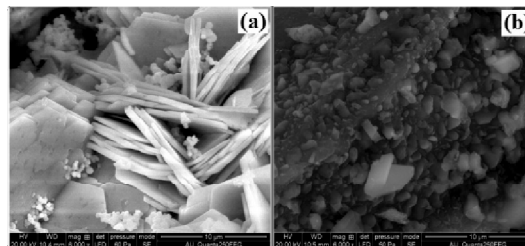


Fig. 3. SEM images of (a) SnO₂ and (b) PDMA/SnO₂.

Optical properties of PDMA/SnO₂ nanocomposites:

In Fig. 4A and B shows that optical spectroscopy analysis enabled us to understand the optical properties of the synthesised pure tin oxide and its composite samples. The UV-Visible spectra of the samples of PDMA shows the peaks at 265, 350 and 665 nm can be attributed to the π - π^* transition of the aromatic benzene ring (leucoemeraldine), polaron- π , π - π (emeraldine), and polaron- π^* transition (pernigraniline), respectively¹⁷. The absorption peak of SnO₂ nanoparticle is one sharp absorption wavelength of 245 nm¹⁸. The PDMA/SnO₂ nanocomposite was appeared in the absorption wavelength at 294 nm and normal absorption edges at 265, 350 and 665 nm and its interesting note that shifted in the wavelength region 268, 390 and 673 nm, which is reasonably, due to the more number of SnO₂ nanoparticles are well incorporated into the PDMA matrix.

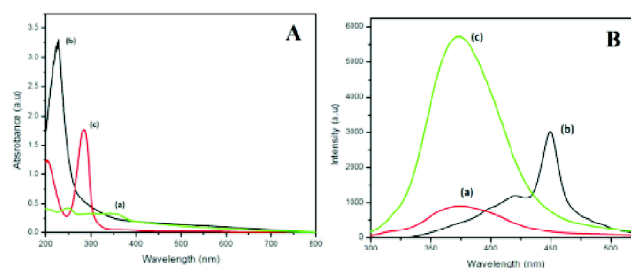


Fig. 4. (A) UV-Visible spectra and (B) FL spectra.

Fig. 4B shows the PL emission spectra of PDMA, SnO₂ nanoparticles and PDMA/SnO₂ nanocomposite, which were taken under an excitation wavelength of 300 nm. Two prominent peaks at 414 and 442 nm have been observed in the range 350–500 nm. After multiple Gaussian fit, the emission spectrum presents three bands 356, 372 and 452 nm respectively. A weak UV emission peak was observed at 439 nm, which attributed to the free exciton electron-hole recombination.

nation. Two prominent peaks at 356 and 372 nm have been observed in the range 300–450 nm. Earlier reports have indicated that SnO₂ exhibited a broad band peak near 396 nm¹⁹. Since PDMA/SnO₂ samples maxima 452 nm (2.74 eV) are lower than the band gap of SnO₂ nanoparticles. In these visible emissions cannot be assigned to the direct recombination of a conduction electron in the Sn 4p band and a hole in the O 2p valence band. The peaks at 452 nm might originate from the luminescence centers formed by such tin interstitials or dangling bonds in the SnO₂ nanocrystals, but that is not yet clear. We attribute the emission at 356 nm to electron transitions mediated by defects levels in the band gap, such as oxygen vacancies²⁰. From Fig. 4B, it can be observed that the PDMA/SnO₂ nanocomposites result in the free excitation electron-hole recombination peak at 372 nm with sharp and high intensity, while the characteristic peaks of PDMA could not be observed. In pure SnO₂ nanoparticles, the emission attributes to electron transition, mediated by defects levels in the band gap, such as oxygen vacancies. Probably the defects play a role after introducing SnO₂ into the PDMA leads to the reduction in the peak intensity at 397 nm and 456 nm due to the luminescence processes²¹. It is concluded that, the synthesis of PDMA/SnO₂ nanocomposite with high UV emission in the blue-violet region, and it may be used for light emitting applications.

Conclusions

The PDMA/SnO₂ nanocomposite was successfully synthesized by using *in situ* chemical polymerization of DMA using potassium peroxodisulfate as an oxidant. The results of the FTIR, XRD and SEM studies reveal that the polymerization of PDMA has been successfully achieved on the surface of the SnO₂ nanoparticles and indicates that there is some interaction between PDMA and SnO₂ nanoparticles. The optical properties of the PDMA/SnO₂ nanocomposites were analyzed by UV-Visible and spectroscopy. The optical properties characteristics of the PDMA/SnO₂ nanocomposites are observed to be better than those of pure PDMA and SnO₂ nanoparticles. Due to the fact that it has as excellent optical properties and it may be find the application in light emitting diodes.

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References

1. T. A. Skotheim and J. R. Reynolds, 3rd ed., CRC Press, New York, 2007.
2. H. S. Nalwa, John Wiley and Sons Ltd., 1997, Vols. 1- 4.
3. L. M. Huang, T. C. Wen and A. Gopalan, *Mater. Chem. Phys.*, 2002, **77**, 726.
4. D. W. Hatchett, R. Wijeratne and J. M. Kinyanjui, *J. Electroanal. Chem.*, 2006, **593**, 203.
5. J. M. Kinyanjui, N. R. Wijeratne, J. Hanks and D. W. Hatchett, *Electrochim. Acta*, 2006, **51**, 2825.
6. V. Juttukonda, R. L. Paddock, J. E. Raymond, D. Denomme, A. E. Richardson, L. E. Slusher and B. D. Fahlman, *J. Am. Chem. Soc.*, 2006, **128**, 420.
7. J. K. Jian, X. L. Chen, T. Xu, Y. P. Xu, L. Dai and M. He, *Appl. Phys.*, 2002, **75**, 695.
8. J. Q. Hu, X. L. Ma, N. G. Shang, Z. Y. Xie, N. B. Wong, C. S. Lee, and S. T. Lee, *J. Phys. Chem. B*, 2002, **106**, 3823.
9. D. W. Hatchett and M. Josowicz, *Chem. Rev.*, 2008, **108**, 746.
10. M. Alam, A. A. Ansari, M. R. Shaik and N. M. Alandis, *Ara-bian J. Chem.*, 2013, **6**, 341.
11. N. I. Elakhya, G. I. Gayatri, S. I. Aparna, P. I. Rajesh and P. Ramasamy, *Opt. I. J. Light and Electron Optics.*, 2017, **142**, 436.
12. N. G. Deshpandea, Y. G. Gudagea, Ramphal Sharmaa, J. C. Vyasb, J. B. Kimc and Y. P. Leec, *Sens. Actuators, B*, 2009, **138**, 76.
13. D. Patil, Y.-K. Seo, Y. K. Hwang, J. S. Chang and P. Patil, *Sens. Actuators, B*, 2008, **132**, 116.
14. D. Patil, P. Patil, Y. K. Seo and Y. K. Hwang, *Sens. Actuators, B*, 2010, **148**, 41.
15. A. Hamrouni, N. Moussa, F. Parrino, A. Di Paola, A. Houas and L. Palmisano, *J. Mol. Catal. A: Chem.*, 2014, **390**, 133.
16. V. H. Nguyena and J. J. Shima, *Synth. Met.*, 2015, **207**, 110.
17. T. K. Changa, C. C. Chang and T. C. Wena, *J. Power Sources*, 2008, **185**, 603.
18. G. Yang, Z. Yan and T. Xiao, *Appl. Surf. Sci.*, 2012, **258**, 8704.
19. T. W. Kim, D. U. Lee and Y. S. Yoon, *J. Appl. Phys.*, 2000, **88**, 3759.
20. F. Gu, S. F. Wang, M. K. Lu, Y. X. Qi, G. J. Zhou, D. Xu and D. R. Yuan, *Inorg. Chem. Commun.*, 2003, **6**, 882.
21. P. Manivel, S. Ramakrishnan, Nikhil K. Kothurkar, A. Balamurugan, N. Ponpandian, D. Mangalaraj and C. Viswanathan, *Mater. Res. Bull.*, 2013, **48**, 640.