

Photoluminescence Properties of Polyphenylenediamine Doped with TiO₂ Nanoparticles

S. ARCHANA^{1,*} and MANJUNATHAN MUNISAMY²

¹Department of Chemistry, Veltech Rangarajan Dr. Sagunthala R&D Institute of Science and Technology, Avadi, Chennai-600062, India

²Department of Chemistry, B.W.D.A. Arts and Science College, Tindivanam-604304, India

*Corresponding author: Tel: +91 44 33870055, E-mail: drsarchana@veltech.edu.in

Received: 23 August 2018;

Accepted: 25 September 2018;

Published online: 31 December 2018;

AJC-19206

A series of poly(*o*-phenylenediamine) doped with TiO₂ nanoparticles were synthesized by chemical oxidative polymerization method using ferric chloride as an oxidant. The structural, morphological and optical properties were investigated by transmission electron microscope (TEM), FTIR, UV-visible, photoluminescence spectroscopies. It was found that the photoluminescence spectra of polymer nanocomposites emit radiation at 540 nm which corresponds to the emission of green light. The polymer and its nanocomposites exhibit interesting concentration-dependent optical properties.

Keywords: Polyphenylenediamine, TiO₂, Photoluminescence, Nanocomposites.

INTRODUCTION

The unique optical and electronic properties of metal nanoparticles are due to their high surface area to volume ratio and it exhibits excellent catalytic activity than the respective bulk metals [1,2]. Recently, conducting polymer nanocomposites has attracted much attention because of its ability to enhance the electrical and mechanical properties of the polymer through interaction with nanoparticles by synergistic effects [3]. Polymer nanocomposites show quite different properties from the constituent materials due to interfacial interactions between nanostructured semiconductors and polymers.

Polyphenylenediamines are conducting polymers which have reported to have high gas separation ability [4,5] and lyotropic liquid crystallinity [6,7]. Among various metal oxide semiconductor materials, TiO₂ has been widely used due to its unique physical and chemical properties as well as their low cost and extensive applications in diverse areas [8-10].

Poly(*o*-phenylenediamine) (PoPDA) doped with TiO₂ and flyash cenospheres composites have been reported for the photocatalytic activity and degradation of antibiotics waste water under visible light [11]. The layered structure of PoPDA and its TiO₂ composite were synthesized and their hydrogen storage capacity has been estimated by Abdel Rehim *et al.* [12]. The photocatalytic study of PoPDA/TiO₂ composite exhibited

significantly higher photocatalytic activity for photo-decolorization of methylene blue than TiO₂ material under visible light irradiation [13]. The nanocomposites, TiO₂-PoPDA core-shell morphology type was prepared by *in situ* chemical oxidative polymerization method using ammonium persulfate as oxidant. The photocatalytic activities of PoPDA-TiO₂ nanocomposites on rhodamine B in solar light [14] were remarkably enhanced than the use of TiO₂ nanoparticles.

In present study, PoPDA/TiO₂ nanocomposites were synthesized by *in situ* chemical polymerization method using FeCl₃ as an oxidant. The luminescence properties were recorded by varying the concentrations of the synthesized polymers and their nanocomposites and it was found that as the concentration of polymer decreased, its emission intensity found to increase.

EXPERIMENTAL

The chemicals *viz.*, *o*-phenylenediamine, ferric chloride, sodium dodecyl sulfate (SDS) are of analytical grade and used as received without further treatment. The nanoparticles of TiO₂ (60-70 nm) were purchased from Sigma Aldrich.

The FT-IR spectra were analyzed by ABB-MB-3000 FT-IR spectrometer using KBr pellet method. The UV-visible spectra of polymers were analyzed using Perkin Elmer Lambda UV-visible spectrometer using DMSO as solvent. The XRD patterns

were obtained by using Bruker AXS D8 Advance using Cu as an X-ray source at the wavelength of 1.5406 Å of angular ranges from 3° to 135°. High-resolution transmission electron microscopy was imaged using Tecnai T20 G2 S-TWIN having the operating voltage of 250 kV. Spectrofluorometer of model FLUOROLOG-FL3-11 was used to measure the fluorescence of the isolated polymer nanocomposites using Xenon lamp 450W as a source. The samples were analyzed in the range of 180-1550 nm and the detector used was PMT for UV-visible (180 to 850 nm) region.

Preparation of PoPDA/TiO₂ nanocomposites: To the solution of *o*-phenylenediamine (0.05 mol), surfactant SDS at its CMC value of 0.008 mol was added and stirred, to this 0.5 M, HCl was added. The TiO₂ nanoparticles were added in 10, 20 or 30 wt. % to above solution and the content was kept for vigorous stirring in order to make TiO₂ nanoparticles suspended in the solution. Ferric chloride (0.05 mol) was added to the above mixture drop by drop for about 30 min. The final mixture was kept for 6 h at room temperature with constant stirring to favour polymerization of monomers. The poly(*o*-phenylenediamine) with 10, 20 and 30 wt. % TiO₂ nanocomposites precipitate obtained by *in situ* polymerization method was filtered, washed with deionized water and finally with methanol in order to remove the monomer contaminations and oligomers [15-17].

RESULTS AND DISCUSSION

The FT-IR, UV-visible, XRD, spectroscopy of prepared nanocomposites have been discussed previously [15-19]. In the present study, the photoluminescence properties were recorded by varying the concentrations of synthesized polymers and their nanocomposites. It was found that as the concentration of polymer decreased, its emission intensity was found to increase.

FT-IR spectra of poly(*o*-phenylenediamine)/TiO₂ nanocomposites: The FT-IR spectral data of PoPDA with 10, 20 and 30 % TiO₂ nanoparticles were assigned as PoPDA/10 % TiO₂, PoPDA/20 % TiO₂ and PoPDA/30 % TiO₂. The spectral results show a single band in the region of 3352 cm⁻¹ is due to the N-H stretching of NH-group. The bands at 3413, 3195 cm⁻¹ are due to the presence of asymmetrical and symmetrical stretching modes of N-H bond in NH₂ moiety. The presence of peaks at 1688 and 1520 cm⁻¹ is due to characteristic stretching vibrations of C=N and C=C group in phenazine skeleton. The peaks at 1374 and 1244 cm⁻¹ can be associated with C-N-C stretching vibrations in the repeated benzenoid units and quinoid imine moiety. Furthermore, the presence of peaks at 752 and 582 cm⁻¹ are due to out-of-plane bending vibrations C-H bond in benzene nuclei in phenazine moiety (Fig. 1). When compared to polymer, the wave numbers of composites were slightly shifted to longer a value which is attributed to the formation of hydrogen bond between the oxygen of TiO₂ and hydrogen of -NH- group of polymer. In addition, the presence of band 486 cm⁻¹ is due to Ti-O bond stretching vibration of TiO₂ metal oxides confirms the incorporation of TiO₂ into the polymeric matrix. The peak at 1049 cm⁻¹ is assigned to S=O bond vibration of incorporated SDS in the polymeric skeleton.

UV-visible spectra of poly(*o*-phenylenediamine)/TiO₂ nanocomposites: The UV-visible spectra of PoPDA 10 %,

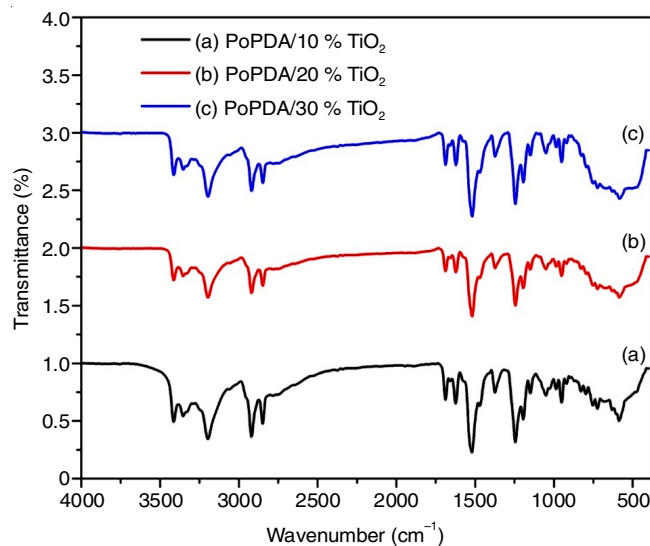


Fig. 1. FT-IR spectra of poly(*o*-phenylenediamine)/TiO₂ nanocomposites

PoPDA 20 % and PoPDA 30 % of TiO₂ nanoparticles were observed with two peaks at about 282 and 441 nm. The one nearer to 441 nm is assigned to π - π^* transition of phenazine skeleton conjugated to the two lone pairs of electrons present on nitrogen of NH₂ groups, the broadening of peak suggests the presence of quinoneimine moieties. The other peak at about 282 nm is due to the π - π^* transitions of benzenoid and quinoid repeating units. The UV-visible spectra of PoPDA with various wt. % of TiO₂ nanoparticles are presented in Fig. 2.

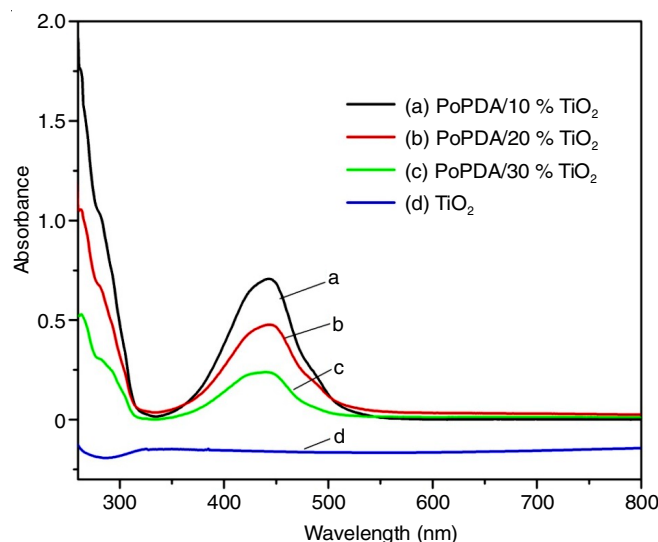


Fig. 2. UV-visible spectra of poly(*o*-phenylenediamine)/TiO₂ nanocomposites

X-ray diffraction RD of poly(*o*-phenylenediamine)/TiO₂ nanocomposites: The XRD pattern of TiO₂ and PoPDA/TiO₂ nanocomposites are shown in Fig. 3. The X-ray patterns at $2\theta = 25.38^\circ, 37.88^\circ, 48.08^\circ, 53.98^\circ$ and 55.18° were attributed to the diffractions lines of the (1 0 1), (0 0 4), (2 0 0), (1 0 5) and (2 1 1) crystal lattice planes of TiO₂ metal oxide anatase phase. The sharp lines observed 27.48° and 36.18° due to (1 1 0) and (1 0 1) faces of rutile phase in TiO₂ [19].

The XRD patterns of PoPDA nanocomposites includes diffraction patterns of both PoPDA lines in the region of $5^\circ < 2\theta < 35^\circ$ and also the lines corresponds to TiO₂ nanoparticles,

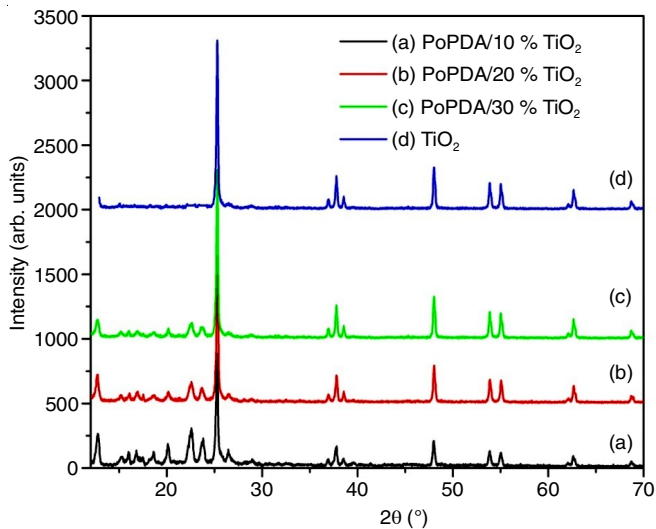


Fig. 3. XRD spectra of poly(*o*-phenylenediamine)/TiO₂ nanocomposites

proving the incorporation of TiO₂ nanoparticles in the polymer moiety by forming nanocomposites. The XRD patterns of PoPDA nanocomposites shows no broad reflection, indicates that the obtained sample has well crystalline and long range ordering.

Transmission electron microscopy analysis of PoPDA/30 % TiO₂ nanocomposite: The TEM image of poly(*o*-phenylenediamine) with 30 wt. % of TiO₂ nanoparticles is shown in Fig. 4. The HRTEM image of PoPDA with 30 % TiO₂ nanoparticles has aggregated spherical particles exhibiting the core-shell type of morphology. The particle size of synthesized polymer nanocomposites was of 60-70 nm range as it is evident from Fig. 4. The entire surfaces of TiO₂ nanoparticles were surrounded by a uniform thin layer of PoPDA and TiO₂ nanoparticles are well dispersed in the polymeric matrix. The outer shell of TiO₂ nanoparticle shows increment in brightness due to the presence of polymeric chain when compared with dark inner core, confirms the formation of core-shell morphology of PoPDA/30 % TiO₂ nanocomposites. The formation core-shell type of PoPDA encapsulated TiO₂ nanocomposites were mainly attributed to the strong electrostatic interaction between the polymeric matrix and the nanoparticles TiO₂ [20].

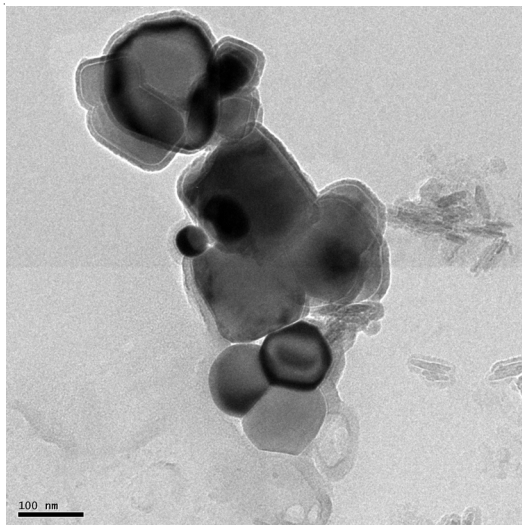


Fig. 4. TEM image of poly(*o*-phenylenediamine)/30 % TiO₂ nanocomposites at 100 nm scale

Photoluminescence: The fluorescence spectra of poly(*o*-phenylenediamine) and its 10, 20 and 30 % of TiO₂ nanocomposites were studied. It is observed from the spectra that the intensity of photoluminescence increases with increase in wt.% of TiO₂ nanoparticles [21]. The polymer and its nanocomposites are excited in the range of 440-450 nm and the corresponding photoluminescence response exhibits strong emission in the range of 522-527 nm, which fall under the green light emitting range. The emission is obtained due to π - π^* transition of benzenoid/amine groups of oxidized/reduced polymer [22]. The π spectrum of PoPDA (Fig. 5) and PoPDA/TiO₂ nanocomposites was measured using different concentrations (1000, 50 and 20 ppm).

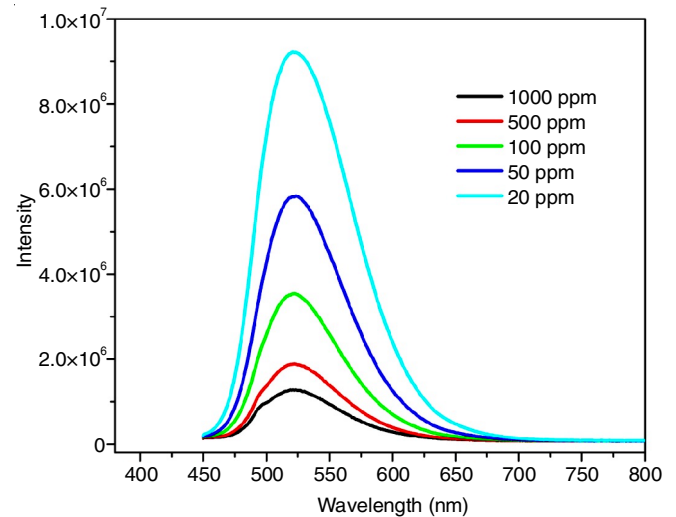


Fig. 5. Photoluminescence spectra of poly(*o*-phenylenediamine) at different concentrations

It is found that luminescence behaviour of poly(*o*-phenylenediamine)/10 % TiO₂ nanocomposites (Fig. 6) depends upon the concentration of nanocomposites. The photoluminescence measurement of PoPDA/10 % TiO₂ at 20 ppm concentration shows stronger emission of intensity 1,03,42,140 arb. units whereas if the concentration is increased to 50 ppm the emission intensity is decreased to 68,14,856 arb. units. Further, increases

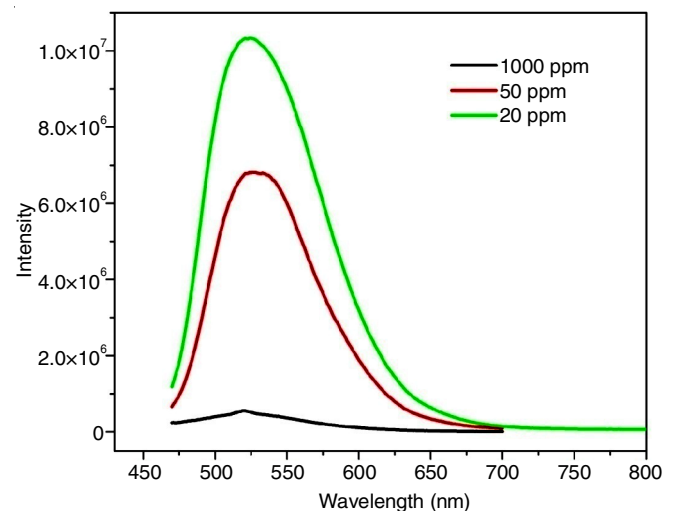


Fig. 6. Photoluminescence spectra of poly(*o*-phenylenediamine)/10 % TiO₂ nanocomposites at different concentrations

of concentration to 1000 ppm, photoluminescence efficiency quenched to a greater extent of 5,57,203 arb. units.

The concentration-dependent photoluminescence spectrum of PoPDA with 20 % of TiO₂ nanoparticles (Fig. 7) shows a similar trend as PoPDA prepared with 10 % TiO₂ nanoparticles. At the concentration of 20 ppm, it emits maximum intensity of 1,07,26,340 arb. units and further increase of concentration to 50 and 1000 ppm the intensity decreased enormously to 84,71,018 arb. units and 8,47,889 arb. units, respectively.

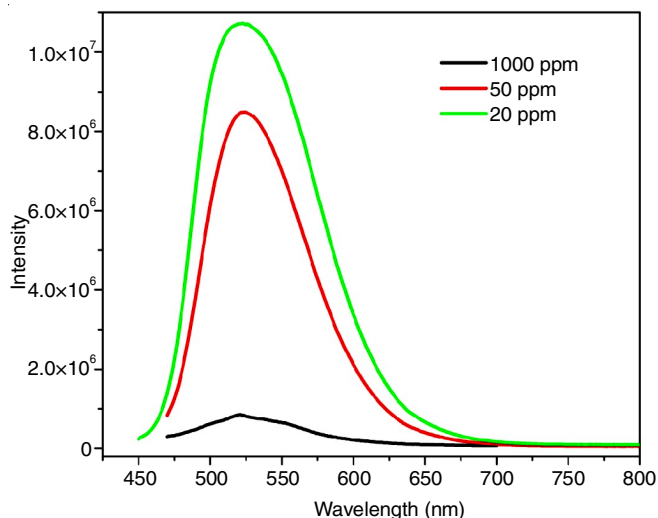


Fig. 7. Photoluminescence spectra of poly(*o*-phenylenediamine)/20 % TiO₂ nanocomposites

The photoluminescence spectrum of PoPDA nanocomposites with 30 % of TiO₂ nanoparticles was illustrated in Fig. 8. The concentrations used for the study are 1000, 500, 100, 50 and 20 ppm. The observed emission peak falls under the range of green light emission region of 525 nm. The maximum emission intensity was found at 20 ppm concentration of 1,11,50,510 arb. units. The emission intensities correspond to 1000, 500, 100 and 50 were 19,88,323, 26,59,257, 55,39,110 and 94,94,935 arb. units, respectively.

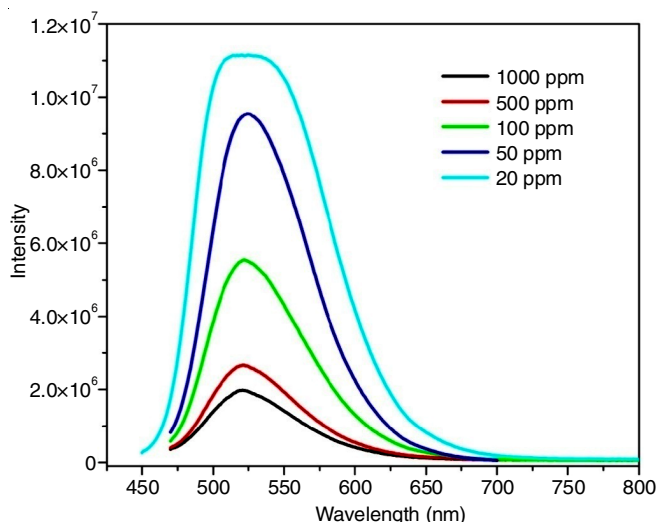


Fig. 8. Photoluminescence spectra of poly(*o*-phenylenediamine)/30 % TiO₂ nanocomposites at different concentrations

The polymer and its nanocomposites exhibit interesting concentration-dependent optical properties. The reason may be due to the dispersion of nanocomposites in the solution, if the nanocomposites are well dispersed in solution, the optical emission is more pronounced.

Conclusion

The prepared polymer nanocomposites were characterized using various spectroscopic techniques. The experimental results agreed with the literature value suggested that the polymer is formed. The polymer nanocomposites with 10, 20 and 30 wt. % TiO₂ was prepared by an *in situ* polymerization method. The core-shell featured nanocomposites exhibited excellent optical properties and found to be concentration dependent. The emission intensity of nanocomposites at 1000 ppm was a low and further decrease in concentration to 500, 100 and 20 ppm emission intensity was likely increased this may be due to the phenomenon of increase in a surface volume ratio of nanoparticles in a polymer matrix at a lower concentration. A comparison of emission intensity measured at 20 ppm concentration, of 10, 20 and 30 wt. % TiO₂ was found to have 1,03,42,140 arb. units, 1,07,26,340 arb. units and 1,11,50,510 arb. units respectively.

ACKNOWLEDGEMENTS

The authors are grateful to the STIC, Cochin and CIF, Pondicherry, University for providing instrumental facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- S. Chen, J. Zhu, T. Zhou, B. He, W. Huang and B. Wang, *Int. J. Electrochem. Sci.*, **7**, 8170 (2012).
- K. Crowley, A. Morrin, R.L. Shepherd, M. in het Panhuis, G.G. Wallace, M.R. Smyth and A.J. Killard, *IEEE Sens. J.*, **10**, 1419 (2010); <https://doi.org/10.1109/JSEN.2010.2044996>.
- T.-Y. Wu, W.-B. Li, C.-W. Kuo, C.-F. Chou, J.-W. Liao, H.-R. Chen and C.-G. Tseng, *Int. J. Electrochem. Sci.*, **8**, 10720 (2013).
- M.S. Tamboli, M.V. Kulkarni, R.H. Patil, W.N. Gade, S.C. Navale and B.B. Kale, *Colloids Surf. B Biointerfaces*, **92**, 35 (2012); <https://doi.org/10.1016/j.colsurfb.2011.11.006>.
- P. Boomi, H.G. Prabu, P. Manisankar and S. Ravikumar, *Appl. Surf. Sci.*, **300**, 66 (2014); <https://doi.org/10.1016/j.apsusc.2014.02.003>.
- P. Boomi, H.G. Prabu and J. Mathiyarasu, *Colloids Surf. B Biointerfaces*, **103**, 9 (2013); <https://doi.org/10.1016/j.colsurfb.2012.10.044>.
- P. Boomi, H.G. Prabu and J. Mathiyarasu, *Eur. J. Med. Chem.*, **72**, 18 (2014); <https://doi.org/10.1016/j.ejmech.2013.09.049>.
- M. Baibarac, I. Baltog, M. Scocioreanu, B. Ballesteros, J.Y. Mevellec and S. Lefrant, *Synth. Metals*, **161**, 2344 (2011); <https://doi.org/10.1016/j.synthmet.2011.09.001>.
- Q. Hao, B. Sun, X. Yang, L. Lu and X. Wang, *Mater. Lett.*, **63**, 334 (2009); <https://doi.org/10.1016/j.matlet.2008.10.041>.
- S. Archana and R. Jaya Shanthi, *Int. J. Chemtech Res.*, **8**, 85 (2015).
- X.-G. Li, M.-R. Huang and Y.-L. Yang, *Polymer*, **42**, 4099 (2001); [https://doi.org/10.1016/S0032-3861\(00\)00661-3](https://doi.org/10.1016/S0032-3861(00)00661-3).
- M.H. Abdel Rehim, N. Ismail, A. El-Rahman, A.A. Badawy and G. Turkey, *Mater. Chem. Phys.*, **128**, 507 (2011); <https://doi.org/10.1016/j.matchemphys.2011.03.037>.

13. F. Cataldo, *Eur. Polym. J.*, **32**, 43 (1996);
[https://doi.org/10.1016/0014-3057\(95\)00118-2](https://doi.org/10.1016/0014-3057(95)00118-2).
14. X.-G. Li and M.-R. Huang, *J. Appl. Polym. Sci.*, **66**, 2139 (1997);
[https://doi.org/10.1002/\(SICI\)1097-4628\(19971219\)66:11<2139::AID-APP10>3.0.CO;2-X](https://doi.org/10.1002/(SICI)1097-4628(19971219)66:11<2139::AID-APP10>3.0.CO;2-X).
15. S. Archana and R. Jaya Shanthi, *Int. J. Adv. Res.*, **2**, 778 (2014).
16. S. Archana, *Int. J. Adv. Chem.*, **5**, 29 (2017);
<https://doi.org/10.14419/ijac.v5i1.7437>.
17. S. Archana, *Int. J. Appl. Res.*, **3**, 661 (2017).
18. S. Archana and R. Jaya Shanthi, *Indian J. Adv. Chem. Sci.*, **2**, 83 (2013).
19. S. Archana and R. Jaya Shanthi, *Res. J. Chem. Sci.*, **4**, 60 (2014).
20. M. Wang, H. Zhang, C. Wang and G. Wang, *Electrochim. Acta*, **106**, 301 (2013);
<https://doi.org/10.1016/j.electacta.2013.05.097>.
21. K. Gupta, P.C. Jana and A.K. Meikap, *Synth. Met.*, **160**, 1566 (2010);
<https://doi.org/10.1016/j.synthmet.2010.05.026>.
22. S. Goswami, U.N. Maiti, S. Maiti, S. Nandy, M.K. Mitra and K.K. Chattopadhyay, *Carbon*, **49**, 2245 (2011);
<https://doi.org/10.1016/j.carbon.2011.01.055>.