

Synthesis and Characterization of Polyaniline Doped Metal Oxide Nanocomposites

Megha Sawarkar¹, S A Pande², P S Agrawal³

¹ Research Scholar, Dept of Applied Chemistry, Laxminarayan Institute of Technology, Nagpur-440 033, India

² Associate Prof., Dept of Applied Physics, Laxminarayan Institute of Technology, Nagpur-440 033, India

³ Associate Prof., Dept of Applied Chemistry, Laxminarayan Institute of Technology, Nagpur-440 033, India

Abstract - The ZnO-Pani and CdO-Pani nanocomposites were prepared by sol-gel method using their respective nitrates. It is a simple and low cost method to prepare nanocomposite. The prepared samples were characterized by using Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and Fourier Transform Spectroscopy (FTIR) to get surface morphology, idea of getting particles of nanosized range so that further characterization can be done, to study the electrical properties of synthesized nanocomposite and measure the resistivity.

Key words: Metal Oxide nanoparticles, polyaniline, structural properties.

1. Introduction

Mutual interactions between inorganic semiconductors and conducting polymers may give rise to interesting properties which are significantly different from those of individual components [1]. Nanostructures and nanocomposites of conducting polymers have emerged as a new field dedicated to the creation of smart materials for use in future technologies [2-3]. Blending or encapsulation of inorganic nanoparticles in Intrinsically conducting polymer matrix is believed to be an easy route to prepare and design nanocomposites where delocalized π -electrons can interact with inorganic nanoparticles, resulting in materials of unique or better properties [4]. Many studies on preparation of polymer nanocomposite have been reported in the quest to develop new advanced materials with improved mechanical, electrical, optical and catalytic properties or to improve conduction mechanism in electronic devices. These materials have found their use in many electronic and nanoelctronic devices.

Polyaniline (PANI) is a promising conducting polymer due to its easy synthesis, environmental stability and high electrical conductivity on doping with protonic acids [5-6]. The highly ordered structures such as crystalline or self assembled structures of ideal conducting polymer with π -conjugated structure is expected to have metal-like electrical conductivity. To induce an ordered structure, other materials acting as filler for the composite are required [7-12]. The preparation of PANI composites with various materials has received great attention because of their unique properties and applications in various electrical and electronic devices. Several reports dealing with the preparation of conducting composites such as Fe₃O₄:PANI, MnO₂:PANI, TiO₂:PANI and ZrO₂:PANI [13,14], as well as preparation and characterization of ZnO:PANI composites have been published [15-17]. Due to these properties it has been studied extensively for making optical and electronic devices [18- 20] like: light emitting diodes, solar cells, transducers, photo detectors, etc. In particular, ZnO nanostructures (NSs) are of intense interest since they can be grown by a variety of methods with different morphologies. Nanostructure ZnO can be synthesized by various methods such as physical, chemical, electrochemical, etc. but chemical route has attracted much attention due to the flexibility of controlling the shape and size of the structures by tuning the different growth conditions. [21- 26] To utilize these properties of ZnO in LEDs application, another p-type material is necessary as ZnO NRs is unintentionally n-type material. Since mostly polymers are p-type and their special properties like low cost, low power consumption, flexible and easy manufacturing all makes polymers a better choice to use with ZnO NPs to fabricate a flexible device that utilizes the properties of both materials for large area lighting and display application. [27, 28]

On the other hand Cadmium oxide (CdO) is n-type semiconductor used as a transparent conductive material prepared as a transparent conducting film back. Cadmium oxide has been used in applications such as photodiodes,

phototransistors, photovoltaic cells, transparent electrodes, liquid crystal displays, IR detectors, and anti reflection coat. CdO micro particles undergo band gap excitation when exposed to UV-A light and is also selective in phenol photo degradation. With this background of multifunctionality CdO, it was thought worthwhile to use the nano-sized CdO as an inorganic counterpart in the composite preparation.

In the present work ZnO, CdO nanoparticles are prepared by sol-gel method. The structural and morphological properties of ZnO-PANI, CdO- PANI nanocomposites based on ZnO and CdO nanoparticles as inorganic filler material and PANI as the main matrix were studied. The synthesized nanocomposites were subjected for spectroscopic and structural characterization using FTIR, SEM and XRD respectively. The structure of CdO was found to be cubic with lattice parameter 4.689 Å which was confirmed from XRD. The average crystallite size was found to be 56 nm which was supported by SEM images.

2. EXPERIMENTAL

2.1 Synthesis of ZnO nanoparticles

Zinc chloride (assay > 98%), Aniline (assay > 99%), Ammonium peroxydisulfate (APS) (assay > 98%), methyl orange, Sodium hydroxide (assay 99%), Hydrochloric acid (assay>37%) and 2-propanol (assay > 99.8%) of analytical grade were taken and used as it is, except aniline which was distilled prior to use. Double distilled water was used for preparation of various solutions.

5.5g of ZnCl₂ was dissolved in 200 ml of water at 90°C in a beaker and 16 ml of 5M NaOH aqueous solution was added dropwise to the ZnCl₂ solution with a gentle stirring over a period of 10 minutes. The particles were separated from the supernatant by sedimentation. The supernatant solution was discarded and the solid residue was washed five times with distilled water to remove NaCl. The particles were peptized with 2-propanol for 10 minutes at room temperature. Then the particles were collected by centrifugation at 6,000 rpm for 15 minutes and then washed three times with distilled water. Finally, the product was thermally treated at 250°C for 5 hours to form ZnO powder.

2.2 Synthesis of PANI -ZnO composites

To prepare PANI-ZnO nanocomposite, during polymerisation, ZnO nanoparticles (50% by wt of aniline) were dispersed in the solution. 0.9313 g of ZnO powder was added into 20 mL aqueous solution of 0.01 mol aniline monomer and 0.01 mol hydrochloric acid. 0.01 mol APS was dissolved in a 15 ml distilled water and added drop wise to the mixture of ZnO and aniline with stirring in an ice bath. Polymerization proceeded for 5.5 hours. The

composite of PANI modified ZnO was obtained as precipitate. The precipitate was isolated by filtration, washed with distilled water and ethanol several times, and dried at 50°C. Pure PANI was also synthesized, by using an identical method but without using ZnO.

2.3 Synthesis of CdO nanoparticles

Nanostructure of CdO was synthesized by sol – gel method using respective metal precursor cadmium acetate . Cadmium acetate was added slowly in 500 ml clear solution of starch and distilled water and the solution was stirred. While stirring, equimolar ammonia in aqueous solution was added drop by drop. Then stirring was carried for another two hours and the solution was kept overnight. Then the solution was filtered and precipitate of CdO was obtained which was heated overnight at 80°C. Next day, crystalline form of CdO was sintered up to 600°C. At 80°C the colour of CdO was light red and at 600°C, it was reddish brown.

2.4 Synthesis of PANI -CdO nanocomposites

PANI-CdO nanocomposite was obtained by in-situ polymerization. Initially polymerization of monomer aniline was initiated by drop wise addition of APS in acidic medium in which specific quantity of synthesized CdO powder was added. The stirring was continued for 2 hours and then solution was kept overnight. Next day, the mixture was filtered, washed with distilled water and the methanol and then dried at 80°C for overnight.

3. CHARACTERIZATION TECHNIQUES

3.1 Wide angle x-ray diffraction

X-ray diffraction (XRD) studies were carried out using a Philips powder X-ray diffractometer (Model: PW1710). The XRD patterns were recorded in the 2θ range of 10° - 80° with step width 0.02° and step time 1.25 sec using CuK α radiation (λ = 1.5406 Å). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by JCPDS file.

3.2 Fourier Transform Infra red Spectroscopy

Fourier Transform Infra Red (FTIR) spectroscopy (Model: Perkin Elmer 100) PANI-metal oxide (50%) nanocomposite was studied in the frequency range of 400 - 4000 cm⁻¹.

3.3 Scanning Electron Microscopy

Morphological study of doped PANI- metal oxide nanocomposite was carried out using scanning electron

microscopy (SEM Model: JEOL JSM 6360) operating at 20 kV.

4. RESULTS AND DISCUSSION

4.1. Structural Analysis

Figure. 1 shows the typical XRD patterns of nanoparticles and its nanocomposites. The XRD pattern of PANI in figure 1 reveals two weak peaks, observed at $2\theta=20^\circ$ and $2\theta=25^\circ$. The peak at $2\theta = 20^\circ$ represents the characteristic distance between the ring planes of benzene rings in adjacent chains or the close contact inter-chain distance [29]. The peak centered at $2\theta=25^\circ$ may be assigned to the scattering from PANI chains at interplanar spacing [30,31] and very low intensity of the observed peak indicates that the PANI has amorphous structure with low crystallinity.

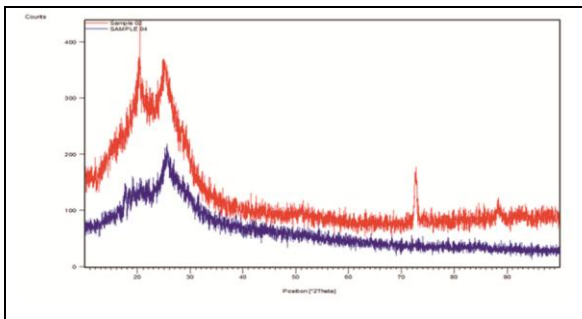


Fig 1: XRD patterns of ZnO nanoparticles and PANI/ZnO nanocomposites

The diffraction peaks of ZnO nanoparticles and PANI/ZnO composites have been indexed to the hexagonally wurtzite structured ZnO which were well matched with that in JCPDS, 36-1451. The crystallite sizes of the ZnO nanoparticles and PANI/ZnO nanocomposites were estimated from X-ray line broadening using Scherer's equation [32] and found 32 nm and 48 nm, respectively. The increasing trend of lattice parameters indicating that the volume of unit cell for ZnO is greatly increased due to the adsorption of PANI molecular chains on the surface of the ZnO nanoparticles. In order to study the effect of addition of ZnO nanoparticles in PANI matrix, a careful analysis of the position of the XRD peak indicates that there is a shifting in peak's position towards lower 2θ value. These results are in good agreement with the results reported earlier [33] but in this case, the crystallinity of ZnO nanoparticles was found to be disturbed in the PANI/ZnO nanocomposites. However, in the present work the crystallinity of ZnO is not disturbed by PANI molecular chain on the surface of ZnO nanoparticles as can be seen from Figure 1. The shifting of the peak's position clearly indicates that ZnO nanoparticles are incorporating into the PANI polymer matrix. The X ray diffraction pattern of the composite revealed that the degree of crystallinity of PANI-ZnO composite was higher than that of the PANI but lower than

ZnO showing that the amorphous nature of PANI may inhibit crystallisation of ZnO

It can be seen from Figure 2a that all of the peaks can be indexed to the cubic CdO crystal (JCPDS Card No. 05-0640). The XRD curve of the CdO nanoparticles reveals that the relatively strong diffraction peaks are (111) and (200). The sharp peaks of the XRD patterns indicate that the fabricated CdO nanostructures possess good crystallinity.

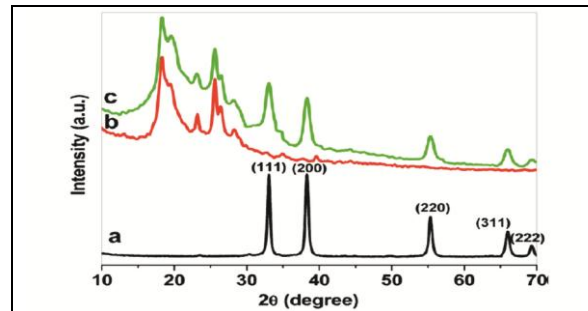


Fig 2: XRD patterns of (a) CdO nanoparticles, (b) PANI, and (c) PANI/CdO nanocomposite.

In Figure 2(b), (c), the XRD patterns of Pure PANI and PANI/CdO nanocomposite are represented. Four peaks can be observed in the region $2\theta = 15-30^\circ$. For the XRD pattern of PANI, the maximum peak around $2\theta = 18.5^\circ$ can be ascribed to periodically parallel and perpendicular polymer (PANI) chains. The peak at $2\theta = 20^\circ$ is evidence of the characteristic distance between the ring planes of benzene rings in adjacent chains or close contact interchains [29]. The peak centered at $2\theta = 25^\circ$ can be assigned to the scattering from PANI chains at interplanar spacing [30,31] and indicates that Pure PANI also has some degree of crystallinity (Figure 2b). As can be seen in Figure 2c, two phases are identified in the PANI/CdO nanocomposite. One is the cubic structure of CdO and the other is PANI with characteristic peaks.

4.2 MORPHOLOGICAL STUDIES

4.2.1 SEM of PANI and PANI-ZnO nanocomposite

Fig. 3 (a), (b) and (c) shows the scanning electron micrographs of PANI (EB), ZnO and PANI-ZnO nanocomposites respectively. The pure PANI displays micrometer sized irregular sheetlike morphology as seen in Figure 3(a)

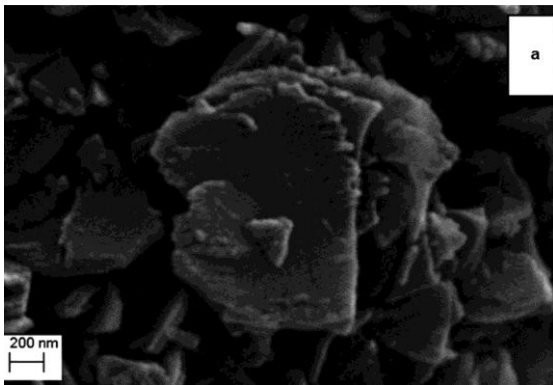


Fig. 3(a): SEM image of Pure PANI

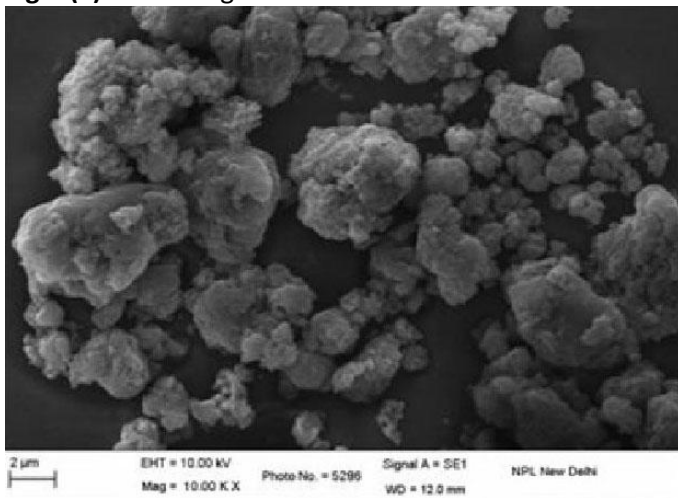


Fig. 3(b): SEM image of Pani/ZnO

SEM micrographs shows morphology of PANI has changed with the introduction of ZnO nanostructures of morphologies.

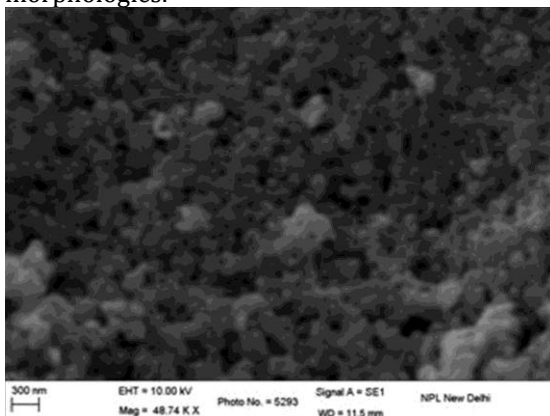


Fig 3(c): SEM image of ZnO nanoparticles

And Figure 3(c) depict the uniform distribution of spherical shaped ZnO into the polymer matrix, respectively. Figure 3(b) shows the incorporation of ZnO nanoparticless synthesized into the polymer matrix. SEM analysis of ZnO showed a particle size distribution of about 50-70 nm. From the SEM image of composite, it is observed that ZnO particles are surrounded by polyaniline

matrix and hence it appears as agglomerated macromolecules.

4.2.1 SEM of PANI-CdO nanocomposite

Part a and b of Figure 4 show the SEM images of the PANI/CdO nanocomposite, and Pure CdO respectively. The pure PANI displays micrometer sized irregular sheet like morphology as seen in Figure 3(a). CdO nanoparticles can be seen on PANI sheets as shown in Figure 4(a). It is observed that the distribution of CdO nanoparticles in the PANI matrix is homogeneous and the sizes of the CdO nanoparticles are measured as 52 and 67 nm as indicated by the rectangle.

5. FOURIER TRANSFORM INFRA-RED SPECTROSCOPY (FTIR) STUDIES

5.1 FTIR of pure PANI, ZnO nanoparticles and PANI-ZnO Nanocomposites

FTIR spectrum is the feature of a particular compound that gives the information about its functional groups, molecular geometry and inter/intermolecular interactions. Figure 5 shows the FTIR spectra of pure PANI, ZnO nanoparticles and PANI/ZnO nanocomposites.

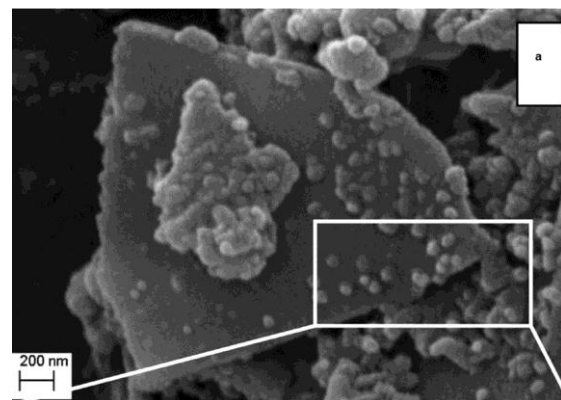


Fig 4(a): SEM image of CdO/PANI nanoparticles

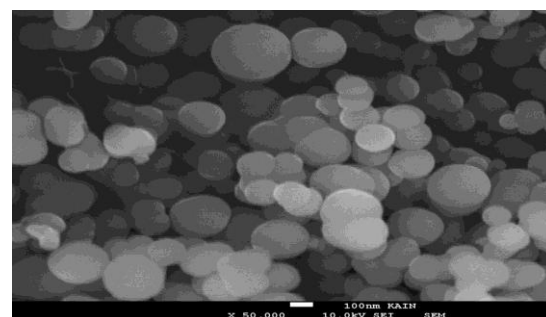


Fig 4(b): SEM image of CdO nanoparticles

Figure 5(a) shows that the characteristic peaks of pure PANI appear at 1586, 1475, 1295 and 1151 cm^{-1} . FTIR spectra of ZnO nanoparticles as shown in Fig. 5(b) depict the broad peak between 3343 and 3566 cm^{-1} which is associated to the adsorbed H₂O molecule whereas, the absorption band at 501 cm^{-1} is the stretching mode of ZnO.[34]

Figure 5(c) shows that the absorption peaks for PANI/ZnO nanocomposites appear at 1572 cm^{-1} (C=C stretching mode of the quinoid rings), 1461 cm^{-1} (C=C stretching mode of benzenoid rings), 1234 cm^{-1} (C-N stretching mode) and 1148 cm^{-1} (N = Q = N, where Q represents the quinoid ring) [35, 36], indicating the formation of PANI in the composites. Comparing to the corresponding peaks of pure PANI, the peaks of PANI/ZnO shifted towards lower wavenumber. This shifting of absorption bands may be due to the action of hydrogen bonding between the hydroxyl groups on the surface of ZnO nanoparticles and the amine groups in the PANI molecular chains [37]. Similar observations of shifting of absorption peaks of PANI/ZnO towards lower wavenumber were also reported earlier. [38]

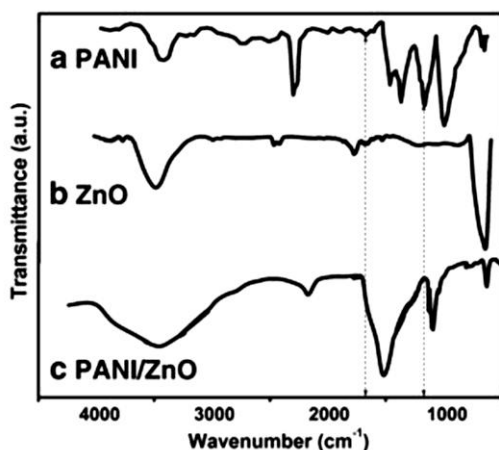


Fig 5: FTIR of (a) ZnO nanoparticles, (b) Pure PANI (c) PANI-ZnO nanocomposites.

5.2 FTIR OF CdO NANOPARTICLES and PANI-CdO nanocomposites

FTIR spectroscopic analyses were carried out to characterize the prepared PANI, CdO nanoparticles, and PANI/CdO nanocomposite. The FTIR spectrum of CdO is represented in Figure 6. The bands at 833, 686, and 631 cm^{-1} are related to the stretching vibration of Cd-O bonds. As seen in Figure 6(b), the FTIR spectrum of the pure PANI exhibits a characteristic peak around 3263 cm^{-1} which is attributed to the N-H stretching mode (39). The peaks of the C=N and C=C stretching vibrations of quinoid and benzenoid units are observed at 1578 and 1490 cm^{-1} , respectively. The band at 1297 cm^{-1} is assigned to the C-N

stretching of the benzenoid, while the band at 1041 cm^{-1} is due to the quinoid unit of PANI.

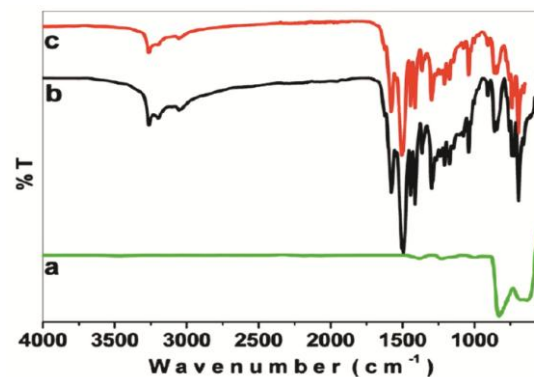


Fig 6 : FTIR spectra of (a) CdO nanoparticle, (b) Pure PANI, and (c) PANI/CdO nanocomposite.

The presence of the benzenoid and quinoid units is evidence of the emeraldine form of PANI. In Figure 6(c), the FTIR spectrum of the PANI/CdO nanocomposite is represented. The corresponding spectrum has the same characteristic bands as the PANI homopolymer, but some of the bands shifted to higher wave numbers after the addition of CdO nanoparticles. The bands at 1578, 1490, and 1041 cm^{-1} shifted to 1587, 1499, and 1049 cm^{-1} , respectively. These shifts of characteristic bands can be attributed to the interactions between PANI homopolymer chains and CdO nanoparticles which decrease the electron density and bond energy of the PANI after the addition of CdO nanoparticles [40].

6. CONCLUSION

In this work pure PANI, ZnO and CdO nanoparticles along with PANI/ZnO, PANI /CdO nanocomposites had been successfully synthesized by a simple, cost effective technique. ZnO and CdO nanoparticles were synthesised by sol gel method. XRD studies clearly showed the crystalline and hexagonal quartzite nature of the ZnO nanoparticles and PANI/ZnO nanocomposites of 32 nm and 48 nm, respectively. A change in the lattice parameters of ZnO in the PANI/ZnO nanocomposites was observed which also indicated the interaction between ZnO particles and PANI matrix. The SEM study of PANI/ZnO nanocomposites revealed uniform distribution of ZnO nanoparticles in PANI matrix. FTIR spectra revealed that the absorption peaks of PANI/ZnO nanocomposite were found to shift towards lower wave number as compared to those observed in pure PANI. The shifting of absorption bands were attributed to the interaction of ZnO nanoparticles with the PANI molecular chains.

Pure PANI and PANI/CdO nanocomposites have been successfully prepared by a chemical polymerization method. The SEM observations revealed that PANI has irregular sheet like morphology and the morphology remained stable after the combination with CdO nanoparticles. The FTIR confirm that there is an interaction between PANI chains and CdO nanoparticles which affect electron density and bond energy. Overall, PANI/Metaloxide nanocomposites present a promising material which may be applicable in optoelectronic devices which have the dual advantages of low dimension and organic conductors.

REFERENCES

- [1] Dutta, K., Manna, S., & De, S. K. , *Synthetic Metals*, 2009, 159, 315–319.
- [2] Malinauskas, A., Malinauskiene, J. , & Ramanavicius, A. , *Nanotechnology*, 2005,16, 51–62.
- [3] Rajesh A. T., & Kumar D., *Sensors and Actuators B*, 2009, 136, 275–286.
- [4] Lei X., & Su Z., *Polymer Advanced Technology*, 2007, 18, 472-476.
- [5] Ahmed A. A., Mohammad F. & Rahman M. Z. A., *Synthetic Metals*, 2004, 144, 29–4.
- [6] Qiang J., Yu Z., Wu H., & Yun D, *Synthetic Metals*, 2008, 158, 544–547.
- [7] Kim D. K., Oh K. W. & Kim S. H., *Journal of Polymer Science. B*, 2008, 46, 2255-2266.
- [8] Mittal H., Kaith B., & Jindal R., *Advances in Applied Science Research*, 2010, 1, 56-66.
- [9] Ramaswamy V., Vimalathithan R. M., & Ponnusamy V, *Advances in Applied Science Research*, 2010, 1, 197-204.
- [10] Igwe H.U., & Ugwu E.I., *Journal of Advance in Applied Science Research*, 2010, 1, 240-246. ISSN: 0976-8610
- [11] Tomar A.K., Mahendia S., & Kumar S., *Advances in Applied Science Research*, 2011, 2, 327- 333. ISSN: 0976-8610
- [12] Lanje A.S., Sharma S.J., Pode R.B., & Ningthoujam R.S., *Advances in Applied Science Research*, 2010, 1 , 36-40. ISSN: 0976-8610.
- [13] Gok A., Omatsova M., & Prokes J., *European Polymer Journal*, 2007, 43, 2471–2480.
- [14] Yavuz A., & Gok A., *Synthetic Metals*, 2007, 157, 235–242.
- [15] Paul G. K., Bhaumik A., Patra A. S., & Bera S. K, *Materials Chemistry and Physics*, 2007, 106, 360–363.
- [16] Jeng J., Chen T. , & Lee C. , *Polymer*, 2008, 49, 3265–3271.
- [17] Zhang H., Zong R. & Zhu, *The Journal of Physical Chemistry*, 2009, 113, 4605–4611.
- [18] Yang P., Yan H., Mao S., Russo R., Johnson J., Saykally R., Morris N., Pham J., He R., & Choi H., *Advanced Function Materials*, 2002, 12, 323-331.
- [19] Park W. I., Yi G., Kim M., & Pennycok S. L., *Advanced Materials*, 2002, 14, 1841-1843.
- [20] Vayssieres L., Keis K., Hagfeldt A., & Lindquist S., *Chemistry of Materials*, 2001, 13, 4395-4398.
- [21] Pacholski C., Kornowski A., & Weller H., *Angewandte Chemie*, 2002, 114, 1234-1237.
- [22] Patil V. B., Pawar S. G., Patil S. L. & Krupanidhi S. B., *Journal of Materials Science: Materials Electronics*, 2010, 41, 355-359.
- [23] Lee J. H. Ko, K. H., & Park B. O, *Journal of Crystal Growth*, 2003, 247, 119-12.
- [24] Chougule M. A., Patil S. L., Pawar S. G., Raut B. T., Godse P. R., Sen S., & Patil V. B., *Ceramic International*, 2012, 28, 2685-2692.
- [25] Gupta V. & Mansingh, A., *Journal of Applied Physics*, 1996, 80, 1063-1073.
- [26] Chougule M. A., Patil, S. L., Pawar S. G., Raut B. T., Godse P. R., Sen S., & Patil V. B. , Mane, A. T. *Journal of Materials Science: Materials in Electronics*, 2010, 21, 1332-1336.
- [27] Gurunathan, K., Murugan A.V., Marimuthu R., Mulik, U.P. & Amalnerkar D.P., *Material Chemica Physics*, 1999, 61, 173-191.
- [28] Amin, G., Sandberg M., Zainelabdin A., Zaman S., Nur O. & Willander M., *Journal of Material Science*, 2012, 47, 4726-4731.
- [29] Pouget J.P., Hsu C.H., MacDiarmid A.G., & Epstein, A. J. , *Synthetic Metals*, 1995, 69, 119-120.
- [30] Feng W., Sun E., Fujii A., Wu H., Nihara K., & Yoshino K., *Bulletin of the Chemical Society of Japan*, 2000, 73, 2627-2633.
- [31] Min S., Wang F., & Han Y., *Journal of Materials Science*, 2007, 42, 9966-9972.
- [32] Ahmed F., Kumar S., Arshi N., Anwar M.S., Su-Yeon L., Gyung-Suk Kilb, Dae-Won Park Bon Heun Kooa, & Chan Gyu Lee, *Thin Solid Films*, 2011, 519, 8375–8378.
- [33] Sharma B.K., Khare N., Dhawan S.K., & Gupta H.C., *Journal of Alloys and Compounds* , 2009, 477, 370–373.
- [34] Silva R. F., & D Zaniquelli , M. E. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2002, 198, 551–558.
- [35] Mathewa R., Mattesb B. R., & Matthew P. E. , *Synthetic Metals*, 2002, 131, 141–147.
- [36] Monkman A.P., & Adams, P., *Synthetic Metals*, 1991, 40, 87–96.
- [37] He Y., *Applied Surface Science*, 2005, 249, 1–6.
- [38] He Y., *Powder Technology*, 2004, 147, 59–63.
- [39] Zheng W, Angelopoulos M, Epstein A. J. & A. G., *Macromolecules*, 1997, 30, 2953–2955.
- [40] Niu Z., Yang Z., Hu Z., Lu Y. and Han C.C , *Advanced Functional Materials*, 2003, 13, 949–954.