Synthesis, Characterization, and Applications of Polymer-Based Poly Aniline Zinc Oxide Nanocomposites by Sol-Gel Method and their Photocatalytic Activity.

Kalpana Ginne, Madan Kumar Gundala, Dr. S. Kavitha*

Chaitanya (Deemed to be University), Kishanpura, Hanamakonda, Warangal – 506 001 (T.S). India.

Email ID: kavitha.cdu@gmail.com

Abstract:

Using the Sol-Gel process and in-situ chemical oxidation polymerization, PAZO (polyaniline zinc oxide nanocomposite) was fabricated from zinc nitrate. PAZO is an acronym for "Polyaniline Zinc oxide Nanocomposite." When $K_2S_2O_8$ is used as an oxidant in an acidic media, the reaction results in 0.1, 0.2, 0.3, 0.4, and 0.5 moles of ZnO being produced at room temperature. FTIR, XRD, SEM, and TEM analysis were used to characterize the PANZO nanocomposites that were produced. During the photo degradation of potassium permanganate (KMnO4) dye supply, the polymer ZnO Nanocomposite showed superior photocatalytic activity compared to nitrogen-doped TiO_2. Nanocomposites made using PAZO exhibited both ferromagnetic and semiconducting properties. For the first time, we have investigated how NiO's presence influences PANO nanocomposites' photocatalytic capability. According to the data that was collected, the Polyaniline Zinc Oxide nanocomposite that was developed has the potential to be used as a useful photocatalyst.

Keywords: Polyaniline-Zinc Oxide, nanocomposites, Sol-Gel method, Spectroscopic methods, and Photocatalytic activity.

1. Introduction

Inorganic semiconductors and conducting polymers may combine to provide novel and fascinating properties that aren't found in either substance by itself [1]. A developing field is the creation of conducting polymer nanostructures and nanocomposites for use in future technologies [2–3]. Inorganic nanoparticles may be blended or enclosed in an innately conducting polymer matrix to create nanocomposites, in which delocalized -electrons may interact with inorganic nanoparticles [4]. Numerous studies on the production of polymer nanocomposite have been reported in an attempt to develop unique, complex materials with improved mechanical, electrical, optical, and catalytic characteristics or to improve the conduction mechanism in electronic devices. These materials are used in several electrical and nanoelectronics devices.

After being doped with protonic acids, polyaniline (PANI) has high electrical conductivity, is easily synthesized, and is ecologically safe. Highly structured structures include crystalline or self-assembling structures of an ideal conducting polymer. A conjugated structure is expected to exhibit metal-like electrical conductivity. To create an ordered structure, additional components acting as filler for the composite are required [7–11]. The creation of PANI composites using a variety of materials has sparked a lot of attention because of its distinctive properties and applications in a broad range of electrical and electronic devices [12,13]. In addition to reports on the production of additional conducting composites including Fe_3O_4: PANI, MnO_2: PANI, TiO_2: PANI, and ZrO_2: PANI, ZnO: PANI composites have also been manufactured and characterized [14–16].

It has been the focus of many studies because of these qualities for application in a broad range of optical and electrical devices [17–19], such as LEDs, solar cells, transducers, photodetectors, and many more. ZnO nanocomposites, which may be created using a variety of methods and in a broad range of sizes and forms, are particularly fascinating. Physical, chemical, electrochemical, and other methods can all be used to create nanostructures of ZnO. Still, the sol-gel route has attracted the most attention due to how easily the form and size of the structures can be altered by changing the growing conditions [20–25]. Since ZnO nano-composites are n-type semiconductors, a different p-type material is needed to take advantage of these ZnO characteristics in LED applications. To create a flexible device that utilizes both materials for wide-area illumination and displays, polymers, which are mostly p-type, are preferred over ZnO NPs due to their affordability, low power consumption, flexibility, and simplicity of production [26 and 27].

Polyaniline zinc oxide nanocomposites have emerged as one of the most well-liked conductive polymers due to their reversible redox, pH-switching, and sensing properties as well as their simple manufacture [28]. However, materials in this class often have materials with weak physical properties and thermal stability. Polyaniline Zinc Oxide nanocomposites can only be produced via a spinning process since melt techniques like extrusion are too difficult to use. The PAZO has attracted the attention of researchers because of its enticing qualities and the broad range of prospective applications [30–32]. Polymer-based nanocomposites have found use in a variety of industries, including photocatalysis, filtration, protective textiles, and medicinal substrates [33]. One example is the PAZO nanocomposite, successfully produced via the Sol-Gel process. To the best of our knowledge, this study represents the first instance of in-situ reduction of aniline, N, and N-dimethyl formamide, incorporating zinc nitrate, while the combination is being heated and magnetically agitated. PAZO nanocomposites may be made utilizing a special, simple, rapid, and affordable approach by altering the percentage of zinc nitrate solution.

Here, ZnO nanocomposites are made using the sol-gel method. Inorganic filler materials including ZnO nanoparticles were combined with a polyaniline (PANI) matrix to generate nanocomposites, and their structural and morphological characteristics were studied. FTIR, SEM, TEM, and XRD were used to characterize the generated nanocomposites' spectral and structural properties. It was confirmed by X-ray diffraction investigation that the cubic structure of ZnO, with a lattice value of 4.689, exists. A crystallite's average size was 90 nm, and scanning electron microscopy supported this finding.

2. Experimental:

2.1. Materials:

Aniline (S. D. Fine-Chem. Ltd., 99.5%) was used after double distillation. Other chemicals such as Zinc nitrate (99%), Potassium persulphate, Ethanol (99.9%), H_2SO_4(98.9%), Starch, N, and N-Dimethyl formamide were bought from a local company, Ammonia used was of AR grade. The water used in this investigation was de-ionized.

2.2. Synthesis method of PAZO nanocomposites:

Step-1(Preparation of Zinc Oxide Nanoparticles)

A 100 ml starch solution and 0.1 M zinc nitrate solution were given a dropwise addition of ammonia while continuously stirred. After the ammonia addition was finished and the sample was allowed to settle overnight, the colour of the sample changed from white to light yellow. The sample is first collected, and then it is filtered using Whatman filter paper. Take a sample of the ZnO nanoparticles and wash them in ethanol and deionized water to remove any impurities. They were then dried at 65^0C in hot air furnaces.

Step-2(Preparation of Poly aniline Zinc Oxide Nanocomposites)

Synthesized ZnO nanoparticles undergo in-situ chemical oxidative polymerization to create the PAZO matrix. Then, after heating the mixture for an hour while stirring continuously, we added 10 ml of the previously made sonicated ZnO solution. After two hours of stirring, we noticed that the solution had changed from yellow to dark green, indicating that polymerization had taken place and the formation of PAZO nanocomposites.

To allow the solution to completely develop, the sample was left in a dark area overnight after it was obtained. Cleaning the sample could include using ethanol and deionized water—the effective fabrication of polyaniline-zinc oxide nanocomposites with adjustable zinc oxide concentration. Per mole, these values varied between 0.1 to 0.5 moles of PAZO.

3. RESULT AND DISCUSSIONS:

3.1. Scanning Electron Microscopy (SEM):

Images of PANI, ZnO, and PAZO nanocomposites taken with a scanning electron microscope are shown in **Fig.1, 2, and 3,** respectively. The shape of pure PANI may be seen in **Fig. 1**, where it is shown as looking like uneven sheets on a micrometer scale. In **Fig.3,** the ZnO spheres are shown as being uniformly dispersed throughout the polymer matrix. In **Fig.2,** a simplified representation of the process of incorporating ZnO nanoparticles into a polymer matrix is shown. According to the results of an SEM examination, the particle size distribution of ZnO falls somewhere between 70 and 90. The composite was photographed using an SEM, and the resulting image indicates that the ZnO particles included inside it have a polyaniline shell.

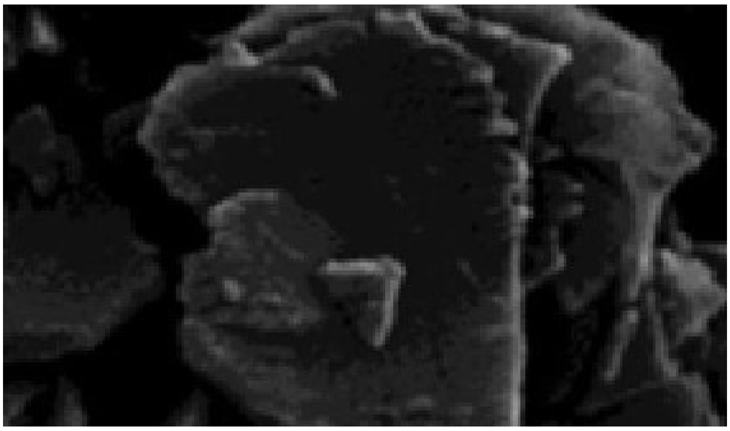

Fig.1. SEM image of polyaniline

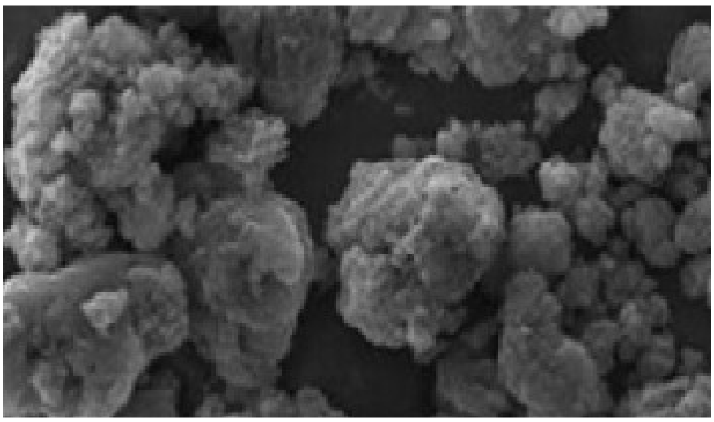

Fig.2. SEM image of polyaniline Zinc Oxide nanocomposites

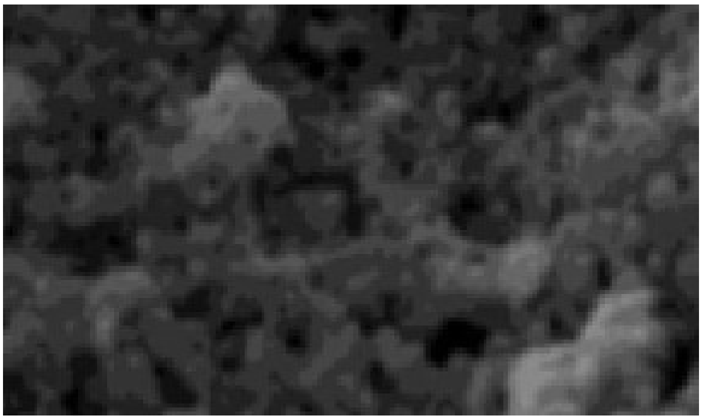

Fig. 3. SEM image of zinc oxide nanoparticles

3.2. Transmission Electron Microscopy (TEM):

TEM is then used to inspect the sample in order to determine if the Polyaniline Zinc Oxide nanocomposite was effectively created. During this study, images of the PAZO nanocomposites are obtained. In ImageJ, the images are processed to provide a histogram of particle diameter and a computation of the average particle size. TEM electron diffraction may be used to identify the orientation of both PANI and nano-zinc oxide and its components.

The morphological results for PANI and ZnO nanocomposites from the research as mentioned earlier demonstrate that they are spherical and amorphous, with a size of 90 nm, as shown in **Fig. 4.** Finally, we can state that decreased particle sizes were a direct effect of the sol-gel process.

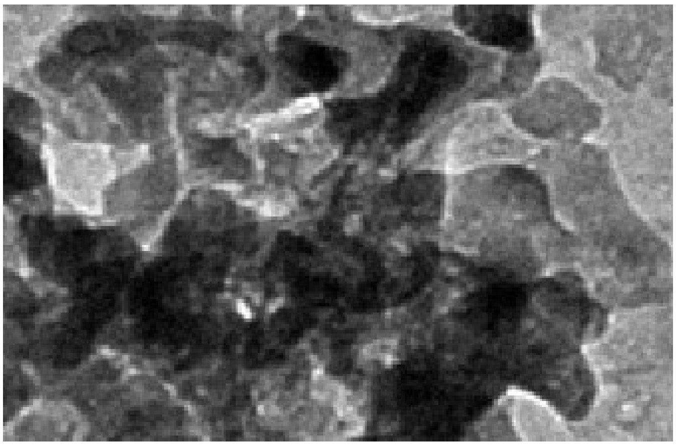

Fig. 4. TEM image of polyaniline ZnO nanocomposite

3.3. X-Ray Diffraction (XRD):

The usage of an X-ray diffractometer is a versatile and non-corrosive approach for quantitatively detecting the phase of crystalline material. The unit cell dimensions and the size of the crystalline structure are provided. The polyaniline Zinc Oxide nanocomposites are homogenized and crushed into a fine powder after the examination. After filtering to obtain a monochromatic picture, the average bulk composition of cathode rays from a cathode ray tube may be calculated.

Fig.5. depicts the results of the X-ray diffractometer, which reveal the existence of crystalline zinc oxide nanopowder. The maxima, as shown in **Fig. 5,** are 31.77°, 34.44°, and 47.60°. Based on the evidence and peaks, the generated PAZO structure was concluded to be the hexagonal phase of zinc oxide. The data supported this point of view. The solid Zinc Oxide material was affected by the broadening of the XRD peak patterns. We determined the average crystal size of the polyaniline Zinc Oxide nanocomposite using the Scherrer equation. We measured the Diffraction peak widths to within full width at half the maximum (FWHM) to do this.

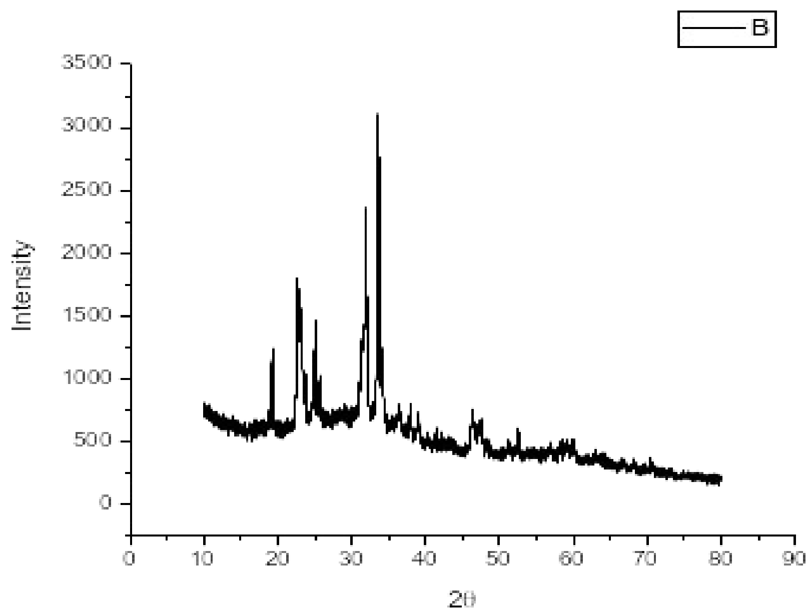

Fig.5. X-ray Diffraction graph of Nano-Zinc Oxide particles

3.4. Fourier Transform Infrared Spectroscopy (FTIR):

Fourier transform infrared spectroscopy (FTIR) was used to identify the FTIR peaks for polymer-based polyaniline zinc oxide nanocomposites and their values in **Table 1**. The presence of polyaniline in the PAZO nanocomposite, which was recovered after multiple extractions with DMF, **Fig.5.** can be explained by the FTIR peaks at 2975 cm^{-1}, 2923 cm^{-1}, and 2852 cm^{-1}, which matched and matched an FTIR spectrum of pure ZnO nanoparticles, the peak at 618.38 cm^{-1}, which was the characteristic absorption of the Zn-O bond, and the broadband peak at 3434.96 cm^{-1}.

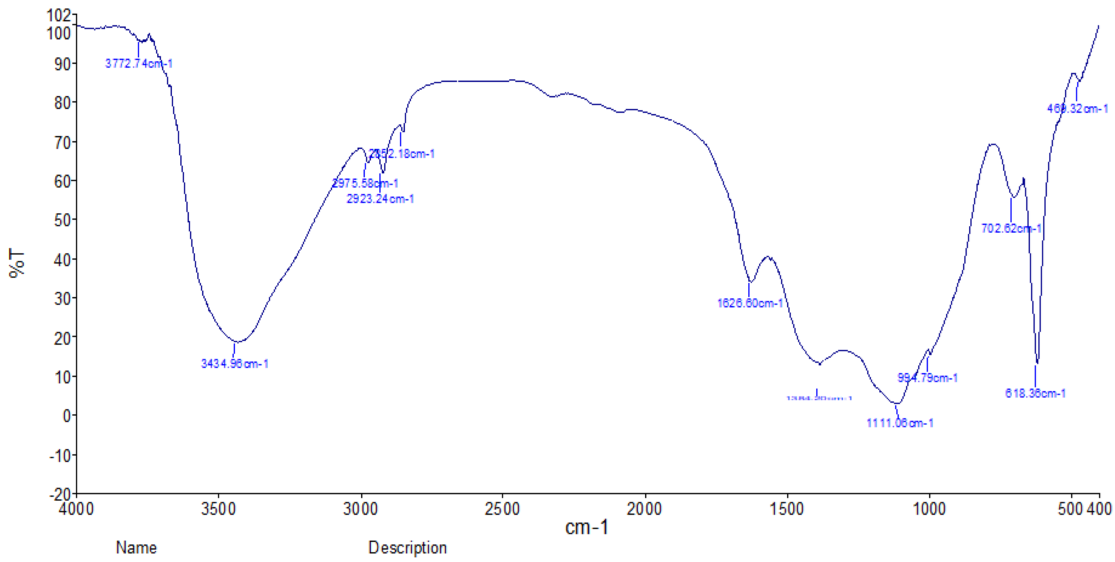

Fig.5. FTIR-Spectra of Polymer-based Polyaniline Zinc Oxide (PAZO) nanocomposites.

Table-1. FTIR absorption characteristics of PAZO nanocomposites:

PAN	PANO Nanocomposite in cm^{-1}	Assignments
2939	2975	C-H Stretching vibration
2245	2923	C=N Stretching vibration
1454	2852	C-H bending vibration
	618.38	ZnO peak

3.5. Photocatalytic Activity of Polyaniline Zinc Oxide Nanocomposites:

It was found that PAZO nanocomposites may be made with strong photocatalytic activity by photo-degrading a 0.2 M dye concentration using potassium permanganate as the light source. A common chemical that is simple and inexpensive to make in labs is potassium permanganate. The potassium permanganate was poured onto a Petri dish before being dissolved in the distilled water. These two operations were followed by discarding the potassium permanganate. You should get the following outcomes after producing several samples of PAZO nanocomposite at various concentrations, adding them to a solution of ($KMnO_4$), and then exposing each sample to UV light sources: **Fig.6.** depicts the relationship between $KMnO_4$ absorbance and UV exposure. This association gets increasingly obvious as the minutes pass 10-minute intervals for up to 1.5 hours. The sample's absorbance was assessed upon annealing in PAZO nanocomposites at 650^0C. **Fig.6.** demonstrates how the regularity and integrity of the PAZO nanocomposite structure have a significant impact on the pace at which photodegradation takes place. The polymer nanocomposite catalyst produced fewer photo-generated electron-hole pairs on its surface because of its poor crystallinity and uneven crystal structure.

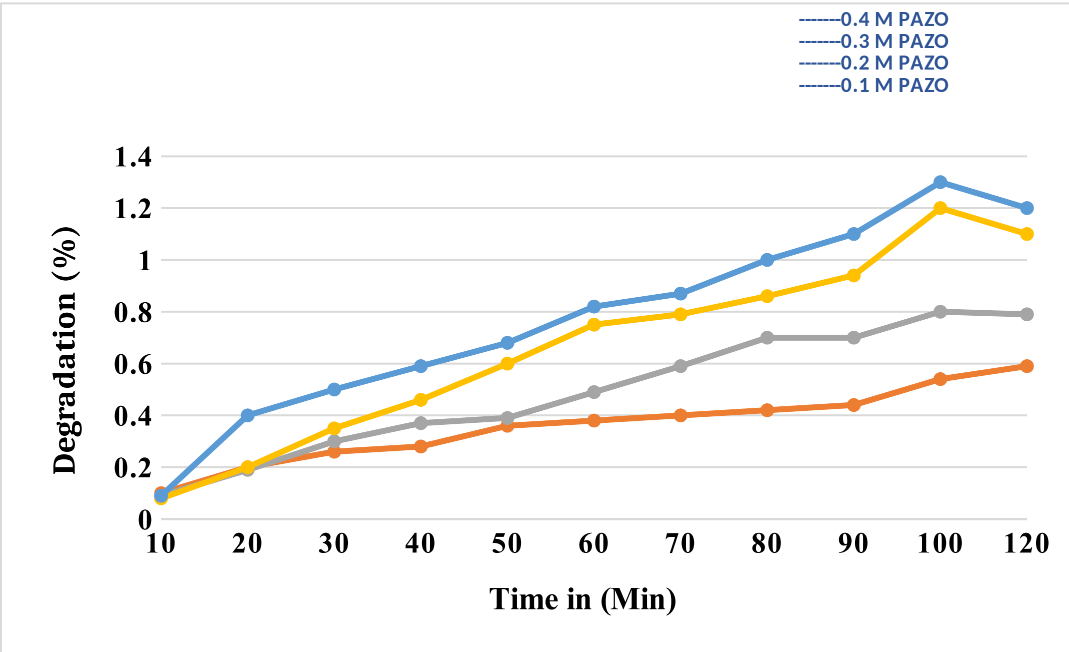

Fig. 6. Image of photocatalysis with respective time (Min)

Table-2. Values obtained from experiments about the use of PAZO nanocomposites in

Photocatalysis

ISSN: 2366-1313

S.No	Time in (Min)	Con. 0.1 M	Con. 0.2 M	Con. 0.3 M	Con. 0.4 M
1.	10	0.1	0.09	0.08	0.09
2.	20	0.2	0.19	0.2	0.4
3.	30	0.26	0.3	0.35	0.5
4.	40	0.28	0.37	0.46	0.59
5.	50	0.36	0.39	0.6	0.68
6.	60	0.38	0.49	0.75	0.82
7.	70	0.4	0.59	0.79	0.87
8.	80	0.42	0.7	0.86	1
9.	90	0.44	0.7	0.94	1.1
10.	100	0.54	0.8	1.2	1.3
11.	120	0.59	0.79	1.1	1.2

Conclusion:

One of the many possible ways that may be taken to attain the appropriate degree of uniformity is dictated by the type and qualities of the particles employed in the creation of polymer nanocomposites. The current work showed that polymer nanocomposite materials based on ZnO nanocomposites may be synthesized by the Sol-Gel technique. A variety of unique tactics were put together in conjunction to achieve this objective. This study was able to establish that the morphology and topology of PAZO nanocomposites in the 70-90 nm size range are the most crucial factors using TEM and TEM. Scientists were able to demonstrate that nanocomposites crystallize into the monoclinic space group C2/c using X-ray diffraction. FTIR was utilized to confirm that the chemical grafting of the PAZO nanocomposite to the polymer had been effective. The development of technology has made this feasible. The photocatalytic activity data show that 0.4 M PAZO nanocomposites can absorb light for 10 minutes. Additionally, photocatalytic activity was shown, making it a prime candidate for incorporation into a semiconducting device. This finding was obtained using ultraviolet light, which encouraged the creation of oxygen radicals.

References:

1. Sanico, Fedil G.; Candidato, Rolando T.; Vequizo, Reynaldo M.; Alguno, Arnold C. (2014). Morphological and Optical Characteristics of Zinc Sulfide on Silica-Modified Polyaniline Grown on Glass and Platinum-Coated Substrates. *Applied Mechanics and Materials,* 548-549, 201–205. DOI: 10.4028/www.scientific.net/amm.548-549.201
2. Malinauskas, A; Malinauskiene, J; Ramanavičius, A (2005). Conducting polymer-based nanostructured materials: *electrochemical aspects. Nanotechnology*, 16(10), R51–R62. DOI:10.1088/0957-4484/16/10/R01
3. Rajesh; Tarushee Ahuja; Devendra Kumar (2009). Recent progress in the development of nano-structured conducting polymers/nanocomposites for sensor applications., 136(1), 275–286. DOI: 10.1016/j.snb.2008.09.014_
4. Xiping Lei; Zhixing Su (2007). Conducting polyaniline-coated nano silica by in-sit chemical oxidative grafting polymerization., 18(6), 472–476. doi:10.1002/pat.905_
5. Ahmed A. A., Mohammad F. & Rahman M. Z. A., Electrical Studies on the Composite of Polyaniline with Zinc Oxide Nanoparticles., *Synthetic Metals*, 2004, 144, 29–4.
6. Junfeng Qiang; Zhuhuan Yu; Hongcai Wu; Daqin Yun (2008). Polyaniline nanofibers synthesized by rapid mixing polymerization., 158(13), 0–547. DOI: 10.1016/j.synthmet.2008.03.023

7. Kim, D.K., Oh, K.W. and Kim, S.H. (2008) Synthesis of Polyaniline/Multiwall Carbon Nanotube Composite via Inverse Emulsion Polymerization. *Journal of Polymer Science Part B: Polymer Physics*, 46, 2255-2266. DOI.org/10.1002/polb.21557
8. Mittal H., Kaith B., & Jindal R., Synthesis, characterization and swelling behaviour of poly (acrylamide-co-methacrylic acid) grafted Gum ghatti based superabsorbent hydrogels., *Advances in Applied Science Research*, 2010, 1, 56-66.
9. Ramaswamy V., Vimalathithan R. M., & Ponnusamy V, Synthesis and characterization of BaSO4 nanoparticles using microemulsion technique., *Advances in Applied Science Research*, 2010, 1, 197-204.
10. Igwe H.U., & Ugwu E.I., Optical Characteristics of Nanocrystalline Thermal Annealed Tin Oxide (SO2) Thin Film samples Prepared by Chemical Bath Deposition Technique., *Journal of Advance in Applied Science Research*, 2010, 1, 240-246. ISSN: 0976-8610
11. Lanje A.S., Sharma S.J., Pode R.B., & Ningthoujam R.S., Advances in Applied Science Research, 2010, 1, 36-40. ISSN: 0976-8610.
12. Gok A., Omatsova M., & Prokes J., Synthesis, Characterization and CO2 Gas Sensing Response of 5% SnO2 Doped Polyaniline Nano Composite., *European Polymer Journal*, 2007, 43, 2471–2480.
13. Ayşe Gül Yavuz; Ayşegül Gök (2007). Preparation of TiO2/PANI composites in the presence of surfactants and investigation of electrical properties., 157(4-5), 0–242. DOI: 10.1016/j.synthmet.2007.03.001
14. A. Chakraborty; T. Mondal; S.K. Bera; S.K. Sen; R. Ghosh; G.K. Paul (2008). Effects of aluminum and indium incorporation on the structural and optical properties of ZnO thin films synthesized by spray pyrolysis technique., 112(1), 162–166. DOI: 10.1016/j.matchemphys.2008.05.047
15. Jauder Jeng; Tai-You Chen; Chia-Fen Lee; Nai-Yun Liang; Wen-Yen Chiu (2008). Growth mechanism and pH-regulation characteristics of composite latex particles prepared from Pickering emulsion polymerization of aniline/ZnO using different hydrophilicity of oil phases., 49(15), 3265–3271. DOI: 10.1016/j.polymer.2008.05.027
16. Zhang, Hao; Zong, Ruilong; Zhu, Yongfa (2009). Photo Corrosion Inhibition and Photoactivity Enhancement for Zinc Oxide via Hybridization with Monolayer

Polyaniline. *The Journal of Physical Chemistry* C, 113(11), 4605–4611. DOI:10.1021/jp810748u

17. Yang, P.D., Yan, H.Q., Mao, S., Russo, R., Johnson, J., Saykally, R., Morris, N., Pham, J., He, R.R. and Choi, H.J. (2002) Controlled Growth of ZnO Nanowires and Their Optical Properties. *Advanced Functional Materials*, 12, 323-331. DOI: org/10.1002/1616-3028(20020517)
18. W.I. Park; G.-C. Yi; M. Kim; S.J. Pennycook (2002). ZnO Nanoneedles Grown Vertically on Si Substrates by Non-Catalytic Vapor-Phase Epitaxy., 14(24), 1841–1843. DOI:10.1002/adma.200290015
19. Vayssieres L., Keis K., Hagfeldt A., & Lindquist S., Chemistry of Materials, 2001, 13, 4395-4398.
20. Claudia Pacholski; Andreas Karnowski; Horst Weller (2002). Suborganization von ZnO: *von Nanopartikeln Zu Nanostäbchen*., 114(7), 1234–1237. DOI:10.1002/1521-3757(20020402)114:7<1234: aid-ange1234>3.0.co;2-d_
21. Patil V. B., Pawar S. G., Patil S. L. & Krupanidhi S. B., Effect of Camphor Sulfonic Acid Doping on Structural, Morphological, Optical, and Electrical Transport Properties on Polyaniline-ZnO Nanocomposites., *Journal of Materials Science*: Materials Electronics, 2010, 41, 355-359. DOI: 10.4236/snl.2012.23009
22. Lee J. H. Ko, K. H., & Park B. O, Journal of Crystal Growth, 2003, 247, 119-12.
23. Chougule M. A., Patil S. L., Pawar S. G., Raut B. T., Godse P. R., Sen S., & Patil V. B., Effect of Camphor Sulfonic Acid Doping on Structural, Morphological, Optical, and Electrical Transport Properties on Polyaniline-ZnO Nanocomposites., *Ceramic International*, 2012, 28, 2685-2692. DOI: org/10.4236/snl.2012.23009 P
24. Gupta, Vinay; Mansingh, Abhai (1996). Influence of postdeposition annealing on the structural and optical properties of sputtered zinc oxide film. *Journal of Applied Physics*, 80(2), 1063–1073. DOI:10.1063/1.362842
25. Chougule M. A., Patil, S. L., Pawar S. G., Raut B. T., Godse P. R., Sen S., & Patil V. B., Mane, A. T. Effect of Camphor Sulfonic Acid Doping on Structural, Morphological, Optical and Electrical Transport Properties on Polyaniline-ZnO Nanocomposites., *Journal of Materials Science*: Materials in Electronics, 2010, 21, 1332-1336. **DOI:** 10.4236/snl.2012.23009
26. Hosseiny, Seyed; van Rijn, Patrick (2013). Surface Initiated Polymerizations via e-ATRP in Pure Water. Polymers, 5(4), 1229–1240. DOI:10.3390/polym5041229

27. Amin, G., Sandberg M., Zainelabdin A., Zaman S., Nur O. & Willander M., ZnO and CuO Nanostructures: Low-Temperature Growth, Characterization, their Optoelectronic and Sensing Applications., *Journal of Material Science*, 2012, 47, 4726-4731.
28. J. Foroughi, G.M. Spinks, G.G. Wallace, Nanotechnology and Conducting Polymer Fibres: Towards the Development of Nano-structured Conducting Polymers and Nano-composite Fibres; LAP Lambert Academic Publishing: Germany, 2010. DOI: 10.1007/978-981-4451-45-1_14
29. Mohamed Rehan, Amr A. Nada, Tawfik A. Khattab, A.M. Abdelwahed, Amira Adel Abou El-Kheir. Development of multifunctional polyacrylonitrile/silver nanocomposite films: Antimicrobial activity, catalytic activity, electrical conductivity, UV protection, and SERS-active sensor. DOI: 10.1016/j.jmrt.2020.05.079
30. J-J. Hwang, T-W Ma. Preparation, morphology, and antibacterial properties of polyacrylonitrile/montmorillonite/silver nanocomposites. *Mater Chem Phys* 2012;136(2–3):613. DOI: 10.1016/j.matchemphys.2012.07.034
31. S. Ren, L. Dong, X. Zhang, T. Lei, F. Ehrenhauser, K. Song, et al. Electrospun nanofibers made of silver nanoparticles, cellulose nanocrystals, and polyacrylonitrile as substrates for surface-enhanced Raman scattering. Materials 2017;10(1):68. DOI: 10.3390/ma10010068.
32. Y. Wang, Q. Yang, G. Shan, C. Wang, J. Du, S. Wang, et al. Preparation of silver nanoparticles dispersed in polyacrylonitrile nanofiber film spun by electrospinning. Mater Lett 2005;59(24–25):3046. DOI: 10.1007/s10971-010-2158-0
33. Nandapure, B.; Kondawar, S.; Salunkhe, M.; Nandapure, A. (2013). Nanostructure cobalt oxide reinforced conductive and magnetic polyaniline nanocomposites. *Journal of Composite Materials*, 47(5), 559–567. DOI:10.1177/0021998312442559.