Research Journal of Chemical Sciences E-ISSN 2231-606X
Vol. **6(5),** 27-33, May **(2016)** *Res. J. Chem. Sci.*

Synthesis and Structural Properties of Nanocomposite of PANI/ZnO by *in – Situ* polymerization

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Available online at: www.isca.in, www.isca.me
Received 22nd March 2016, revised 2nd April 2016, accepted 11th May 2016

Abstract

Hybrid PANI/ZnO synthesized by typical oxidative polymerization. This nanocomposite of PANI/ ZnO has been investigated for their structural properties because of hybrid structures. This adopted synthesis method is calledin –situ polymerization. XRD patterns of pure zinc oxide, pure polyaniline and nanocomposites PANI/ZnO gives confirmation of elements were present in compound. SEM micrographs shownanocomposite material PANI/ZnO nanotube formation PANI and in situ deposition of ZnO. EDX gives confirmation of nanocomposites material PANI/ZnO. This nanotube structures enhances the active and passive properties.

Keywords: Nanostructure Pure PANI, ZnO, *in –situ polymerization* of PANI/ZnO, XRD, SEM, EDX.

Introduction

Now days, All polymers are thought to be excellent insulating materials until the l970's, when Hideshishirakawaand their associates reported the high conductance of polyacetylene doped with AsF_5[1-3]. Sincethen, broad research has been carried out on conducting polymers because of theirexcellent electrical and optical properties. These materials have broad application in areasranging from anticorrosion coatings, to chemical sensors and biosensors, light-emittingdevices, and solar cells, as well as many others[4]. Among the variety of conducting polymers due to unique electrical properties, stability and easy fabrication process polyaniline is one of the most attractive materials. Because of these interesting properties, polyaniline has been a potential candidate in sensor applications[5,6]. However, the difficulties with these conducting polymers are their low processing ability, poor chemical stability and mechanical strength[7]. As an option, there are a plenty of space to fabricate hetero junctions, to enhancement of the sensor characteristics and mechanical strength. By usingpolymerization, polyaniline and its nanocomposite have been synthesized in a bulk form.

Polyaniline which can besynthesized either by chemical oxidization polymerization[8-10] or electro polymerization[11]. Conventional chemical polymerization is conducted by polymerizing aniline monomersin the presence of a free radical activator. Polyaniline, prepared via chemicalpolymerization with a protonic acid, is typically called doped polyaniline or ernemldinesalt. Generally, conventional bulk chemical synthesis produces only bull-likepolyaniline. One dimensional (1D) nanostructures of conducting polymers such as nanowires, nanofibers, and nanotubes, have been intensively investigated because theypossess superior properties due to their high surface area-to-volume ratio. In past twodecades, a variety of methods have been used to synthesize polyaniline nanofibers, including electrospinning[12], interfacial polymerization[13] rapid- mixing[14], nanofibers seeding[15] templates[16] and surfactants[17] or oligomer-assisted polymerization[18].

Among the various semiconductor oxides materials, Zinc Oxide (ZnO) has been chosen as the key sensing material. Zinc Oxide is among the extensively studied metal oxide outstandingbecause of their unique properties and important characteristics for example low cost, easy availability and wide range of applications. Several researchers have studied this Zinc Oxide either individually or along with some dopant. Metal oxide ZnO is usually semiconductor.Zinc oxide has received forceful attention due to its significant combination of physical and optical properties among the group of II-VI compound semiconductors. Its wide band gap, high exciton binding energy (60 meV), and its assorted growth morphologies make ZnO a key material in the fields of nanotechnology.

There are growing interests to combine both organic and inorganic materials for applications in electro-optic[19]. Combination of nanosized metal oxides and polyaniline has the potential to enhance the property of the conducting polymer. Such composites can operate at room temperature due to its optimized volume to surface ratio of nanosized metal oxides. The properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics[20].

In present work ZnO and PANI nanoparticles synthesized and structural properties were studied.The choice of materials in any research work is an extremely crucial issue which, in turn, is governed by several theoretical as well as practical considerations such as their suitability and compatibility under the given laboratory conditions.

Methodology

Synthesis of Conducting Polymer: Polyaniline: In present work, use International Union of Pure Applied Chemistry (IUPAC) method is used prepare polyaniline in which aniline hydrochloride (5.18gm) is dissolved in 100 ml distilled water to make up volume. Ammonium peroxydisulphate (11.42gm) is dissolved in 100 ml distilled H_2O in a volumetric flask. The solutions are kept for 1 hour at room temperature. The above solutions are mixed together in equally proportion with constant stirring.

This solution kept under Ultrasonic wave treatment (Sonication process) for period of 10 minutes at room temperature. The precipitated is collected by filtration and washed with 0.2 M HCl, to remove all residual monomers, oxidant and its decomposing products. Finally it is washed with acetone to removes low –molecular-weight organic intermediates and oligomers. It also prevents the aggregation of PANI precipitated during drying. The precipitated is dried at 60^0C for 12 hours.The resultant material is a polyemeraldine salt.

Synthesis of Nanomaterial Metal Oxide: Zinc Oxide: All the chemicals used in this study were of GR grade purchase from Sd-Fine, India (purity 99%). The chemicals are used without any further purification. Synthesis method adopted from S.D. Charpe*etal*liquid –phase method. Finally we get product of ZnO nanoparticles.

Synthesis of Nanocomposite (PANI/ZnO): In this synthesis we used *in –situ polymerization* method[21-22] to prepare nanocomposite PANI/ZnO. First we prepare 1 M HCl solution in distilled water. Here we used Zinc Oxide which prepared in steps II.

In preparation we add Zinc Oxide (ZnO) in 1M HCl solution to achieved 0.1 M gel solution of Zinc Oxide then this solution under treatment of sonication for 1 hour. Now prepared 100 ml 0.1 M Aniline hydrochloride Solution then add 10 ml sonicated ZnO solution. Again go for sonication for 10 minutes then add 100 ml Ammonium peroxydisulphate (APS) solution slowly with continues stirring, after 3 hours we achieved polymerization. This type polymerization is called as *in-situ Polymerization*.

After 3 hours filter, washed above solution with 1 M HCl solution and dried under vacuum for 12 hours. Final we get nanocomposite of PANI/ ZnO.

Results and Discussion

X-Ray Diffraction Studies: Polyaniline (PANI): The polycrystalline structure of the nano polyaniline (PANI) was characterized by powder X-ray diffraction (Rigaku X-ray diffractometer) with Cu-α source and 2θ range of 10° - 90°. Figure1show XRD pattern of synthesized polyaniline (PANI) which confirmed that PANI has polycrystalline nature which showsthat ithasamorphousnature.

Zinc Oxide (ZnO): The crystallographic structure of the synthesized ZnO nanostructure was characterized by powder XRD.Figure 2show XRD pattern of ZnO. The corresponding X-ray diffraction peak for (100), (002), (101), (102) (110), (103), (200), (112), (201), (004), (202) and (104) planes confirm the formation of hexagonal wurtzite structure of ZnO (DB card no.-2300013).Hence XRD pattern confirmed that synthesized ZnO are highly crystalline in nature. The domain size of the crystal can be estimated by Scherrer form. The average particle size was calculated from (101) peak ZnO is found to be 35nm.Fromsoftware analysis it is confirm that prepared zinc oxide powder contains Zn and O elements only, not any impurity[23].

PANI/ZnO Composite: The semi-crystalline structure of the synthesized nanocomposite of Polyaniline (PANI) and Zinc Oxide (PANI/ ZnO) was characterized by XRD. The recorded XRD pattern confirmed that synthesized composite of Polyaniline (PANI)/Zinc Oxide (ZnO) is polycrystalline that is semi amorphous in nature. Figure 3 shows XRD pattern of zinc oxide nanoparticles and that of various nanocomposites showed similar peak patterns, therefore, it may be assumed that presence of polyaniline did not cause any change in crystal structure of zinc oxide or negligible change which may be ignored[24,25].

These results show that polyaniline present in nanomatrix is amorphous in nature which supports the previous reports. Moreover above discussion also supports that the incorporation of supporting polymer into polyaniline does not affect the crystal structure of ZnO. However, presence of such polymers seems to cause the decrease in the size of ZnO nanoparticles this is due to formation of polymer-Zn complex on the surface of ZnOnanoparticles present within/on the surface. This superficial property of the nanocomposites as has also been suggested by Tang*et al*[26] in the study of x-rays patterns of Polymethylmethacrylate (PMMA) and zinc oxide composites.

Scanning Electron Microscopy Studies: SEM of Polyaniline (PANI): Scanning Electron Microscope (SEM) images of selected sample was obtained using SEM-JEOL 840 A. The surface morphology of nano size Polyaniline by SEM and its micrographsare shown in figure 4 (a,b). From SEM image PANI is more porous in nature. Due to small pores size, its surface area is more which helps to enhance properties.

SEM of Pure Zinc Oxide (ZnO): Figure-5 (a, b) shows SEM micrograph of the pure ZnO. From micrograph it is observed that there is randomly distribution of nanospheres ZnO. Due to such a distribution of nanospheres, surface to volume ratio of the ZnO may be increase.

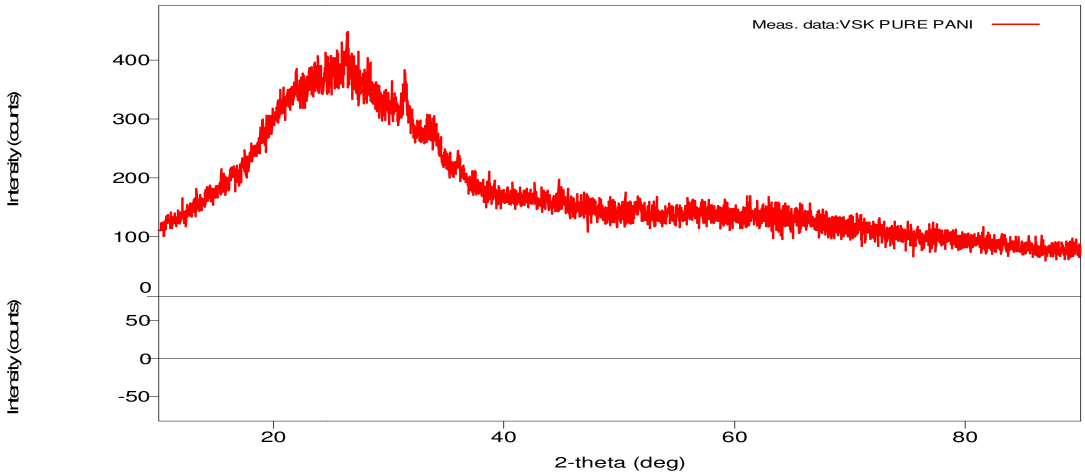

Figure-1
XRD of Pure Nanostructure PANI

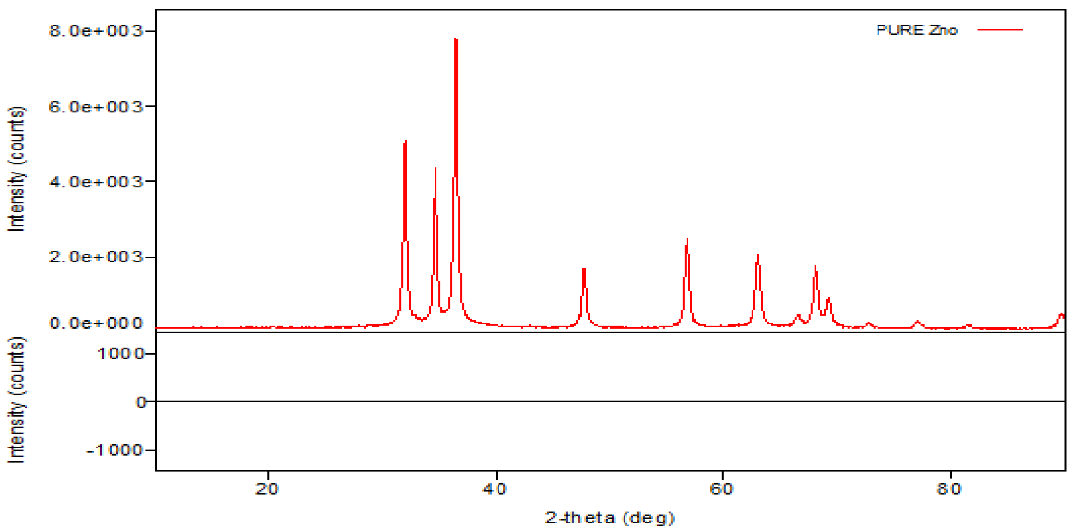

Figure-2
XRD Pattern of Pure Nanostructured ZnO

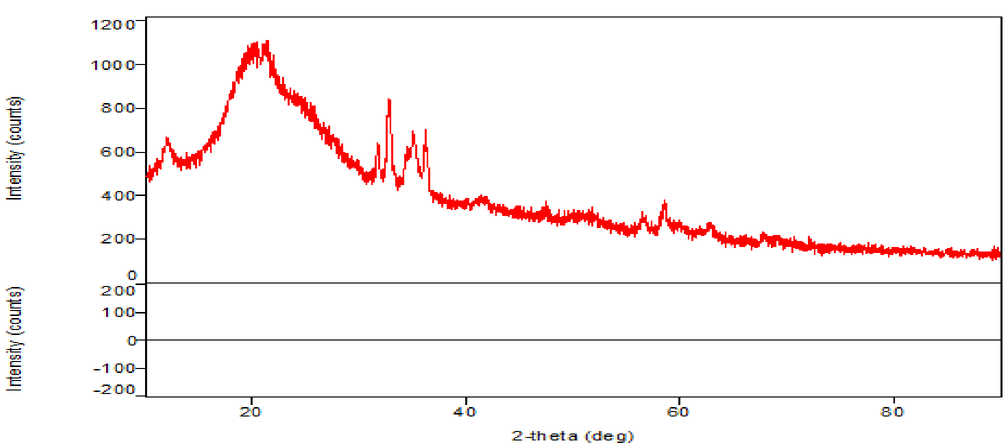

Figure-3
XRD Pattern of Nanocomposite of PANI/ ZnO

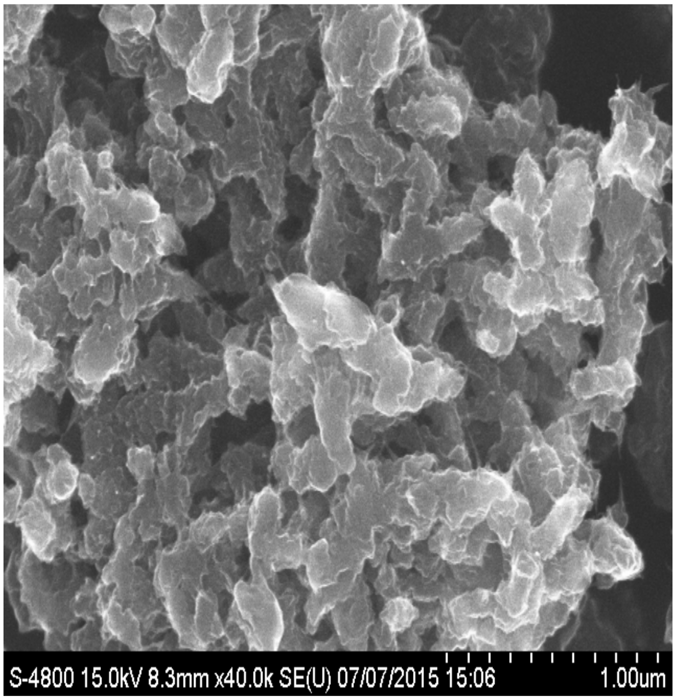

Figure-4(a)
SEM micrograph of PANI

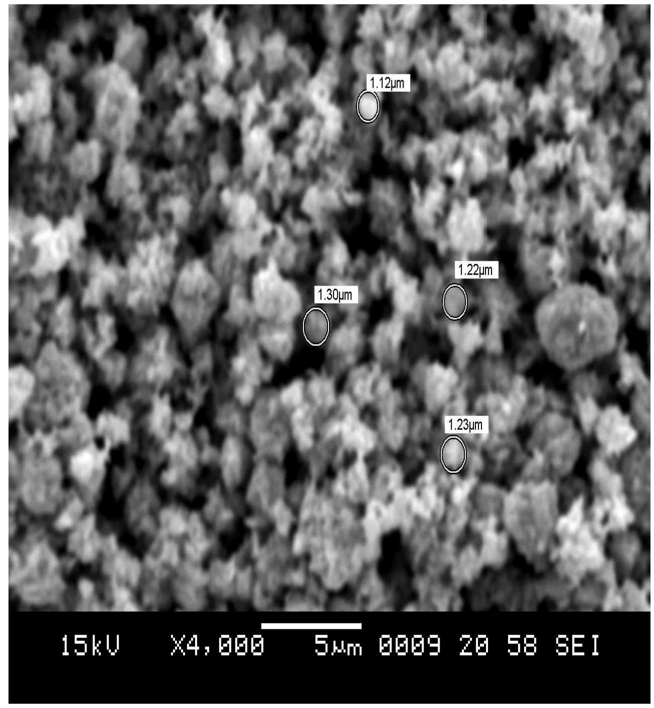

Figure-5(a)
SEM micrograph of ZnO

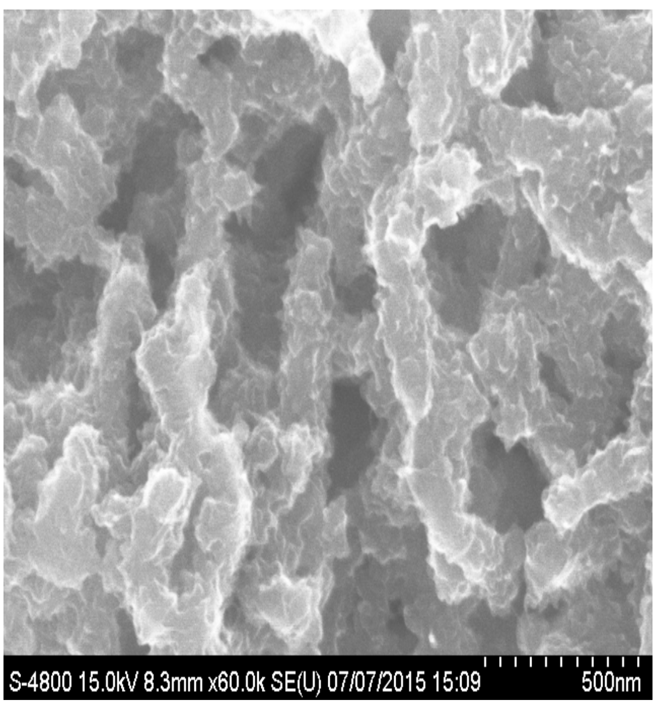

Figure-4(b)
SEM micrograph of PANI

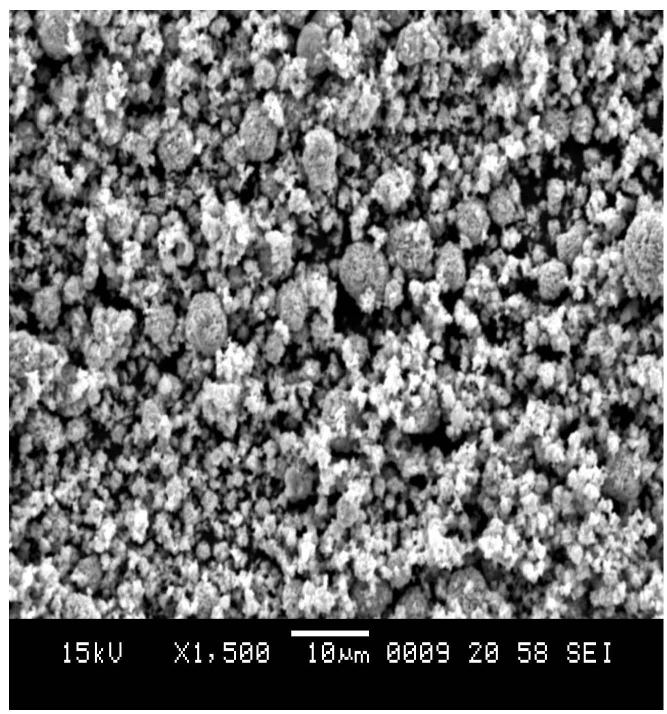

Figure-5(b)
SEM micrograph of ZnO

SEM of Nanocomposite PANI/ZnO: Figure-6 (a,b,c,d) shows SEM micrograph of nanocomposite of polyaniline and zinc oxide.From micrographs it is cleared that there were formation of nanotubes of nanocomposite material PANI/ZnO. It is observed that from image 6 (aand d) on head of polyaniline nanotube there is decomposition of nanosized Zinc Oxide. This is evidencefor *in –situ polymerization*method of PANI and ZnO to synthesis nanocomposite of PANI/ZnO.

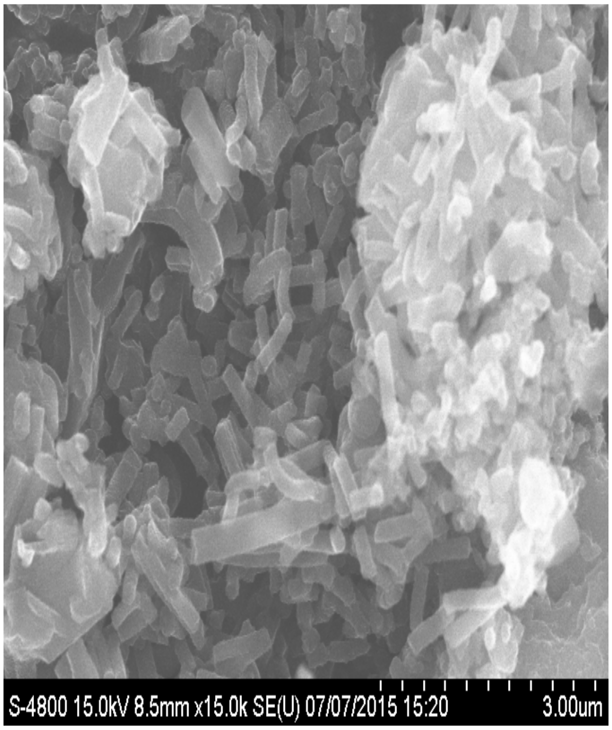

Figure-6(a)
SEM micrograph of PANI/ZnO

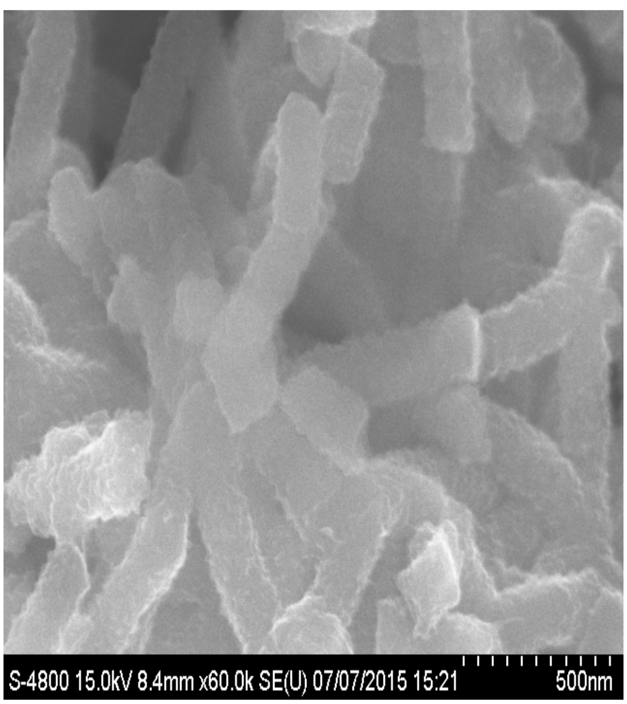

Figure-6(b)
SEM micrograph of PANI/ZnO

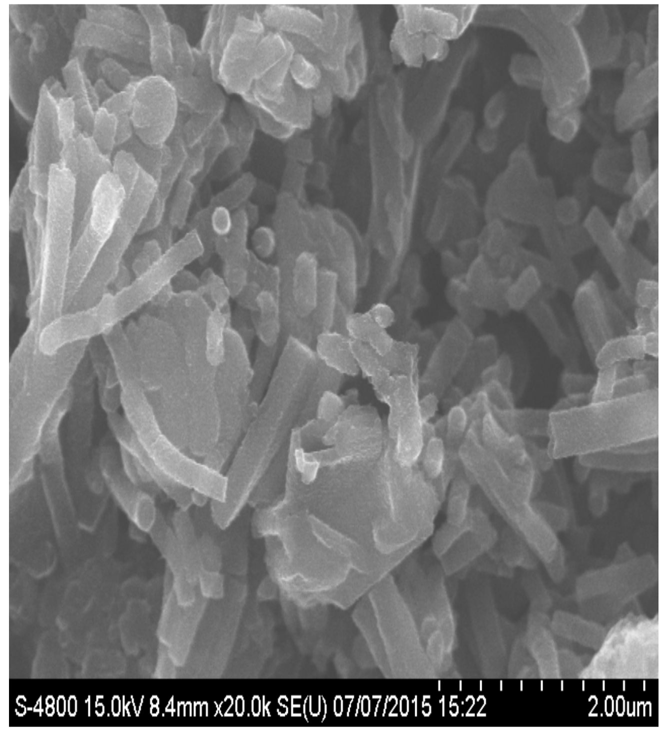

Figure-6(c)
SEM micrograph of PANI/ZnO

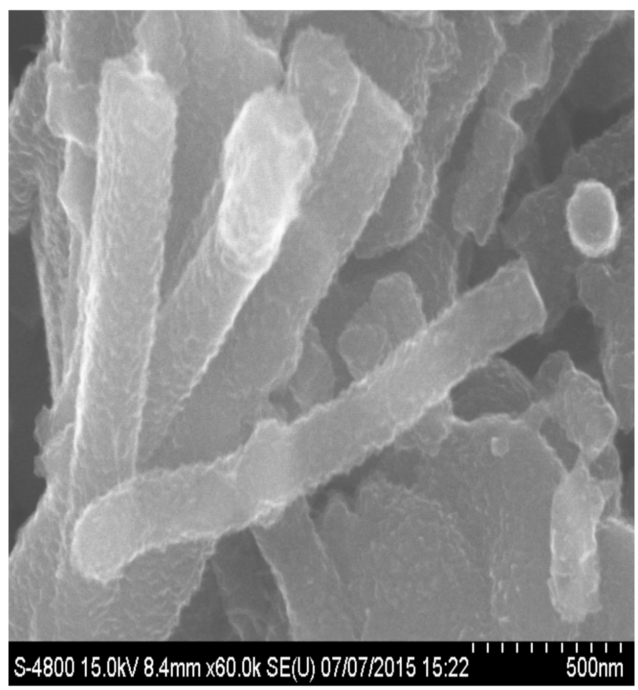

Figure-6(d)
SEM micrograph of PANI/ZnO

EDX of Nanocomposite of PANI/ZnO: An energy dispersive Spectroscopy (EDX) image of selected sample wasobtained using SEM-JEOL 840 A. Elemental compositions of PANI/ZnO from spectrum: 4417 are given in Table-1. From table is cleared that no other elements were present in given sample of nanocomposite PANI/ZnO.

Table-1
EDX of Nanocomposite of PANI/ZnO

Sr.No	Element	Atomic Number	Weight by %	Atomic Weight by %
1	C	6	57.47	64.50
2	N	7	19.95	19.20
3	O	8	15.61	13.15
4	Na	11	2.83	1.66
5	S	16	2.97	1.25
6	Zn	30	1.17	0.24
Total			100	100

Conclusion

The Pure Zinc Oxide, Pure Polyaniline andPANI/ZnO nanocomposites have been successfully synthesized. PANI nanotubes were successfully covered with PANI byprocess of '*in situ'* chemical oxidative polymerization of aniline. Due to interfacial interactions between nanocomposite ZnO and PANI, there is formation of PANI and ZnO matrix. This type of hybridmaterialwill use in many applications.

Acknowledgement

I pay respect and express indebtedness to Dr. V.S. Kalymwar because of their guidance, consistent supervision as well as suggestions at every phase of this thesis work that made it possible to materialize. Authors would like to thanks University Grant Commission (UGC), New Delhi (India) and UGC DAE CSR Indore for financial support.

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