2.1 INTRODUCTION

Recently, scientific and research community have shown their great interest on metal oxide nanostructures and their applications due to their easy, safe, environmental friendly, cheap synthesis procedure and technological applications in the fabrication of devices for energy harvesting and storage, photonics, sensors as well as medical and biological applications.

Since the discovery of the first conducting polymers, polyacetylene in 1977, the conducting polymers research field has been established and developed in an unexpectedly accelerated rate [1-5]. Conducting polymers are unique photonic and electronic functional materials owing to their high \( \pi \)-conjugated length, unusual conducting mechanism and reversible redox doping/de-doping process. Conducting polymers show various promising applications, such as in transistors [6], sensors [7-10], memories [11], actuators/artificial muscles [12-14], supercapacitors [15], and lithium ionic batteries [16]. In the past decade, conducting polymers nanostructures have become a rapidly growing field of research, because they display new properties related to their nanoscale size and have greatly improved the performance of devices [17-21]. Conducting polymer nanostructures can be synthesized by several approaches, such as well-controlled solution synthesis [22-25], soft-template methods [26], hard-template methods [27-28], and electrospinning technology [29-30].

The most preferred method of preparation of polymer is either chemical or electrochemical oxidation of monomer in aqueous medium. The synthesis of polymer by either of these methods depends upon the intended application of the polymer. In the case of chemical synthesis chemical oxidants such as ammonium persulfate \([(NH_4)_2S_2O_8]\) is employed and the polymer precipitates out of the chemical reaction solution [31].
2.2 MATERIALS AND METHODS

Analytical-reagent-grade Aniline, Ammonium Per Sulphate, Hydrochloric acid, Nickel chloride, Oxalic acid, Polyethylene glycol of molecular weight 6,000 was obtained commercially, Ferrous ammonium sulphate, Zinc nitrate, Ferric nitrate, Citric acid, Ammonia Solution are used in the present study.

2.3 CHEMICAL SYNTHESIS OF POLYANILINE.

The synthesis was based on mixing aqueous solution of aniline hydrochloride and ammonium persulphate at room temperature, followed by the separation of PANI hydrochloride precipitate by filtration and drying. Aniline hydrochloride (equi molar volume of aniline and hydrochloride acid) was dissolved in distilled water in a volumetric flask to 100 ml of solution. Ammoniumpersulphate (0.25M) was dissolved in water also to 100ml of solution. Both solutions were kept for 1 hour at room temperature, then mixed in a beaker, stirred with a mechanical stirrer, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter, washed with 0.2 M HCL, and similarly with acetone. Polyaniline hydrochloride powder was dried in air and then in vacuum at 60°C for 24 hours. Polyaniline prepare under these reaction and processing conditions are further referred to as “standard” samples.

2.3.1 SYNTHESIS OF NICKEL OXIDE NANOPARTICLES
The nickel oxide nanoparticles were synthesized by self-propagating low temperature combustion method, employing nickel oxalate as precursor. Precursor is prepared by dissolving equimolar quantity of Nickel chloride and oxalic acid in distilled water. This solution is stirred for ½ hour on magnetic stirrer. Light green precipitate of nickel oxalate dehydrate so obtained is filtered and washed with distilled water. The prepared Nickel Oxalate was mixed with Polyethylene glycol (PEG) in the weight ratio 1:5. The resultant compound was placed in a crucible and heated in air by using electrical heater and it was observed that initially PEG is melted, then frothed and finally ignited to give nickel oxide as a residue, then the prepared compound was then calcinated for 2 hours to remove impurities. Finally pure nickel oxide nanoparticles were obtained.

2.3.2 SYNTHESIS OF POLYANILINE/NICKEL OXIDE NANOCOMPOSITES

Synthesis of the Polyaniline–nickel oxide nanocomposites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. Nickel oxide nanoparticles were added in the mass fraction to the above solution with vigorous stirring in order to keep the nickel oxide homogeneously suspended in the solution. To this solution, 0.1 M of ammoniumpersulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at -5°C for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24 h to achieve a constant mass. In these way, Polyaniline–Nickel oxidenanocomposites containing various weight percentage of Nickel oxide (10 %, 20 %, 30 %, 40 %, and 50 %)wt% in PANI were synthesized.
2.3.3 SYNTHESIS OF IRON OXIDE NANOPARTICLES.

The iron oxide nanoparticles were synthesized by self-propagating low temperature combustion method, employing iron oxalate as precursor. The Precursor is prepared by dissolving equimolar quantity of ferrous ammonium sulphate and oxalic acid in distilled water. This solution is stirred for ½ hour on magnetic stirrer. Yellow precipitate of iron oxalate dehydrate obtained is filtered and washed with distilled water. The prepared iron oxalate was mixed with Polyethylene glycol (PEG) in the weight ratio 1:5. The resultant compound was placed in a crucible and heated by using electrical heater and it was observed that initially PEG is melted, then frothed and finally ignited to give iron oxide as a residue, then the prepared compound was then calcinated for 2 hours to remove impurities. Finally pure nickel oxide nanoparticles were obtained.

2.3.4 SYNTHESIS OF PANI/IRON OXIDENANOCOMPOSITES.

Synthesis of the Polyaniline– iron oxide nanocomposites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. Iron oxide nanoparticles were added in the mass fraction to the above solution with vigorous stirring in order to keep the iron oxide homogeneously suspended in the solution. To this solution, 0.1 M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at -5°C for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water, acetone, and finally dried in an oven for 24 h to achieve a constant mass. In these way, Polyaniline– iron nanocomposites containing various weight percentage of iron oxide(10 %, 20 %, 30 %, 40 %, and 50 %)wt% in PANI were synthesized.
2.3.5 SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Zinc oxide nanoparticles are synthesized by sol-gel method. First, a sol solution consisting zinc nitrate, citric acid, with specific weight percentage was prepared. The prepared citric acid solution is mixed drop wise to zinc nitrate solution at constant stirrer for 3h at T=80°C. Then ammonia is added to the above solution to maintain (pH 4.5). The completion of both the reaction gives rise to the development of the complex and the evaporation of the solvents forms a spongy gel. Further, the spongy gel was slowly heated at T=150°C for 1 h in a hot oven and the obtained compound was grounded well and calcinated for 2 hours to remove impurities and finally, pure zinc oxide nanoparticles were obtained.

2.3.6 SYNTHESIS OF POLYANILINE/ZINC OXIDE NANOCOMPOSITES

Synthesis of the PANI/Zinc oxide nanocomposites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. Zinc oxide particles were added in the mass fraction to the above solution with vigorous stirring in order to keep the Zinc oxide homogeneously suspended in the solution. To this solution, 0.1 M of ammonium persulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at -5°C for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24h to achieve a constant mass. In this way, PANI–Zinc oxide composites containing various weight percentages of ZnO (10, 20, 30, 40 and 50 wt%) in PANI were synthesized.
2.3.7 SYNTHESIS ZINC FERRITE NANOPARTICLES

ZnFe$_2$O$_4$ nanoparticles were prepared by the sol-gel method, using zinc nitrate and ferric nitrate in the molar ratio 1:2. A certain amount of citric acid was dissolved in distilled water then the prepared Zn(NO$_3$)$_2$·6H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O solution were dissolved in it with a molar ratio 1:1 of nitrate to citric acid. A small amount of ammonia was then added to the solution to adjust the pH value to 7 and stabilize the nitrate-citrate solution. During this process the solution was continuously stirred using magnetic stirrer for 5–6 hours at 120°C, resulting in a gel. This gel is heated at a temperature of about 150°C for 1 h to remove water molecules. Finally, the gel is completely transformed into a foam powder. The foampowder was then grounded into a fine powder. The synthesized powder was calcinated for 2 hours to remove impurities and finally pure zinc ferrite nanoparticles are obtained.

2.3.8 SYNTHESIS OF POLYANILINE/ZINC FERRITE NANOCOMPOSITES

Synthesis of the Polyaniline/Zinc ferritenanocomposites was carried out by in-situ polymerization method. Aniline (0.1 M) was mixed in 1 M HCl and stirred for 15 min to form aniline hydrochloride. Zinc ferritenanoparticles were added in the mass fraction to the above solution with vigorous stirring in order to keep the Zinc ferrite homogeneously suspended in the solution. To this solution, 0.1 M of ammoniumpersulphate, which acts as an oxidizer was slowly added drop-wise with continuous stirring at 5°C for 4 hours to completely polymerize. The precipitate was filtered, washed with deionized water, Acetone, and finally dried in an oven for 24 h to achieve a constant mass. In these way, Polyaniline/Zinc ferritenanocomposites containing
various weight percentage of Zinc ferrite (10, 20, 30, 40 and 50) wt% in Polyaniline were obtained.

2.3.9 PREPARATION OF ZINC FERRITE NANOCOMPOSITE FILM:

Polyvinyl alcohol (PVA) with molecular weight Approx. 1,25,000 was obtained commercially with AR grade, and Polyaniline/Zinc ferrite was synthesized by In-situ polymerization method. Powdered PVA of about 2.5 g was dissolved in 50ml of double distilled water by stirring. The solution was then warmed up to 333°K and thoroughly stirred, using a magnetic stirrer, for about 1h until the polymer became completely soluble.

A thick film of the sample was prepared by solution casting method in the following manner. The synthesized Polyaniline/Zinc ferrite nanocomposites powder was dissolved in PVA solution and this was sonicated for 15-20 min. The sonicated solution was stirred for ½ hour and then the paste of PVA/Polyaniline/Zinc ferrite nanocomposites was formed. Then known volume of viscous PVA/Polyaniline/Zinc ferrite nanocomposites solution was poured onto a leveled clean glass plate and left to dry at room temperature for about 48 h. The dried films were peeled off from the glass plate and cut into suitable pieces for characterization and applications.

2.3.10 PREPARATION OF PELLETS

The powders of Polyaniline, Polyaniline/Nickel Oxide nanocomposites, Polyaniline/Iron Oxide nanocomposites, Polyaniline/Zinc Oxide nanocomposites, Polyaniline/Zinc Ferrite nanocomposites so obtained from synthesis techniques discussed in early sections were crushed and finely ground in agate mortar in the presence of acetonemedium. The powder is then pressed to form pellets of 10 mm diameter and thickness varying up to 2 mm by applying
pressure of 90 MPa in a hydraulic press. For temperature dependent conductivity and sensor studies, the pellets of Polyaniline and its metal oxide nanocomposites are coated with silver paste on either side of the surface to obtain better contacts.
References


