CHAPTER – II

LITERATURE REVIEW

2.1.   RELEVANT LITERATURE SURVEY

Conducting electro-active polymers has attracted attention in recent years because of their potential applications in new technologies such as electrochemical displays, sensors, catalysis, redox capacitors, antistatic coatings, electromagnetic shielding, optical, photoelectrical properties, and secondary batteries (Malinaukas 2001, Skotheim et al 1998). And these polymers are usually used to prepare organic–inorganic hybrid materials due to their good stability and controllable thickness and they can be chemically bonded to inorganic materials by method of polysorption. This method is limited to inorganic materials that have active groups (such as hydroxyl group) on their surface (Werne and patten 2001, Zhang and Ruhe 2005, Sandra et al 2006). Among organic conducting polymers, polyaniline (PANI) has attracted intense interest because of its high conductivity, excellent stability, and relatively high transparency to visible light. These properties make it one of the most applied conducting polymers (Molapo et al 2012). For application in optoelectronics, normally the polymeric matrices are the most desirous as the film of the polymer/ nanoparticles composite can be cast easily and thus offer direct use in devices. The re-dispersed nanoparticles when loaded in polymer by dissolution of the as-synthesized particles cannot be guaranteed and this leads to difficulties in knowing the concentration of nanoparticles within the polymer. If the nanoparticles are synthesize in polymeric reaction medium. Such issues can be tackled with much ease (Du et al 2007). The use of polymers is a prominent method for the synthesis of nanoparticles. The reason for using the polymers to prepare nanocomposite

is to control the growth and morphology of the nanoparticles. Inorganic nanoparticles stand for a class of new materials having enormous applications in broad fields. To obtain the materials with synergetic or complementary behavior between polymer and inorganic nanoparticles, various composites of polymer with inorganic nanoparticles have been synthesized in recent years (Hesheng and Qi 2002, Danielle et al 2003, Li et al 2010, Jeon and Baek 2010, Zhu and Chen 2014, Hanemann and Sazbo 2010). Among those inorganic nanoparticles, metal oxide like Manganesedioxide (MnO_2) and Titanium dioxide (TiO_2) are considered for a study in this work and most of the literature survey is carried out for oxide nanomaterials.

Metal oxides play a very important role in many areas of chemistry, physics, and material science (Noguera 1996, Kung 1989, Henrich and Cox 1994, Wells 1987, Harrison 1989, Garca et al 2004). The metal elements can form a large diversity of oxide compounds (Wyckoff 1964). These elements can adopt much structural geometry with an electronic structure that can exhibit metallic, semiconductor, or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysis. For example, almost all catalysis used in industrial applications involves an oxide as active phase, promoter, or support. In the chemical and petrochemical industries, products worth billions of dollars are generated every year through processes that use oxide and metal/oxide catalysis (Ertl et al 1997). For the control of environmental pollution, catalysis or adsorbents, that contain oxides, are employed to remove the CO_x, NO_x and SO_x species formed during the combustion of fossil-derived fuels (Shelef et al 2002, Stirling 2000). Furthermore, the most active areas of the semiconductor industry involve the use of oxides (Sherman

1987). Thus, most of the chips, used in computers, contain an oxide component. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single-particle species (Gleiter 1995, Valden et al 1998, Rodriguez et al 2002, Baumer and Freund 1999, Trudeau and Ying 1996). Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surfaced sites. Particle size is expected to influence three important groups of properties in any material. The first one comprises of the structural characteristics, namely the lattice symmetry and cell parameters (Ayyub et al 1885). Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface-free energy and stress with decreasing particle size must be considered. Changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations (Millot et al 2003, Schoiswohl et al 2004, Mchale et al 1997, Zhang and Bandfield 1998), and in extreme cases, the nanoparticle can disappear because of interactions with its surrounding environment and a high surface-free energy (Samsonov et al 2003). To display mechanical or structural stability, a nanoparticle must have a low surface-free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in TiO_2, VO_x, Al_2O_3, or MnO oxides (Zhang and Bandfield 1998, Samsonov et al 2003, Song et al 2003). Size-induced structural distortions, associated with changes in cell parameters, have been observed in nanoparticles of Ceria (Yang et al 2005), Fe_2O_3 (Ayyub et al 1988), ZrO_2 (Garvie and Goss 1986), CeO_2 (Alonso et al 2004), and Y_2O_3 (Skandan et al 1992). As the particle size decreases, the increasing number of surface and interface atoms generates instrinsic

stress/strain (Cammarata and Sieradki 1989) and there may be also extrinsic strain associated with a particular synthesis method that may be partially relieved by annealing or calcination (Garca et al 2005). On the other hand, interactions with the substrate on which the nanoparticles are supported can complicate the situation and induce structural perturbations or phases which are not observed for the bulk state of the oxide (Song et al 2003, Surnev et al 2001).

The second important effect of size is related to the electronic properties of the oxide. The nanostruture in any material produces the so-called quantum size or confinement effects which essentially arise from the presence of discrete and atom-like electronic states. From a solid-state point of view, these states can be considered as being a superposition of bulk-like states with an increase in oscillator strength (Moriarty 2001). Additional general electronic effects of quantum confinement experimentally probed on oxides are related to the energy shift of exciton levels and optical bandgap (Yoffre 1993, Brus 1986). An important factor is to consider, when dealing with the electronic properties of a bulk oxide surface is the long-range effects of the Madelung field, which are not present or limited in a nanostructured oxide (Pacchioni et al 1996, Mejias et al 1995, Fernendez-Garca et al 1996). Theoretical studies for oxides show a redistribution of charge when going from large periodic structures to small clusters or aggregates, which must be roughly considered to be relatively small for ionic solids while significantly larger for covalent ones (Albaret et al 1999, Rodriguez and Maiti 2000, Rodriguez et al 1999, Bredow et al 1998, Casarin et al 1997, Scamehorn et al 1994). The degree of ionicity or covalency in a metal-oxygen bond can, however, strongly depend on size in systems with partial ionic or covalent character; an increase in the ionic component to the metal-oxygen bond in parallel to the size decreasing has

been proposed. Structural and electronic properties obviously drive the physical and chemical properties of the solid, and the third group of properties is influenced by size in a simple classification. Many oxides in their bulk state have wide band gaps and a low reactivity (Rodriguez 2002). A decrease in the average size of an oxide particle does, in fact, change the magnitude of the band gap (Fernendez-Garca et al 1996, Rodriguez et al 1998), with strong influence on the conductivity and chemical reactivity (Hoffmann 1988, Albright et al 1985). Surface properties are a somewhat particular group included in this subject because of their importance in chemistry. Solid-gas or solid-liquid chemical reactions can be mostly confined to the surface and/or subsurface regions of the solid. The two-dimensional (2D) nature of surfaces as mentioned has (i) notable structural consequences, typically a rearrangement or reconstruction of bulk geometries (Luth 1997), and (ii) electronic consequences such as the presence of mid-gap states (Albright et al 1985, Bardeen 1947). In the case of nanostructured oxides, surface properties are strongly modified with respect to 2D-infinite surfaces, producing solids with unprecedent absorption or acid/base characteristics (Lucas et al 2001). Furthermore, the presence of under-coordinated atoms (like corners or edges) or oxygen vacancies in an oxide nanoparticle should produce specific geometrical arrangements as well as occupied electronic states located above the valence band of the corresponding bulk material, enhancing, in this way, the chemical activity of the system (Anchell and Hess 1996, Rodriguez et al 2001, Ferrari and Pacchioni 1995, Richards et al 2000).

Most of the research in the broad field of nanoscience is dedicated to the development of synthesis routes to nanoparticles and nanostructures. These efforts give access to nanomaterials with a wide range of compositions, monodisperse crystallite sizes, unprecedented crystallite shapes, and with complex assembly properties. But in

spite of all the progress, the most synthesis methodologies were found on an empirical basis, i.e. by trial-and-error experiments, representing isolated efforts without any generally valid basic concepts or mechanistic principles that would allow a rational synthesis strategy. The synthetic chemist is still far away from preparing a certain compound on the nanoscale with a desired composition, structure, size and shape, or even properties, intentionally and in a predicted way. The reasons for this major limitation are manifold and are discussed for some of these issues in the context of liquid-phase routes to metal oxide nanoparticles because their synthesis and application is of particular scientific and technological interest. In contrast to the traditional high temperature preparation of bulk metal oxides, involving the reaction of a mixture of powders, the use of liquid-phase routes bears the advantage that it is possible to obtain metastable materials, to achieve superior compositional homogeneity, and to influence the particle morphology during the chemical transformation of the molecular precursor to the final oxide network (Cushing et al 2004). Especially aqueous sol-gel chemistry was highly successful in the synthesis of bulk metal oxides (Livage et al 1988). However, it turn out as a specific synthesis route and works well for the bulk oxide. It cannot directly be adapted to its corresponding counterpart on the nanoscale. The reason lies in the fact that aqueous sol-gel chemistry typically leads to amorphous precipitates that are transformed into the desired crystalline material by applying a calcination step. Due to uncontrolled crystal growth, this temperature treatment to induce crystallization is not a viable option for size and shape-controlled nanoparticle synthesis. Furthermore, aqueous sol-gel chemistry is rather complex, mainly due to the high reactivity of the metal oxide precursors and the double role of water as ligand and solvent, complicating the synthesis of small structures. Nevertheless, several recent examples reported in the

literature indicate that it is, in general, possible to prepare metal oxide nanoparticles in aqueous medium in a controlled way given that the experimental conditions are strictly kept (Jolivet et al 2004, Brutchey and Morse 2006, Dessombz et al 2007, Yahiro et al 2006). A simple way to avoid many problems of aqueous chemistry is to perform the synthesis procedure in organic solvents under exclusion of water. The rapidly growing number of publications in this field suggests that these so-called nonaqueous (or nonhydrolytic) processes are particularly successful for the size- and shape-controlled preparation of colloidal inorganic nanoparticles (Jun et al 2006, Park et al 2007, Niederberger 2007). The precursor molecules in surfactant-controlled approaches are transformed into the nanocrystallites in the presence of stabilizing surfactants in a typical temperature range of 250-350 ^{o}C (Jun et al 2006, Park et al 2007, De Mello Dongo et al 2005), whereas solvent-directed processes just involve the reaction of metal oxide precursor(s) with a common organic solvent and usually took place at lower temperature (50-250 ^{o}C) (Neiderberger and Garnweitner 2006, Niederberger et al 2007, Pinna and Niederberger 2008). The small numbers of reactants (precursor and solvent) make it possible to study the chemical mechanisms involved in metal oxide formation through the characterization of the organic by-products (Neiderberger and Garnweitner 2006). Parallel to the formation of the inorganic nanoparticles, also the initial organic species (i.e. solvent and/or the organic part of the precursor) undergo transformation reactions. In many cases, the formation of the organic compounds can easily be correlated to the growth of the inorganic nanoparticles. It means that chemical reaction pathways for inorganic nanoparticles can be elaborated based on the organic side reactions (Garnweitner and Neiderberger 2008). The main function of the organic species is to act as oxygen source for the oxide formation; however they are actively

involved during all stages of particle growth and crystallization, strongly influencing the composition, size, shape, and surface properties of the nanocrystals (Garnweitner and Neiderberger 2008). Another important advantage of nonaqueous sol-gel processes in comparison to aqueous systems is the accessibility of ternary, multi, and doped metal oxide nanoparticles (Pinna and Niederberger 2008). The different reactivity of metal oxide precursors towards a specific solvent complicates the synthesis of oxides containing two or more metals. In organic solvents it is easier to match the reactivity of the metal oxide precursors and of the dopants in comparison to aqueous systems, which is crucial for obtaining phase pure products. Nanometer-scale structures exhibit many unique optical, mechanical, catalytic, and electrical properties that can be exploited in a wide range of application from Micro Electro Mechanical System (MEMS) to biological sensor. Recent approaches in the synthesis of nanostructured arrays are of a significant importance for the development of advanced nanotechnology. Nanoporous anodic alumina membrane has especially gained much attention due to the simplicity in fabrication of well-defined nanoarrays (Abel sandos et al 2014, Chu et al 2003). The nanopore diameters of alumina, ranging from about tens to several hundreds of nanometers, could easily be controlled by varying the parameters like the anodizing voltage, anodizing time, temperature and chemical treated time (Piao and Kim 2003). Various kinds of nanotubes or nanowires like metal (Luo et al 2004), metal oxide (Wu et al 2004), polymer (Lakshmi 1997), and others (Tian et al 2004, Wang et al 2004) have been expediently fabricated.

Nanomaterials feature high surface energy and reactivity resulting from their high specific surfaces and exhibit special electric, magnetic, absorptive, and catalytic properties (Pan et al 2007, Huang et al 2002, Wang and Li 2002, Jain et al 2005, Tang et

al 2003, Zitoun et al 2005). Manganese oxides have different forms such as MnO_2, Mn_2O_3, Mn_3O_4, and MnO due to its different oxidation states. Manganese Dioxide among the above mentioned structures is particularly interesting in view of its widespread use in many applications, such as batteries, high-density magnetic storage media, electro-chromic materials and catalysts (Shen et al 1993, Bernard et al 1993, Berkowitz et al 2008, Grootendorst et al 1995, Gandhe et al 2007, Cheng et al 2006). The properties of semiconductor nanostructured materials depend not only on their chemical composition but also on their shape and size. In the last decade, various different shape and size MnO_2 nanocrystals have been synthesized by various techniques, for instance, single-crystal MnO_2 nanorods were obtained by a simple chemical method (Chen et al 2005); nanoparticles are prepared by co-precipitation method (Kumar et al 2013), hydrothermal method (Ramprasath et al 2016, Karthikeyan et al 2014) and thermal decomposition (Kalamuei et al 2016, Kim et al 1999); thin films are prepared by chemical bath deposition (Aref and Tang 2014); nano fibers are prepared by spray pyrolysis technique (Vijalakshmi et al 2015); three dimensional nanostructures are synthesized by hydrothermal process (Bag and Raj 2016). However, the exploration of low-temperature routes for the synthesis of MnO_2 has, therefore, been worth attempting.

Environmental problems associated with organic pollutants promote the development of fundamental and applied research in the area of environment (Yin Obrien 2003). Hence, various methods have been developed to remove organic pollutants like biodegradation, adsorption, and photoca talytic oxidation (Ahmad et al 2011, Suwanchawalit et al 2012, El-Naas et al 2009). Among them, using semiconductor photo catalysis technology for degradation of organic pollutants has

drawn an increasing interest attributing to its great potentials such as environmental friendly, low cost, and sustainable treatment. Although significant progress has been made, there is still much research needed to be undertaken like the availability of highly efficient photo catalysts for water purification (Hu et al 2010, Cho et al 2011, Xiang et al 2010). Among the various semiconductor materials, titanium dioxide (TiO_2) has received considerable attention due to a large number of technical applications like photo catalysis, gas-sensing, and so on (Maria et al 2009, Wang et al 2017, Elsalamony 2016). Especially, proper band potentials of TiO_2 thermodynamic conditions for photo catalytic redox reaction make it an efficient photo catalyst (Elsalamony 2016, Bagheri 2014). In general, the photo catalytic activity of TiO_2 is strongly dependent on its nanostructure. Owing to the efforts from many research groups, a variety of methods have been used to obtain TiO_2 nanostructures such as hydrothermal method, solvo thermalmethod and sol-gel method (Mohan et al 2013, Kavitha et al 2013). Among the various synthesis methods, microwave assisted method and sol-gel solution method possess the added advantage of faster reaction time than the conventional solvothermal method. Here, the MnO_2 and TiO_2 nanoparticles are prepared at a less reaction time compared to the reaction time of other methods. However, in this study, the MnO_2 and TiO_2 nanoparticles are prepared using microwave assisted solution method and Sol-Gel method. The characteristics such as crystallinity, presence of functional groups, thermogravity, morphology, and dielectric are analyzed using various techniques.

In this work, the samples have been synthesized by microwave-assisted solution method using domestic microwave oven. Microwave is electromagnetic radiation with frequency range of 0.3-300 GHz and corresponding wavelengths from 1 mm to 1 m. In the microwave irradiation region, the frequency of the applied irradiation is low enough

so that the dipoles have time to respond to the alternating electric field and therefore rotation. However, the frequency is not high enough for the rotation to precisely follow the field. It causes energy to be lost from the dipole by molecular friction and collision giving rise to dielectric heating. Due to the properties of internal and volumetric heating, thermal gradients, during microwave processing are avoided providing a uniform environment for reaction. This method has been successfully applied for the preparation of a variety of nanosized inorganic materials (Lidstro et al 2001). Compared with conventional heating, microwave heating has an advantage of high-efficiency and rapid formation of nanoparticles with a narrow size distribution and no serious agglomeration.
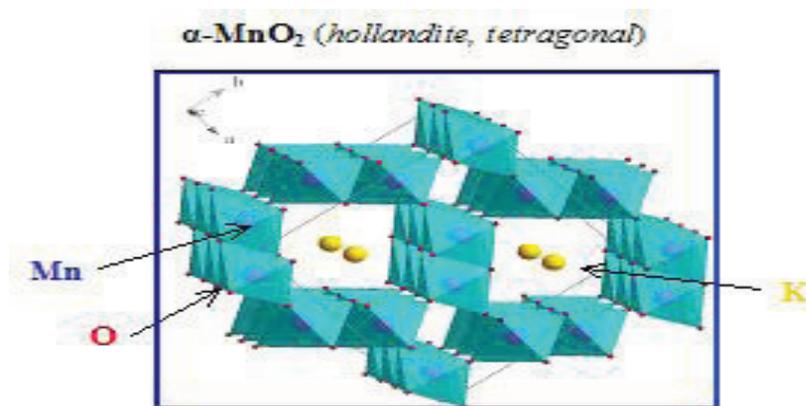

Fig. 2.1. The Tetragonal structure of Manganese dioxide.

2.2. AIMS AND SCOPE OF THE PRESENT WORK

Conducting electro-active polymers have attracted considerable attention in recent years because of their potential applications in new technologies such as electrochemical displays, sensors, catalysis, redox capacitors, antistatic coatings, electromagnetic shielding, optical, photoelectrical properties, and secondary batteries. These polymers are usually used to prepare organic–inorganic hybrid materials due to their good stability and controllable thickness and they can be chemically bonded to

inorganic materials by method of polysorption. This method is limited to inorganic materials that have active groups (such as hydroxyl group) on their surface. Among organic conducting polymers, polyaniline (PANI) has attracted intense interest because of its high conductivity, excellent stability, and relatively high transparency to visible light. These properties make it one of the most applied conducting polymers. For application in optoelectronics, the polymeric matrices are normally the most desirous as the film of the nanoparticles/polymer composite can be cast easily and thus offer direct use in devices. The re-dispersed nanoparticles when loaded in polymer by dissolution of the as-synthesized particles cannot be guaranteed and this leads to difficulties in knowing the concentration of nanoparticles within the polymer. If the nanoparticles are synthesized in polymeric reaction medium, such issues can be tackled with much ease. The use of polymers is a prominent method for the synthesis of nanoparticles. The reason for using the polymers to prepare nanocomposite is to control the growth and morphology of the nanoparticles. Inorganic nanoparticles stand for a class of new materials having enormous applications in broad fields. To obtain the materials with synergetic or complementary behavior between polymer and inorganic nanoparticles, various composites of polymer with inorganic nanoparticles have been synthesized in recent years. Among those inorganic nanoparticles, Manganese dioxide (MnO_2) and Tidanium Dioxide (TiO_2) nanoparticles have been intensively studied due to their unique catalytic, electrical, and optic properties, as well as their extensive applications in diverse areas. A variety of methods such as co-precipitation, hydrothermal, sol–gel method, microemulsion method etc. based on wet chemical routes has been extensively employed to synthesize of these nanoparticles. The synthesis of Manganese Dioxide (MnO_2) and Tidanium Dioxide (TiO_2) nanoparticles by microwave-assisted and Sol-Gel

solution method is repoted in this wrok. PANI/ MnO_2 and PANI/TiO_2 nanocomposite are synthesized by in situ polymerization of aniline in the presence of as prepared nanoparticles and the prepared nanomaterials are characterized by various studies.

In a typical synthesis of MnO_2 nanoparticle, the microwave-assisted solution method is performed by using maganese of two different salts which are manganese (II) sulphate[$MnSO_4$] and manganese oxalate[MnC_2O_4]. Both salts have different concentration, i.e. manganese (II) sulphate and manganese oxalate are mixed with continuous rousing at the temperature of 40°C at one hour. While stirring, NaOH solution is added till the pH of the solution becomes 12. Then the solution is kept in microwave oven (900W, 2450MHz, Ondia, India) at a temperature of 30°C for about 30min and is kept out for two hours for cooling. After two hours, brown precipitates (MnO_2) are obtained. This is filtered out and washed with deionized water and ethanol. It is dried for three days at room temperature.

In typical synthesis of TiO_2 nanoparticles, all the reagents, used, are of analytical grade and no further purification is done before use. TiO_2 nanoparticles are prepared via sol–gel method using titanium tetraisopropoxide (TTIP), distilled water and Acetic acid (CH_3COOH) as the starting materials. The sol-gel synthesized TiO_2 is obtained from titanium tetraisopropoxide (Ti(OiPr)4) is dissolved in absolute de-ionized water is added to the acetic acid solution in terms of a molar ratio. Acetic acid (CH_3COOH) is used for restraining the hydrolysis process of the solution. The obtained solutions are kept under slow-speed constant stirring on a magnetic stirrer for 30 min at room temperature. In order to obtain nanoparticles, the gels are dried under room temperature for 24 hr to evaporate water and organic material to the maximum extent. After the dried powders

obtained precipitate are at room temperature for two days to carry out and to obtain desired TiO_2 nanocrystalline.

PANI/MnO_2 and PANI/TiO_2 nanocomposites are prepared as follows, PANI/ MnO_2, PANI/ TiO_2 nanocomposite are synthesized by in-situ polymerization. As prepared MnO_2 and TiO_2 nanoparticles are in the concentrations of 1wt%, 2wt%, 5 wt %, 10 wt %, 20 wt % and 50 wt % are added separately to the 4.5 ml, aniline is injected to 70 ml, of 2 M HCl under ultrasonic action to reduce the aggregation of nanoparticles. After 12 h, 4.5 g Ammonium Persulphate (APS) (dissolved in 20 ml de-ionized water) is dropped into solution with constant stirring for about 20 minutes. The polymerization is allowed to proceed for 6 hour at 40^0 C. Reaction mixture is filtered under gravity and washed with 2 M HCL and de-ionized water. Afterwards, It is dried at 90^0 C for 12 hour in vacuum to obtain a fine tint green powder. Total number of samples synthesized in thi work is eleven and as-synthesized nanocomposite materials are subjected to various studies like XRD, HRTEM, FT-IR, TG/DTA, UV-Visible spectroscopic studies and Impedance spectral studies.

A report of the present investigation is provided in this thesis. The entire work has been organized into five chapters.

First chapter gives the general introduction, and aim, and scope of the present work. The methods of synthesis and various experimental techniques of nanoparticles have been explained in the second chapter. Third and Fourth chapters give the detail about preparation and studies of PANI/ MnO_2 and PANI/TiO_2 nanocomposites. Chapter five contains the summary and conclusions derived out of the present study and scope for future work in the same area of the research.