Chapter 5

Conclusions and Future Scope
Conclusions

Nanocomposite materials have attracted much attention recently, as they are novel materials, which combine the advantages of different constituting materials. In this kind of material, the nano-size fillers influence the composite’s properties to a much greater extent than corresponding conventional composites with micro-size fillers. Specially, the nanomaterials with their host polymer are often synthesized by embedding nanoparticles of metal or semiconductors in polymers.

Nanocomposites show properties different from bulk polymers because of the small size of the filler and the corresponding increase in the surface area. Polymers are able to provide required immobilization of nanoparticles avoiding their coalescence, thus protecting the novel size dependent properties of nanomaterials. A variety of polymer-inorganic nanocomposites have attracted considerable interests due to enhanced mechanical, thermal, optical and electric properties.

Among many nanocomposite precursors, zinc oxide nanoparticles are being investigated because of it’s many favorable properties such as wide bandgap, high catalysis activity good transparency, strong room temperature luminescence, high electron mobility, intensive ultraviolet and infrared adsorption, and effective bactericide and antibacterial function etc.

Literature has also shown that the incorporation of small amount of ZnO significantly improve the properties of polymer matrix which make zinc oxide-polymer nanocomposites a promising new class of materials beneficial for widespread fields. Moreover, ZnO can be simply obtained through simple chemical route. Thus, ZnO nanoparticles become a more efficient choice for preparing high performance ZnO-Polymer nanocomposites. For this purpose we have chosen ZnO nanoparticles to investigate the composites of zinc oxide nanoparticles with various polymers for their structural, optical and electrical properties.

In this regard we have carried out chemical synthesis of ZnO nanoparticles and prepared a series of ZnO-Polymer nanocomposite samples with various concentrations of nano ZnO by an ex-situ process. Hence, this thesis includes the results obtained on investigations of ZnO-Polymer nanocomposites.

ZnO nanoparticles were synthesized by wet chemical route and reaction parameters were altered to produce particles of different sizes. Polymethyl methacrylate (PMMA), Polyvinylalcohol (PVA), Polyvinyl pyrrolidone (PVP),
Polyaniline (PANI) were the polymers chosen as the host matrix. Comprehensive characterization of ZnO nanoparticles and its nanocomposites has been undertaken using various characterization techniques: PL, UV-vis, XRD, FT-IR, SEM, TEM, XPS and four probe electrical conductivity measurements.

First uncapped ZnO nanoparticles were synthesized.Basically, ZnO nanoparticles are prepared by hydrolyzing zinc chloride in NaOH / methanol solution. Three different sizes of ZnO nanoparticles were synthesized by varying the concentration of reactants. Formation of zinc oxide particles in the nano regime has taken place indicated by blue shift in the absorption edge. However as can be seen from the UV-vis figure, ageing affects both the peak position and shape of the absorption spectrum. As the ageing times were prolonged, the absorption peak undergoes a series of red shifts. Sharpness of the excitonic peak also decreases with ageing and tailing at longer wavelength region also increases due to agglomeration of the particles, which are dispersed in methanol. Moreover, the aggregated clusters were accompanied with turbid suspension in the solution. XRD results indicate that the crystal growth easily occurs during aging, which agrees with previous results. Thus it is necessary to somehow protect the particles from agglomerating.

Hence, Stability of the size of the nanoparticles has been achieved using 2-mercaptoethanol (ME) as surface capping molecules. Various sizes of ZnO nanoparticles have been synthesized by changing the amount of the mercaptoethanol. It was found that for different sizes, the excitonic peak appears quite sharp without any tailing observed. Blue shift in absorption peaks (i.e. a shift towards lower wavelength), with increase in the concentration of ME is seen which indicates that the particles are in nano regime having size less than the Bohr diameter of exciton, 5.1 nm for ZnO. Moreover, there is no change in the shape of the absorption spectrum with ageing which confirms that by capping the particles with ME their stability has increased.

Results shows that particles are stable and with narrow size distribution. The size of the nanoparticles determined from the X-ray diffraction and effective mass approximation were found to be in agreement with each other. The morphology was determined using TEM which showed the presence of spherical monodispersed particles, no agglomeration was detected. Structural investigations show that ZnO nanoparticles are having hexagonal Wurtzite structure.
Presence of 2-mercaptoethanol was detected using FTIR, PL investigations show intense green luminescence for the samples synthesized in methanol. When these particles were incorporated in various polymer matrices to form ZnO-Polymer nanocomposites, variation in optical properties, electrical properties could be noticed. Hence, Besides the work on zinc oxide nanoparticles, composites of nano ZnO-with different Polymers have also been investigated. Here, we fabricated a series of novel Zinc oxide-Polymer nanocomposite films with different ZnO contents through incorporation of pre-made ZnO particles into polymer matrix.

In case of ZnO-PVA nanocomposites, Polyvinyl alcohol (PVA) was chosen as the polymer matrix for its aqueous solubility. Also, it is a unique synthetic biocompatible polymer and it has a large number of hydroxyl groups that react with many kinds of functional groups. Due to large range hydrogen bond formation ability it is extensively used as a binder for the synthesis of composite materials.

In the study of ZnO/PVA nanocomposites, the purpose was to prepare PVA nanocomposites with ZnO by the ex situ method and to investigate the influences of loading percent of ZnO on the properties and morphology of PVA nanocomposites. In this study, the relevant nanocomposites were prepared by ex situ method. The measurements of FTIR, XRD, SEM, and UV-visible transmission spectra were used for the characterization of the nanocomposite samples. The effect of ZnO/polymer ratio was examined in terms of changes in the properties of the composites.

A standard four-probe method is performed to characterize the electrical conductivity of the resulting ZnO/PVA nanocomposites. The ability to tune the electrical conductivity of the nanocomposites is achieved by varying the ZnO particle concentrations. The dc conductivity of all the samples follows a simple hopping type of charge conduction mechanism.

At lower temperature, there is a very weak variation in dc conductivity with temperature but the variation becomes larger beyond T >130 K. Two different excitation energy was calculated to explain such temperature dependence of dc conductivity. The hopping conduction mechanism is justified by the temperature-dependent conductivity investigation. It was also found that the electrical conductivity in the polymer nanocomposites filled with nanorods is lower than that of the nanocomposites filled with nanoparticles. XRD and FT-IR analyses demonstrate a strong interaction between ZnO nanoparticles and PVA.
A poorer crystalline structure of PVA in the nanocomposites than that of pure PVA is inferred from XRD analysis. i.e. XRD data indicated an increase in the crystallinity of the PVA film with the presence of ZnO. The FTIR measurements showed that ZnO nanoparticles were dispersed inside the PVA matrix, causing the PVA to undergo significant changes on exfoliation with nano ZnO. The XRD patterns, the SEM images confirmed the dispersion of ZnO nanoparticles in the matrix. The SEM images showed that the original structure of ZnO nanoparticles was preserved in the PVA matrix and that the oxide was uniformly distributed on the film surface. SEM photographs showed the aggregates of the particles, which were formed because of the high surface energy of the monometer-sized crystals.

Particles with an average size of ~50 nm were observed. However, some smaller particles with an average size of less than 10 nm can also be found in the micrograph. The optical clarity was investigated by UV-visible transmission spectra. The presence of ZnO in the PVA film caused changes in the optical properties of the polymer. As ZnO content increases, the particles tend to aggregate to the increasing extent. The nanocomposite films exhibit very small transmittance in the ~260-320 nm range except 1:1 ZnO/PVA composition.

The polymers can effectively inhibit the aggregation of the ZnO nanoparticles and keep the ZnO nanoparticles well dispersed in PVA matrix at nanometer level. The grafting of polymers improves the stability of composite particle dispersion and its compatibility within polymeric matrix. In addition, the concentration of zinc oxide nanoparticles is found to have a significant effect on the electrical conductivity of the polymer nanocomposites.

At lower temperature range the activation energies are smaller in compare to higher temperature range. Thus, the interaction between ZnO nanoparticles and polymer becomes more prominent at higher temperature. It is also observed that the activation energy increases with the increase in nano ZnO content. Thus, it may be concluded that, the nano ZnO takes part in conduction mechanism at lower temperature but both ZnO and polymer dominate the charge transport mechanism at the higher temperature range. Thus observed two slopes in conductivity versus temperature curve may be due to the above two charge transport mechanisms The ability to tune the electrical conductivity of the nanocomposites is achieved by varying the particle loadings.
Another polymer Poly (vinylpyrrolidone) (PVP) was chosen as an organic component for the composite because of its unique characteristics. PVP is highly soluble in polar solvents such as alcohol, so it is preferable to avoid phase separation in the reaction. The pyrrolidone group of PVP prefers to complex with many inorganic salts resulting in fine dispersion and surface passivation of them. It has good film--forming ability and its films exhibit good optical quality and mechanical strength.

In ZnO/PVP nanocomposites, surface sensitive technique ‘XPS’ proved that there occurs an interaction between ZnO nanoparticles and PVP. The electrical behaviour of the nanocomposites shows a transition at ~170 K. The electrical resistivity exhibits a semiconductor-like conductivity at higher temperatures and temperature independent conductivity at lower temperatures. This may be caused by the formation of chains of particles or islands of ZnO nanoparticles in the polymer matrix. The hopping conduction mechanism is justified by the temperature-dependent conductivity investigation. SEM was utilized for gathering information about the morphology of the sample, which showed a uniform dispersion of spherical shaped particles through the ZnO/PVP nanocomposite film.

XRD and SEM results indicated that all the ZnO nanoparticles with a polycrystalline hexagonal wurzite structure were well separated from each other and were dispersed in the polymeric matrix homogeneously and randomly. As the percentage of ZnO increases, the size of the ZnO increases and it may be that this ZnO network forms good path for electrons and may help in explaining why the electrical resistivity of ZnO/PVP nanocomposites goes on decreasing as the ZnO concentration increases.

The shifts of infrared bands for PVP in the hybrid film should be attributed to strong coulombic interaction between ZnO and polymeric matrix. The ultraviolet-visible adsorption (UV-vis) showed distinct excitonic features. Thus, ZnO/ PVP nanocomposite films have been fabricated based on the stabilization of functional materials ZnO in the PVP matrix. ZnO nanoparticles are homogeneously and randomly distributed in the matrix, maintain the primary structure, and consist strong Coulombic interaction with polymeric matrix. Temperature dependent electrical responses of the ZnO/PVP films were successfully demonstrated.
The results thus indicate that ZnO/PVP composite thin films can be used as biosensors for solution containing superoxide anion radicals (SOR) and potentially for characterizing the antioxidant properties of fluids. Thus, these particles were investigated using electron microscopy, FTIR spectroscopy and absorption spectroscopy. Comparison of obtained results was made with the literature. These results are important for controlling the growth of ZnO structures in their applications for various devices.

In case of ZnO/PMMA nanocomposites, polymethylmethacrylate (PMMA) is selected as a supporting matrix in the current study because it has superior intrinsic physico-chemical properties as well as biocompatibility and dimensional stability. It is also widely used as a housing material or surface coating material of machinery because of its excellent weather resistance and high transparency.

In the present work, the high-quality ZnO/PMMA nanocomposite films were prepared by embedding of ZnO nanoparticles into PMMA polymeric matrix by modified spin coating method. The prepared nanocomposite films are highly transparent and a clear excitonic peak is observed in their absorption spectra. The absorbance spectrum of the nanocomposites suggested that increasing the amount of nano-ZnO in composite particles could enhance the UV-shielding properties of the polymers.

The surface of the ZnO/PMMA nanocomposite films has been investigated using SEM and TEM. It was clearly found from SEM that ZnO nanoparticles can be homogeneously dispersed in the PMMA matrix. The structure of ZnO/PMMA nanocomposite films was characterized using X-ray diffractometry. These nanocomposites show excellent luminescent performance, which can be further used for various applications. By optimising the synthesis of ZnO-PMMA nanocomposites and the concentration of nano ZnO, we prepared with high UV absorption and a substantial transparency for visible light.

Such materials have potential as UV stabilized PMMA materials for various outdoor applications with high sun light loads. These results indicate that the composite particles have potentially remarkable features of interest. This synthesis method can be used for the fabrication of different polymer-inorganic nanocomposites with other functionalities. It would be interesting in future to investigate nonlinear optical properties, electrical and magnetic properties.
It has been possible to prepare composites of ZnO nanoparticles with polyaniline by an ex-situ process. Polyaniline (PANI) was chosen as the polymer matrix because amongst the family of conducting polymers and organic semiconductors, it is unique due to its ease of synthesis, environmental stability, good electrical conductivity and simple doping/dedoping chemistry.

Herein, ZnO-PANI nanocomposites has been synthesized and were well characterized. The ZnO nanoparticles are embedded in a matrix of polyaniline as evident from the SEM images. It is important to notice that the concentration of ZnO nanoparticles plays a critical role in the growth of the structure of the materials in the nanocomposites. With the increase in the content of the inorganic phase, the growth of the branches of the structure is restrained. UV absorbance increased as the nano ZnO content increased in composites.

Also, the intensity of absorption band increases as the concentration of ZnO increases in the nanocomposites. The absorption peaks in FTIR spectra of nanocomposites were found to shift to higher or lower wavenumber as compared to those observed in pure PANI. The observed shifts were attributed to the interaction between the ZnO and PANI molecular chains. The incorporated ZnO nanoparticles played a significant role by enhancement in the surface activities of the composite material. The electrical property of nanocomposites is a function of the filler as well as the matrix. In the case of zinc oxide-polyaniline composites, the electrical conductivity is predominantly due to PANI.

These nanocomposites show slightly lower resistivities than that of the polymer. The change in the conductivity of the composites indicates a change in the doping state of the polymer due to incorporation of ZnO in the polymer chain. It was found that the morphology, size, electrical properties of ZnO-PANI nanocomposites were affected by the concentration of ZnO. The ZnO-PANI nanocomposites are also semiconducting. Thus, our simple, inexpensive method can be easily tapped for industrial applications. These nanocomposites can be exploited in various fields such as in electric devices, sensors. There is clearly great room for further studies on these materials for potential applications.

Thus, in this work, the nanocomposites can improve the dispersion stability of ZnO and increase interfacial adhesion between the polymers and ZnO nanoparticles.
FTIR, SEM and UV-Vis, XRD were employed to provide the proof for the success of chemical bonding, their particle size and morphology structure and properties. Also, a standard four-probe method is performed to characterize the electrical conductivity of the resulting zinc oxide-polymer nanocomposites.

During this research, conductivity ($\sigma$) change with temperature has been found to follow the Arrhenius equation. However two or three distinct regimes are observed. This study suggests that in different temperature regimes, the conduction mechanism in zinc oxide-polymer nanocomposites is controlled through charge transport in the conduction band, or through electronic hopping between the nearest neighbour donor levels. The activation energies of the charge transport are a few times those of hopping because of the ease of hopping compared with charge transport.

There are different energy barriers for the different conduction mechanisms. The hopping conduction mechanism is justified by the temperature-dependent conductivity investigation. In addition, an increase in ZnO nanoparticle loading is found to have a significant effect on the electrical conductivity of the polymer nanocomposites.

By adding ZnO nanoparticles with Polyvinyl alcohol the electrical resistivity of the nanocomposites can be lowered to about $\sim 10^9$-$10^{11}$ $\Omega$.cm; with Polyvinyl pyrrolidone the resistivity values of $\sim 10^8$-$10^{10}$ $\Omega$.cm can be reached. For the ZnO-PANI nanocomposites the resistivity values of $10^4$ $\Omega$.cm can be reached PANI has a large influence on the obtained resistivity values. The decrease of resistivity reflects more aggregation of 2:1 and 5:1 ZnO-PVA composites compared to 1:1 ZnO-PVA composition. The lower resistivity of ZnO-PVP films is likely due to its smaller grain size. In case of ZnO-PVP films, it may happen that the incorporation of point and textured defects, Porosity of the film however, might be the reasons for lower conductivity. Our results indicate that ZnO-PVA films have better conductivity than ZnO-PVP films to a more homogeneous distribution of grains.

In the summary, ZnO nanoparticles and their nanocomposites assemblies have been synthesized by chemical route. Tuning conductivity with temperature offers functionality to the composite systems, which could be exploited in high tech applications.
Future Scope

ZnO is a cheap, safe and good UV blocker. It can also improve the mechanical properties of polymer composites. So, there is potential for further development of ZnO as a UV protection system, specially in the polymer industry. For these nanocomposites more optical properties are to be investigated such as nonlinear optical properties. Other properties such as electrical conductivity, magnetic properties are also be studied. The introduction of nano-ZnO into polymers could improve the mechanical, electrical and optical properties of the polymers due to a strong interfacial interaction between the organic polymer and the inorganic nanoparticles because of it’s small size, large specific area and quantum effect respectively. These nanocomposites therefore could be widely applied in coatings, plastics, rubbers and other applications.

ZnO nanoparticles are found to be useful in various biological applications such as tagging, chemical libraries etc. Attempts should be made in utilizing these particles in the biological applications such as DNA detection or cancer cell detection. These particles can also be utilized in fabrication of optoelectronic devices such as LEDs. This requires detailed studies on the aspects like quantum yield, decay time etc. Attempts should also be made to understand the effect of particle size on the luminescence properties of the material in such system.

This synthesis method can be used for the fabrication of different polymer-inorganic nanocomposites with other functionalities with some modifications in it. Attempt to utilize these nanocomposites as biosensors should also be made. Extensive study on these materials is necessary for their further applications.