Structural, Dielectric and Spectroscopic Investigations of Sol-gel derived Titania/Poly (vinyl-pyrrolidone) Hybrids

The recent research on hybrid materials has been obviously dedicated to significant efforts on the synthesis and characterization of inorganic/organic based composite materials. When such synergic materials are combined to form heterogeneous structures, the properties of the resulting composites depend on the properties as well as the chemical and morphological details of the constituents. Additionally, the inclusion of nanoscale entities in such composite materials is found to have accomplished remarkable variations in their properties compared to the bulk counter parts. Nanocomposites can be defined as multicomponent materials, in which at least one of the phases has dimension in the nanometer range. The extraordinary interest in nanocomposite materials is mainly due to the vast range of properties that can arise from the combination of the peculiar characteristics of each component, nanoparticles (NPs) and host polymer. Indeed, the original size-dependent physical and chemical properties of the NPs, together with the high processability and defined chemical and morphological structure of the polymers, finally result in innovative materials. Such materials possess unique and tunable characteristics that cannot be achieved by traditional materials. In addition, nanocomposites can also show original properties, not fully envisioned from the properties of the single components, deriving from the local micro-structural arrangements of the nanosized objects in the polymer. The formation of a composite by combining a polymer with an inorganic material has been suggested to meet the demands of balanced properties by using both organic and inorganic materials. The overall properties of a composite material are determined not only by the properties of the parent components but also by the morphology, volume fractions and connectivity of the phases as well as their interfacial properties.
Sol–gel chemistry has been widely used for over two decades as a method to prepare ceramic precursors and inorganic glasses. The sol–gel process has been used to synthesise novel inorganic/organic composite (hybrid) materials often called ‘o’ by Wilkes et al. and ‘ormosils’ or ‘ormocers’ by Schmidt et al. In the case of composites, the objective is to carry out the sol–gel reaction in the presence of organic molecules of typically polymeric functional groups to get better bonding to the ceramic-like phase. This is very useful and novel technique that can produce reinforcing particles within a polymeric environment. Moreover, these novel hybrid sol–gel materials are normally nanocomposites and have the potential for providing exclusive combinations of properties that cannot be achieved by other materials. The preparation, characterization, and applications of inorganic/organic hybrid materials are rapidly expanding areas of research in materials science.

In this perspective, the thesis presents the structural, dielectric and spectroscopic investigations of sol-gel derived titania/poly(vinyl- pyrrolidone) hybrids. These hybrid materials have been characterized using absorption and fluorescence spectroscopy, Fourier Transform Infrared Spectroscopy, Thermo gravimetric and differential thermal analysis, X- Ray diffraction techniques, Raman spectroscopy, Scanning electron microscopy, Atomic force microscopy, Transmission electron microscopy, Energy-dispersive X-ray spectroscopy, dielectric spectroscopy and colorimetric studies.

The thesis is divided into five chapters and the chapter wise summary is given below.

Chapter 1 begins with a brief introduction of hybrid materials, its synthetic strategies and their general applications. Sol- gel processing for the preparation of hybrid materials is discussed in detail. A brief discussion on polymer poly (vinyl-pyrrolidone) and titanium dioxide and their various properties are presented. Spectroscopic properties of rare earth ions, principally samarium, terbium and
europium ions are described. The different characterization techniques employed in the present work are also briefly touched upon.

Chapter 2 describes the non hydrolytic sol-gel synthesis and characterization of TiO$_2$/PVP hybrid nanocomposites using tetra isopropyl orthotitanate and poly(vinyl-pyrrolidone) as precursors. The structural and optical characterizations of the prepared samples have been carried out using different experimental techniques. The capping of PVP around TiO$_2$ nanoparticles was confirmed by FT-IR spectroscopy, the interaction being via bridging oxygens of the carbonyl (C=O) and the nanoparticle surface. The XRD, Raman and TEM results indicate that the prepared samples are formed in pure anatase nano-TiO$_2$ structure. The particle size analysed by TEM ranges between 7 and 12 nm. The size of the nanocrystals as estimated from the XRD spectra is found to be well in agreement with the TEM micrograph. The spacing for the crystal planes is also determined using the ImageJ program applied to the TEM micrographs. The optical absorption study reveals a direct band gap for the TiO$_2$ nanoparticles and the estimated band gap is 3.55 eV. The photoluminescence peaks of the sample were observed at 364 nm, which is due to the band to band transitions of TiO$_2$ and at 465nm, which is associated with the surface trap states.

Chapter 3 depicts the synthesis and characterization of TiO$_2$/PVP: Sm$^{3+}$ and TiO$_2$/PVP: Eu$^{3+}$ hybrid composites. The TEM and XRD of the samples confirm the formation of TiO$_2$ nanocrystals in the hybrid composites. The prepared composites contain TiO$_2$ nanocrystallites in the anatase phase and exhibit Ti-O-Ln bond. The absorption spectra of all the prepared samples reflect the increasing photoresponse of doped samples to visible light over pure TiO$_2$. Surface area is remarkably increased due to lanthanide ion-doping. Two newly prepared Ln(III):TiO$_2$/PVP (Ln = Eu, Sm) luminescent composites exhibit enhanced pure red or orange light emission due to energy transfer from TiO$_2$ to Eu(III) or Sm(III), respectively. The photoluminescence spectra clearly reveal an energy transfer from the TiO$_2$
nanocrystals to Sm$^{3+}$ ions and to Eu$^{3+}$ ions. The energy transfer kinetics involves the harvesting of the optical energy by the TiO$_2$ nanoparticles and the transfer of energy to the ions from the surface states of the nanocrystals.

Chapter 4 contains the dielectric and ac conductivity studies of titania/poly(vinyl-pyrrolidone) nanocomposites with varying concentrations of TiO$_2$. The dielectric response and the ac electrical conductivity of the samples are investigated for the frequency range 100Hz -2MHz at room temperature. The dielectric studies show low values for dielectric constant and loss at high frequencies. Both dielectric constant and dielectric loss decreased with increasing wt% of TiO$_2$. AC conductivity is found to have obeyed the Jonscher’s power law, which further decreased with increasing wt% of TiO$_2$. The ac conductivity is found to have values of the order of $10^{-7} - 10^{-8}$ S/cm for the nanocomposites. In addition, the experimental dielectric data have been analyzed by considering electric modulus formalism. The Cole-Cole parameters were calculated and the semi arcs observed in the plots indicate a single relaxation process and can be modeled by an equivalent parallel RC circuit. The complex impedance plots indicate the presence of ionic contribution to the electrical conductivity of these materials.

Chapter 5 reports the preparation, characterization and energy transfer mechanisms from Tb$^{3+}$ ions to Eu$^{3+}$ ions in the TiO$_2$/PVP hybrid matrix. Co-doped rare earth cations Tb$^{3+}$ and Eu$^{3+}$ aggregated as luminescent centers within the hybrid matrix in a controlled manner resulted in the white-light phosphors with tunable emission properties. Down-conversion of light is used for the generation of white light which involves the conversion of UV into visible light by the involvement of rare earth ions. Due to the energy overlap between Tb$^{3+}$ and Eu$^{3+}$, an efficient energy transfer occurs from Tb$^{3+}$ to Eu$^{3+}$. The increase of Eu$^{3+}$ concentration leads to the increase of the energy transfer efficiency from Tb$^{3+}$ to Eu$^{3+}$. The photoluminescence colours of TiO$_2$/PVP:Tb$^{3+}$:Eu$^{3+}$ samples can be easily tuned from green to red by changing the doping concentration of Eu$^{3+}$ and Tb$^{3+}$. The white light luminescence
colour could be changed by varying the excitation wavelength also. The emission spectrum for the sample has been converted to the CIE 1931 color coordinate system. The color coordinates corresponding to the prominent emissions are determined. The CIE chromaticity calculation demonstrated its potential as white LED-based near-UV excitation.

The research work presented in the thesis has either been published in or communicated to reputed international journals and presented in various national/international seminars.

**Research papers published/ communicated**


