Abstract

Nanotechnology deals with natural and artificial structures on the nanometer scale, i.e. in the range from 1 μm down to 10 Å. One nanometer, 1 nm = 10^{-9} m, is roughly the distance from one end to the other of a line of five neighboring atoms in an ordinary solid. Particle size is expected to influence structural and electronic properties of Nanomaterials, which are important driving forces in deciding physical and chemical properties of the material. Semiconductor nanocrystals have attracted lot of attention in the recent years in both fundamental research and technical applications, because of their unique size dependent optical and electronic properties arising from quantum confinement effects, and structural properties as well.

The civilian, commercial and defense sectors of most advanced industrialized nations are faced with a tremendous set of environmental problems. Organic chemicals which may be found as pollutants in waste water effluents from industrial or domestic sources must be removed or destroyed before discharge to the environment. Many processes have been proposed over the years and are currently used to remove organic toxins from wastewaters, current treatment methods for these contaminants such as adsorption by activated carbon and air stripping, merely concentrate the chemicals present by transferring them to the adsorbent or air but they do not convert them into nontoxic wastes. Thus, one of the major advantages of the photocatalytic process over existing technologies is that there is no further requirement for secondary disposal methods. Another advantage of this process is that expensive oxidizing chemicals are not required as
ambient oxygen is the oxidant. Photocatalysts are also self regenerated and can be reused or recycled. As the most promising photocatalyst, TiO$_2$ based materials are expected to play an important role in helping to solve many serious environmental and pollution challenges.

Ferrite nanoparticles have been the emerging focus of the recent scientific research because of their potential technological applications in storage media, biomedical fields and magnetic nanofluids. Magnetic properties of nanoparticles have recently attracted considerable attention from both scientific and technological points of view. Particularly, ZnFe$_2$O$_4$ nanoparticles have generated a large research effort in the past 10 years due to their intriguing magnetic and catalytic properties and also due to their enhanced chemical reactivity which makes them ideal candidates for many technological applications. The earlier studies revealed that the stoichiometric ZnFe$_2$O$_4$ possesses a normal spinel structure where the diamagnetic Zn$^{2+}$ ions prefer the A site in oxide crystals with spinel structure due to their affinity for strong, nearly covalent, sp$^3$ bonding with oxygen ions. The band gap energy of ZnFe$_2$O$_4$ is 1.9eV.

On the other hand TiO$_2$ is a wide bandgap semiconductor (3.03 eV for rutile and 3.18 eV for anatase) and can only absorb about 5% of sunlight in the ultraviolet region, which greatly limits its practical applications. Extensive efforts have been made in the development of TiO$_2$ photocatalysts that can efficiently utilize visible light. An ideal photocatalyst should be stable, inexpensive, nontoxic and highly photoactive. For the degradation of organic compounds, the redox potential lies within the bandgap of the semiconductor. Several semiconductors have bandgap energies sufficient for catalysing a wide range of chemical reactions. These include TiO$_2$, WO$_3$, SrTiO$_3$, α-Fe$_2$O$_3$, ZnO and ZnS. During the photocatalytic process, the illumination of a semiconductor photocatalyst with UV/visible radiation activates the catalyst, establishing a redox environment in the aqueous solution. The semiconductor visible photocatalysis with a primary focus on TiO$_2$ has been applied to a variety of problems of environmental interest in addition to water and air purification. TiO$_2$, most thoroughly investigated in
Thus the main objectives of the present investigation are:

1) Synthesis of ZnFe$_2$O$_4$ nanoparticles by polyol / sonochemical method and to study their optical, structural and magnetic properties.
2) Synthesis and characterization of TiO$_2$ and TiO$_2$-ZnFe$_2$O$_4$ nanocomposite in nanosize regime by Polyol / Electrochemical / Sonochemical method.
3) To overcome the serious drawbacks of low efficiency and narrow visible light-response range in TiO$_2$ photocatalyst
4) Study the photocatalytic activity of ZnFe$_2$O$_4$, TiO$_2$ and TiO$_2$-ZnFe$_2$O$_4$ in visible region by dye degradation and compare the efficiency with degussa TiO$_2$ photocatalyst

With these objectives, the thesis is structured into five chapters:

Chapter 1: Introduction

This chapter introduces nanoscience and nanotechnology. It also explains how properties of material changes with particle size. It gives in detail the literature survey of TiO$_2$ and ZnFe$_2$O$_4$ as a photocatalyst respectively. The effect of size of ZnFe$_2$O$_4$ semiconductor on the magnetic properties has been discussed. A detailed discussion of TiO$_2$ as a photocatalyst and its optical properties has been given based on rigorous literature survey. Especially on: the current UV activated photocatalysts, Efforts to increase the photoactivity of pure TiO$_2$, particle size optimization, crystal structure optimization, increase in the photoactivity through surface modifications, current visible light activated photocatalysts, ion implantation, synthetic techniques, metal and non-metal dopants, semiconductor coupling. It gives in detail the history of photocatalysis and motivation for visible photocatalysis. The process of photocatalysis has been discussed in detail on the following points: Band gap excitation, band-edge positions, electron-hole pair recombination, role of photogenerated electrons and holes in photocatalysis and photocatalytic oxidation of organics. The chapter describes different methods of synthesis of nanostructured metal oxides and composites.
At the end of the chapter, scope of the thesis has been discussed.

Chapter 2: Experimental Methods and Characterization techniques

This chapter discusses the detailed procedure for the synthesis of semiconductor nanostructures, and characterization techniques used. The synthesis is done by Polyol process for ZnFe$_2$O$_4$ and TiO$_2$. Synthesis of ZnFe$_2$O$_4$ and TiO$_2$ is also done by sonochemical process and electrochemical process respectively. TiO$_2$-ZnFe$_2$O$_4$ nanocomposite is synthesized by sonochemically assisted polyol process.

The chemical, structural, and morphological characterization of the samples was performed using various characterization techniques. X-ray diffraction (XRD) analysis of powder samples was done on an Philips PW 1840 powder X-ray diffractometer, operating at a voltage of 20 kV (with CuKα radiation, λ=1.5401Å) in the range (2θ) from 20° to 80° with a scanning rate of 1° per minute. Diffuse reflectance spectroscopy (DRS) was used to observe the band edge absorption of the photocatalyst. DRS spectra were acquired using JASCO V-670 UV/VIS Spectrophotometer. BaSO$_4$ was used as standard reference. Fourier Transform Infrared Spectroscopy (FTIR) was used to study the chemical composition of the sample. Thermogravimetric and Differential thermal analysis (TG-DTA) was done to study the thermal stability and phase changes in the samples. Scanning Electron Microscopy (SEM) was used to study the morphology of the sample. The Transmission Electron Microscopy (TEM), High-Resolution Transmission Electron Microscopy (HRTEM), and Electron Diffraction patterns were obtained on a Tecnai F30 FEG machine operated at 200 kV. Room temperature magnetic study (VSM) was done for ZnFe$_2$O$_4$ samples. The Brunauer-Emmett-Teller (BET) method was used to measure the total surface area of the samples. Room Temperature - Photoluminescence Spectra (RT-PL) were scanned on Perkin Elmer Lamda 650. X-ray photoelectron spectroscopy (XPS) was used for elemental analysis. Photoelectron spectra were recorded with a V. G. Microtech unit ESCA 3000 spectrometer equipped with Al Kα X-ray source (hν = 1486.6 eV) and a hemispherical electron
analyser. The X-ray source was operated at 150 W. The residual pressure in the ion pumped analysis chamber was maintained below 1.0×10−9 Torr during data acquisition. The C 1s peak at a binding energy 284.6 eV was taken as an internal standard. A detailed description of the photocatalytic setup fabricated in the laboratory has been given.

Chapter 3: Section-I: ZnFe$_2$O$_4$ Synthesized by Polyol method

In this chapter, superparamagnetic ZnFe$_2$O$_4$ nanoparticles with size range of 28-38 nm were synthesized by polyol process based on use of varying chain length glycols as solvent. The plausible mechanism behind in situ formation of zinc ferric oxalate hydroxide hydrate [Fe$_2$Zn(C$_2$O$_4$)$_2$(OH)$_3$]$^+$ 4H$_2$O complex from diethylene and polyethylene glycol has been discussed. The magnetic properties of above complexes are explained in this chapter. We have found a ferromagnetic ordering in precursor complex compounds. The intermediate hydrocarbon chain between the oxalato bridged metal cations play crucial role in obtaining anomalous magnetic behavior. ZnFe$_2$O$_4$ nanoparticles obtained after annealing the DEGylated precursor complex showed highest superparamagnetic (SPM) behavior (22.4 emu/g) among others. The reason for anomalous SPM behavior of ZnFe$_2$O$_4$ nanoparticles are explained on the basis of the degree of inversion of the spinel structure, high surface-to-volume ratio, which causes non-collinear spin arrangement in a surface layer and higher oxygen concentration on the surface of dead organic layer, which increases the unpaired valence electrons leading to uncompensated surface spins.

Chapter 3: Section-II: ZnFe$_2$O$_4$ Synthesized by Sonochemical method

In this chapter, we have synthesized zinc ferrite nanoparticles using sonochemical route using sonochemically assisted coprecipitation reaction. The same procedure was carried out for 50W, 100W and 150W energy keeping all other parameters same. The as prepared samples are ∼12-18nm and after annealing at 400°C crystallite size increases to ∼25nm. Governable
parameters that are critical for the coprecipitation of ZnFe$_2$O$_4$ were determined primarily, they are the pH of the solution and the final calcination temperature, and along with these usual conditions horn energy was varied. All three parameters have affected the crystallinity and particle size of the sample.

UV-DRS study reveals that samples prepared by 50 and 100W energy showed same trend in absorption at 672nm in visible region but after annealing at 400°C it is red shifted to 722nm. A sample prepared by 150W energy is further red shifted to 750nm. X-ray diffraction study of as synthesized zinc ferrite reveals that powder is completely gone into spinel structure and matches well with cubic system of zinc ferrite ZnFe$_2$O$_4$ (JCPDS card no. 22-1012). Sample prepared at 100W energy shows smallest crystallite size. Thermogravimatric graph shows continuous weight loss upto 400°C and a stable formation after that. Exothermic fluctuations are seen from 430 to 700°C might be because of lattice rearrangements and Fe$^{3+}$ cations hopping from octahedral to tetrahedral sites in a spinel structure. Vibrational bands around 410 and 570 cm$^{-1}$ indicate Zn-O and Fe-O-Fe bonds thereby confirming formation of ZnFe$_2$O$_4$. From SEM images it is clear, that as energy of horn increases agglomeration in the particles decreases might be because of high speed Brownian motion of formed radicals during synthesis and thereby creating higher cavitational temperature. Sonochemical synthesis gives pure phased, 10-15 nm sized spinel oxide.

ZnFe$_2$O$_4$ nanoparticles synthesize by polyol as well as sonochemically assisted coprecipitation method as photocatalyst in visible light gives poor results as compare to coupled system. The photoactivity of ZnFe$_2$O$_4$ ceases after a short duration. This phenomenon has been attributed to poor separation ability of photogenerated electrons and holes As well as high surface charge recombination.

**Chapter 4: Section-I: TiO$_2$ Synthesized by Polyol method**

In this chapter, we have described synthesis of TiO$_2$ nanoparticles using ethylene glycol as solvent, capping agent as well as reducing agent. Here we have used Ti(Bux)4 as titanium precursor and heated slowly in EG at 180°C.
for 2 hrs. As synthesized precursor powder matches with titanium glycolate complex with wirelike-rod shape having size of 5-10 micron. This precursor on annealing at 300 and 500°C shows rod like morphology made up of small naocrystalline TiO$_2$ particles. The onset absorption edges for annealed samples shifts to visible region. The sample annealed at 300°C show a huge absorbance in the whole visible light region, while sample annealed at 500°C is again slightly red shifted towards visible region. The precursor glycolate complex annealed at 300 and 500°C goes in pure anatase phase of TiO$_2$. During annealing at 300°C in static air carbon from ethylene glycol must have been doped in the lattice of TiO$_2$ and thereby reducing the band gap, giving tail like absorbance in entire visible region.

The photoactivity of TiO$_2$ by polyol shows best results when annealed at 300°C. Due to annealing carbon from EG must have been doped, thus degrades fast in visible region.

**Chapter 4: Section-II: TiO$_2$ Synthesized by Electrochemical method**

The quality of TiO$_2$ nanocrystals yielded by non-hydrolytic electrochemical method is better than that of the TiO$_2$ nanocrystals synthesized by polyol method. This is an easy, low cost, clean and easily reproducible method. Here we have used Titanium sheet and Platinum sheets as cathode and anode respectively. Current density was varied from 10 to 40 mA. Tetra butyl and tetra Pentyl ammonium bromide were used as capping agent and stabilizing agent, in the mixture of THF and acetonitrile. As synthesized samples were characterized by UV-DRS, XRD, FTIR, TG-DTA and TEM. Monodispersed ~3-4 nm sized particles are obtained by using TBAB and TPAB capping agent, confirmed by XRD and TEM, showing mixed phase of anatase and rutile. FTIR confirms formation of TiO$_2$ by Ti-O stretching peak at 520 cm$^{-1}$ and shoulder peak at 720 cm$^{-1}$. TG-DTA show stable formation at 800°C. The extended, long tail like absorbance in visible region seen in UV-DRS spectra after annealing in static air at 300°C might be because of doping of carbon atom from TBAB into TiO$_2$ crystal. After annealing at 300 and 500°C in static air pure anatase phase is formed for all samples HRTEM
lattice spacing matches well with XRD results. TiO$_2$ synthesized at 40mA current density with TBAB as capping agent shows optimum size with 50% anatase phase.

Electrochemically synthesized TiO$_2$ shows good catalysis for TBAB capped-40mA sample after annealing at 300°C. Above said sample shows good catalysis than D-25.

Chapter 5: Results and Discussion of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites by sonochemically assisted polyol synthesis

In this chapter a novel sonochemically assisted polyol synthesis route is used to create TiO$_2$-ZnFe$_2$O$_4$ nanocomposite that is directed towards extending the photoresponse of TiO$_2$ from UV to visible wavelengths. Our aim was to increase the anatase content while maintaining an adequate amount of ZnFe$_2$O$_4$ to create a composite with the potential of visible light absorption. As the concentration of ZnFe$_2$O$_4$ increases, the anatase-to-rutile transformation begins to occur. The anatase-to-rutile transformation involves a collapse of the open anatase structure to a closed rutile structure instigated by the rupture of two of the six Ti-O bonds of the titanium coordination octahedral (TiO$_6^{2-}$) in anatase to form new bonds in the rutile structure. The transformation is most probably attributed to the diffusion of Fe$^{3+}$ into surface Ti$^{4+}$ forming an oxygen vacancy that promotes nucleation. This substitutional process may occur due to the similar ionic radii for Fe$^{3+}$ (64pm) and Ti$^{4+}$ (68pm).

This chapter deals with detailed photocatalytic study of TiO$_2$-ZnFe$_2$O$_4$ nanocomposites. The visible light photoactivity for a TiO$_2$-ZnFe$_2$O$_4$ coupled system follows a bell curve with the maximum degradation being achieved with X equal to 1 and 3 (where X is the % of ZnFe$_2$O$_4$ in 100% TiO$_2$). The increased photoactivity of X values for 1 to 3 can be attributed to the role of ZnFe$_2$O$_4$ in extending the photoresponse of the catalyst to visible. In conclusion, TiO$_2$-ZnFe$_2$O$_4$ nanocomposite has been proved to be an efficient photocatalyst for degradation of organic compounds like phenolic or azo dyes.