Studies on optoelectronic, photocatalytic and energetic ion irradiation aspects of nanotitania systems

PREFACE

Over the years, nanoscale semiconductor oxides have received extensive research interest owing to their unusual physical, optical and electrical properties and their impending application in the fields of optoelectronics, non-linear optics, photocatalysis and bio-sensing. The synthesis of diverse structures of nanoscale systems is currently attracting a great deal of attention. Whether in the form of one-dimensional nanorods/nanotubes or two-dimensional nanoplates/nanosheets, their pivotal role as regards controlled charge transport is not only sound, also highly reliable. On the other hand, photocatalysis has become a general utterance over the years and in order to improve its efficiency materials of diverse kinds and structures are considered at a large.

Titania (TiO_2) has been a widely studied system amidst other semiconductor oxides, for its low toxicity, environmental stability and cost effectiveness. More commonly it is used as white pigments as it shows no absorbance in the visible region. The most promising characteristics of TiO_2 is in its high photocatalytic efficiency which is due to the generation of electron and hole pairs under UV light thereby inducing surface reactivity at large. The photocatalytic response is however restricted due to its wide bandgap (E_g~3.2 eV, anatase) nature along with the long life time (~μs) of photogenerated carriers. Numerous efforts have been made by researchers in order to improve its optical absorption, and consequently photocatalytic activity in the visible to near-infrared (IR) region. With a purpose of lowering the band gap, numerous attempts have been made by varying its chemical composition with metal, nonmetal or self-doping or by structural and surface modifications. It may be noted that, the physicochemical properties of titania largely depend on its crystalline structure, lattice imperfections, morphology, texture and dopant present.

This thesis highlights structural, morphological and optoelectronic responses of nanotitania systems of diverse structures and also that exist in pure and doped forms. Primarily, hydrothermal route and microwave heating techniques have been employed for growing different morphologies such as, (1D) nanotubes, and (2D) nanosheets from the nanoparticles under suitable reaction conditions. The effect of low energy ion irradiation on titania nanoparticles and nanosheets has been investigated to exploit morphological and optoelectronic features. Moreover, the creation of disordered layer upon hydrogenation is illustrated for different % of H_2 gas concentration with N_2 as the carrier gas. Photochromic, photocatalytic and hemolytic activity of specific nanotitania structures have also been evaluated.

The *Chapter I* is an introductory chapter which highlights fundamental aspects of nanotitania systems of diverse structures. Several important features, like optical response, irradiation effect, hydrogenation effect are being discussed in the light of existing literature and recent reports. Photoactivity and bio-physical activity of nanotitania based systems are also described. This chapter as a whole gives an account on the assertive role, new properties, as well as the challenges ahead for desired applications at large.

In *Chapter II*, the synthesis and basic characterization of pure and doped (Ag^+ and Cr^{3+}) titania nanoparticles have been discussed. The structural analyses of the synthesized samples were investigated by X-ray diffractrogram (XRD). Molecular vibrational characteristics have been assessed by Fourier transform infrared (FT-IR) spectroscopy studies. The optical absorption and emission response were revealed by UV-visible spectroscopy and photoluminescence spectroscopy working at room temperature. The temperature dependent study, in response to the weight loss of the samples, was carried out using thermogravimetric analysis. Latter, the photochromic and thermochromic behaviour of doped titania nanosystems are being discussed in sequence. The dopant concentration dependent photochromic behaviour of the undoped and Cr^{3+} doped TiO_2 nanoparticles are described using CIE colour diagram by studying the transmitted response of three different lasers of known wavelengths. Thermochromism feature, as studied for 1% Cr^{3+} doped nano-titania system and within a temperature range 0–55^{o}C, displayed reversible colouration characteristics when subjected to heat, or removal of heat.

In *Chapter III*, growth of TiO_2 nanotubes and nanosheets derived from nanoparticles are discussed in sequence. The visible evidence of formation of different nanostructures, like nanoparticles, nanotubes and nanosheets has been presented using Transmission electron microscopy data. Other characterization techniques, like XRD, UV, PL have also been employed to reveal its properties.

The *Chapter IV* highlights the effect of low energy ion irradiation on morphological and optical responses of titania nanosystems with emphasis on nanoparticles and nanosheets. In general, positive ions are used for implantation. The use of negative ions facilitates free ion implantation. TiO_2 nanoparticles were irradiated with two different kinds of ions (80 keV Xe^+, 80 keV Ag^-) with Xe exhibiting a higher nuclear energy loss. Particle growth is predicted as a consequence of swelling behavior accompanied by the formation of Van der Waals crystals in isolated regions of nano-titania with Xe^+ ion irradiation. Similarly, implantation of Ag into titania nanoparticles has been substantiated from the TEM images. 80 keV Ag^- ion irradiated nanoparticles exhibited plasmonic response with a strongest response at a fluence of 5×10^{15} ions/cm^2. The growth of homogeneous micron size spheres was perceived upon 100 keV Au^- ion irradiation on the nanosheets. Au^- ion irradiated nanosheets exhibited hydrophobic character with superhydrobhopic feature at the highest fluence (5×10^{16} ions/cm^2).

The *Chapter V* focuses on the effect of hydrogenation on sol–gel derived anatase-phase white TiO_2 nanoparticles. The hydrogenated black titania confirms the anatase phase, but with weak diffraction signals. Upon hydrogenation, nanotitania system acquires a disordered phase in the form of a thin amorphous layer surrounding the nanoparticles owing to the formation of TiO_2:H_x complexes. The optical band gap of black TiO_2 is reduced to 1.53 eV and a higher thermal stability has been revealed. The BET surface analysis of hydrogenated nano-titania sample has shown a more-open hysteretic isotherm and consequently, very high surface area as compared to the untreated one. Hydrogenated nanotitania could find scope in infrared optics, hydrogen storage and desired photocatalytic applications.

In *Chapter VI*, the application aspects of different structures of nanotitania in the field of photocatalysis and hemolysis are presented. Methyl orange (MO) and methylene blue (MB) dyes were chosen as the target to make a comparative study of the photocatalytic activity of nanoparticles, nanotubes and nanosheets under UV irradiation. Titania nanosheets exhibited a pronounced photocatalytic degradation efficiency (87% in case of MB dye and 69% in case of MO dye) followed by nanotubes and nanoparticles. Moreover, a comparative view is given between white and black TiO_2 nanoparticles in which the latter showed a degradation efficiency of 51% in case of MO dye, whereas white TiO_2 showed only 12 % degradation efficiency. The catalytic activity, under UV light illumination, is discussed in the light of pseudo-first order kinetics. Further, hemolytic activity was considered as regards biophysical relevance of the synthesized products. A comparative analysis was made considering the hemolytic activity with increase in concentration of various forms of titania: nanoparticles, nanotubes and nanosheets. TiO_2 nanosheets displayed highest membrane stability of ~56% as compared to nanoparticles and nanotubes which showed ~46% and ~44% stability respectively in hemolysis of red blood cells.

Finally, in *Chapter VII*, the conclusions drawn from the present study are highlighted along with some important findings. The future scope of our work is also presented at the end followed by appendices, list of publications and addenda.