In recent years, intensive research attention has been drawn to design and develop Nanostructured Materials for applications in the field of materials science, microelectronics, bioengineering, pharmaceutical industry etc. Nanostructured materials may be defined as structural elements having dimensions in the range of 1 to 100 nm. The low dimensionality, high surface to volume ratio and morphology combined with quantum confinement results in unique physical, chemical, electrical, optical and magnetic properties. These distinctive properties are being exploited to develop new products, devices and technologies. The challenge lies in controlled manipulation of size and shape with appropriate synthetic methods, functionalizations etc. and development of basic understanding to engineer custom designed materials with defined properties for specific applications.

Metal oxide nanostructures, in particular, titanium dioxide, represent one of the most potential materials, because of their unique structural, physical and chemical characteristics suitable for a variety of applications. Ancient paintings suggest titanium oxide as an artist’s pigment because of its suitable refractive index, hiding characteristics and nontoxicity. Presently TiO\textsubscript{2} finds usage in a wide range of applications such as coatings, cosmetics, ceramics, textiles, food-contact material, leather, pharmaceuticals, photoelectrochromics, photoconductors, sensors, polymer electrolytes and more recently, in several biological and biomedical areas. An upcoming area envisaged for titania as a photocatalyst is to play a major role in addressing several environmental and pollution challenges along with the prospects of cost effective utilization of solar energy based on photovoltaic and water-splitting devices. The development of advanced hybrids of TiO\textsubscript{2} with metals, organics and polymers etc. enriches the list of potentially new applications.
To ascertain the different parameters that control the properties of TiO$_2$ it is important to have a comprehensive understanding of the physico-chemical properties as a function of the structural composition. Currently, research in this field is wide-ranging, with activities extending from fundamental work involving synthesis of novel titania based structures to engineering solid-state devices of the future. The physical and chemical properties of titania nanocrystals are greatly influenced by the synthetic route and processing; therefore control on synthesis is an important parameter to modify material properties. However, literature suggests that relatively less attention has been paid to low temperature wet chemical processing which is simple, highly energy efficient, can be scaled up easily and hence industrially viable. The success of the process, nevertheless, depends on the establishment of a reaction pathway for controlled formation of nanostructures through a rational theoretical and experimental understanding.

The present thesis is hence conceived with the central theme of synthesizing nano sized TiO$_2$ with tailored phase and morphology to achieve exotic properties followed by several demonstration of its desired applicability in both chemistry and biology. Theoretical approximation and calculations to provide insight into the formation mechanism of various phases of titania have been undertaken. The influence of synthetic conditions in controlling the properties and the effect of impurities (metal and nonmetal) on the optical band gap is studied in detail and subsequently the photochemical activity is correlated with the physico-chemical properties. Attempts have been made towards surface modification of these nanoparticles to impart high dispersity in specific solvents that is highly desirable in many applications. Surface modified nanosized TiO$_2$ has been utilized in designing easily recoverable and reusable catalyst systems for a range of industrially important organic reactions. Initial efforts to
show the potential for the synthesized nanoparticles as biofunctional materials is also undertaken. To sum up, the work described in this thesis is a systematic attempt right from conceptualization to tailoring and designing of the properties of nanostructured TiO$_2$ for specific end uses.

The Thesis is divided into six chapters:

**Chapter 1** is an introduction to the field of nanoscience and technology and the importance of titanium dioxide nanoparticles in present day. This chapter briefly describes the popular methods of synthesis, the characterization techniques employed in establishing the size, morphology, various physical and chemical properties as well as the different applications of TiO$_2$. The reasons for the continued interest in titania, the challenges involved in suitably tailoring the properties along with the scientific concepts proposed are also discussed.

**Chapter 2** deals with the synthesis and characterization of phase-pure rutile, mixed phase and anatase titania nanocrystals at low temperature. In **Part A** of this chapter, a simple and efficient methodology for the low temperature synthesis of phase-pure nanocrystalline rutile TiO$_2$ with tuned morphology is reported. Control on morphology has been achieved by simple variation of the hydrothermal process, starting with titanium-tetrachloride without using mineralizers, additives or templating agents. The X-ray Diffraction (XRD) and Selected Area Electron Diffraction (SAED) patterns show the formation of phase-pure rutile titania in the entire temperature range of synthesis (40 °C to 150 °C). The major highlight in this methodology was to achieve phase-pure rutile even at a considerably low temperature (40 °C). Fourier Transform Infrared (FTIR) spectra strongly indicate the presence of hydroxyl group or surface adsorbed water. Thermogravimetry along with differential analysis (TG-DTG) shows no phase change upto 1000 °C. A combination of reaction parameters (temperature, time) with a thorough Transmission Electron Microscopy (TEM) study demonstrates
the formation of phase-pure rutile titania nanocrystals as nano-rods, bunched nanospindles or spherical nanoparticles depending on the hydrothermal reaction conditions.

Scheme 1. The proposed pathway for formation of phase-pure rutile titania with different morphology.

Ultra-Violet-Diffuse Reflectance Spectroscopy (UV-DRS) shows the optical band gap in the range of ~2.8-3.1 eV and BET specific surface area is found to be between 70-140 m²/g depending on the synthesis conditions. Raman spectroscopic analyses of the samples provide valuable insights into the structural and stoichiometric details.

Part B is a detailed study on controlling the phase, crystallinity, shape and effective band gap of nanocrystalline titanium dioxide using hydrogen peroxide via a solvothermal process. As a convenient and environmentally benign system the peroxotitanium complex has gained attention for the preparation of titania and titanium-containing multicomponent functional materials.

Figure 1. The effects of H₂O₂ on titania formation.
This chapter deals with a simple, economical, clean and environmentally friendly process leading to titania with desired properties through an energy efficient low temperature wet chemical method. Study of all the reaction parameters concludes that primarily the H$_2$O$_2$: Ti ratio ($r_p$) is the controlling factor to obtain crystalline titania with different phase composition. The evolution of phase and the crystallite size of the synthesized materials have been determined from XRD and Raman spectroscopy. The phase related morphology of the materials observed by TEM is truncated anatase and rod-like rutile (Figure 2 b&c).

![Figure 2](image)

**Figure 2.** TEM images (a) phase-pure anatase without H$_2$O$_2$, (b) anatase and rutile with intermediate $r_p$ and (c) predominant anatase with excess H$_2$O$_2$.

The solvothermal synthesis in presence of the oxidizing agent H$_2$O$_2$ resulted in titania with slight carbon incorporation and the source of carbon is presumed to be either the precursor or the solvent. The percentage of carbon obtained from Elemental analysis is $\leq 1\%$. FTIR and X-ray photoelectron spectroscopy (XPS) established the presence of both carbide and carbonate species in titania matrix. The effect of carbon incorporation is manifested as a red-shift in band edge for UV-DRS ($\sim 2.7$ eV). The BET surface area of the catalysts is estimated in the range of 100-125 m$^2$/g.

**Chapter 3** is a comprehensive theoretical study of Titania formed by solvothermal method with hydrogen peroxide to provide appropriate insight into the probable reaction pathway and formation of the polymorphs.
Quantum mechanical calculations using Density Functional Theory (DFT) with B3LYP/LANL2DZ provide all possible structures of the intermediate complexes. Based on the energy value of these intermediate structures a probable reaction mechanism is proposed for the final phase composition.

Optimization of the structures explains that the formation of various Ti-complexes (Figure 4) is the predominant controlling factor for the different TiO₂ crystal phases both in absence and presence of peroxide.

Broadly the modification of TIP (titanium isopropoxide) with H₂O₂ reduces the availability of groups that hydrolyze and condense easily through the formation of the complex. Therefore, the use of H₂O₂ as mineraliser allows the control of both the condensation and oligomerization leading to the preferential crystallization of TiO₂ in the preferred phase.
Chapter 4 evaluates the photocatalytic activities of various phases of titania. Part A describes the use of phase pure rutile as photocatalyst for the degradation of the pollutant azo-dye, Methyl orange (MO) under UV irradiation.

Figure 5. The (A) TEM image of the best rutile-titania catalyst and (B) the Liquid Chromatogram of MO.

Dependence of dye photodegradation rate on the morphology, specific surface area, surface nonstoichiometry and acidity are investigated in detail. Catalyst performance is compared for rate constants obtained for each reaction using non-linear least square fits to the experimental data that reveals a pseudo-first order reaction kinetics. The result shows extraordinarily high activity for all nanosized synthesized samples compared to
commercial TiO$_2$. Interestingly the catalyst synthesized at 40 $^\circ$C for 16 hrs shows best activity (Figure 5).

![Scheme 3. The proposed mechanism of photocatalytic reaction.](image)

The enhancement of the photocatalytic rate in presence of oxygen established that the degradation is an oxidative process.

**Part B** of Chapter 4 demonstrates visible light activity of the mixed phase and anatase TiO$_2$. This synthesized TiO$_2$ shows a far superior activity compared to Degussa P25 under similar experimental conditions for the photodegradation reaction of 2-mercaptobenzothiazole (2MBT). The complete decomposition is confirmed by High Performance Liquid Chromatography (HPLC) (Figure 6).

![Figure 6. HPLC of 2MBT (a) Initial, after (b) 15 and (c) 45 minutes of photodegradation.](image)
Chapter 5 is a study on the role of metal incorporated titania nanoparticles in photocatalysis as well as catalytic reactions. The chapter has been divided into two parts.

Part A deals with the use of metal (Ag and Pd) on TiO$_2$ for photocatalytic application. Literature studies have documented that the deposition of noble metals onto TiO$_2$ surfaces is a dynamic research area to modify the photocatalytic activity of TiO$_2$. The addition of a metal in low percentage is often proposed to enhance the photocatalytic efficiency of TiO$_2$. The Ag and Pd loaded (in different weight percentage) on TiO$_2$ nanoparticles are prepared by reduction with hydrazine hydrate followed by detailed characterization (XRD, Raman, TEM, UV-DRS, XPS, etc). The activity of metal-titania nanoparticles on the photodegradation of the odorous pollutant 2MBT is studied under solar light. Figure 7 shows the presence of metals when titania nanotubes are used as support.

Results show that the presence of metal on TiO$_2$ influences the photodegradation rate. In particular, the presence of Ag on titania significantly improves the degradation reaction of 2-MBT.

Part B comprises the application of surface modified nanosized titania as an effective catalyst support for the Pd (0). Suzuki coupling reactions of a wide range of materials...
substituted aromatic chloro, bromo and iodo compounds using the synthesized material are enlisted.

**Scheme 4.** Preparation method with visual image of the catalyst

![Scheme 4](image)

A facile route is adopted for Pd immobilization on the surface of amine terminated TiO$_2$ nanoparticles. XRD pattern showed the presence of crystalline Pd and anatase TiO$_2$. Metallic nature of Pd is confirmed by XPS and its weight percentage is determined by Atomic Absorption Spectroscopy (AAS). The morphology of the material is evaluated by TEM while FTIR spectroscopic analysis affirms the grafting of dopamine (DA) on titania. The catalysts are completely recoverable by decantation giving solvent specific solubility and the efficiency of the catalyst remains unaltered even after 3 repeated cycles.
Abstract

Scheme 5. Representative Suzuki cross coupling reaction

\[
\begin{align*}
\text{X} = \text{Cl, Br, I}
\end{align*}
\]

The TiO\textsubscript{2}-DA-Pd catalyst system shows remarkable possibility because of (1) the high surface area of the nano-sized catalyst; (2) free active sites of Pd nanoparticles in absence of protective ligands; (3) facile mass transfer because of the well-dispersed Pd nanoparticles; (4) ease of handling and separation; (5) reusability. Hence this study provides a future incentive for developing an efficient and cost effective catalyst system that can be exploited for industrial applications in the synthesis of various drug intermediates.

Chapter 6 presents the use of titania and modified titania based materials for biofunctional applications. The chapter is divided into two parts each dealing with specific application addressed.

Part A of the chapter deals with development of an antibacterial system. Metal nanoparticles (such as silver, copper and gold) are known to have antimicrobial properties. The nanoparticles supported in inorganic or polymeric matrix can offer high antibacterial activity, low toxicity, easy handling, chemical stability, selectivity, long lasting action period and thermal resistance versus organic antibacterial agents. Part A is a comparative study of metal loaded (Ag, Au and Cu) Titania as antibacterial system. The light-induced reduction-deposition of the metal nanoparticles from their corresponding salt has been performed on synthesized TiO\textsubscript{2} nanoparticles. The synthesized nanocomposite materials are characterized by XRD, Raman, TEM, UV-DRS and XPS. The antimicrobial activities of the synthesized Metal-TiO\textsubscript{2} (M-TiO\textsubscript{2}) nanocomposite materials are assayed under aerobic conditions. Microbial growth was
determined by the increase in (optical density at $\lambda = 600 \text{ nm}$) $\text{OD}_{600}$ after incubation of the samples at 37 °C for 6-8 hrs in nutrient broth. The lowest concentration that resulted in complete inhibition of bacterial growth was recorded as 100% minimal inhibitory concentration (MIC). The metal-titania nanocomposites showed almost complete killing of bacterial colonies for both the Gram positive and Gram negative bacteria. The bactericidal effect of the nanocomposites against *P. aeruginosa* and *S. aureus* was determined by plating suitably diluted aliquots of the culture upon exposure to different concentrations of the M-TiO$_2$ after specified time intervals on nutrient agar plates. The plates were incubated for 12-15 hrs at 37 °C for colony counting. All the M-TiO$_2$ samples showed appreciable antibacterial effect which is supported by the TEM image of the Cu-TiO$_2$ treated cells (Figure 9).

![Figure 9](image.png)

**Figure 9.** (a) TEM image of bacteria (*P. aeruginosa*) in presence of Cu-TiO$_2$ & (b) inhibition by Cu-TiO$_2$ particles.

**Part B** consists of Protein Separation using titania composite material. This Part deals with the synthesis, characterization and application of Au-TiO$_2$ nanocomposite. Au (0) nanoparticles are known to specifically bind to cysteine containing protein in a protein mixture and have earlier been reported as an effective tool to study their binding with cysteine containing proteins. Here we have deposited Au nanoparticles on nanocrystalline titania particles via photoreduction method. The presence of gold is confirmed by XRD, Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDAX) and Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-
OES) studies. The zero oxidation state is confirmed by XPS analysis (Figure 10a). The morphology and size of the support and active nanoparticle is observed by TEM images (Figure 10(b)). The optical property of Au as well as that of the support TiO$_2$ is studied by UV-DRS. The synthesized materials are tried for binding of cysteine containing proteins.

![Figure 10. The (a) XPS and (b) TEM image of Au-TiO$_2$](image)

The binding of protein has been ensured by UV-Vis spectroscopy by monitoring the decrease in OD$_{280}$ of the supernatant protein solution after incubated with the nanocomposites at 37 °C for specific time. The Au-TiO$_2$ nanocomposite materials show effective binding with cysteine containing proteins. The attachment was kinetically monitored and the maximum attachment was obtained only after 48 hrs. Finally the inferences from the complete study and the scope for future work have been included.