CHAPTER I

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This chapter deals with the overview of titanium dioxide (TiO$_2$) nanoparticles, TiO$_2$ films, TiO$_2$-polyoxometalate composite films and their photocatalytic behaviour on the degradation of dyes.

Research in nanoscience and technology is one of the most active research areas for diverse applications. Precise manipulation of matter at the nano level can accelerate the development of newer products with novel properties. Nanoscience comprises the use of nano scale materials in electronics, catalysis and biomedicine [1]. Nanostructured materials, with particle size less than 100 nm, possess special characteristic properties like structural (network symmetry, unit cell size), electronic (band gap, quantum size effect) and physicochemical (crystalline structure, particle size, surface area, chemical reactivity, stability). Metal oxides are playing an important role in the field of microelectronic circuits, sensors, piezoelectric devices and catalysts. The bulk state of the oxides usually leads to a robust and stable system with well-defined crystalline structures [2].

Semiconducting materials have been the subject of great interest due to their numerous practical applications, and they provide fundamental insight into the electronic processes involved. Semiconductor photocatalysis uses sunlight to activate nanoparticle catalysts to break-down the chemicals. Photocatalysis works on the principle that light falling on a semiconductor with an appropriate band gap, or energy difference between the conduction and the valance bands will create positive (holes) and negative (electrons) charge carriers, which in turn used to initiate reduction (electrons) and oxidation (holes) reactions at the catalyst surface. The positively charged holes and negatively charged
electrons tend to recombine to yield a neutral state. This can occur via volumetric and surface recombination. Nanostructured (20-30 nm) particles provide the optimal balance between these effects and are thus best suited to photocatalysis. An advantage obtained in nanoparticles is that the large surface to volume ratio makes possible the timely utilization of photogenerated carriers in interfacial processes [3, 4]. Titanium dioxide (TiO$_2$) is the widely investigated semiconductor metal oxide. It has got a wide range of applications in our day-to-day life. It is also called as titania, the naturally occurring oxide of titanium. It is present in three stable polymorphic states: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic).

![Crystal structures of rutile, anatase, and brookite](image)

TiO$_2$ powders of rutile and anatase forms are n-type semiconductors. Anatase is commonly used for photocatalysis owing to its higher photocatalytic activity. This higher photocatalytic activity is related to its lattice structure. Each titanium atom is coordinated to six oxygen atoms in anatase tetragonal unit cell. A significant degree of buckling is associated with O-Ti-O bonds in anatase as compared to rutile TiO$_2$ [5]. Titanium and oxygen atoms are more tightly packed in the rutile crystal. Each Ti$^{4+}$ ion is surrounded by...
an octahedron of six $O^{2-}$ ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distance in anatase is greater, whereas the Ti-O distance is shorter in rutile. In the rutile structure, each octahedron is in contact with 10 neighbour octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms); while in the anatase structure each octahedron is in contact with eight neighbours (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO$_2$. Anatase can be conceived as an arrangement of parallel octahedral, while in the case of rutile some octahedral are rotated by 90°. A symmetry change occurs during the conversion from anatase to rutile phase. As a consequence, the ionic mobility that occurs during phase transition results in increased densification and coarsening of the TiO$_2$ nanoparticles.

Rutile is the most stable phase for particles above 35 nm in size. Anatase is the most stable phase for nanoparticles below 11 nm. Brookite has been found to be the most stable for nanoparticles in the 11-35 nm range. All the three forms have different activities for photocatalytic reactions.

Rutile has three main crystal faces, two (110) and (100) are quite low in energy and are thus considered to be important for practical polycrystalline or powder materials, the most thermally stable phase is (110). It has rows of bridging oxygens (connected to just two Ti atoms), the corresponding Ti atoms are 6-coordinate. In contrast, there are rows of 5-coordinate Ti atoms running parallel to the rows of bridging oxygens and alternating with these. The exposed Ti atoms are low in electron density (Lewis acid sites). The (100) surface also has alternating rows of bridging oxygen and 5-coordinate Ti atoms, but these exist in a different geometric relationship with each other. The (001) face is thermally less
stable, restructuring above 475°C. There are double rows of bridging oxygen alternating with single rows of exposed Ti atoms, which are of the equatorial type rather than the axial type [6].

Anatase has two low energy surfaces (101) and (001), which are common for natural crystals. The (101) surface is thermodynamically low-energy which is the most prevalent face for anatase nanocrystals. This phase is corrugated with alternating rows of 5-coordinate Ti atoms and bridging oxygen, which are at the edges of the corrugations [7].

Titanium dioxide is applied in the photoelectrochemical field owing to its special properties like chemical stability, non-toxicity, biocompatibility, high dielectric constant, increased electrical conductivity and very high refractive index. Nanoscale TiO₂ may enhance the potential to synthesize materials with tailor-designed properties and functionalities for environmental applications. TiO₂ has the ability to turn super hydrophilic in the presence of sun light [8].

Photocatalysis is a spontaneous chemical reaction where light is required for the catalyst to function. A photocatalyst can transform the light energy into chemical energy by creating strong oxidative and reductive species which greatly enhance the rate of the spontaneous reaction; during transformation, the photocatalyst itself remains unchanged. The intrinsic photocatalytic properties of TiO₂ are directly related to its crystal phase, crystallite size, defect structures, structural properties (surface area, porosity, morphology) and pore size distribution. The photocatalytic process of TiO₂ is characterised by high reaction rates and short treatment times due to rapid oxidation reactions by hydroxyl radicals. Photocatalysts are heterogeneous catalysts usually in the form of a powder or a thin film [9, 10]. Photocatalysts have been used in ceramic tiles, glass, concrete, gypsum, roofing tiles, sealers, blends of cements (to create composites with self-cleaning), decontamination and anti-bacterial [11].
Mechanism of TiO$_2$ photocatalysis: The anatase form has a band gap energy of 3.2eV. When irradiated with light of equal or greater energy (i.e. a wavelength less than approximately 385 nm), electrons in the valence band (VB) of the TiO$_2$ semiconductor can be excited to the conduction band (CB) and leave a positively charged electron vacancy (hole) in the valence band [12]. As a result, free electrons ($e^{-}_{CB}$) and positively charged holes ($h^{+}_{VB}$), with strong reducing and oxidizing potentials are generated.

\[ TiO_2 + hv \rightarrow e^{-}_{CB} + h^{+}_{VB} \]

![Mechanism of TiO$_2$ photocatalysis](image)

Electron-hole recombination is likely to occur with the re-emission of a photon (light) or a phonon (heat). Conversely if the charge separation is maintained, the electrons and the holes migrate to the surface of the crystal they can take part in various oxidation or reduction reactions with molecules adsorbed to the surface of the catalyst, such as oxygen, water or organic species. Specially, $h^{+}_{VB}$ may react with surface-bound H$_2$O or OH to produce the hydroxyl radical and $e^{-}_{CB}$ is picked up by oxygen to generate superoxide radical anion (O$_2^-$);

formation of superoxide radical anion: $O_2 + e^{-}_{CB} \rightarrow O_2^-$

neutralization of OH$^-$ into OH by the hole: $(H_2O \leftrightarrow H^+ + OH^-) + h^{+}_{VB} \rightarrow OH + H^+$
The hydroxyl radical and the superoxide radical anions are the primary oxidising species in the photocatalytic oxidation processes resulting in the degradation of the pollutants. TiO₂ is stable in aqueous media and is tolerant of both acidic and alkaline solutions. It can also be synthesized in nanostructure forms more readily than many other catalysts. Furthermore, its band gap is appropriate to initiate a variety of organic reactions. The probability and rate of the charge transfer processes for electrons and holes depend on the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbed species. The three main factors in oxide semiconductor selection are band gap, band edge position and stability. Anatase has a larger optical band gap (3.2 eV) than rutile (3.0 eV) [13]. Rutile samples have a direct band gap as well as an indirect band gap, while anatase samples have an indirect band gap only [14].

The photocatalytic efficiency of TiO₂ is limited due to the high recombination ratio of photogenerated electrons (e⁻) and holes (h⁺) on the surface of TiO₂ under ultraviolet (UV) light irradiation and null photoresponse of TiO₂ under visible light irradiation, which severely limits on the development of solar photocatalysis for environmental applications.

The photocatalytic activity of TiO₂ could be enhanced by modification with different materials such as transition metals, non-metal atoms, semiconductors, polyoxometalates, and noble metals [15].

Polyoxometalates (POMs) are inorganic cluster-like complexes and constituted from oxide anion and transition metal cation. The most useful properties and applications of POMs have been based on acid-base chemistry that leads to a wealth of condensed anions and the redox chemistry that those anions undergo, frequently with very small structural distortion. The unique physical and chemical properties of POMs including molecular and electronic versatility, reactivity and stability make them ideal photocatalyst candidates. POMs share the general photochemical characteristics as that of the semiconductor
photocatalysts due to their similar electronic attribute. Suitable light energy excitation of the ligand to metal charge transfer band of POMs can be considered as a parallel process to the band gap excitation of TiO$_2$. The HOMO–LUMO gap (semiconductor band gap) of the Keggin unit is higher than that of TiO$_2$, and they must be photoactivated by the light energy with the excited wavelength lower than 260 nm [16]. A synergistic effect exists between POM and TiO$_2$ that can improve the efficiency of the catalysts. This effect originates from the interfacial electron transfer taking place from the conduction band of TiO$_2$ to POM after UV irradiation. Such effective electron transfer can inhibit fast electron-hole recommendation in TiO$_2$ and the tapped holes have sufficient time to react with H$_2$O to generate OH$^-$ radicals. The OH radicals oxidize dye which results in decolourization of the dye solution [17]. Consequently POM acts as homogeneous photocatalyst and TiO$_2$ acts as heterogeneous photocatalyst [18].

The ability to accept electrons giving rise to mixed-valence species is one of the most important properties of the structurally well-defined POM clusters [19]. The major drawback of POM photocatalytic system is the high solubility of the POM, which impedes the recovery and reuse of the catalysts. Incorporation of POM into the solid matrix is interesting because the support makes POM easily handled and recycled [20]. Powdery photocatalysts have high surface area and good activity but their separation after a water purification process is time consuming and poses problems. TiO$_2$ has been widely investigated either in the suspension or immobilized forms in the treatment of broad range of aqueous pollutants. The advantage of using the immobilising technique is that the material can be easily recycled. The stability of nanometer size particles is very often subjected to regeneration that is known to be very expensive and complicated procedure. Thin films on suitable substrates have shown good storage stability than the nanosized particles. The immobilization technique has become a
better option due to TiO$_2$ in slurry or suspension has to go through separation of dispersed TiO$_2$ particles after the treatment.

Titanium dioxide thin films have attracted a great deal of attention. They have many advanced functions in photocatalysis, sterilizing, solar energy cells, gas sensors and self-cleaning effect. Moreover, **TiO$_2$ film supported on a conductive material could exhibit interesting photoelectrochemical properties** [21]. All modern electronic devices rely on thin film technologies that allow the preparation of integrated circuits, where a huge number of transistors or other devices are prepared simultaneously on a single silicon wafer. **Thin films on suitable substrate show very good storability.** The porous TiO$_2$ film in anatase phase could accomplish the photocatalytic degradation of organic compounds under the radiation of UV. It has many application prospects in the field of environmental protection such as sterilization and sewage disposal [22]. A low-cost preparation and fixation of the TiO$_2$ photocatalyst with small sized particle is necessary for practical applications. Various deposition methods such as electron beam evaporation, ion sputtering, chemical vapour deposition and the sol-gel techniques have been utilised for obtaining TiO$_2$ thin films [23].

**Among the various methods in use for the production of porous as well as compact titanium oxide thin films, the electrodeposition appears to be a simple and low cost method.** The main advantage is the easy control of film thickness, morphology, composition through electrical quantities such as deposition current and applied potential. 

**Processes such as sol-gel and electrochemical deposition have emerged as alternative routes for the preparation of nanocrystalline TiO$_2$ thin films** [24].

The term “transparent conducting oxide” (TCO) refers to heavily doped oxide semiconductors that have a band gap sufficiently large (≥ 3 eV) to make them transparent over the visible spectral range and conductivity high enough such that they exhibit metal
like behaviour. Due to their high conductivities, the films show high reflectivity in the near infrared. The dominant TCOs which have found applications in wide areas of electronic and optoelectronic fields are tin oxide, indium oxide, indium tin oxide and zinc oxide. Indium tin oxide (ITO) is a well-known transparent conducting oxide (TCO). It is a highly degenerate n-type wide gap semiconductor that is produced by doping Sn atoms in In₂O₃ [25-27]. ITO films show an interesting and technologically important combination of properties such as high luminous transmittance, high infrared reflectance, good electrical conductivity, excellent substrate adherence, hardness, and chemical inertness [28]. Indium tin oxide is essentially formed by substitutional doping of In₂O₃ with Sn. Tin atoms preferentially occupy the less distorted lattice sites in the expanded In₂O₃ lattice [29]. The electrical characteristics of ITO films are dependent on the presence of oxygen vacancies and substitutional tin atoms. Since a compromise between electrical conductivity and optical transmittance is encountered for ITO film, a careful balance between the properties is required [30].

Synthetic dyes are used in colouring industries. They are important parts of industrial water effluent, as they are discharged in abundance by many manufacturing industries. Dye pollutants can have dramatic effects on the environment. The impact of these dyes on the environment is a major concern because of the potentially carcinogenic properties of these chemicals. Some dyes may undergo anaerobic decolouration to form potential carcinogens. Different approaches are handled to treat these coloured effluents before discharging them to various water bodies. Physical, chemical and biological unit operations are the treatment methods to remove suspended and floatable materials and to eliminate any pathogenic organisms. Classical techniques involved in the treatment processes are adsorption, coagulation, flotation and sedimentation. All these techniques
are versatile and useful, but they all end up in producing a secondary waste product which needs to be processed further.

The removal of azo dyes requires either the adsorption of the dye onto a material or chemical reactions. The application of these methods is limited due to high cost, poor degradation efficiency and secondary pollutant generation. A set of techniques which are relatively newer, more powerful, and very promising is called Advanced Oxidation Processes (AOPs) which has been developed and employed to treat dye-contaminated wastewater. This methodology would normally utilize a strong oxidizing species such as OH$^-$ radicals produced in situ, which causes a sequence of reactions thereafter to break down the macromolecules into smaller and less harmful substances. In many cases, the macromolecule is completely mineralized into water and carbon dioxide. The AOP technique has drawn considerable attention from various quarters of scientific community as it is easy to handle and produces significantly less residuals as compared to the classical approaches. The various techniques employed in the AOP approaches are UV photolytic, Fenton, photo-Fenton, ozonation, sonolysis and photocatalytic [31].

Based on the above details, it is inferred that POM supported on TiO$_2$ as composite material would exhibit better photocatalytic degradation of dyes. In this study, it is aimed

- To synthesis TiO$_2$ powder of nanosize by a simple sol-gel process and to test the photocatalytic activity against dye solution.

- To prepare TiO$_2$ film on a conductive support (ITO plate) by electrodeposition for the reuse in wastewater treatment in order to avoid problems related to solid catalyst residue in the conventional method.

- To prepare TiO$_2$-POM composite film (Molybdenum, Tungsten and Copper based) on a conductive ITO plate by the said electrodeposition method for improved photocatalytic efficiency.
References


