Chapter 1

Introduction
The delicate equilibrium in the energy-environment correlation needs close surveillance, perpetual consolidation and consistent effort for improvement. This chapter presents the brief background of the energy-environment relationship and the role of semiconducting photocatalytic materials in improving this. Initially the most viable renewable energy source has been kept in mind while identifying different strategies to use the same. Titania, one of the most well known photocatalyst with promises to have high influence on the future course of development of the renewable energy for mitigation of environmental problems, has been thoroughly explored. The rationale of the thesis was formed after reviewing the current literature on its synthesis and strategies adopted for the improvement of its activity in visible range. Subsequently on the basis of detailed characterization results and after proper understanding the current scenario of possibility of use of nanostructures for this, the motivation of the thesis has been defined. Finally, with the help of the current literature the aims and objectives of the work have been set and the outline of the thesis has been concluded.

1.1 Energy and environment

Energy is the lifeline of civilizations with their qualitative growth linked with quantitative increase in the energy supply availability. But direct relation of environmental degradation with the energy consumption has put the mankind into a paradoxical situation on its quest for better quality of life – Should it be driven by more supply of energy or physical environment conducive to quality growth of civilization? It appears that the only way out from this situation is to explore the technologies which help us in striking a balance between the two. Develop the technology around abundant energy resource and make sure that it does not affect the physical environment.
Since ages nature has its own pace of maintaining the delicate equilibrium between the various environmental components. For mankind the learning path for the need to maintain this equilibrium has been steady but may take longer than desirable. Overexploitation and contamination of fresh water resources is becoming a more pressing concern now. Among all current environmental problems, availability of clean drinking water is probably the hardest to approach scientifically and is expected to have the worst consequences in shorter term than the one driven by energy scarcity. If the energy outlook is worrying, problems related to water shortage are even bad. If the present trend continues, a major part of the globe will be water-stressed soon. According to Vorosmarty et al.[1] nearly 80% of the world’s population is already exposed to high levels of threat to water security (Figure 1.1).

![Global geography of incident threat to human water security][1]

Figure 1.1: Global geography of incident threat to human water security [1]

The need of large investment in clean water technology makes less developed countries vulnerable. One of the alternatives to recycle the available water using conventional power appears to be a short term solution. During this phase of transition the only solution is to use the abundant renewable energy resource available to the major inhabited parts of the globe and see the possibility of recycling the water at faster than the natural pace to ensure the net availability of clean water.
1.2 Solar Energy

But generally speaking renewable energy is the replenishable energy available from the nature at a matching pace. The global share of renewable energy consumption is less because of techno-economic reasons (Figure 1.2).

![Total World Energy Consumption, 2010](image)

**Figure 1.2:** Total world energy consumption[2]

However the reports suggest that the old renewables (biomass) are being replaced by new renewables (small hydro, modern biomass, wind, solar, geothermal and biofuels) at a faster rate than ever[2,4]. Among the new renewables both potential and growth of solar has been reported to be higher than others [2,4].

![Yearly sum of global irradiance](image)

**Figure 1.3:** The yearly global irradiation of the world
The solar energy received much attention due to the several favorable factors like availability and greenness. The average daily solar irradiation over the globe is 6 kWh/m², and over India it is 4 to 7 kWh/m². The total annual and daily solar irradiation over the globe and India, respectively, is shown in Figure 1.3 and 1.4. Its cumulative value over the land area is far more than the current total energy consumption of the world. The solar energy can be utilized mainly through three different conversion routes as shown in Figure 1.5. Also a careful observation shows that it is consistent with the fact that the water-scarce regions are solar-rich regions. Therefore, it is pertinent to develop suitable technologies which permit the use of solar energy to help solve energy and water problems simultaneously. Among the different solar energy conversion techniques, the challenge of addressing two problems with one technology may be met with the help of solar photocatalytic conversion. This technology can be used in host of energy and environmental applications.
1.3 Solar photocatalysis

It is the process in which a catalyst, normally a semiconductor, produces electron-hole pairs under the exposure of photons and these electron/hole pairs participate in chemical reactions. It is different from normal catalysts as the heterogeneous photocatalysts perform the dual function of initiator and accelerator of the chemical reaction as a catalyst. Its reusability makes it a potent sustainable technology capable to address both energy and environmental issues. The mechanism of a semiconductor photocatalysis is shown in figure 1.6. When a photon is incident on a semiconducting material electrons are generated and excited from the
valence band to the conduction band which results in the formation of holes in the valence band. If the band edges are suitably placed the excited electrons react with oxygen in the atmosphere forming superoxide anions ($O_2^{-}$), and the holes react with moisture in the atmosphere producing hydroxyl radicals (OH•) [5]. These active hydroxyl species are extremely reactive, are capable of and reducing and decomposing organic substances (Figure 1.6).

![Figure 1.6: Mechanism of solar photocatalysis](image)

**1.4 Solar photocatalytic materials and applications**

1.4.1 Selection of the photocatalytic materials

According to semiconductor photochemistry, the role of photocatalysis is to initiate or accelerate any specific reduction and oxidation (redox) in the presence of irradiated semiconductors. The generation of electron-hole pairs in semiconductor takes place when the energy of the incident photons matches or exceeds the band gap value [5–8]. In the case of semiconductors, if the conduction band (CB) electrons ($e_{cb}^{-}$) have a chemical potential of +0.5 to −1.5 V with respect to the normal hydrogen electrode (NHE) then they can act as reductants. The valence-band (VB) holes ($h_{vb}^{+}$)
have a strong oxidative potential of +1.0 to +3.5 V with respect to NHE [5]. That means for a semiconductor in order to be photo-chemically active as a photocatalyst the redox potential of the photo-generated valance band hole must be sufficiently positive to generate OH• radicals, which can then oxidize the organic pollutants. The redox potential of the photo-generated conductance band electron must be sufficiently negative to be able to reduce the adsorbed O₂ to superoxide [9]. The chemical potential of different semiconductors with respect to the NHE is shown in Figure 1.7.

![Figure 1.7: Different semiconducting materials with their redox potential value with respect to NHE [11]](image-url)

For H₂ production to occur, CB bottom-edge must be more negative than the reduction potential of H⁺ to H₂ (E_{H⁺/H₂} = 0 V vs NHE at pH=0), while the VB top-edge should be more positive than the oxidation potential of H₂O to O₂ (E_{O₂/H₂O}=1.23 V vs NHE at pH=0) for O₂ formation from water to occur [10]. So the selection of semiconductors is very important in accordance with the different applications. TiO₂, ZnO, WO₃, CdS, ZnS, SrTiO₃, SnO₂, WSe₂, and Fe₂O₃ can be used as the photocatalysts. Figure 1.7 gives the band gap and redox potential of the H₂/H₂O and H₂O/O₂ couples. Also the stability, photo corrosion, and availability, has to be taken care of [8]. Many high activity semiconductor photocatalysts have been proposed.
which can be used for both energy production and environmental treatments. But among different semiconductor photocatalysts studied till date titania still remains the best catalyst due to its stability, inertness, corrosion-resistance, non-toxicity, abundance and low cost after the important discovery of titania based heterogeneous photocatalysis by Fujishima and Honda in 1972[5, 12-13].

1.4.2 Applications of the semiconducting photocatalytic materials

After going through the trend of research the commercially potential applications of semiconductor photocatalysis emerge as self-cleaning surfaces, air purification and deodorization, water purification, hydrogen production, buildings cooling, corrosion protection and medical applications [14]. Many of these materials are used in new generation photovoltaics [15]. Hence the major applications of the photocatalysts can be classified under i) detoxification, ii) disinfection, iii) Hydrogen production, iii) photovoltaics.

1.4.2.1 Detoxification

Since the discovery of semiconductor photocatalysis by Fujishima and Honda tremendous research is going on to improve the photocatalytic performance as well as to find different areas for environmental application. The photocatalysis finds lots of applications in this area due to the widespread applicability and greenness of the technique. The major applications are color removal [14-17]; COD(chemical oxygen demand) reduction [18,19]; mineralization of hazardous organics[20-22]; destruction of hazardous inorganic such as cyanides [23]; treatment of heavy metals [24]; degradation of harmful fungicides, herbicides, and pesticides [25]; destruction of malodorous compounds [26] ; decontamination of soil [27] ; and decontamination of indoor air [28].

1.4.2.2 Disinfection

The photocatalysis can be effectively used for killing bacteria, fungi, prions and cancer cells using photocatalytic reaction with titanium dioxide. There are many circumstances, where removing or killing microorganisms in water, air and on surfaces is necessary or desirable. For example, water disinfection requires deactivation of pathogenic organisms. The potential use of titanium dioxide
nanoparticles in daily life and in development of new self-cleaning and antimicrobial surfaces and paints. The semiconducting photocatalyst finds many applications in this area and the reported applications are destruction of cancer cells [29]; bacterial inactivation [30]; virus inactivation [31]; and algal inactivation [32].

1.4.2.3 Hydrogen Production

Presently hydrogen production is mainly done by using non-renewable resources (e.g., fossil fuels) or the high-energy consumption process, and these process are neither environmental friendly nor economical. Therefore, there is a great interest in the development of sustainable and economic methods for the production of hydrogen. Since the first report by Fujishima and Honda on the photoelectrochemical water splitting on a TiO$_2$ electrode, the photocatalytic water splitting has emerged as a promising way for a clean, low-cost, and environmentally friendly production of hydrogen by using solar energy [33-34].

1.4.2.4 Photovoltaics

Many researchers reported the use of photocatalyst materials as a photo-anode in photo-electrochemical cells. One-dimensional (1D) nanostructures of TiO$_2$ grown directly on transparent, conductive glass substrate using hydrothermal/solvothermal methods have been reported for this [15]. The new generation solar cells have also use TiO$_2$ in their architecture.

1.5 Strategies for functional improvement of the titania photocatalyst

Titania has three crystalline phases anatase, rutile and brookite with varying energy band gap (3.2 eV for anatase and brookite, 3.0 eV for rutile) and thermodynamic stability. The most stable form of TiO$_2$ is rutile. At higher temperature the metastable anatase and brookite get transformed to the thermodynamically stable rutile at the calcination temperature exceeding ~600 °C [35]. Titanium dioxide generally is an n-type semiconductor due to oxygen deficiency [36]. As stated earlier TiO$_2$ is the most widely investigated photocatalyst due to its high photoactivity, low cost, low toxicity, and good chemical and thermal stability [37]. In the last few years there have been several exciting breakthroughs with respect
to titanium dioxide. Various strategies have been employed for the improvement of the photocatalytic performance of TiO$_2$ and some of them are shown in Figure 1.8.

![Diagram of various strategies for the functional improvement of TiO$_2$ photocatalytic activity](image)

**Figure 1.8:** Various reported strategies for the functional improvement of TiO$_2$ photocatalytic activity

They can be summarized as morphological modifications such as increasing surface area and porosity and as chemical modifications such as deposition/incorporation of additional chemical components on TiO$_2$ in the TiO$_2$ matrix. Due to large band gap, high carrier recombination and low surface area, the pristine TiO$_2$ photocatalyst showed limited photoactivity.

### 1.5.1 Development of multiphases/phase complexes

Numerous research efforts have been made to develop coupled semiconductors like Bi$_2$S$_3$/TiO$_2$, ZnO/TiO$_2$ and CdS/TiO$_2$. The resultant complex materials considerably enhance the photocatalytic efficiency by reducing the photogenerated electron-hole pair recombination rate. They have applications in hydrogen production, detoxification, disinfection and photovoltaic devices. These complex composites are also considered as the key materials in developing high efficiency photocatalysts under visible light. It can also deal with the problems of the individual
components, and stimulate a synergistic effect in efficient charge separation and improvement of photo-stability [38]. The trend of scientific publications in the area of multiphases/phase complexes [40] is shown in the Figure 1.9.

The studies on influence of phase and phase composition on the photocatalytic activity has produced contrasting results. Different works reported show that anatase works better than rutile and some authors reported the best results for rutile. Many experimental results support the existence of a synergistic effect in the bicrystalline titania containing anatase-rutile, anatase-brookite, rutile-brookite, or tricrystalline anatase rutile brookite in enhancing the photocatalytic activity[39].

Figure 1.9: Shows the number of papers published in scientific journals in the area of metal/phase complex and doping of titania for photocatalysis from January 1999 to November 2012 (Search done through ISI, Web of Science)[40]

The composites of different semiconductors has received a great attention for the development of highly active photocatalysts due to its better charge separation, bicrystals and tricrystals of heterogeneous titania nanostructures are interesting since they involve only a change in the crystal structure of the same material. Two distinct mechanisms on the interfacial charge transfer process in the bicrystal of anatase and rutile were proposed by Bickley et al.[41] and Hurum et al[42]. The reports related to the phase complexes are contradicting and the exact mechanism is still under debate.
1.5.2 Doping

Due to wide band gap of this catalyst, it is active only in the UV region. As shown in solar radiation spectrum (Figure 1.10). As per the radiation data only 5% of terrestrial solar flux lies in UV region, 43 % is in visible and the remaining 52% is in infrared range. Thus the utilization of natural solar light for a photocatalytic process needs to be enhanced by engineering the band gap so as to extend the response of titania to the visible region. Designing, fabricating, and tailoring the physico-chemical and optical properties of titania is essential to utilize a major fraction of the solar spectrum. With respect to the above, the modification of the TiO$_2$ has been reported by various techniques like coupling with a narrow band gap semiconductor, metal ion/nonmetal ion doping, co-doping with two or more foreign ions, surface sensitization by organic dyes or metal complexes, surface fluorination, which exerts a substantial influence modifying the electronic band structure and construction of favorable surface structure resulting in higher quantum efficiency and reaction rates for the degradation of organic pollutants under UV/solar light illumination.

Figure 1.10: Solar radiation spectrum[42]
Doping with transition metals like Cr, Co, V and Fe can result in extending the spectral response of TiO₂ well into the visible region and also in improving photocatalytic activity [44]. However, these dopants may also act as recombination sites. Another techniques involves modifying titania with transition metal like Fe, Cu, Co, Ni, Cr, V, Mn, Mo, Nb, W, Ru, Pt and Au [45-47]. The incorporation of transition metals in the titania matrix may result in the creation of new energy levels in the band gap region which may induce a red-shift in the absorption spectrum towards the visible light region. In these cases photocatalytic activity generally depends on the type of the dopant and the level of doping agent. The possible limitations of metal doping are photo-corrosion and supported charge recombination at metal sites [48]. As one of the typical transition metals, V has been frequently investigated because it can lead to conspicuous absorption in the visible region [46-47, 50-53].

Non-metal doping of TiO₂ has been attempted to induce visible light activity in photocatalysts, and nitrogen is one of the most promising dopant [54, 55]. Nitrogen can be easily incorporated in the TiO₂ matrix, because of its comparable atomic size with oxygen, small ionization energy and high stability. The N-TiO₂ has been prepared in anatase and anatase-rutile mixed phase by tuning the parameters of the sol-gel synthesis. The mixed phase hetero-junction photocatalysts have been reported to be more effective in transfer of photo-excited electrons from the conduction band of anatase to that of rutile, favoring electron-hole separation under visible light irradiation as well [56]. Other potent non-metals dopants like carbon, phosphorous and sulphur have also been successfully used for enhancing the visible light activity in TiO₂. The non-metal dopants effectively narrow the band gap of TiO₂. The alteration in the lattice parameters, and the presence of trap states within the conduction and valence bands from electronic perturbations, give rise to band gap narrowing. Thus these non-metal dopants not only allow for visible light absorption but also the presence of trap sites within the TiO₂ bands which increases the lifetime of photo-generated charge carriers[38]. Also N-F co-doped TiO₂ has been investigated in visible light photocatalysis due to the similar structural inclinations of the two dopants. In addition, the collective structure preserves the advantages of N-doping in high visible light response while the F-doping plays important role in
charge-carrier separation[38]. The trend of scientific contribution towards doped-titania research [40] is shown in the Figure 1.9.

1.5.3 Sensitization

Sensitization of TiO$_2$ with noble metals like Ag, Au, Pt and Pd has been shown to enhance and extend the photocatalytic activity of titania in visible range by acting as an electron trap, consequently, facilitating interfacial charge transfer through resultant delay in recombination of the electron-hole pair [38, 57]. Seery et al., reported improved visible light photocatalysis with Ag modified TiO$_2$ [57]. Gunawan et al. reported an opposite effect in which reduced silver deposited on a TiO$_2$ support resulted in excitation and reverse electron flow from silver to the TiO$_2$ support, when exposed to visible light (> 450 nm), oxidizing silver ($\text{Ag}^0 \rightarrow \text{Ag}^+$) in the process [38]. The visible light responsiveness of TiO$_2$ was accredited to the surface plasmon resonance of silver nanoparticles [59].

To extend the photo-response of TiO$_2$ into the visible region, dye-photo-sensitization has been reported as one of the most effective way by different groups. The excited dye molecule later transfers electrons into the conduction band of TiO$_2$, while the dye itself is converted to its cationic radical. The TiO$_2$ acts only as a third party for transferring electrons from the sensitizer to the substrate on the TiO$_2$ surface.
as electron acceptors, and the valence band of TiO\textsubscript{2} remains unaffected. In this process, the lowest unoccupied molecular orbital (LUMO) of the dye molecules should be more negative than the conduction band of TiO\textsubscript{2}. The electrons transferred to the CB of titania are scavenged by molecular oxygen to form superoxide radical O\textsubscript{2}\textsuperscript{-} and hydrogen peroxide radical OH\textsuperscript{·} [38, 60]. The trend of scientific publications in the area of sensitization of titania [40] is shown in the Figure 1.11.

1.5.4 Templating

Photocatalysis is basically a type of system engineering dealing with a series of sub-tasks involving optoelectronic conversion, surface/interface catalysis and sorption of reactants/products. The photocatalytic materials with hierarchical composite nanostructures have inherent design features which can influence all the sub-tasks. The idea to develop a single composition/structure capable to perform all the sub-tasks optimally is far-fetched. A number of reports on development of semiconductor metal or semiconductor-semiconductor composite hierarchical nanostructures in order to facilitate charge rectification and to improve carrier separation in semiconductor photocatalysts, are available [61-63]. Biological materials found in nature provide many examples with complicated, optimized, and efficient hierarchical morphologies and a large variety of porous structures from nanometer to macroscopic scale. They have been found to exhibit superior performance and efficiency in chemical and physical processes [64]. Biomimetic synthesis of material offers a new promising method to develop morphologies which may play important role in efficiency improvements. Biological resources have basic structure made of highly ordered functional units which may be used as biological templates. Through replication of such templates biostructures of inorganic materials of low dimensionalities can be fabricated with high reproducibility and low-cost [65]. Figure. 1.11 shows the recent trend of scientific publications in the area of templating of titania.

1.6. Solar photocatalytic reactor

Several types of solar photocatalytic reactors design and performance have been reported. The results are available as some review paper[65]. The major reported
types of solar photo-reactors are Parabolic Trough Reactors, Compound Parabolic Collector (CPC), Inclined Plate Collectors (IPC), Double-Skin Sheet Photo-reactor (DSS), Rotating Disk Reactors (RDR), Water Bell Reactors (WBR), Optical Fiber Photo-reactors (OF) and Fixed and Fluidized Bed Photo-reactors (FFB). Among them, those based on CPC technology are currently most suited for operation at pilot scale and beyond. Significant knowledge and experience in the design and operation of photocatalytic systems using CPC photo-reactors already exist from studies in photocatalysis, making the design and scale-up of a plant based on this technology relatively straightforward. The current performance of CPC photo-reactors is similar to, or marginally greater than, most other photo-reactor designs, and they are suited for use with supported catalysts [67]. A number of research institutions have chosen CPC photo-reactors as the basis for their pilot-plants [66]. IPC photo-reactors have been reported to be an efficient photo-reactor design for small scale treatment because of their low flow rates. But they have simple design, low capital cost and may be installed at almost any location [68]. DSS photo-reactors can also performance identical to that of CPC photo-reactors at low capital cost but have not been rigorously tested at pilot-scale which has left many issues unresolved. The work of Dillert et al. [69] is not supported by other studies and there is wide variation in the efficiency of such systems. The other complex designs such as RDR, water bell,
and fiber optic photo-reactor designs are less likely to see light of the day because of additional difficulties in material handling, environmental problems and efficiency issues. Suitability of fiber-optic photo-reactor design in a number of specialized application has been reported where the photon collector the target are separated. The fluidized/fixed bed photo-reactors described by Pozzo et al.[70] appear to be an optimal method of photocatalyst handling and high quantum efficiencies. But efficient utilization of solar radiation in fluidized bed is a challenge. Once this and other issues, e.g. optimum particle size and photocatalyst attachment methods, are addressed, the fluidized bed photo-reactor may prove to be a highly effective, especially for photoreactions involving gas streams such as CO₂ reformation reactions. The design development and testing of CPC reactors in the light of new developments and under different weather conditions also remains an issue which needs attention of researchers. The trend of scientific publications contributing to solar photocatalytic reactors is shown in the Figure 1.12.

1.7 Origin of the present work and objectives

A number of reports are available with conflicting and inconsistent claims about the activity of the phases. It is not surprising because a heterogeneous photocatalysis system represents a complex interaction of catalyst and reactant phases under irradiation. The catalyst may exist in pristine or mixed phase. The current issues in the literature may be attributed to this. A quest to resolve this issue forms the primary objective of the thesis. It has been approached through the changes in the reaction kinetics attributable to carrier recombination, particle size and absorption spectrum of phases. But different titania phases, pristine or mixed, show activity mainly under UV irradiation while a major part of solar radiation is in visible range.

To extend the absorption range to visible spectrum researchers have employed a number of techniques such as doping(anionic/cationic), co-doping, making metal oxide complexes, and grain size control. A number of the titania based visible active systems have been reported. The present work attempts to handle this issue in the light of the conclusions of the work on different phases of titania. This forms the second major objective of the
thesis. It may be noted that the absorption of the catalyst in visible range doesn’t ensure the high visible light photoactivity due to charge carrier recombination and specific surface area issues.

Recombination of carriers may be reduced by utilizing techniques such as noble metal/dye sensitization, making metal oxide complexes, and phase complexes. One or more of these options may be implemented like i) doping along with sensitization, ii) metal oxide complex with sensitization, and iii) metal oxide and phase complex along with sensitization. It is desirable here to use a technique which ensures stability, low energy intensity and simplicity of implementation. It is obvious that incorporation of any foreign atom to any metal oxide will reduce the total specific surface area of the metal oxide. It requires optimization of the level of incorporation of foreign atom. While this is one of the objectives of the thesis it has to keep in mind the issues of radiation absorption, titania phase composition are all intertwined with this.

Increasing the specific surface area of the photocatalyst has always offered technical challenges and provided positive results. For this many researchers have exploited different techniques such as using high surface area substrate, preparing mesoporous materials, templating and synthesizing nano-sized catalysts. Throughout the present report endeavors to achieve this by keeping surface area as high as possible as well as the size of the catalyst as small as possible. But conventional sol-gel technique has its own limitation. It is needed to explore some novel technique to achieve this objective. It should be noted that the use of efficient solar photocatalyst without an efficient solar reactor system will result in poor overall efficiency.

For diverse applications of solar photocatalysis different researchers have proposed different reactor systems. Among them solar compound parabolic reactor (CPR) appears to be the best option for field operation. This report attempts to test the photocatalysts on a reactor designed for the purpose.
The present thesis attempt to sort out the above mentioned problems. The main aim of the thesis is to prepare a highly visible active photocatalyst for solar energy applications. However the specific objectives are:

i) To Synthesize and investigate the dependence of photoactivity of titania with different anatase/rutile phase ratio

ii) To study the impact of metal doping on the photocatalytic activity of pristine and mixed phase titania

iii) To study the impact of silver sensitization on the photocatalytic activity of mixed phase metal doped titania

iv) To attempt to develop the titania photocatalyst with hierarchical superstructure through bio-templating using non-hydrolytic synthesis route and test its performance.

v) To design, fabricate and evaluate the performance of solar photocatalytic detoxification reactor for industrial effluent.

1.8 Summary of the thesis

The thesis consist of seven chapters and two appendices based upon the above mentioned issues in detain are outlined here.

Chapter 2: This chapter reports the detailed investigation on different phases of titania. It includes synthesis of a set of anatase, rutile and mixed phase (anatase+rutile) titania nanomaterials through simple sol-gel technique. The physico-chemical characterization results of the samples with the detailed analysis have been presented to understand the material. The photocatalytic activity of samples was assessed under both UV and visible radiation flux using an aqueous pollutant probe. The study carried out on a series of mixed phase titania with varying ratio of anatase-rutile phases (A/R ratio) including the pristine phases helped the present work in correlating the A/R ratio with their unique photocatalytic response to UV and visible radiation. The mixed phases show high activity across the wavelength range. This unique result helped in formulating a model reported herein as “Interface model”. The model is reasonably successful in explaining high activity of mixed phases including the large difference in optimum A/R ratio
for the photocatalysts under UV and visible light irradiation wavelength ranges.

**Chapter 3:** Any phase of titania (pristine anatase, pristine rutile, mixed phase) may be engineered using a range of techniques to make it active in visible range. However the present chapter explores the activity of different phases in the light of the earlier conclusion regarding the mixed phase. For this the visible active anatase, rutile and mixed phase titania photocatalyst were synthesized by doping a suitable metal through an intermediate step in sol-gel technique. Characterization and the photocatalytic performance determination of these metal doped titania phases was done. Both disinfection and detoxification activities were compared under visible irradiation using suitable probe pollutant and bacterium, respectively.

A consistent superior photocatalytic detoxification and disinfection activity of metal doped mixed phase titania catalyst compared to metal doped pristine titania samples was observed. This chapter also fills a gap in literature by defining a new performance parameter *microbicidal photonic efficiency*(MPE) to facilitate quantification of the performance of the photocatalyst and the disinfection system by taking into account the response of the catalyst to the radiation intensity.

**Chapter 4:** Even the most suitable photocatalyst have been reported to show poor activity attributable to recombination of a large amount of photo-generated charges. They need to be separated by providing a suitable scavenging or separation mechanism. Sensitization by a noble metal on titania has shown encouraging result. The present chapter presents the results of an investigation on impact of sensitization on the photoactivity of visible active doped titania phases synthesized in the present study. The probes used for detoxification and disinfection studies were the same as reported earlier.

The sensitization of noble metal on mixed phase metal doped titania resulted in enhancement in the photoactivity compared to an identically synthesized metal doped mixed phase titania sample. Thus Ag assisted charge separation complements the high activity of the photocatalyst.
Chapter 5: This chapter reports a successful attempt to synthesize nanostructured titania micro-fibers using non-hydrolytic sol-gel technique using cotton as both oxygen donor and template. Reasonable success was achieved in synthesizing a high surface area pristine anatase titania with small mesoporosity showing very high UV photoactivity compared to Degussa P-25.

This enhancement in the photoactivity is ascribed to the small particle size, high specific surface area, and the effect of templating. However, high stability of the resultant catalyst phase, even at very high temperatures, rendered it difficult to get mixed or rutile phase titania having small and acceptable grain size. Significant drop in the surface area made it impossible to derive any conclusion vis-a-vis mixed phase titania based templating and non-hydrolytic process.

Chapter 6: Testing of the catalyst in a prototype reactor system is considered necessary to simulate its employability and predict its performance in the field conditions. This chapter presents the details of the design of components and materials used in a compound parabolic reactor (CPR) constructed with an aim to use the photocatalyst for solar photocatalytic applications. The CPR has been engineered to exploit both UV and visible part of the solar irradiation. The performance of the CPR has been demonstrated in terms of degradation of a probe pollutant. The system performances have been reported in terms of rate constant, residence time and photonic efficiency. An attempt has been made to assess its performance in different ranges of solar spectrum. This finding may result in the development of an efficient commercial CPR.

Chapter 7: This chapter concludes about the strengths and discusses about the scope of improvement in different aspects of the proposed photocatalytic systems for different applications using entire range of solar radiation spectrum. The prospects and limitations of phase composition, sensitization, and templating have been discussed. Finally, the future scope of the present work in the possible energy applications has been discussed.
Appendix A:

A study on the effect of the modification of the electrode system using the titania developed in the present work in a dye-sensitized solar cell has been presented.

Appendix B:

This appendix presents the primary attempt to develop photoactive material through non-hydrolytic templating technique and may be considered as a prelude to the work reported in Chapter 5.
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