Abstract

Mixed phase titania based visible active photocatalyst for solar energy applications

Energy is the lifeline of civilizations with their qualitative growth defined by the quantitative increase in the energy supply. 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. Physical environment may be understood in the wider connotation of this term as it includes air, water, soil and other social capitals as essential components.

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. Water, one of the components, is the medium for a number of physico-chemical process occurring inside the human body and is a basic requirement for maintaining the quality of life. In fact the contamination of atmospheric air and soil also influence the level of water contamination with a small phase lag. 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. During this phase of transition the only solution is to shift
towards the abundant renewable energy resource available to the major inhabited parts of the globe in the form of solar energy to recycle the clean surface water. Also it is consistent with the fact that the water-scarce regions are solar-rich regions. Therefore, as solar energy has the highest potential of all the renewable, suitable technologies must be developed to permit the use of solar energy to simultaneously help solve energy and water problems.

This challenge of addressing two problems with one technology may be met with the help of an important discovery of titania based heterogeneous photocatalysis by Fujishima and Honda in 1972. This technology can be used in host of energy and environmental applications. The possibility to use solar energy makes it all important consequently, after this discovery a number of high activity semiconductor photocatalyst have been proposed which can be used for both energy production and environmental treatments. But among different semiconductor photocatalyst studied till date titania still remains the best catalyst due to its stability, inertness, easy availability and environmental-friendly nature. The main drawbacks of titania photocatalyst are high charge carrier recombination, small absorption wavelength band limited to UV region, and low specific surface area. It may be noted here that the favorable band-edge positions, and availability of multiple phases of titania provide additional opportunities as a photocatalyst.

Titania has three phases anatase, rutile and brookite. 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 be kept in mind that the issues of radiation absorption and 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 work, present in this 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 and the most popular 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. This report attempts to test the photocatalysts on a reactor designed for the purpose.

Chapter I: It introduces the theme of the thesis including information about the mechanism of photocatalysis, type of photocatalysts, and the methods of their synthesis and characterization. A detailed literature survey has been done with regard to different phases of titania photocatalyst, schemes to make them visible active, methods to sensitize them to have selective affinity towards different photogenerated particles, and techniques to restrict the grain size to have high specific surface area. In addition to these a survey of different types of solar reactors has also been done with a view to provide rationale of the work and to set the objectives of the thesis.

Chapter II: 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 III: 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 photocatalysts 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 IV: Even the most suitable photocatalysts have been reported to show poor activity attributable to recombination of a large amount of photogenerated 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 V: 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 VI: 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 was made to assess its performance in different ranges of solar spectrum. This finding may result in the development of an efficient commercial CPR.

Chapter VII: 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.