Summary and Conclusions

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8.1 Summary

Catalysis is a phenomenon which enhances the rate of reaction by a substance without itself undergoing any change after the completion of the reaction. The substance behind the process is called catalyst. Photocatalysis is the process in which the catalytic reaction is activated by absorption of light energy by the catalyst. Semiconductor materials become a very good photocatalyst based on its bandgap. Among the various semiconductor materials, titania becomes the prominent one. The high photocatalytic efficiency, eco friendliness, chemical inertness, low cost of preparation, thermal stability etc are the advantages of titania compared to others. In photocatalytic process, titania catalyst absorb light energy and create photo excited species such as holes and electrons in valence band and conduction band respectively. These photo excited species are very good oxidants and reductants (i.e., act as redox system) and also they create more powerful oxidant and reductant by reaction with adsorbed water, hydroxyl and oxygen species, which help for the degradation of adsorbed species on their surfaces.

Band gap, surface area, crystallite size, morphology, phase purity, method of preparation etc are other of the factors which affect the activity of photocatalyst. Titania exists mainly in three crystallite phases such as anatase, rutile and brookite. Among which anatase phase exhibits better photocatalytic activity than others with band gap of 3.2 eV. Even though titania is a very good photocatalyst, its activity is limited to UV irradiation based on its band gap. In order to bring its activity in visible region, we modify the titania by doping non-metals such as nitrogen and co-doping with nitrogen and sulphur. The prepared catalysts are characterized by various techniques such as XRD, UV-Visible DRS, Surface area, SEM, TEM, XPS, Raman and TG analysis and the results are correlated to their activities.
One of the major applications of this technology is the degradation of organic pollutants in water and air streams which is considered as one of the so-called advance oxidation processes (AOP). In AOP methods the driving material for the degradation of pollutants is the powerful oxidizing agent such as hydroxyl radical obtained by the oxidation of photo excited holes with adsorbed water or surface hydroxyl groups on titania materials. This research work includes degradation of some selected dyes such as crystal violet, rhodamine B, methylene blue and acid red1 and pesticides such 2,4-D, 2,4,5-T, aldicarb and monolinuron etc in aqueous media which produces harmful effects on aquatic life. The research also contributes the antibacterial study of E-coli and the generation of hydrogen through photocatalytic splitting of water.

8.2 Conclusions

Chapter 1 This chapter contains a general introduction about photocatalysis by semiconductors. This includes a brief history of catalysis, photocatalysis, and the mechanism behind the photocatalysis. It also explains the importance of titania as photocatalyst with its structure, different methods of preparation, advantages, drawback etc. The advantages and limitations of sol-gel method are described briefly. The necessity for modification and different methods available for the modification with its merits and demerits are also highlighted. An outline of present research work was also incorporated.

Chapter 2 This chapter contains a detailed description about the experimental conditions, chemicals and technologies used for the preparation of catalysts with its notation using sol-gel method. We also discussed the theory and experimental basis behind various techniques adopted for the characterisation of prepared catalysts such as XRD, UV-Visible DRS, SEM-EDX, TEM, XPS, Elemental analysis,
Raman spectra, TG etc. The instrument with its specification and the experimental set up for the measure of photocatalytic activity are well discussed.

**Chapter 3** We have successfully synthesized pure titania, nitrogen doped titania and nitrogen, sulphur co-doped titania through sol-gel methods using titanium tetraisopropoxide, urea and thiourea as the main chemicals. The phase purity and the crystalline nature of the prepared catalysts are obtained from XRD analysis. All the prepared catalysts give purely anatase phase. It is also confirmed by HRTEM, SAED and Raman analysis. The crystallite size calculated using Scherrer equation from the XRD data. It gives very good correlation of particle size obtained from TEM. Particle size histogram showed that they are in nano scale with average size of 8-13 nm. The band gap reductions of the modified catalysts are calculated from UV-Vis.DRS spectrum. The visible light absorption of the modified catalysts is correlated to their bandgap. The presence of dopant impurities such as nitrogen and sulphur are qualitatively confirmed from the C, H, N, S elemental analysis and EDX analysis. The physical colour change of the modified catalyst also reinforces the presence of the dopant impurities in the modified catalysts. The chemical composition and oxidation states of elements are obtained from XPS analysis. Surface area is measured using BET method. The surface morphologies of the catalysts are obtained from SEM and TEM images, which show spherical and rectangular particles. HRTEM and SAED images showed particles to be crystalline and highly ordered in nature. Finally the thermal stability of the samples are confirmed from the TG analysis and the calcination temperature of catalysts are fixed to 400 °C.
**Chapter 4** This chapter is mainly discussing the photocatalytic degradation of dyes materials in aqueous solution using visible light irradiation. We have reported the efficiency of the modified catalyst with high percent photocatalytic degradation of dyes such as Crystal violet, Rhodamine B, Methylene blue and Acid red1. The optimum catalyst amount for this study is 3 g/L. The synergetic effect of the dopants N and S confirms the better activity of NS-TiO$_2$ compared to others in visible light. Around 75% of dyes are degraded with visible light irradiation of one hour. The effect of catalyst amount, effect of time, effect light sources and effect of dopant concentration are successfully explained. Thus the application of modified titania photocatalyst proves better efficiency in the degradation of dyes using visible light irradiation which is correlated to its bandgap.

**Chapter 5** In this chapter we are discussing the photocatalytic degradation of few organic pollutants (collectively called pesticides) in aqueous medium. Compounds such 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, aldicarb and monolinuron are selected and their photocatalytic degradation using the modified and pure titania are studied well. More than 80% of all the pollutants are photocatalytically degraded using modified catalyst with a visible light irradiation with time less than one hour. Factors affecting photocatalytic degradation such as catalyst amount, irradiation time, light source, dopant concentration, lamp power and reusability of the catalysts are well studied and discussed successfully. The photocatalytic activity of the catalyst also tested for reusability. The high correlation between the activity and lamp power also observed. The phase purity, smaller particle size, high surface area etc contribute to higher activity.
Chapter 6 In this chapter we discuss the brief history about the hydrogen production through photocatalytic water splitting reaction. This includes the different materials and technologies for the production of hydrogen, the general mechanism behind the photocatalytic water splitting reaction on semiconductor materials. The advantages of titania as photocatalyst with its drawbacks and modifications are also discussed. The results indicated that 0.1 g of NS-TiO₂ catalyst gives a good yield of hydrogen with visible light irradiation of 4 hours when compared with the same quantity and time of irradiation of others catalysts. The higher surface area, high purity anatase crystalline nature, small band gap etc. contributes the higher activity of the modified catalysts.

Chapter 7 One of the major advantageous of photo catalytic disinfection is that it completely ensures the deactivation of bacteria and inhibits its re-emergence. This has a crucial role in commercial application of disinfection process. Thus the application of photocatalytic process is an effective substitute for normal disinfection method to prevent the reappearance of bacteria in treated water. In this section we have successfully deactivated the Escherichia coli bacteria by irradiation of visible light using both N and N S co-doped titania. Increasing the photocatalyst concentration and time of irradiation provided more rapid deactivation and it is optimized with catalyst dosage of 5.0 mg

Disinfection by titania photocatalyst with its modified forms become a promising technology which has proven to be very effective for the treatment of a wide range of biological species in potable water. The technique can be used for the disinfection
of water and wastewater even in areas which lack electricity and other infrastructures. Concurrent removal of organic, inorganic and bacterial pollutants from water is an added advantage of titania photocatalysts. Its application is not limited its still on continue.

8.3 Future Outlook

- The present photocatalytic degradation studies are limited to few dyes, pesticides and bacteria species based on the duration of course. A lot of systems are still pending to be evaluated.
- Moreover this study is limited only to the percent degradation; their mechanical pathway for the degradation and existence of any intermediate products is still not understood.
- This study is limited to doping with nonmetals. Nowadays the co-doping with metal and non-metal, multi elemental doping are the hot topics.
- This study is limited to sol-gel method for the preparation of catalysts. Other methods are still opens for comparison of the activity of catalysts.
- This thesis discusses the photocatalytic applications of powdered catalyst which lacks a complete recovery of catalyst after its application. Thus new technologies are needed for complete recovery of the catalyst without any loss of activity.
- Thoroughly detailed mechanisms behind the photocatalytic application with pure and modified catalyst are still a debate among the researchers.

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