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"Synthesis of TiO₂ based nanoparticles for photocatalytic applications"



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CHAPTER 1

1.1 INTRODUCTION

Interest in the study of TiO₂ as photocatalyst was triggered in 1972 by Fujishima and Honda, who first demonstrated its use for photo-oxidation of water (Fujishima and Honda, 1972). Since then considerable research has been done from both fundamental and an applied perspective. Typical photocatalytic reactions are quite complex with a lot of parameters influencing the resultant activity. Many studies have been carried out to investigate the effect of physical and chemical properties of TiO₂ nanoparticles on their photocatalytic activity (Tanaka et al., 1991; Tanaka and Suganuma 2001; Kato. 1992; Damm et al., 2005; Ohtani et al., 1997). Such studies have revealed that for efficient photocatalytic activity of TiO₂, the parameters and the species (charge carriers) responsible for surface reactions have to be optimized.

Parameter 1: Surface area

Parameter 2: Intrinsic prevention of charge carrier recombination

Parameter 3: Extrinsic prevention of charge carrier recombination

Parameter 4: Increasing the adsorption affinity of the surface towards a pollutant.

Photocatalysis being a surface phenomenon, surface area is very important to determine the amount of reaction sites interacting with the pollutant and the charge carriers (e⁻ and h⁺) have to be utilized properly to improve their ability to initiate surface reactions. For the latter case crystallinity of the TiO₂ should be high to prevent the recombination of e⁻ and h⁺. Highly crystalline TiO₂ prevents the recombination of charge carriers relative to amorphous and less crystalline TiO₂ and due to this it can be termed as “*intrinsic prevention of charge carrier recombination*”. As a working hypothesis, surface area and crystallinity of the TiO₂ powder have to be improved for efficient photocatalysis.

As the liquid phase nanopowder production techniques are carried out at or near room temperature, the resultant material is often amorphous or less crystalline. Calcination of the as-synthesized powder will be carried out to improve the crystallinity at the expense of surface area. Several authors reported the increase of the photocatalytic activity with the calcination temperature and reach a maximum where both the surface area and crystallinity are at an optimum level (Inagaki et al., 2001; Porter et al. 1999; Yu et al., 2000; Zhang et al., 2000). Toyoda et al. (2004) reported the qualitative information on the crystallinity from the FWHM (Full Width at Half Maximum) of (101) anatase reflection of TiO₂ with respect to the calcination temperature. On the other hand, Yeung et al. (2003) reported the qualitative crystallinity information on TiO₂ nanoparticles by merely taking the reflection intensity of the XRD pattern. But apparently, the crystallinity of a particular powder depends on the combination of the FWHM and the intensity of the reflection. In other words, it should not be taken as granted that higher FWHM and lower reflection intensity corresponds to lower crystallinity of the powder and vice versa. Depending on the nanoparticle synthesis route, powder of the similar particle size can be synthesized with varied degree of crystallinity (Kruis et al., 1998).

In contrast, to the liquid phase processes, process parameters of the gas phase synthesis methods can be adjusted to produce nanoparticles with varied crystallinity and surface area without the necessity of post treatments. Well known example of gas phase synthesized TiO₂ nanopowder is Degussa P-25 which was tested by several research groups for the photocatalytic decomposition of various pollutants/reactants and mechanistic studies (Lee et al., 2003; Mills and Wang 1998; Micic et al., 1993; Canela et al., 1998). Several authors reported the synthesis of modified TiO₂ i.e. mixed oxides (Fresno et al., 2005), composites (Yang et al., 2002) metal deposited TiO₂ (Teoh et al., 2005; Moonsiri et al., 2004) etc that show better photocatalytic activity than P25 TiO₂. Very few groups have reported the

synthesis of pure TiO₂ that exhibits better activity than P-25 (Xie and Yuan 2003; Kim et al., 2001; Kominani et al., 2002 & 2003). Out of which HyCOM (Hydrothermal Crystallization in Organic media) TiO₂ was synthesized strategically by optimizing the characteristics necessary for improving the photocatalytic activity i.e. producing nanopowder with much higher surface area and crystallinity than P-25 TiO₂. Crystallinity of the as-synthesized HyCOM powder is not as high as P-25 TiO₂, but it is subjected to post-calcination treatment to control the surface area and crystallinity.

Optimization of the “*Parameter 1* and *Parameter 2*” (refer Page. 1) have been studied in the fifth chapter, in which pure TiO₂ powders with high crystallinity and surface area, compared to P-25, has been produced in a single step which avoids the post treatment. Improved PCA of the as-synthesized nanoparticles compared to P25 TiO₂ has been shown and factors contributing to this enhancement are discussed. More over, the relative degree of crystallinity of each powder is measured (by taking both FWHM and reflection intensity into account) quantitatively and compared with P-25 TiO₂ which is something not reported with HyCOM TiO₂ and other studies which showed improved PCA.

It is known that the photocatalytic degradation of a pollutant is the consequence of a series of oxidation and reduction reactions initiated by the photogenerated holes and electrons, respectively. The characteristic times necessary for the oxidation and reductions reaction is estimated to be 30 ps and 250 ns (Hoffmann et al., 1995), respectively, which means that electrons get accumulated and recombine with the holes due to the sluggishness of the reduction reactions. Intrinsic prevention of charge carrier recombination by highly crystalline TiO₂ doesn't have control on this time-sensitive recombination of charge carriers and this necessitates employing an extrinsic trapping of electrons.

Modification of TiO₂ by noble metal deposition i.e. Au (Wood et al., 2001; Jakob et al., 2003; Subramanian et al., 2004), Ag (Hirakawa and Kamat, 2004), Pt (Johannessen and

Koutsopoulos, 2002) is one example of the extrinsic trapping system. When the deposited metal particle interacts with the photoexcited TiO_2 , the two particles undergo charge equilibration. The shift in the Fermi level towards the conduction band energy enhances the catalytic efficiency of the composite system. However, the associated processes and reagents are expensive which makes it difficult to scale-up the process.

Extrinsic trapping can also be employed by coupling two semiconductors that have suitable conduction and valence band potentials. In the past years, a number of studies related to TiO_2 coupled with other semiconductors like SnO_2 (Tennakone and Bandara, 2001; Vinodgopal et al., 1996), WO_3 (Do et al., 1994; Li et al., 2001), Fe_2O_3 (Pal et al., 1999; Pal et al., 2001), ZnO (Wang et al., 2002), CdS (Spanhel et al., 1987) were performed. Among them, coupling TiO_2 with SnO_2 attracts much attention. The band gaps of SnO_2 and TiO_2 are 3.88 and 3.2 eV, respectively, and the conduction band edge of SnO_2 is approximately 0.5V above that of TiO_2 (Vinodgopal and Kamat, 1995). When the two semiconductor particles are coupled, the conduction band of SnO_2 acts as a sink for photogenerated electrons. Since the photogenerated holes move in the opposite direction, they accumulate in the valence band of the TiO_2 particle, thereby increasing the efficiency of charge separation. Two variants of $\text{SnO}_2/\text{TiO}_2$ system has been studied for the improvement of PCA i.e. composite $\text{SnO}_2/\text{TiO}_2$ particles/films (Shang et al., 2004; Kanai et al., 2004; Cao et al., 2001; Tai 2001) and mixed oxides of $\text{SnO}_2/\text{TiO}_2$ (substitution of Sn for Ti in TiO_2 lattice) (Lin et al., 1999). The increase of the PCA with the mixed oxides is due to the increased band gap and subsequently the conduction band potential of the solid solution, which necessitates the use of light of much higher energy (Sensato et al., 2003). On the other hand, theoretical band gaps of the SnO_2 and TiO_2 are preserved in the particles/films and due to this composite particles/films are interesting systems to study in more detail. Some authors reported the synthesis of $\text{SnO}_2/\text{TiO}_2$ particulate films and particles by using mixed suspensions of separate TiO_2 , SnO_2 particles

and calcining finally (Shang et al., 2004; Kanai et al., 2004; Cao et al., 2001). Shi et al., (2000) reported the synthesis of SnO₂/TiO₂ coupled nanoparticles by homogenous solution precipitation methods which includes multiple steps of adding SnCl₄ precursor to TiO₂ powder externally and subjecting the resultant powder to calcination. Resultant composite particles showed better PCA than pure and commercial TiO₂ and SnO₂ particles, and the optimum loading of SnO₂ on TiO₂ was reported as 18.4 wt%. Though Sn substitution enhances the transformation of anatase to rutile, Yang et al., (2002) reported the synthesis of SnO₂/TiO₂ binary oxides by a novel stearic acid method (SAM) which stabilizes the anatase phase and showed better photocatalytic activity than P25. The above method is also a wet chemical synthesis route which needs calcination to improve the crystallinity of the resultant powder.

Collectively, “*Parameters 1, 2 and 3*” are optimized in the sixth chapter to reap the advantages of intrinsic and extrinsic prevention of charge carriers by synthesizing SnO₂/TiO₂ composite nanoparticles. Gas phase process employed in this study enable the mixing of the constituents at a molecular level to achieve better chemical homogeneity.

Utilizing the advantages of the nanoparticles to its maximum extent is possible by facilitating the reactants to interact with the available high surface area of the photocatalyst. In other words it can be said that the photocatalytic activity of SnO₂ modified TiO₂ photocatalysts can be further improved if the SnO₂/TiO₂ composite system adsorbs more pollutant on to its surface along with the function of electron trapping. But unfortunately, deposited SnO₂ only serves as electron trapping agent but are not effective to enhance the adsorption of the pollutants. However, TiO₂ coupled with other semiconductors has been reported to perform both the above mentioned functions. This has been realized by coupling the WO₃ semiconductor with TiO₂. As a basic function, WO₃ has a suitable conduction band potential to allow the transfer of photogenerated electrons from TiO₂ facilitating effective

charge separation. Additionally, formation of a monolayer of WO_x species on TiO_2 can significantly increase the surface acidity (Kwon et al., 2000). Because of this increased acidity WO_3/TiO_2 particles generate higher affinity for species with unpaired electrons and hence can adsorb more OH^- or H_2O , which is prerequisite for OH radical formation necessary for photooxidation reactions. To date, WO_3/TiO_2 has been synthesized by sol-gel (Li et al., 2001; Yang et al., 2005), ball milling (Shifu et al., 2005), incipient wetness impregnation (Do et al., 1994; Song et al., 2001), multiple grafting (Engweiler et al., 1996). Thin films of WO_3/TiO_2 have also been produced by dip coating (Rampaul et al., 2003) and spin coating (Tatsuma et al., 2003). Kwon et al. (2000) reported that with increasing amount of WO_3 , acidity increases and reaches a maximum value for a WO_3 concentration of 3.2 mol%. A further increase in WO_3 concentration does not have any influence on the acidity of WO_3/TiO_2 composite particles. Interestingly, the photocatalytic activity also followed the same hysteresis as the acidity dependence. Li et al. (2001) synthesized the WO_3/TiO_2 by sol-gel process using ethanol solutions of $\text{Ti}(\text{O-Bu})_4$ and aqueous solutions of ammonium metatungstate. The resultant amorphous $\text{WO}_x\text{-TiO}_2$ gel was calcined at 973K for 2 h to produce crystalline WO_3/TiO_2 nanocomposites. They also measured the isoelectric points and found them to be at pH 6.40 and 5 for pure TiO_2 and 3 mol% WO_3/TiO_2 respectively. This variation in the isoelectric point can greatly enhance the adsorption of organic reactants on the surface of the WO_x/TiO_2 photocatalysts. All the process routes investigated so far employed multiple step synthesis by using pure TiO_2 as a starting material.

In chapter seven, flame spray synthesis (FSS) route has been followed to synthesize the WO_3/TiO_2 nanocomposites in a single step. All the above mentioned “*Parameters 1, 2, 3 and 4*” have been optimized by adjusting the WO_3 concentration and process parameters of the synthesis route.