Chapter 3

Study of impact of vanadium doping on the photocatalytic activity of pristine and mixed phase titania
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Any phase of titania (pristine anatase, pristine rutile, mixed) 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. To make the phases visible active there may be two approaches i) Dope the material with suitable cationic or anionic dopant thereby creating intermediate and localized level in the band gap ii) Prepare photocatalyst semiconductor composites with suitable band gap and work function iii) Control the crystallite size of the nanomaterials iv) Sensitize the material with noble metals to take advantage of plasmonic resonance effect. This chapter reports the work done to study the impact of doping on the visible light photocatalytic activity of TiO$_2$ of different phases. This chapter also attempts to facilitate quantification of the performance of the photocatalytic disinfection system by taking into account the response of the catalyst to the radiation intensity.

3.1. Introduction

In the earlier chapter, the potency of mixed phase titania for photocatalysis was outlined with details of synthesis and characterization of pristine and mixed phase titania. Also the high activity of mixed phase titania was explained through a model called *interface model*. The pristine and mixed phases of titania show photoactivity mainly in UV range while the major part of solar spectra is in visible range. Thus, it becomes very important to explore the possibility of developing visible active photocatalyst. Many attempts were made by researchers to develop visible active photocatalyst by modifying titania for efficient use of solar radiation. Different approaches such as doping (anions/cations); co-doping, sensitization and development of a variety of semiconductor composites have been employed to achieve this objective [1-15]. Among them doping (or co-doping) of TiO$_2$ with
cationic elements such as V, Fe, W, Cr, Mo, Nb, Zn, Sn, Zr or anionic elements such as B, N, S and C received great interest [3,4].

Among the different cationic dopants used in titania V is the most studied as it gives highly active photocatalyst with elevated and red-shifted absorption spectrum [16-35]. The is mainly due to high charge-to-volume ratio of V compared to Ti and existence of higher number of valence states of V. Also high relative polarisability of V makes transfer of photogenerated electrons easier as well as the scavenging of electrons more probable thereby increasing the average lifetime of holes [25]. However the low solubility of V in anatase (about 5 at. %) phase has been reported [4]. Most of the reported works on photocatalytic activity of Ti-V systems are for this upper limit of V solubility. Visible active V doped titania photocatalysts have been reported in pristine anatase [17-23], rutile [24-25] or in mixed phases [29,31-32] along with their photoactivity. Also many attempts have been made to develop titania-vanadia complexes and study their visible light activity [36-41]. No work has been noticed which compares the activity of pristine and mixed phase V-doped titania photocatalysts.

V doped pristine and mixed phase titania nanoparticles were synthesized through modified sol-gel technique and their photocatalytic activities were compared both for detoxification and disinfection applications. Photocatalyst systems with different Ti-V ratio were prepared for this. The photocatalytic potency of each one of them was examined in terms of rate constant and photonic efficiency for detoxification application. For disinfection a new performance parameter called microbicidal photonic efficiency (MPE), proposed in this work, along with disinfection rate constant was used.

3.2. Experimental

3.2.1 Materials and synthesis

V-doped titania systems were synthesized using the reagents vanadium pentaoxide (V₂O₅) from Loba chemicals (India), hydrogen peroxide (H₂O₂, 30%) from Merck (India) and the other reagents were same as discussed in the Chapter 2. All the
reagents were of analytical grade and double distilled water was used in all the processes.

Many synthesis methods are reported to synthesize V doped titania nanoparticles\cite{17,22,31-32}. In the present work sol-gel method was employed to keep the uniformity in synthesis as in the case of pure titania. Pristine and mixed phase V-doped titania nanoparticles were synthesized using modified sol-gel method as shown in flow diagram (Figure 3.1).

![Flow diagram of the vanadium modified titanium dioxide preparation](image)

Figure 3.1: Flow diagram of the vanadium modified titanium dioxide preparation

Initially titanium sol was prepared as discussed in Chapter 2. Vanadium sol was prepared by taking V$_2$O$_5$ powder and H$_2$O$_2$ in the ratio 1:13 (w/V). H$_2$O$_2$ was mixed drop wise with the V$_2$O$_5$ under continuous shaking. After complete mixing of the reagent, the prepared solution was heated for 1hr at 60-70 $^\circ$C. The vanadium sol was mixed into the mother sol of the titanium in three different ratio (1:0.5 v/v, 1:0.75 v/v, 1:1v/v). The solution was left for aging for 12 h at room temperature under constant stirring. Finally after drying the sol the gel was heated at the ramping rate of 4 $^\circ$C/min and calcined at 100 $^\circ$C, 200 $^\circ$C and at 400 $^\circ$C for 1hr each and then at 550 $^\circ$C for 30 min. Hereafter the samples are labeled as TiV(A), TiV(M) and TiV(R), respectively. For a given calcination temperature the phase of the resultant TiV oxide
nanoparticles is sensitive to the amount of vanadium used in the sol [31]. Hence to get pristine anatase phase of Ti-V the mixed sol was prepared with very low amount of vanadium sol, keeping all other conditions same.

3.2.2 Characterization

XRD, FTIR, PL and UV-DRS analyses were carried out using the instruments as discussed in Chapter 2. The TEM and FESEM images were recorded using Transmission Electron Microscope (JEM-100CX II, JEOL, Japan) and Field Emission Scanning Electron Microscope (Hitachi S-4800), respectively. Energy Dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) of the Scanning Electron Microscope system.

3.2.3 Photocatalytic detoxification experiments

The detoxification experiment set-up was similar to the one reported in Chapter 2 and shown in Figure 2.2. The experiments were carried out under identical conditions and sampling rate.

3.2.4 Photocatalytic disinfection experiments

A gram-negative bacterium, E. coli was considered to study the bactericidal/disinfection activity of the photocatalyst under visible light irradiation (393 W/m²). The schematic representation of the set-up is given in Figure 3.2. The model bacterium under study was grown in Luria Broth (LB) media at 37 °C for 24 hrs at a constant shaking of 200 rpm. The cells were harvested post incubation by centrifugation at 5000 rpm for 5 min and then washed thrice with 0.9 % (w/v) normal saline before being used to study disinfection activity of the photocatalyst. All the materials were autoclaved at 16 psi and at 121 °C for 40 min to ensure sterility before using them in the experiments. The pellet obtained after centrifugation was diluted to a cell suspension of $8.6 \times 10^6$ cfu/ml with the 0.9% normal saline. The final concentration of photocatalyst and a reference catalyst was adjusted to 0.25 mg/mL. The reaction mixture was stirred continuously with a magnetic stirrer to prevent settling of the photocatalysts. To ensure sterility and maintain the temperature of the bacterial environment, the reaction was carried out in a 37 °C incubator for one hour.
Light and dark control both in presence and absence of catalyst were maintained under the same environment, respectively. After an interval of 30 min an aliquot of the reaction mixture was withdrawn from each experiment and was immediately diluted up to a suitable dilution with 0.9% saline and plated on LB-agar plates. The colonies were counted in terms of colony forming unit (CFU) after incubation at 37 °C for 24 h. All of the above experiments were performed in triplicate. The average values of results are reported in each case.

3.3. Results and discussion

The X-ray diffraction (XRD) patterns of the synthesized vanadium doped titania samples are depicted in Figure 3.3. All the spectra show crystalline nature of the samples with high degree of crystallinity. The TiV(A) oxide sample showed pure anatase phase [JCPDS File No. 211272] and the sample TiV (R) oxide showed pure rutile phase [JCPDS File No. 870710]. The sample TiV (M) oxide showed a mixed phase with predominantly anatase phase peaks comparable with the JCPDS files of pure anatase [JCPDS File No. 211272] and rutile phase [JCPDS File No. 870710].

![Schematic diagram of the disinfection batch reactor](image)}
The small shift observed in the XRD peaks may be attributed to the incorporation of V inside the titania lattice. Anatase to rutile transformation of pure titania begins at about 700 °C, though TiV oxide samples show the onset of transformation at lower temperature [29,31]. This clearly indicates the incorporation of vanadium inside the titania lattice. No other peaks from possible impurities/surface vanadium are detected. The crystallite sizes, calculated by the Scherrer formula, are given in Table 3.1. The phase composition of the TiV(M) sample, calculated using Spurr formula, is also given in Table 3.1.

The morphology and particle size were investigated through SEM and TEM as depicted in Figure 3.4. The SEM and TEM micrographs of all the TiV oxide samples show the particle size distribution in nano-range (~ 30-100 nm). The average particle size is small in the case of pristine anatase phase and increases with its transformation to mixed and then to rutile phase. This is consistent with the earlier reports [23]. In the case of TiV (M) the phase composites are clearly identifiable in the TEM micrograph. The particle sizes observed in TEM agree well with the grain size calculated through XRD analysis. The EDAX spectrum corroborates the
Figure 3.4: SEM and TEM spectra of V doped titania samples (a1 and b1) TiV(A), (a2 and b2) TiV(M), (a3 and b3). TiV(R)

Table 3.1 Physico-chemical characteristics of the samples

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample</th>
<th>Crystallite Size (nm)</th>
<th>Mass Fraction (%)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anatase</td>
<td>Rutile</td>
<td>Anatase</td>
</tr>
<tr>
<td>1.</td>
<td>TiV (A)</td>
<td>41.00</td>
<td>NA</td>
<td>100</td>
</tr>
<tr>
<td>2.</td>
<td>TiV (M)</td>
<td>35.40</td>
<td>51.40</td>
<td>79</td>
</tr>
<tr>
<td>3.</td>
<td>TiV (R)</td>
<td>NA</td>
<td>50.70</td>
<td>0</td>
</tr>
</tbody>
</table>
presence of Ti with Kα line at 4.5 keV and V with Lα line at 0.5 keV in all the TiV oxide system. The EDAX spectra of TiV oxide also shows an atomic percentage of vanadium to be ~5% and is comparable with the earlier report [4, 31].

![Figure 3.5: UV-DRS Spectra of V doped titania samples](image)

Diffuse reflectance spectroscopy were carried out to investigate the optical spectral response of the pristine and mixed phase TiV oxide samples. The DRS spectra of the TiV oxide samples along with Degussa P25 are depicted in Figure 3.5. All the TiV oxide samples showed marked red shift in the absorption spectra compared to Degussa P25. This variation in the absorption spectra may be attributed to the incorporation of vanadium inside the titania matrix [19, 27, 31, 38-39]. Energy band gap of the material is related to its absorption coefficient and energy of the photon by the Tauc’s relation as discussed in Chapter 2. The band gap of the materials is calculated and is given in Table 3.1. The values are in good agreement with the earlier reports [23, 32].

The photoluminescence responses of the samples carried out at an excitation wavelength of 380 nm are shown in Figure 3.6. All the samples showed an emission
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peak of direct transition corresponding to the band gap value found from UV-DRS spectra. The trap levels identified in the PL spectra between 530 nm to 550nm,

Figure 3.6: PL spectra of the V doped titania samples at an excitation wavelength of 380nm corresponding to 2.38 to 2.25 eV are attributed to oxygen vacancy levels [5]. The trap levels play a positive role in reducing the recombination. This may play a positive role in the photocatalytic activity.

FTIR analysis was done for the TiV oxide samples. The FTIR spectra for all the three samples are depicted in Figure 3.7. The broad band at 3430 cm$^{-1}$ is assigned to the hydroxyl groups. The bands at 3750 and 3840 cm$^{-1}$ are the characteristic peaks of octahedral vacancies assigned to 6Ti$^{3+}$-OH while the band at 3680 cm$^{-1}$ corresponds to tetrahedral-coordinated vacancies identified as 4Ti$^{4+}$-OH[42]. It is observed that the transformation from octahedral vacancies to tetrahedral coordinated vacancies is maximum in the case of mixed phase as observed in the case of pristine mixed phase titania reported in Chapter 2. It may play a positive role in reduction of recombination. The band at 1628 cm$^{-1}$ is ascribed to surface absorbed water molecules and -OH groups [36]. The band at 1630 cm$^{-1}$ could also belong to Ti-O [6].
The conversion of mixed phase to rutile is observed in the spectra wherein a shoulder at 550 cm\(^{-1}\) corresponding to anatase (present in the mixed phase) gets converted to sharp peaks at 530 and 640 cm\(^{-1}\) corresponding to rutile phase [7] confirming the XRD results. The band at 985 and 598 cm\(^{-1}\) could be due to V=O and V-O vibrations, respectively [39].

3.3.1 Degradation kinetics and photonic efficiency

The photocatalytic activity of the materials was studied on aqueous phenol. The phenol solution with the catalyst loading was irradiated with the visible light flux for duration of 120 min along with the reference catalyst Degussa P25. All the TiV oxide samples show photoactivity as depicted in Figure 3.8. The TiV(M) catalyst showed high rate of degradation compared to the pristine TiV oxide systems and the reference catalyst Degussa P-25. The rate constants for photodegradation of phenol as per pseudo first order kinetics were calculated to compare the performance of the mixed phase TiV oxide with its pristine systems as well as Degussa P25. Using the linear transformation \( \ln \left( \frac{C}{C_0} \right) = -kt \), where \( C_0 \) is the initial concentration, \( C \) is the final concentration and \( k \) is kinetic constant, the rate constants are calculated by \(-\ln(C/C_0)\) vs. time plot (Figure 3.9) the values of which are given in Table 3.2.
The mixed TiV oxide sample showed 2.2, 1.7 and 2.8 times higher activity in the rate of degradation of phenol compared to TiV(A), TiV(R), and Degussa P-25, respectively. The high rate of degradation of phenol observed in the case of mixed phase TiV oxide may be due to its enhanced visible light functional property attributable to narrowing of band gap and effective charge separations occurring in the case of mixed phase systems.

Table 3.2 Rate constants, photonic efficiency and microbicidal photonic efficiency of the samples

<table>
<thead>
<tr>
<th>S. N</th>
<th>Sample</th>
<th>Detoxification of Phenol</th>
<th>Disinfection of E.coli</th>
<th></th>
<th></th>
<th>Microbicidal photonic efficiency (bCFU*/Einstein)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rate Constant (min⁻¹)</td>
<td>Photonic efficiency (%)</td>
<td>Rate constant (min⁻¹)</td>
<td>Light</td>
<td>Dark</td>
</tr>
<tr>
<td>1</td>
<td>Degussa P25</td>
<td>0.0017</td>
<td>0.0273</td>
<td>0.014</td>
<td>0.005</td>
<td>0.139</td>
</tr>
<tr>
<td>2</td>
<td>TiV oxide (A)</td>
<td>0.0022</td>
<td>0.0338</td>
<td>0.015</td>
<td>0.005</td>
<td>0.143</td>
</tr>
<tr>
<td>3</td>
<td>TiV oxide (M)</td>
<td>0.0048</td>
<td>0.0550</td>
<td>0.031</td>
<td>0.005</td>
<td>0.161</td>
</tr>
<tr>
<td>4</td>
<td>TiV oxide (R)</td>
<td>0.0029</td>
<td>0.0416</td>
<td>0.018</td>
<td>0.004</td>
<td>0.150</td>
</tr>
</tbody>
</table>
Figure 3.9: Rate constant calculation spectra of V doped titania samples

To compare the performance of the photocatalysts with respect to the radiation intensity and spectrum the photonic efficiency has been calculated using the expression discussed in Chapter 2. The values are given in Table 3.2 and are identical to the earlier report [43]. The photonic efficiency of the mixed TiV oxide system are 2, 1.6 and 1.3 times than Degussa P25, TiV(A) and TiV(R), respectively. Relative values of photonic efficiencies are significant which reflect the suitability of the type and design of the reactor as well.

3.3.2 Kinetic study for E. coli inactivation and microbicidal photonic efficiency:

The bactericidal activity of the TiV oxide samples was investigated by evaluating the inactivation of E. coli bacterium under dark and visible light irradiation. The results of the comparison of TiV oxide samples with Degussa P25 photocatalyst are depicted in Figure 3.10. The Gram negative bacterium E. coli can be almost completely inactivated within one hour with mixed TiV oxide photocatalysts under visible light irradiation. The decrease of the cfu count on an agar plate was used for evaluation of bactericidal activities as shown in (Figure.3.11). The Chick-Watson model is simple and easy to be applied as a disinfection kinetic model [44].
The rate constant is calculated by plotting $-\ln N_t/N_0$ vs time (Figure 3.12) and is given in Table 3.2. All the TiV oxide samples showed high rate constant compared to Degussa P25. A small increase in rate constant is observed in the case of mixed phase TiV oxide compared to its pristine phases as well as reference catalyst Degussa P25. The rate constant values are comparable with the earlier reports [1,9]. This result clearly indicates the role of mixed phase in the photoactivity as discussed in Chapter 2.

3.3.3 Microbicidal photonic efficiency (MPE)

For comparing the photocatalysts and for optimizing performance of a photocatalysts, there is a need to have a robust performance parameter which precisely and consistently represents photocatalytic disinfection. For system performance calculations the catalyst loading and intensity of light must also be the affecting design and operational parameters. An excellent review on the mechanisms and modeling of photocatalytic disinfection is available in the literature which concludes that none of the existing models is adequate to address the effect of catalyst loading and light intensity together [45]. The mechanistic kinetic model proposed by...
Figure 3.11: *E. coli* culture at different time of exposure

Figure 3.12: Disinfection rate constant calculation spectra of V doped titania samples
Marugan et al 2008 was shown to represent and respond to the rate of inactivation and to the amount of catalyst loading in terms of Chick-Watson model kinetic constant $k_i$, pseudo-absorption constant $K_i$, and inhibition coefficient $n_i$ (i represents the level of population of bacteria) at constant radiation intensity. It does not take into account the variation in radiation intensity. Since the rate of disinfection is based on the rate of change in CFU counts (after plating the reaction mixture on a known area), it is difficult to relate it to the irradiated area of the reactor, which is different. Hence MPE, a different parameter, is proposed in this work. This can take into account the effect of radiation flux and may be incorporated in future mechanistic kinetic models. Its efficacy is probed and presented.

Killing of each microbes involves rupturing of cell wall/membrane, protein oxidation and interruption of electron transport. Each of these processes involves oxidation of a number of different molecules. It is difficult to determine the number of molecules oxidized in this process. Therefore, for quantifying the performance of the catalyst, MPE (which is identical with the photonic efficiency [43]), is defined, as the change in the number of colony counts, $\Delta N$, per photon. But in this case the colony count is done by counting the number of colonies plated on a specific area (say $A_p$). The photocatalytic disinfection experiment is however carried out by irradiating the microbes in a given volume of the reactor through its aperture of area, $A$, by a known flux of photons, $J$. Here $\Delta N$ is identical to $\Delta C$. The only difference here is in area of plating and area of exposure which are not the same. To overcome this problem $\Delta N$ is normalized with the area of exposure ($A \Delta N/A_p$) which provides a net change in colony counts approximately representing the change in the microbial count in the given volume of the reactor. Dividing this by the number of photons will give the microbicidal photonic efficiency as shown below.

\[
\zeta_{mb} = \frac{\Delta N}{(J.A_p.\Delta t)}
\]  

(3.1)

where $\Delta N =$ change in colony count in the effective plating area adjusted to $10^0$ dilution (CFU); $J =$ flux of photons (Einstein/m$^2$/sec); $A_p =$ effective plating area (m$^2$); $\Delta t =$ change in time (s).
The flux of photons ($J$) is calculated using the equation

$$J = \frac{(I \lambda)}{(N_A h c)}$$  \hspace{1cm} (3.2)

where $I=$ light intensity (W/m$^2$); $\lambda=600$ nm; $N_A=$ Avogadro constant; $h=$ Planck’s constant (J/sec); and $c=$ speed of light(m/s). The microbicidal photonic efficiency values are given in Table-3.2. From the values it can be seen that the TiV oxides are far superior than Degussa P-25 in showing the bactericidal activities. As expected the mixed TiV oxide showed better performance for disinfection also compared to all pristine samples. However, it should be noted that the bactericidal activity will depend upon the type and configuration of the reactor as well.

The high detoxification and disinfection activity of mixed phase V doped titania can be explained using the generalized mechanism which has been proposed for mixed phase pure titania in the earlier chapter. According to this model under visible light irradiation both the phases of TiV oxide samples will generate electron-hole pairs and the electrons will be successfully separated at the junction. Hence holes can effectively participate in photocatalytic oxidation of pollutants/ microbicides. The mechanism of charge separation will be identical to the one developed earlier for pure titania system[Chapter-2]. However two aspects need further investigation – one the exact mechanism in TiV system, and two, the optimum ratio of phases in TiV(M). It is expected that this understanding may lead to the development of visible active anion/ cation doped mixed phase titanium dioxide based catalysts for energy and environmental applications

3.4. Conclusions:

This chapter discussed the preparation of vanadium doped mixed and pristine phases of titania were prepared using sol-gel technique to take advantage of red-shift in such systems. All the TiV oxide samples were in nanoscale with a grain size distribution of ~ 30-100nm and showed extended absorption in visible range. The analysis of photocatalytic performance of the samples for the detoxification and disinfection applications showed high visible light photoactivity compared to
Degussa P25. The mixed phase TiV oxide sample showed high rate of degradation for both the applications. The enhancement observed in the case of mixed phase TiV oxide is attributable to the extended and elevated absorption in the visible range and the reduction in the carrier recombination due to effective charge separation in accordance with interface model for mixed phase titania systems. This new finding may help in developing highly visible active mixed phase TiV oxide photocatalyst with optimized anatase-rutile phase ratio for commercial detoxification and disinfection applications. To enhance the performance of such system further resort to some other method may be taken. Sensitization, one of the methods mentioned earlier appears to be a logical step ahead.
References:


