Chapter 4

Study of impact of silver sensitization on the photocatalytic activity of mixed phase V doped titania
Chapter 4

Study of impact of silver sensitization on the photocatalytic activity of mixed phase V doped titania

Even the most suitable photocatalyst systems with suitable band edge position and wide absorption spectrum have been reported to show poor activity attributable to recombination of a large amount of photo-generated charges. The mixed phase system reduces the recombination to a large extent. They need to be completely isolated by providing a suitable scavenging or isolation mechanism. Sensitization by a noble metal on pristine titania phases has shown encouraging result. V– doped mixed phase is one of the most active photocatalyst. It is to be seen if their activity can be improved further by sensitization. The present chapter presents the results of an investigation on impact of silver sensitization on the photoactivity of visible active V doped mixed phase titania synthesized in the present study for both detoxification and disinfection applications. The probes used for detoxification and disinfection studies were the same as reported in earlier chapter. 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 Ti-V photocatalyst.

4.1 Introduction

In previous chapters the high activity of pristine mixed phase as well as V doped mixed phase titania with respect to pristine titania phases have been outlined with details of synthesis and characterization. A model was also proposed to explain the high activity of mixed phase titania. As discussed in Chapter 3, V doped mixed phase titania nanoparticles show relatively high visible light activity compared to pristine V doped titania as well as to the pristine and mixed phase pure titania. As proposed the mixed phase of all these system is successful in reducing the
recombination to some extent of charge carriers though intraphase band bending and intermediate trap levels due to presence of oxygen vacancies. Some of the recent results on isolation of charge carriers by suitable noble metal scavengers/ sensitizers, it was felt that there is a further scope of reducing charge carrier recombination and, consequently, enhancing the photoactivity.

As stated earlier a red-shift in the absorption spectrum does not ensure a proportional increase in the photocatalytic activity, due to carrier recombination. This calls for development of a photocatalyst which shows visible light response as well as decreased charge carrier recombination. Loading of noble metals like Au[1-5], Pt[6-10], Pd[10-16] and Ag[17-49] on titania have been reported to be very effective in enhancing the photocatalytic activity. When the noble metal is loaded on titania, the photo-excited titania electrons migrate toward the noble metal Fermi levels leaving the holes in the valence band as the Fermi levels of the noble metals are lower than the titania conduction band. It results in reduction in the electron-hole recombination rate and thus enhancement in the photocatalytic efficiency. Among the different noble metal electron scavengers silver is the most studied and reported. It shows the enhancement in the photocatalytic activity of titania [17-49], which is attributed to increased specific surface area, improved electron-hole pair separation and enhanced absorption spectrum due to induced surface plasmon resonance(SPR) of Ag-nanoparticles in the visible region[22,23]. This SPR effect is the combined oscillation of conduction electrons in the nanoparticles which resonate with the electromagnetic field of the incident light. Also these excited electrons will return to their thermal equilibrium states and release heat to the lattice and surrounding medium[22]. This heating effect may also induce reactions of the molecules adsorbed on the particles. Also it has been reported that silver loaded titania photocatalyst shows high photoactivity than the pristine titania[18,37]. On careful observation it was found that the active systems were in mixed phase which support the results presented in Chapter 2 and 3.

This chapter report synthesis and characterization of silver sensitized V-doped mixed phase titania nanoparticles with an aim to investigate the effect of sensitization
on its photocatalytic activity for both detoxification and disinfection applications. For this purpose initially silver sensitized identical V doped mixed phase naonoparticles were synthesized under the conditions identical to the one used for V doped mixed phase titania and reported in the earlier chapter. Here Ag is expected to work as an electron scavenger to reduce the charge carrier recombination. A simple and versatile sol-gel method was used to synthesize nanoscale photocatalyst as it provides sufficient temporal and spatial flexibility for inter-atomic interaction and hence makes incorporation of dopant material easier at low temperature while the support material is in sol phase. The photocatalytic activity of the sample was evaluated by studying the degradation of phenol for detoxification and inactivation of E. coli for disinfection applications. The results were compared with Degussa P25 and TiV oxide in visible light for both the applications.

4.2. Experimental

4.2.1 Materials and Synthesis

The silver sensitized V doped titanium dioxide were synthesized by using silver chloride (AgCl), ammonium hydroxide (NH₄OH 25%) and sodium hydroxide (NaOH), all from Merck (India). The remaining reagents and the reference were same as reported in Chapter 2 and Chapter 3.

Among the methods already reported for the synthesis of silver loaded titania [18,19,35]. The method of photo-reduction is the most studied one. However, the photo-reduction needs quite a long time of exposure and the metal particles are likely to fall off during their repeated utilization. Moreover, photo-reduced Ag cannot be highly dispersed on the surface of TiO₂, so that the amount of active sites on the Ag/TiO₂ surface cannot markedly increase and the electronic structure of TiO₂ photocatalyst cannot change greatly. To overcome these difficulties and disadvantages, in this chapter silver doped mixed phase titania nanoparticles were prepared using a modified sol-gel method as shown in Figure. 4.1. For the preparation of silver sensitized V doped mixed phase titania, the titanium sol, vanadium sol were prepared as reported in Chapter 2 and 3. The silver solution was prepared by adding
30% solution of the ammonium hydroxide in silver chloride drop wise at room temperature under stirred condition till complete dissolution of the AgCl.

Finally the vanadium sol and titanium sol were mixed in 1:0.75 ratio and there after the prepared silver solution were added together to get the final sol. The resultant solution was left for aging for 12 h at room temperature under constant stirring. Finally the sol was heated at a ramping rate of 4 °C/min and calcined at 100 °C, 200 °C and at 400 °C for 1 h each and then at 550 °C for 30 min. The final sample hereafter named as Ag/TiV oxide (A).

Also an attempt was made to prepare silver sensitized V doped titania in basic medium so as to get another phase ratio. Normally it is difficult to get desired phase ratio through thermal treatment in highly doped system. This approach involved the preparation of vanadium sol using NaOH. Vanadium sol was prepared by drop wise mixing of NaOH into the V$_2$O$_5$ powder in the ratio 1:13 (w/V) under continuous
shaking. After complete mixing of the reagent, the prepared solution was heated for 1 hr at 60-70 °C. The titanium sol was prepared as reported earlier. The resultant vanadium sol, titanium sol were mixed in 1:0.75 ratio and finally silver solution were added to the above mixture to get final sol. The solutions were left for aging for 12 h at room temperature under constant stirring. Finally the sols were heated at a ramping rate of 4 °C/min and calcined at 100 °C, 200 °C and at 400 °C for 1 h each and then at 550 °C for 30 min. The resultant sample is named as Ag/TiV oxide (B).

4.2.2 Characterization

XRD, SEM, UV-DRS and PL analyses were carried out using the instruments as discussed in Chapter 2 and 3. HR-TEM images were taken by High Resolution Transmission Electron Microscope (Jeol JEM-1000CX II, Japan) operated at an accelerating voltage of 200 kV. The XPS spectra of the catalysts were measured on a XPS spectrometer (Kratos-Axis 165, Shimadzu, Japan) with Al Kα radiation (hγ = 1486.6 eV) at 75W.

4.2.3 Photocatalytic degradation experiments

The experimental set up conditions and the procedure for photocatalytic degradation studies including probe pollutant, the visible light source, the radiation level, catalyst loading, average reactor temperature, pollutant concentration, adsorption-desorption time and exposure interval were same as discussed in Chapter 3. The experiments were carried out under constant stirring by the simultaneous exposure of the blank solution, the solutions with the reference catalysts (Degussa P 25), and Ag/TiV oxide catalyst, each having 60 ml of 1 mM phenol.

4.2.4 Photocatalytic disinfection experiments

The set-up, conditions and the procedure for photocatalytic disinfection experiments were exactly the same as discussed in Chapter 3. The only difference here was that instead of V doped titania catalyst, silver modified V doped titania were employed in the experiments.
4.3. Results and discussion

The two calcined samples prepared under acidic and basic conditions were examined by powder X-ray diffraction analysis (Figure 4.2). The spectra show high degree of crystallinity in each case. The sample Ag/TiV(A) shows a predominantly anatase mixed phase and the peaks are in good agreement with the anatase [JCPDS#211272] and rutile [JCPDS#870710] phase systems of TiO$_2$. There are no distinct peaks for vanadium. In the present case the calcination temperature was much lower than the reported value for onset of anatase to rutile phase transformation. It is in accordance with the report that anatase-to-rutile transformation temperature reduces with V-doping [49-50]. The increase in the rutile phase composition compared to V doped titania prepared under identical conditions can be attributed to further reduction in the temperature of the onset of phase transformation in the presence of Ag [18,37]. The majority of the peaks of this system are same as that of the V doped titania system. The peaks at 38.12°, 44.30° and 64.50° can be ascribed to the presence of Ag in the system [JCPDS File No. 652871]. The peaks at 32.34°,
46.49° and 50.67° can be attributed to the impurity peaks present in the system in the form of AgCl. The sample Ag/TiV(B) shows a predominantly rutile mixed phase and the peaks are in good agreement with the anatase [JCPDS#211272] and rutile [JCPDS#870710] phase systems of TiO₂. It has other corresponding peaks seen in Ag/TiV (A) as well. The enhanced phase transformation observed in the case of Ag/TiV oxide system compared to TiV system can be attributed to the incorporation of Ag into the system as well as the medium of synthesis. The extra peaks observed in the system are due to AgCl precursors. The mass fraction calculated using the formula Spurr formula and the crystallite size calculated by the Scherrer formula as discussed in Chapter 2 and are given in Table 4.1.

Table 3.1 Physicochemical 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>Ag/TiV (A)</td>
<td>24</td>
<td>35</td>
<td>69</td>
</tr>
<tr>
<td>2.</td>
<td>Ag/TiV (B)</td>
<td>39</td>
<td>63</td>
<td>6</td>
</tr>
</tbody>
</table>

The SEM micrographs of the Ag/TiV samples were obtained to investigate the powder morphology and microstructures (Figure. 4.3). The particle size of the sample Ag/TiV(A) in the micrograph shows a homogeneous distribution of the crystalline material although not fully resolved (Figure.4.3A). The image shows highly dispersed nanoparticles in the system. EDAX spectrum, Figure.4.3A (Inset), confirms the presence of Ti with Kα line at 4.5 keV, V with Lα line at 0.5 keV and Ag with Lα line at 3.0 keV. The less atomic percentage of V observed in the case of Ag/TiV oxide sample can be attributed to the low solubility of vanadium and is in good agreement with the earlier report [50-51]. The SEM micrograph of Ag/TiV(B) sample (Figure.4.3B) showed some spike like structures and the particle sizes could not be ascertained from this. EDAX spectra Figure. 4.3B (Inset) confirms the presence of Ti, V and Ag. The SEM image of Ag/TiV(B) couldn’t reveal about the particle size and their distribution. In the TEM micrograph of the sample it is observed that the size of the particles is non-uniform with a size distribution of
Ag/TiV (A) in the range of 5-20nm (Figure 4.4a1.). The SAED pattern (Figure 4.4a1(inset)) confirms the polycrystalline nature of the prepared sample.

Figure 4.3: SEM spectra of silver sensitized V doped titania samples along with EDAX spectra inset (A). Ag/TiV(A), (B). Ag/TiV(B)

Figure 4.4: TEM, HRTEM and SEAD spectra of silver sensitized V doped titania samples (A). Ag/TiV(A), (B). Ag/TiV(B)
The HRTEM micrograph (Figure. 4.4a2.) reveals the fringes of spacing 0.333 and 0.236 nm which correspond to (110) plane of TiO$_2$ and (111) plane of Ag respectively [53]. The TEM analyses confirmed the presence of silver on the surface. The TEM micrograph of Ag/TiV (B) (Figure 4.4b1) shows the presence of grain size of 20-30 nm in the polycrystalline bulk. SAED pattern shows the polycrystalline nature of the sample (Figure 4.4b1(inset)). Ag is seen dispersed and in close contact with TiV oxide. It may facilitate the scavenging of electrons in the catalyst. The HR-TEM image (Figure. 4.4b2) of the material shows the fringes of spacing 0.322 and 0.236 nm which correspond to (110) plane of rutile TiO$_2$ and (111) plane of Ag, respectively [52]. The Ag/TiV (B) sample showed good uniformity in particle size compared Ag/TiV(A) sample. The small decrease observed in the d-spacing supports the presence of V inside the crystal lattice and is in good agreement with the XRD data.

In order to determine the chemical composition and the valance state of the various species in the surface region of Ag/TiV samples XPS study was carried out as shown in Figure 4.5. The full scan spectra of Ag/TiV samples shows the presence of the C 1s, Ag 3d, Ti 2p, V 2p and O 1s peaks which confirm the presence of these element in the surface region of the material. Ag/TiV(A) sample showed the C 1s core level peak at the 284.598 eV which confirm that there is no charge shift. The binding energy peaks at 458.57 and 464.4 eV correspond to the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ lines, respectively which show that the Ti is present in the IV state. The binding energy peaks at 516.935 and 523.976 eV corresponds to the V 2p$_{3/2}$ and V 2p$_{1/2}$ which depicts the presence of vanadium on the catalyst surface in the IV state [54-55]. The binding energy peaks at the 529.657, 530.702 and 532.176 eV correspond to the O 1s lines. These peaks show the presence of three type of the oxygen atoms. The 529.657eV peak corresponds to the Ti bonded oxygen, 532.176 eV peak corresponds to V-O bond and 530.702 eV peak may be due to presence of silver in the system. The Ag/TiV (B) showed similar kind of energy peaks for C, Ti and V. The peaks at the 529.10 and 530.79 eV correspond to the O 1s lines. These peaks show the presence of two types of oxygen atoms. The 529.10 eV peak corresponds to the
oxygen ions in rutile titania matrix while 530.79 eV peak corresponds to the presence of surface hydroxyls on the titanium surface [51]. Peaks at 368.69 and 374.55 eV correspond to Ag 3d$_{5/2}$ and 3d$_{3/2}$ respectively and they confirm the presence of silver on the system. The powder Ag/TiV samples were characterized by UV-DRS spectrophotometer for its UV-Visible light response along with V doped titania. Both TiV and Ag/TiV oxide system showed extended absorption in the visible region (Figure 4.6).

Figure 4.5: XPS spectra of silver sensitized V doped titania samples (A). Ag/TiV(A), (B). Ag/TiV(B)
The absorption spectrum of Degussa P25 is also given for comparison. A significant red-shift is observed in the case of TiV(M). The reduction in the range of absorption spectrum in Ag/TiV samples compared to TiV(M) (Chapter 3) can be ascribed to the lowering of the V content in the lattice as observed in XRD. The band gaps of these materials were calculated by the Tauc’s relation as discussed in Chapter 2 and are given in Table 4.1.

![UV-DRS spectra](image)

Figure 4.6: UV-DRS spectra of silver sensitized V doped titania along with V doped titania samples

It may be noted that large red shift in the absorption spectrum doesn’t ensure an enhanced photocatalytic activity because unwanted recombination centers may result in non-availability of the oxidizing radicals. Also there is a possibility of lowering of the conduction band edge below the affinity level of O₂ which plays a crucial role in enhancing photocatalytic activity. For Degussa P 25 the value of the band gap is 3.2 eV.

The photoluminescence (PL) analysis were carried out to study the photoluminescence responses of the samples with an excitation wavelength of 390nm
in emission mode (Figure 4.6). The Ag/TiV samples showed distinct peaks at 425, 445, 492, 535 and 594 nm. The trap levels identified in the sample Ag/TiV(A) at 425 nm can be assigned to the band-to-band transition of self-trapped excitons localized on octahedral TiO$_2$ nanoparticles [55]. The remaining trap levels ranging from 445 to 595 nm can be assigned to the oxygen vacancy levels [55]. These trap levels may play a positive role in reducing the recombination. Low PL intensity observed in the sample Ag/TiV(B) may be ascribed to the reduction in electron-hole recombination compared to Ag/TiV(A) which plays a positive role in the photocatalytic activity.

![PL spectra of silver sensitized V doped titania samples](image)

Figure 4.7: PL spectra of silver sensitized V doped titania samples

4.3.1 Degradation kinetics and photonic Efficiency

The study of photocatalytic activity of the material was performed on aqueous phenol. Phenol solution was irradiated with visible light flux for a total duration of 90 min. The results of the photodegradation of phenol solution are depicted in Figure 4.8. The Ag/TiV samples shows high rate of degradation compared to the reference catalyst Degussa P-25. The Ag/TiV(B) showed high photoactivity compared to Ag/TiV(A). The photodegradation of phenol follows pseudo-first-order kinetics, and
hence the rate constants are calculated using log \((C/C_o)\) vs. time plot (Figure. 4.9) and are given in Table-4.2.

![Figure 4.8: Phenol degradation spectra of silver sensitized V doped titania samples](image1)

![Figure 4.9: Rate constant calculation spectra of V doped titania samples](image2)
The values of degradation rate constants of phenol are in accordance with the earlier reports[18,56]. Comparison of the activity of the Ag/TiV(A) with the Degussa P-25 shows an increase of about five times in the rate of degradation of phenol and a small rise in the rate constant with respect to TiV(M) (Chapter 3). Ag/TiV (B) shows 12 times high visible activity compared to Degussa P25 and 2.5 times increase with respect to TiV(M) (Chapter 3). The high rate of degradation in the case of Ag/TiV samples may be due to its enhanced visible light functional property attributable to narrowing of band gap, presence of predominantly anatase/rutile mixed phase and the trap levels, as well as the presence of Ag as sensitizer. Among the two Ag/TiV samples the high activity of Ag/TiV(B), in spite of larger grain size may be ascribed to the presence of high proportion of rutile phase. It further shows that mixed influences the activity of titania catalyst more than many other factors. As stated earlier for the comparative analysis of the performance of heterogeneous photocatalysts with respect to the radiation intensity and spectrum, photonic efficiency appears to be an appropriate and reasonable parameter which is measurable. The photonic efficiency were calculated using the equation mentioned

Table 4.2: Rate constants, photonic efficiency and microbicidal photonic efficiency of the samples

<table>
<thead>
<tr>
<th>S. N</th>
<th>Sample</th>
<th>Detoxification</th>
<th>Disinfection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rate Constant</td>
<td>Rate constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(min⁻¹)</td>
<td>(min⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Photonic efficiency (%)</td>
<td>Light</td>
</tr>
<tr>
<td>1.</td>
<td>Ag/TiV (A)</td>
<td>0.005</td>
<td>NA</td>
</tr>
<tr>
<td>2.</td>
<td>Ag/TiV (B)</td>
<td>0.012</td>
<td>0.086</td>
</tr>
<tr>
<td>3.</td>
<td>Degussa P25</td>
<td>0.001</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.021</td>
<td>0.139</td>
</tr>
</tbody>
</table>

in Chapter 2 and values are given in Table 4.2. These are found to be identical to the earlier report[57]. The photonic efficiency of the Ag/TiV samples also showed an increase compared to Degussa P25 and to TiV(M).
4.3.2 Kinetics of microbial inactivation under visible light irradiation

The microbialidal activity of the Ag/TiV(B) oxide was investigated by evaluating the inactivation of *E. coli* bacterium under dark and visible light irradiation. The sample Ag/TiV(B) was employed for disinfection analyses due to its high detoxification performance compared to Ag/TiV(A). All the results were compared with Degussa P25 photocatalyst. As depicted in Figure 4.10, *E. coli* cells can almost completely be inactivated within one hour with Ag/TiV oxide photocatalysts under visible light irradiation. The decrease in the number of CFU on an agar plate was used for evaluating the performance of the photocatalyst. These plates are shown in a series of photographs presented in the Figure 4.11. In the present work Chick-Watson (CW) model was adopted to model the rate of disinfection process represented by kinetic constant k. This particular model was adopted because at higher loading of catalyst the initial delay in the onset of microbialidal activity may be neglected and also a log-linear region was considered adequate for the purpose as discussed in Chapter 3. It may be noted here that catalyst loading and irradiation flux has been kept constant throughout the experiments. The
rate constants were calculated by plotting $-\ln N_t/N_0$ vs time (see Figure 4.12) and the values are given in Table 2. The rate constant for Ag/TiV(B) was calculated to be 0.086 min$^{-1}$, which is about three times and eight times higher than that of TiV(M) (Chapter 3) and Degussa P25, respectively. These were evaluated under identical conditions and are comparable with the earlier reports [58,59]. This result clearly indicates the role of enhanced and extended absorption because of doping of vanadium and reduced carrier recombination due to Ag sensitization. The $k$ values of

Figure 4.11: *E. coli* culture at different time of exposure a) 0 min, b) Ag/TiV (B) 30 min (light), c) Ag/TiV (B) 60 min (light), d) Ag/TiV (B) 30 min (dark), e) Ag/TiV(B) 60 min (dark), f) Degussa P25 30 min (light), g) Degussa P25 60 min (light), h) Degussa P25 30 min (dark), i) Degussa P25 60 min (dark), j) Light control 30 min k) Light control 60 min,

dark control experiments amply demonstrate that microbicidal activity is dominated by photocatalytic effect of the material and not by biocidal effect of Ag. It may be noted that under very low atomic percentage of Ag the biocidal effect of Ag was reported to be negligible [60]. For the comparative analysis of the performance of heterogeneous photocatalysts with respect to the radiation intensity and spectrum
microbicidal photonic efficiency (MPE) has been proposed to be a suitable parameter for the disinfection systems in Chapter 3. The same equation has been used to calculate the microbicidal photonic efficiency values which are given in Table 4.2. From the values it can be seen that the Ag/TiV oxides are far superior than Degussa P-25 in showing the bactericidal activities. As expected the mixed Ag/TiV oxide showed better performance for disinfection also compared to other samples.

A mechanism showing the role of materials in the enhanced visible light activity is depicted in Figure 4.13. As shown, the photogenerated electrons in the photocatalyst migrate to the surface of the catalyst where they are trapped by the silver nanoparticles because of favorable interfacial conditions which also hinder their recombination with holes. The photogenerated holes are thus available to produce •OH radicals in the presence of water which in turn take part in photocatalytic reaction. The presence of pentavalent vanadium oxide has been reported to make a net contribution in photogenration of holes due to their high charge-to-volume ratio in titania matrix and also the movement of electrons by providing a pathway[61].

Figure 4.12: Disinfection rate constant calculation spectra of Ag/TiV(B) samples.
Figure 4.13: Photocatalytic mechanism of Ag/TiV oxide nanoparticles under visible light irradiation.

4.4. Conclusion:

Silver sensitized mixed phase V doped titania nanoparticles were synthesized under the identical synthesis conditions of V doped titania as discussed in Chapter 3. Both the materials showed enhanced red-shift in their absorption spectrum. Both the Ag/TiV oxide samples showed a marked enhancement in the visible light activity with their activities higher than those of TiV oxide and Degussa P25 for the degradation of phenol under visible light irradiation. The synergy of enhanced visible light absorption, presence of carrier traps in the mixed phase; and the role of silver in sensitization and visible light induced plasmon resonance plays a positive role in improving the photoactivity. The results suggest that silver sensitized V doped titania catalyst is a highly active photocatalyst with its activity extending into the visible range suggesting, thereby, that it may be used fruitfully under solar irradiation. From the identical changes in the two performance parameters i.e. degradation rate constant and photonic efficiency, it may be concluded that either of them may be used to analyze the relative performance of the catalysts. It would be interesting to see the influence of morphology including particle size and specific surface area on such systems. But this will need tuning these features through a suitable technique. The process of sol-gel and thermal treatment does not provide sufficient room for this, while other physical methods may be energy intensive. Also it is appropriate to attempt to synthesize pristine systems.
References


4.21


