Single-Step Synthesis of Silver-Doped Titanium Dioxide: Influence of Silver on Structural, Textural, and Photocatalytic Properties

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ABSTRACT: The silver-doped titanium dioxide (Ag−TiO2) photocatalysts with varied silver content ranging from 0.75 at % to 3.5 at % were synthesized by a single-step sol−gel method. The role of silver content on the properties of photocatalyst has been studied. The doping of 0.75 at % silver in TiO2 produced thermally stable TiO2 anatase phase with smallest particle size, uniform particles size and morphology, high surface area and low-energy excitation characteristics. The Ag−TiO2 sample with 0.75 at % silver possesses predominantly finely dispersed silver species (AgO and AgO) on the surface. The proportion of surface agglomerated silver metal (Ag0) increases as the silver content in the Ag−TiO2 sample increases. The silver oxide species were observed to be responsible for better physicochemical and catalytic properties. The TiO2 with 0.75 at % silver was found to be an efficient photocatalyst showing enhanced photocatalytic activity for aqueous medium photocatalytic degradation of phthalic acid in the presence of UV radiation and air.

1. INTRODUCTION

Titanium dioxide (TiO2) is an extensively studied semiconductor photocatalyst for photocatalytic degradation (PCD) of organic and inorganic pollutants, and disinfecting wastewater. In spite of its nontoxic nature, low cost, and applicability for PCD of a broad range of organic pollutants, the TiO2-based treatment processes could not be adopted at a large scale. The major constraints for the practical application of TiO2 photocatalyst is its low quantum efficiency and short wavelength excitation. When TiO2 particles are irradiated with near-ultraviolet light of energy equal to or greater than the bandgap energy ($\lambda < 380$ nm), electrons from the valence band migrate to the conduction band creating positively charged holes in the valence band.1 The positive holes ($h^+$) and conduction band electrons ($e^-_b$) migrate to the surface of TiO2, where they initiate oxidation and reduction reactions with adsorbed species. The holes and electrons can also recombine, leaving them unavailable for participation in useful redox reactions. The efficiency of TiO2-catalyzed photocatalytic reactions is governed by how effectively electrons and holes are channeled into oxidation and reduction reactions before their recombination takes place.2,3 One of the approaches that has been widely adopted to improve the photocatalytic efficiency of the TiO2 photocatalyst under UV and visible light is the doping/deposition of a minute amount of a suitable metal in TiO2, which enhances the participation of the photogenerated holes and electrons in the photocatalytic reactions.4−8 It has been proposed that the deposited or doped metal in TiO2 have high Schottky barriers at the metal−TiO2 contact region and thus act as electron traps, facilitating electron−hole separation and promote the interfacial electron transfer process, which enhances the efficiency of the photocatalyst.9 Silver doped TiO2 (Ag−TiO2) has been one of the extensively studied doped TiO2 photocatalysts due to its wider applications in environmental remediation, antimicrobial activity, catalytic oxidation reactions, etc.10−27 Generally, Ag−TiO2 catalysts are synthesized by either deposition or doping of silver (in optimum amount) in TiO2 to improve its photocatalytic efficiency. The deposition of silver on TiO2 surface is usually carried out by wet impregnation method using an appropriate silver precursor followed by calcination/photo or chemical reduction.11,13,25−26 In recent years, single-step methods for the synthesis of Ag-doped TiO2 photocatalysts have also been reported, in which silver ions (silver salt) are introduced during hydrolysis of the titanium precursor.14,20,22,27−29 The nanosized Ag−TiO2 particles were prepared by a sol−gel process using titanium tetraisopropoxide and silver nitrate as precursors of TiO2 and silver, respectively and sodium citrate tribasic hydrate as a reduction agent to improve the photodegradation of p-nitrophenol.29 The silver (1 at %), carbon and sulfur-doped TiO2 (Ag/(C, S)−TiO2) nanoparticle photocatalyst was prepared by the sol−gel route for improved degradation of the gaseous acetaldehyde as compared to P25 TiO2 under visible and UV light.19 The Ag−TiO2 with varied silver content (1.5−8.5 atom %) were synthesized using a microemulsion
system (water/AOT/cyclohexane) for enhanced photocatalytic decomposition of phenol from aqueous solution under visible and ultraviolet light irradiation and also for antimicrobial applications. A modified sol–gel preparation method was used for synthesis of Ag–TiO_2 in presence of acetic acid to obtain a thermally stable anatase phase with homogeneously dispersed silver nanoparticles on the surface after calcination. This method produced visible light active silver-doped TiO_2 due to the presence of homogeneously dispersed silver nanoparticles on the surface showing increasing rate of rhodamine 6G degradation with increasing silver content in TiO_2. The nano silver-doped mesoporous titania photocatalysts were synthesized by a sol–gel method using a urea template and a glucose reductant and were found to be having improved structural properties as well as photocatalytic activity for dye degradation. A simple and controllable method for Ag–TiO_2 synthesis is desirable for the viability of the TiO_2-based processes. Therefore, the present study was aimed at establishing a one-pot, single-step, sol–gel method (in basic medium) to synthesize Ag–TiO_2, which could be a convenient route for doping of silver in TiO_2. The effect of silver species (ionic/reduced) and its concentration on the structural, textural, and catalytic properties of Ag–TiO_2 are very significant, which have been reported in most of the previous studies. In the present study an attempt has been made to understand the influence of the presence of an optimum amount of silver and the nature of silver (ionic or oxide species/reduced) on the important physicochemical properties and catalytic efficiency of doped TiO_2 material. In continuation of our work on TiO_2-based PCD of phthalic acid (which is a highly stable and nonbiodegradable water pollutant of dyes and paint industries), we observed almost a 3-fold increase in the rate of phthalic acid degradation with Ag–TiO_2 having an optimum amount of silver (0.75 at % Ag) in the presence of UV radiation and air.

2. EXPERIMENTAL SECTION

2.1. Chemicals. All the chemicals used were of synthesis grade and were used without any further purification. Titanium tetra iso-propoxide (TTIP) was purchased from Sacruchem Pvt. Ltd, India, and aqueous ammonia (25%) and phthalic acid (99%) were obtained from s.d. fine Chem. Ltd., India. Silver nitrate and methanol (99%) were obtained from Merck Ltd., India. Degussa P25 TiO_2 catalyst (AEROSIL TiO_2 P25 with 89% anatase phase, crystallite size of 25 nm, and BET surface area of 50.2 m^2/g) was provided by Degussa (Germany).

2.2. Synthesis of TiO_2 and Ag-Doped TiO_2 (Ag–TiO_2) Samples. The TiO_2 was synthesized by sol–gel technique using titanium tetra iso-propoxide (TTIP) as precursor. Aqueous ammonia was added dropwise in TTIP–methanol solution (36 mL TTIP and 160 mL methanol) and aqueous ammonia was added dropwise in the solution till the pH was 9–10. The gel was filtered and washed with distilled water for several times to remove the nitrates, followed by washing with methanol. The gel was dried at 80 °C for 12 h. The dried sample was calcined at different temperatures (400, 500, and 600 °C) to obtain Ag–TiO_2 samples (Ag(0.75)T-400, Ag(0.75)T-500, and Ag(0.75)T-600, respectively, where the value in parentheses denotes silver content). Similarly other Ag–TiO_2 samples with 1.5, 2.5, 3.0, and 3.5 at % silver content (i.e., Ag(1.5)T, Ag(2.5)T, Ag(3.0)T, and Ag(3.5)T, respectively) were prepared by using 0.30, 0.51, 0.61, and 0.71 g of AgNO_3 in TTIP-methanol solution (36 mL TTIP and 160 mL methanol). The samples were calcined at 400, 500, and 600 °C to obtain Ag–TiO_2 samples.

2.3. Characterization of TiO_2 and Ag–TiO_2 samples.

The silver content in the Ag–TiO_2 samples was estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer Instrument, Optima 200 DV). The sample (100 mg) was dissolved in 40% HF solution (15–20 drops) followed by addition of 5 wt % boric acid solution making up to 100 mL in a volumetric flask, which was analyzed by ICP.

The X-ray diffraction (XRD) study of TiO_2 and Ag–TiO_2 samples was carried out using an X-ray diffractometer (Bruker, Advanced D8) with Cu Kα radiation (λ = 1.5418 Å) and a Lynx Eye detector to study the crystalline nature, types of phases, and the crystallite size in the samples. The sample was scanned in 2θ range of 15–90° with a scanning rate of 0.02° s^{-1} and time per step of 0.1 s/step. The crystallite size of each phase was determined from the peak of maximum intensity of the phase using the Scherrer formula with a shape factor (K) of 0.9 as given below:

\[
\text{crystallite size} = \frac{K\lambda}{W\cdot\cos\theta}
\]

where \( W = W_b - W_d \) is the broadened profile width of experimental sample, and \( W_s \) is the standard profile width of the reference silicon sample.

The average particle size and particle size distribution in the samples were measured by dynamic light scattering using Malvern particle size analyzer by dispersing the sample in isopropanol followed by 10 min sonication. The particle surface charge of the samples was analyzed by measuring the ζ potential of the samples using Zetasizer (Malvern) by dispersing the particles in deionized water.

The BET (Brunauer–Emmett–Teller) surface area (S_{BET}) of the samples was determined from a N_2 adsorption–desorption isotherm study at liquid nitrogen temperature (77 K) using ASAP 2010, Micromeritics. Before the analysis, the samples were degassed under vacuum at 110 °C for 2 h to evacuate the physisorbed moisture. The surface morphology of TiO_2 and Ag–TiO_2 particles was analyzed by a scanning electron microscope (SEM; FEI instruments).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the samples was carried out using a TGA/DSC thermal analyzer (Mettler Toledo, STARe SF1052) by heating the sample from 25 to 800 °C with the heating rate of 10 °C/min in the flow of nitrogen gas (50 mL/min).

The UV–vis–NIR spectrophotometer (Agilent, Carry 5000) was used to record the diffuse reflectance spectra (DRS) of the samples under ambient conditions in the wavelength range of 190–2500 nm. X-ray photoelectron spectroscopy (XPS) studies were carried out using VSW scientific instrument.
(UK), equipped with the Al Kα source (1486.6 eV), in an ultrahigh vacuum chamber (in the range of ~1–9 × 10⁻⁹ Torr), and the photoelectrons were detected using a concentric hemispherical analyzer by keeping constant pass energy (40 eV). Prior to the experiments, the photoelectron spectrometry work function was adjusted to get the Au 4f7/2 peak at 84.0 eV (external reference), while C 1s (graphitic carbon of the sample surface) peak served as an internal reference for all the samples. This peak is also used to correct for charging effect. A full scan covering the range of 0–1400 eV binding energy was recorded for detecting all the elements present in the sample. On this basis, the details scans of the corresponding peaks were recorded.

2.4. Photocatalytic Degradation of Phthalic Acid Using TiO₂ and Ag–TiO₂ Samples. The photocatalytic activity of the TiO₂ and Ag–TiO₂ samples was evaluated for photocatalytic degradation (PCD) of phthalic acid in presence of UV light and air using 100 ppm aqueous solution of phthalic acid (400 mL) and 1 g of sample. The solution of 100 ppm of phthalic acid was prepared in deionized water. The 400 mL of aqueous solution was taken in a photocatalytic reactor equipped with a magnetic stirrer and water cooling jacket (temperature: ~30 °C) from outside the reactor. The UV light (Phillips high-pressure mercury lamp; power: 120 W; light intensity: ~4.0 mW/cm²; wavelength: 280–450 nm) encased in a quartz tube was placed inside the reactor. The whole system was placed in a wooden box for protection from the exposure of the radiation. The TiO₂ sample (1 g) was added in the reactor charged with the aqueous solution of phthalic acid. The reaction was carried out at constant temperature under continuous stirring, aeration, and irradiation of UV light. The reaction progress, i.e. degradation of the phthalic acid, was monitored by analyzing the samples (taken by a syringe at regular time intervals) using high performance liquid chromatograph (Dionex Ultimate 3000®) with a C8 column (Acclaim 120, 5 μm, 120 Å, 4.6 mm × 250 mm), acetonitrile–water eluents 50:50, flow rate of 1 mL/min, and 235 nm wavelength of photodiode array detector at constant column temperature of 25 °C.

3. RESULTS AND DISCUSSION

3.1. Characterization of TiO₂ and Ag–TiO₂ Samples. The silver content in the synthesized Ag–TiO₂ samples, measured by ICP-OES analysis is presented in Table 1. The estimated silver contents in the samples were found to be in good agreement with the theoretical values. The XRD patterns (Figure 1a and b) of TiO₂ and Ag–TiO₂ samples calcined at 400 and 500 °C show the presence of an anatase phase showing the characteristic peaks at 25.5, 37.5, 47.8, 53.8 and 54.9° 2θ for diffraction of X-rays from (1 0 1), (1 1 2), (2 0 0), (1 0 5), and (2 1 1) reflections of anatase phase, respectively. The Ag–TiO₂ samples with 0.75–2.5 at % silver content, calcined at 600 °C, also contain predominantly anatase phase (Figure 1c). But the samples having 3.0 at % and 3.5 at % silver content calcined at 600 °C possess anatase along with a rutile phase showing the reflections corresponding to the rutile phase at 27.5 and 36.4° 2θ (Figure 1c). The pure TiO₂ calcined at 600 °C exhibits only the anatase phase with very high crystallinity.

The XRD patterns of Ag–TiO₂ samples with 2.5 to 3.5 at % silver content calcined at 600 °C showed the additional peaks at 38.1, 44.1 and 64.1° 2θ, which were ascribed to Ag0 [for (1 1 1), (2 0 0), and (2 2 0) reflections, respectively; JCPDS 01-1164] (Figure 1c). The intensity of the peaks for the Ag0 gradually increases with increasing the silver content in the sample. The XRD patterns of Ag–TiO₂ samples with 0.75 at % and 1.5 at % calcined at 600 °C did not show any diffraction peaks corresponding to silver species in the samples as they might be too less as well as small in size to be detected. Similarly, XRD patterns of all Ag–TiO₂ samples (with 0.75 to 3.5 at % silver) calcined at 400 and 500 °C did not exhibit any diffraction peaks for silver species. The XRD results indicate that the doping of silver in the range of 0.75–2.5 at % enhances the stability of anatase phase while the higher silver content in TiO₂ promotes the crystallization of anatase to rutile. It shows that the high silver concentration lowers the anatase–rutile transformation temperature, which may be due to increased level of oxygen vacancies. The results also show that in the Ag–TiO₂ samples having high silver content, high-temperature calcination (600 °C) caused the reduction of silver species and aggregation to produce crystallites of Ag0. The Ag+ ions cannot enter the lattice of TiO₂ to form a stable solid solution as the radius of the Ag+ ion (~126 pm) is much larger than that of the Ti4+ ion (~68 pm). So Ag+ ions can migrate from the volume of the grains to the TiO₂ surface during crystallization. The samples having less silver content (0.75–1.5 at % calcined at 400–600 °C) as well as high silver content and calcined at low temperature (400 and 500 °C) have highly dispersed silver species showing no corresponding diffraction peak in XRD. However, in the samples containing high silver content (>1.5 at %) calcined at 600 °C, the silver ions agglomerate on the surface and are reduced to form Ag0 crystallites (due to the high redox potential for the Ag0 ion).

The crystallite size of anatase phase in the pure TiO₂ and Ag–TiO₂ samples, calculated by using the Scherrer formula, was found to be increasing with the calcination temperature (from 400 to 600 °C), which may be because of nucleation and growth of anatase (Figure 2). The 0.75 at % silver-doped TiO₂ samples had the smallest crystallite size (17 nm) at 400 °C. With increasing silver content from 0.75 at % to 3.5 at %, the crystallite size of the anatase phase in the samples also increased.

The average particle size of pure and doped TiO₂ samples was also measured by dynamic light scattering to observe the effect of silver doping and calcination temperature on particle size. The particle size of pure and silver doped TiO₂ samples calcined at different temperature are given in Figure 3. The trend in variation in particle size of the samples was in accord of crystallite size showing smallest particle size for 0.75 at % silver-doped samples. The particle size also increases with calcination temperature from 400 to 600 °C and with increasing silver content from 0.75 at % to 3.5 at %.

The particle size distribution in 0.75 at % silver-doped samples was found to be narrower than pure TiO₂ sample.

| Table 1. Silver Content in Ag Doped TiO₂ Samples |
| sample | Ag (mol %) input | Ag (mol %) output |
| Ag(0.75)T-400 | 0.75 | 0.74 |
| Ag(1.5)T-400 | 1.5 | 1.45 |
| Ag(2.5)T-400 | 2.5 | 2.44 |
| Ag(3.0)T-400 | 3.0 | 2.94 |
| Ag(3.5)T-400 | 3.5 | 3.51 |

[a] mol of Ag × 100] / mol of Ti in solution during hydrolysis.
[b] Calculated from Ag wt %, obtained from ICP analysis.
It can be seen that the crystallite size and average particle size of the Ag−TiO₂ sample decreased as the silver concentration was increased from 0.0 at % to 0.75 at %. Further increase in the silver concentration from 0.75 at % to 3.5 at % increased the crystallite size and average particle size. The doping of metal ions in optimum concentration usually hinders the growth of crystallites. The effect of Ag dopant on TiO₂ particle size reduction has been attributed to grain-boundary pinning caused by dopant ions, which limits the grain growth by the symmetry-breaking effects of the dopant at the boundary, resulting in smaller particle sizes.

The repulsion between the crystallites/particles due to presence of doped silver ions (electropositive nature) in the crystallites may also be responsible for controlling crystallites/particles growth and aggregation giving small particles with narrow size distribution. Results indicate that 0.75 at % may be the optimum doped amount of silver, which is effective to control the crystallite growth and agglomeration. The excess

Figure 1. XRD patterns of TiO₂ and Ag−TiO₂ samples calcined at (a) 400, (b) 500 and (c) 600 °C [(i) TiO₂, (ii) 0.75 at %, (iii) 1.5 at %, (iv) 2.5 at %, (v) 3.0 at %, and (vi) 3.5 at % Ag−TiO₂ samples].

Figure 2. Crystallite size of anatase phase of TiO₂ samples with varied silver content, calcined at different temperatures.

Figure 3. Variation in average particle size of TiO₂ samples with silver content and calcination temperature.
Figure 4. Particle size distribution in TiO₂ and Ag(0.75)T samples calcined at 400–600 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-400</td>
<td></td>
</tr>
<tr>
<td>Ag(0.75)T-400</td>
<td></td>
</tr>
<tr>
<td>T-500</td>
<td></td>
</tr>
<tr>
<td>Ag(0.75)T-500</td>
<td></td>
</tr>
<tr>
<td>T-600</td>
<td></td>
</tr>
<tr>
<td>Ag(0.75)T-600</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. SEM images of (a) T-400, (b) Ag(0.75)T-400 and (c) Ag(3.5)T-400 samples.
amount of silver species on the surface may promote the growth of crystallites of TiO$_2$ during calcination by coalescence of adjacent anatase crystallites forming larger anatase particles.$^{35,36}$

As the Ag(0.75)T-400 sample showed the smallest crystallite size and particle size with narrow particle size distribution, this sample was analyzed by SEM (Figure 5). The SEM picture of Ag(0.75)T-400 clearly shows the presence of spherical particles of homogeneous shape and size with less agglomeration, whereas SEM image TiO$_2$ (T-400) indicates that particles are agglomerated, not of uniform size, and with irregular shape. The SEM picture of Ag(3.5)T-400 shows the presence of very big agglomerated particles in the sample.

The TGA and DSC profiles of the uncalcined samples (i.e., Ti(OH)$_4$ and silver-doped Ti(OH)$_4$ samples) was carried out in the range of 25−800 °C to examine the crystallization phenomena (dehydroxylation) during thermal treatment (Figure 6a and 6b). The TGA graph of the Ti(OH)$_4$ shows three steps weight loss (Figure 6a); the first step (100−250 °C) is attributed to removal of solvents (i.e., water, methanol and isopropanol), second step (260−330 °C) is due to dehydroxylation of Ti(OH)$_4$, and the third step (385−420 °C) represents the crystallization to anatase phase.$^{30}$ In TGA graphs of doped samples, the third step weight loss was observed to be taking place in broad temperature range (below 400−800 °C), whereas for pure Ti(OH)$_4$ this step was centered at ~400 °C showing sharp weight loss at this temperature. It shows that the dehydroxylation of Ti(OH)$_4$ to the anatase phase of TiO$_2$ (i.e., crystallization) is slowed down by silver. The DSC profile of pure Ti(OH)$_4$ also shows a peak at ~400 °C ascribed to crystallization of amorphous sample to anatase phase of TiO$_2$ (Figure 6b). The DSC graphs for various silver-doped samples show profiles similar to that of pure TiO$_2$; however, doped samples, particularly 0.75 at % silver-doped TiO$_2$ present very slow dehydroxylation and crystallization processes showing a broad peak at slightly higher temperature. It indicates that the 0.75 at % silver-doped in TiO$_2$ slows down the phase transformation and shifts the phase transformation temperature to high temperature. A further increase in silver concentration gradually shifts the exothermic peak to lower temperature, indicating the crystallization of the amorphous to the anatase phase at lower temperature in the samples than for the 0.75 at % doped sample.

Diffuse reflectance spectrum of the pure TiO$_2$ sample (Figure 7) shows an absorption edge at ~403 nm, which is generally ascribed to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d$_{5/2}$ orbitals of the Ti$^{4+}$ cations).$^{37}$ There is a shift in the absorption edge to 414 nm, in the 0.75 at % silver-doped sample. In addition, a broad peak with absorption edge at 530 nm can also be seen in the spectrum, which is ascribed to the formation of impurity energy levels within the band gap. The addition of silver ions in the 0.75 at % produce significant changes in the absorption spectrum of TiO$_2$, resulting in absorbance above 400 nm showing the possibility of lower energy transitions. The valence band electrons of TiO$_2$ are excited to localized energy levels created by doped silver in the band gap of TiO$_2$ at longer wavelength. On increasing the silver content from 0.75 at % to 3.5 at %, the absorption edge shifted to lower wavelength. The visible absorption band also disappeared in the samples containing higher silver content. This shows that the samples with >0.75 at % silver content do not show the effect of silver doping on absorption characteristics of TiO$_2$.
Both absorption edges in Ag(0.75)T-400 sample (i.e., at 414 and 530 nm) correspond to band gaps of 2.99 and 2.35 eV, respectively (Table 2), which were calculated according to the formula of the band gap (optical band gap = 1239.8/wavelength).13 The band gap for TiO2 containing more than 0.75 at % silver content increases with increase in silver content (Table 2). The study reveals that the 0.75 at % doping has significant effect on the absorption properties of TiO2 and effectively makes the band gap narrower, which can promote its photocatalytic activity.

The XPS results (Figure 8, Table 3) show that Ag(0.75)T-400 sample contains predominantly ionic silver species (74.5%; Ag2O and AgO) along with Ag0 (25.5%), while in the Ag(2.5)T-400 sample, the proportion of Ag0 increased to 46.5% and in the Ag(3.5)T-400 sample, only Ag0 was present, showing characteristic peaks at 368.4 and 365.42 eV for Ag 3d5/2 of Ag0. The peak at 365.4 eV may be presenting the Ag0 of silver nanoparticles complexed with titanols (Ti−OH) present on the TiO2 surface, which will reduce the binding energy of Ag0. The gradual increase in binding energy of Ti (Ti 2p) from 458.6 to 459.3 eV and of oxygen (O 1s) from 529.6 to 530.4 eV is an indication of this interaction (Table 4, see Supporting Information). Peng et al. have reported a low-energy band for Ag 3d5/2 at 365.4 eV attributed to Ag0 nanoparticles−carbohydrate complex stabilizing the Ag nanoparticles by noncovalent interaction between the carbohydrate hydroxyls and Ag through the high electronegativity of the hydroxyl groups.38 The XPS results indicate that on increasing silver content, Ag0 content on TiO2 surface increases.

Our observations are in good agreement with others. For Ag−TiO2 photocatalysts synthesized in microemulsion system, it was reported that at lower concentration, Ag species exist as AgO, Ag2O and Ag0, while at high concentration the amount of Ag0 species significantly increased.15

The highest specific area (82 m2/g) was obtained with 0.75 at % doped TiO2 calcined at 400 °C, which decreased for the samples having higher silver content (Table 5). The surface charge on undoped TiO2 particles was found to be −43.5 mV, which increased to −26.2 mV in 0.75 at % silver-doped TiO2 (Table 5). This shows that the doped silver species (Ag2O and AgO) are dispersed on the surface of TiO2 particles reducing the surface charge of particles probably due to the electropositive nature of silver present in oxide form. On increasing the silver content from 0.75 at % to 3.5 at %, the surface charge of particles was observed to be gradually decreasing from −26.2 mV to −35.6 mV (Table 5). The decrease in surface charge is attributed to agglomeration of silver species and reduction to Ag0 particles on the TiO2 surface. The ζ potential analysis results are clearly supporting the XPS results.

**Table 2. Absorption Edges and Band Gap Values of Samples**

<table>
<thead>
<tr>
<th>sample</th>
<th>absorption edge (nm)</th>
<th>band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-400</td>
<td>403</td>
<td>3.08</td>
</tr>
<tr>
<td>Ag(0.75)T-400</td>
<td>414</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>530*</td>
<td>2.34*</td>
</tr>
<tr>
<td>Ag(1.5)T-400</td>
<td>405</td>
<td>3.06</td>
</tr>
<tr>
<td>Ag(2.5)T-400</td>
<td>403</td>
<td>3.08</td>
</tr>
<tr>
<td>Ag(3.0)T-400</td>
<td>400</td>
<td>3.10</td>
</tr>
<tr>
<td>Ag(3.5)T-400</td>
<td>393</td>
<td>3.16</td>
</tr>
</tbody>
</table>

*Second absorption edge. \*Second band gap.

**Table 3. Proportion of Silver Species in Silver-Doped Samples**

<table>
<thead>
<tr>
<th>sample</th>
<th>peak area (%) of the peaks at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>367.19 eV (Ag2O, AgO)</td>
</tr>
<tr>
<td>T-400</td>
<td>–</td>
</tr>
<tr>
<td>Ag(0.75)T-400</td>
<td>74.5</td>
</tr>
<tr>
<td>Ag(2.5)T-400</td>
<td>53.5</td>
</tr>
<tr>
<td>Ag(3.5)T-400</td>
<td>–</td>
</tr>
</tbody>
</table>

*From XPS analysis. \*For Ag0 at 365.42 eV.

**Table 4. Ti 2p and O 1s peak positions in the samples**

<table>
<thead>
<tr>
<th>sample</th>
<th>Ti 2p peak</th>
<th>O 1s peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-400</td>
<td>458.6</td>
<td>529.6</td>
</tr>
<tr>
<td>Ag(0.75)T-400</td>
<td>458.7</td>
<td>529.7</td>
</tr>
<tr>
<td>Ag(2.5)T-400</td>
<td>458.7</td>
<td>529.8</td>
</tr>
<tr>
<td>Ag(3.5)T-400</td>
<td>459.3</td>
<td>530.4</td>
</tr>
</tbody>
</table>

This study shows that ζ potential measurement of doped TiO2 samples can be a good analytical tool to find the optimum metal dopant concentration. It can be concluded that at low
silver concentration (0.75 at %), the doped silver species are in oxide forms dispersed over the TiO2 surface, and at high silver content, the silver species accumulate on the TiO2 surface and get reduced to Ag0, decreasing the silver oxide species on the TiO2 surface (Scheme 1).

It was noticed that the synthesis using high silver concentration showed detrimental effects on the structural and textural properties of doped TiO2 as discussed above. At less concentration of silver, the silver oxide species are highly dispersed on the TiO2 surface. The doped silver oxide species may be responsible for enhanced thermal stability of the anatase phase and good control over particle size and shape, giving high surface area and reduced band gap. The electropositive nature of silver in oxide form will restrict the growth of crystallites/particles due to their attractive interaction with Ti-(O)4− moieties (Scheme 1) as well as reduce the particles agglomeration by repelling them away from each other. The small crystallites of anatase phase, high surface area, low energy absorption characteristics, and highly dispersed silver species (which may be more effective in reduction of charge carrier recombination) of the 0.75 at % TiO2 could show enhanced photocatalytic activity of the doped TiO2.

3.2. Photocatalytic activity of Ag–TiO2 for Degradation of Phthalic Acid. The photocatalytic activity of the silver-doped TiO2 samples was evaluated for photocatalytic degradation (PCD) of phthalic acid in presence of UV light and air. The direct photolysis of phthalic acid in absence of TiO2 catalyst did not show any reduction in the concentration, indicating that phthalic acid is photostable. In the absence of UV light, the adsorption of phthalic acid from aqueous solution (100 ppm) on TiO2 samples was in the range of 4.0−4.5% showing almost similar adsorption capacities of doped and undoped samples for phthalic acid. The TiO2 and Ag–TiO2-catalyzed phthalic acid PCD results (Figure 9) clearly indicate the highest activity of Ag(0.75)T-400 sample showing fastest PCD of phthalic acid (almost 3-fold) than pure as well other Ag–TiO2 samples. The degradation was slightly slower with Ag(1.5)T-400 and was observed to be gradually decreasing with increasing the silver content. The activity of Ag(0.75)T-400 sample was also higher than Degussa P25 TiO2. It indicates that Ag–TiO2 with 0.75 at % silver prepared by the one-step sol–gel method is a more efficient photocatalyst than undoped TiO2 and Ag–TiO2 samples with >0.75 at % silver. As there is no difference in adsorption properties of the TiO2 sample for phthalic acid, the enhanced activity of Ag(0.75)T-400 sample can be due to the presence of an optimum amount of doped silver and better structural and textural properties. The highest activity of Ag(0.75)T-400 sample is attributed to finely dispersed silver oxide species, which acts as an electron trap/electron−hole separation center, reducing recombination of positive holes (h+vb) and conduct conduction band electrons (e−cb) and creating a low-energy band gap.39 A more effective electron transfer can occur to the electron acceptors (O2) and donors (phthalic acid) adsorbed on the surface of the doped TiO2. In addition, the better physicochemical properties such as small particle size, high surface area, and narrow band gap of Ag(0.75)T-400 as compared to those of other doped samples may also be responsible for its higher activity. At high silver content, the silver particles can act as recombination centers, decreasing the photocatalytic activity of TiO2.40 Hamal et al. reported a similar effect of Ag concentration on the production of CO2 from CH3CHO on Ag/(C, S)−TiO2 under visible and UV light illumination showing optimal activity of the catalyst for 1 mol % of Ag.19 They stated that 1 mol % Ag concentration effectively suppresses the recombination of the photogenerated charge-carriers on the surface of the catalyst for oxidation and reduction reactions and higher Ag concentrations have a deleterious effect on the photoactivity of the catalysts because of the creation of recombination centers of charge carriers. Similar to our results, others have also reported that silver loading in the range of 0.5−1.5 mol % is the optimum amount giving the highest activity of silver-doped TiO2 in different photocatalytic degradation reactions.13,14,19,26,41,42 In some of the reports on Ag−TiO2, the optimum silver concentration showing the highest photocatalytic activity was found to be very high (3−6.5 mol %).15,20,43,44

Gunawan et al. reported that on exposure to visible light (>450 nm), the reduced silver nanoparticles on TiO2 surface

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**Table 5. BET Surface Area and Surface Potential of Pure TiO2 and Silver-Doped TiO2 (with different silver content) Calcined at 400°C**

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Surface potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-400</td>
<td>37</td>
<td>−43.5</td>
</tr>
<tr>
<td>Ag(0.75)T-400</td>
<td>82</td>
<td>−26.2</td>
</tr>
<tr>
<td>Ag(1.5)T-400</td>
<td>75</td>
<td>−28.7</td>
</tr>
<tr>
<td>Ag(2.5)T-400</td>
<td>72</td>
<td>−31.2</td>
</tr>
<tr>
<td>Ag(3.0)T-400</td>
<td>64</td>
<td>−34.3</td>
</tr>
<tr>
<td>Ag(3.5)T-400</td>
<td>51</td>
<td>−35.6</td>
</tr>
<tr>
<td>Degussa P25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 9. Photocatalytic degradation of phthalic acid with different photocatalysts.**

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**Scheme 1. Ag–TiO2 Particles Showing Effect of Silver Concentration on Particle Size, and Nature, and Location of Silver Species in Low and High Silver-Containing Samples**

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are excited by oxidation (Ag$^+ \rightarrow \text{Ag}^0$), and the electrons are injected to the TiO$_2$ support. The agglomeration of atomically dispersed silver species (which is the scenario at lower concentration of silver, i.e., 0.75 at %) to a bigger cluster of silver species (Ag$^+$) as a separate phase (i.e., at high silver concentration) on the surface may decrease the amount of actually doped silver in TiO$_2$ and also block the surface reaction sites, reducing the photocatalytic activity. The reason for reduced efficiency of a sample containing a higher silver amount has also been explained to be attributed to the fact that the reduced Ag may not be highly dispersed on the surface of TiO$_2$, which will not increase the number of active sites on the Ag–TiO$_2$ surface and will not change the electronic structure of TiO$_2$ significantly. In addition, further increasing the amount of silver can prevent light absorption and adsorption of reactant molecules by TiO$_2$. The poor photocatalytic activity of doped TiO$_2$ with Pt at higher metal loading has also been reported to account for a “screening effect”, making the photocatalyst surface less accessible for photons.

4. CONCLUSIONS
The Ag–TiO$_2$ samples with varied silver content ranging from 0.75 at % to 3.5 at % were synthesized by a single-step sol–gel route in basic medium. The present route can be a convenient method for the synthesis of silver-doped TiO$_2$. The silver content significantly affects the properties of doped TiO$_2$ photocatalyst. The optimum amount of silver (0.75 at %) effectively controls the particle growth and agglomeration, surface area, thermal stability, band gap, etc. The TiO$_2$ doped with 0.75 at % silver was the efficient photocatalyst showing best physicochemical properties (thermally stable anatase phase with smallest crystallite and particle size, narrow particle size distribution, uniform morphology of particles and highest surface area) and photocatalytic activity in phthalic acid PCD. Almost 3-fold faster PCD of phthalic acid could be achieved with 0.75 at % silver-doped TiO$_2$.

ASSOCIATED CONTENT
Supporting Information
This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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