Study of pure and Ag-doped TiO$_2$ nanoparticles for photocatalytic degradation of methylene blue

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Abstract. Titanium dioxide (TiO$_2$) is one of the most basic materials in our daily life that has wide applications as a whitening agent and an excellent photocatalyst material. Other noticeable applications include dye-sensitized solar cells, sunscreen and UV blocking pigments, cosmetics, paint, paper, food additive and flavor enhancer. Metal doping enhances the photocatalytic activity of nanoparticles. Therefore, we have prepared pure and Ag-doped TiO$_2$ nanoparticles using Ti-(IV)-isopropoxide as precursor. The resulting materials were characterized by x-ray diffraction (XRD) and UV-Visible spectroscopy. The XRD results showed the different structural phases and crystallite size of the nanoparticles. The band gap of the photocatalysts decreased by subsequent addition of the dopant. Further, the photocatalytic degradation of methylene blue (MB) was carried out for both pure and Ag doped TiO$_2$ nanoparticles under sunlight upto 90 minutes. The degradation of MB dye was observed to be directly related to the radiation time.

Keywords: Ag-TiO$_2$, co-precipitation, photocatalytic activity, methylene blue, XRD, UV-Visible.

1. Introduction
Water, one of the basic needs of human beings, has been depleted due to misuse and introduction of various foreign contaminants, leading to decrease in the amount of availability of pure water. Addition of dyes during various production processes in the textile industries affects the quality of water to a very large extent. It is estimated that the dyeing and finishing operations in the textile industry produces approximately 200,000 tons of the dye effluents every year due to the inefficiency of the dyeing process [1]. The dye effluents thus produced, hamper the soil productivity and when mixed with water have been found to be carcinogenic, mutagenic and allergic.

Advanced oxidation processes (AOPs) are advantageous in destroying pollutants by their oxidation into mineral salts and non-toxic compounds. In recent years, the traditional water and wastewater treatment technologies have been replaced by semiconductor-mediated heterogeneous photocatalysis. The most widely used semiconductor oxide photo-catalyst for this purpose is titanium dioxide [2]. Heterogeneous photocatalysis is a low cost process leading to complete mineralization of organics into CO$_2$ when sunlight is used as the source of irradiation [3].

TiO$_2$ has become one of the most studied photocatalyst in the treatment of environmental contaminants owing to its attractive characteristics and applications [4]. Titania exhibits a number of attractive characteristics such as chemical stability, nontoxicity and can decompose toxic organic...
compounds in both aqueous phase and gas phase [5]. In spite of these advantages, large-scale application of titania as a photocatalyst is restricted by its large band-gap (3.2 eV) and high recombination rate of charge-carriers. These limitations of titania have been the major concern among researchers. In recent years, altering the electronic structure of the TiO$_2$, via doping with a suitable dopant, has been the most widely used method to enhance its photocatalytic activity. The noble metals, when doped into semiconductor lattice can harvest the visible light. Besides, the semiconductor and noble metal interface forms Schottky barrier that results in the separation of electron-hole pairs [6]. Silver is the most promising noble metal for this purpose due to its lower cost, inherent antibacterial activity and facile preparation. In this study, we have prepared nano-sized pure and Ag-doped TiO$_2$ nanoparticles and studied the various optical and structural properties of them. The photocatalytic activity of these nanoparticles were studied on degradation of MB under sunlight.

2. Materials and methods

2.1. Chemicals used

The various chemicals used in the synthesis of photocatalysts were of analytical reagent grade. Titanium tetra-isopropoxide (C$_{12}$H$_{28}$O$_4$Ti, 97%, Sigma Aldrich), isopropanol (CH$_3$CHOHCH$_3$, ≥ 99%, Merck), Silver nitrate (AgNO$_3$, 99.8%, CDH), ammonia (NH$_4$OH, 25%, Loba Chemie) were used for the synthesis process. Deionized water was used for hydrolysis and washing. All the chemicals were used as received, without any further purification.

2.2. Synthesis

The co-precipitation method was used for the preparation of pure and Ag-doped TiO$_2$ nanoparticles. Titanium tetraisopropoxide (TTIP) was used as a precursor for titanium and isopropanol was used as its solvent. Water was used as hydrolysis catalyst. For the synthesis, TTIP, isopropanol and water were mixed in the ratio 1:10:100. The mixture was then vigorously stirred at room temperature. For Ag-doping, appropriate amount of AgNO$_3$ was added to the solution. The precipitate formation initiated as soon as the precipitating agent NH$_4$OH was added drop-wise to the mixture till the pH reaches 9. The whole mixture was stirred at room temperature for 1 hour. The mixture was then aged for 2-3 hours resulting in the formation of white colored precipitates. These precipitates were then centrifuged, filtered and dried at 80 °C for 15 hours leading in the formation of Ti(OH)$_4$. The titanium hydroxide was then calcined at 600 °C for 4 hours. The calcined mixture was then grounded to form TiO$_2$ nanoparticles.

2.3. Characterizations

The synthesized pure and Ag-TiO$_2$ nanoparticles were characterized by XRD and UV-visible spectroscopy. The phase purity of the nanoparticles have been characterized by XRD patterns from Panalytical’s X’Pert Pro diffractometer system. The Cu K$_\alpha$ radiation is used and nickel metal is used as beta filter. UV-Vis absorption of the samples was recorded on Shimadzu UV-1800 spectrometer.

2.4. Photocatalytic Activity Assessment

It is the ability of some nano materials to speed up a certain reaction as a catalyst when influenced by light resulting into the formation of radicals and reactive oxygen species (ROS) which decompose organic materials. The photocatalytic activity of the synthesized nanoparticles was determined by investigating the degradation of MB dye solution. For this purpose, a drop of MB solution was dipped in water and was divided into two equal parts. In one of the solution the prepared powder sample was added and the other part of solution was taken as the reference. To establish an adsorption-desorption equilibrium, the suspensions were magnetically stirred in dark for 30 min. The solution was then irradiated under the sunlight and was monitored with the interval of 15 min. The change in concentration of prepared solutions (with and without the TiO$_2$ sample) was determined using
Shimadzu 1800 UV–Vis spectrophotometer. The absorptivity measurements were carried out in the wavelength range of 200 to 800 nm.

3. Results and discussion

3.1. X-Ray diffraction

The phase formation and crystallinity of synthesized pure and Ag-doped TiO₂ nanoparticles were identified through the angular range 10°-60°. The XRD patterns of TiO₂ nanoparticles are shown in the figure 1. The sharpness of the peaks indicates the highly crystalline nature of the nanoparticles. The (hkl) planes of various peaks obtained are indexed in the XRD pattern and matched with the peaks reported by Patle et al.[7]. The dominant peak achieved at 2θ = 25.4° corresponds to (101) plane of TiO₂. The various peaks confirm that the prepared TiO₂ is anatase having tetragonal crystal structure [7]. Some peaks of rutile structures at 27.5° and 36.2° corresponding to (110) and (103) respectively were also observed in doped nanoparticles thus confirming the presence of a mixture of both anatase and rutile phases. The presence of rutile structure peaks in doped nanoparticles may be because of annealing temperature of 600°C which is in confirmation with the reports of Yan Hua Peng et al. who reported the presence of the both anatase and rutile phases as a mixture at 600°C temperature [8]. Also, as the concentration of Ag increases, the intensity of rutile peaks reduces which may be on account of increase in the active surface area of photocatalysts [9]. A large surface area gives rise to the number of active sites making it more reactive. This could be the reason behind the conversion of stable rutile phase into reactive anatase phase. Further, no additional peaks corresponding to impurities were observed.

The higher crystallinity of diffraction peaks reduces the chances of trapping of charge carriers by the crystal defects, thus strengthening the probability of the charge carriers to reach the surface [10]. Further, due to smaller particle size, the charge-carriers can reach the surface before recombination as they have to travel a shorter distance to reach the surface [9, 10].

Figure 1. XRD patterns of TiO₂ and TiO₂:Ag nanoparticles.

The crystallite size (D) is calculated by using Scherer’s equation

\[ D = \frac{k \lambda}{\beta \cos \theta} \]  

(1)
where $K$ is called shape factor and its value in this case is taken as 0.9 and $\lambda$ is the wavelength (1.5418 Å Cu Kα), $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the diffraction angle. The value of $D$ was calculated for the XRD peak (101) having maximum intensity.

The lattice strain and the crystallite sizes of the photocatalysts were also calculated by Williamson-Hall (W-H) method [11] using the relation,

$$\beta \cos \theta = 4 \varepsilon \sin \theta + \frac{K\lambda}{D}$$  \hspace{1cm} (2)

We have seen that by plotting graph between $\beta \cos \theta$ and $4\sin \theta$, the strain component can be obtained from the slope ($\varepsilon$) and the size component from the intercept ($K\lambda/D$). The W-H plots of synthesized nanoparticles are shown in figures 2–4.

![Figure 2. The W-H plot of pure TiO$_2$ nanoparticles.](image)

![Figure 3. The W-H plot of TiO$_2$:Ag (3%) nanoparticles.](image)
Whenever the strain in broadening of the peak is absent, the plot between $\beta \cos \theta$ and $4 \sin \theta$ should be a horizontal line parallel to $4 \sin \theta$ axis. The presence of strain in broadening of the peak is indicated by a non-zero slope of the line of graph. However, the crystallite size obtained from Debye-Scherrer equation and W-H method do vary, which can be ascribed to the peak broadening due to the strain contribution in nanoparticles [12]. Further the variation in strain values of the samples is may be due to the rise in number of unit cells per particle in the Ti-lattice. The obtained grain size and strain values induced in the broadening of the peaks are tabulated in table 1.

Table 1. Various parameters of the samples from Scherrer’s method and W-H method.

| Sample Name       | FWHM (Radians) | Scherrer Method | Williamson Hall Method |
|-------------------|----------------|-----------------|------------------------|
|                   |                | $D$ (nm)        |                        |
| TiO$_2$           | 0.00481        | 29.5            | 10.07                  |
| 3% Ag-TiO$_2$     | 0.00404        | 35.17           | 107.56                 |
| 5% Ag-TiO$_2$     | 0.00526        | 26.97           | 45.95                  |

The interplanar spacing can be calculated from Bragg’s equation:

$$2d \sin \theta = n \lambda$$

The general relation between d-spacing ($d_{hkl}$) and miller indices (hkl) is

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

where $a$, $b$ and $c$ are lattice constants.

$$\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

For tetragonal system, $a=b\neq c$

$$\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

The volume of unit cell can be calculated by using formula

$$V = a^2c$$
The number of unit cell in particle is calculated by using formula given below [13]:

\[ N = \frac{4}{3\pi D^3} \]  

(8)

where \( D \) is the crystallite size and \( V \) is the volume of the unit cell.

The values of d-spacing, lattice parameters (\( a \) and \( c \)), c/a ratio, number of unit cells per particle and the volume of the unit cell of various samples are listed in Table 2.

### Table 2. Lattice Parameters of Pure and TiO\(_2\):Ag samples.

| Sample Name | d-spacing at 2\( \theta \) = 25.4 | Lattice parameters in (Å) | c/a ratio | No. of unit cells per particle | Volume in (Å\(^3\)) |
|-------------|----------------------------------|---------------------------|-----------|-------------------------------|----------------------|
| TiO\(_2\)    | 3.488                            | \( a \) = 6.977, \( c \) = 4.028 | 0.577     | 5.647                         | 196.166              |
| 3% Ag-TiO\(_2\) | 3.489                          | \( a \) = 6.978, \( c \) = 4.028 | 0.577     | 4.737                         | 196.190              |
| 5% Ag-TiO\(_2\) | 3.512                          | \( a \) = 7.023, \( c \) = 4.053 | 0.577     | 6.296                         | 199.960              |

### 3.2. UV-Visible Spectroscopy

Optical absorption coefficient of the synthesized pure and TiO\(_2\):Ag nanoparticles has been computed in the wavelength region 200–800 nm. The UV-Vis spectra of pure and Ag-TiO\(_2\) nanoparticles are shown in the inset of figure 5. There is a slight shift of the absorption edge towards the visible region with increase in Ag concentration in TiO\(_2\) that can be attributed to the presence of rutile phase [14].

The band gap plays a crucial role in deciding the photocatalytic activity of photocatalysts by determining the \( e^-/h^+ \) recombination rate [15]. The optical band gap (\( E_g \)) for synthesized nanoparticles can be determined from Tauc formula.

\[ \alpha h\nu = A(h\nu - E_g)^n \]  

(9)

where \( \alpha \) is absorption coefficient, \( A \) is constant, \( h\nu \) is the energy of light in eV. The value of \( n \) is \( \frac{1}{2} \) for direct band gap and 2 for indirect band gap. The band gap of the nanoparticles can be found by extending the linear portion of the graph intersecting the horizontal axis at any point.

A photocatalyst must be capable of exciting an electron from valence band (VB) to conduction band (CB) even at lower intensities of the incident radiations. This is possible by narrowing the band gap energy to absorb visible light. A band-gap of 1.23-3.0 eV is required for a visible light active photocatalyst. Further, the photocatalyst must absorb the radiation within the visible range (i.e. 400–800 nm) of the electromagnetic spectrum [10]. The calculated band gaps of pure TiO\(_2\), TiO\(_2\):Ag (3%) and TiO\(_2\):Ag (5%) were found to be 2.5 eV, 2.2 eV, and 1.8 eV respectively, thus indicating the photocatalysts may become active in visible region of electromagnetic spectrum (figure 5).
3.3. Photocatalytic Activity of Samples

It has been investigated from the literature that the crystallite size has a significant effect on the photocatalytic activity. Smaller the crystallite size, higher is the photocatalytic activity of anatase TiO$_2$ [16,17]. The introduction of Ag atom to TiO$_2$ lattice shifts the absorbance towards visible light region enhancing the photocatalytic activity. From the study of the figures 6-8, the photodegradation of methylene blue was found to be effective with increase in the Ag concentration. Further, the degradation of MB dye was found in direct relation to the radiation time.

Figure 6. Photocatalytic Activity of the pure TiO$_2$. 
4. Mechanism of Photocatalysis
Photocatalysis is a series of chemical reactions that is usually induced by electromagnetic irradiation which causes the excitation of atoms of the irradiated materials that result in the formation of radicals that affect surroundings [18]. Photocatalysis process consists of two main stages: reduction and oxidation [19]. Whenever a material is irradiated with photons, having energy equal to or higher than its band-gap, the excitation of electrons from VB to CB takes place leading to the formation of holes in the VB. This stage is called reduction. The participation of these photo-generated electrons and holes in useful redox reactions is restricted by the recombination process which can be prevented by doping with metal, non-metal, ions or noble metals like Au, Ag etc [14]. For instance, Ag particles become attached to TiO₂ to obtain the Fermi level equilibration leading in the creation of monovalent Ag. This monovalent Ag is capable of trapping the photo-generated electrons and thus reduces the
probability of electron-hole recombinations with increase in the lifetime of photo-generated pairs. Finally, the generated electrons and holes give rise to the formation of ROS such as $O_2^-$ and $OH^-$ (oxidation). ROS are the molecules of relatively small life span containing oxygen atoms and unpaired electrons that are responsible for their high reactivity [20]. The kind of ROS depends on the type of material and irradiated photons. Figure 9 shows the photocatalytic mechanism of Ag-doped TiO$_2$.

![Figure 9. Photocatalysis process of TiO$_2$:Ag.](image)

The various reactions involved in the photocatalysis process are as follows:

- $TiO_2 + hv \rightarrow e^- + h^+_{vb}$
- $h^+_{vb} \rightarrow h^+_{tr}$
- $O_2 + e^- \rightarrow O_2^-$
- $O_2^- + O_2^+ + 2 H^+ \rightarrow H_2O_2 + O_2$
- $O_2^- + h^+_{vb} \rightarrow O_2$
- $O_2^+ + h^+_{tr} \rightarrow O_2$
- $OH^- + h^+_{vb} \rightarrow OH^-$
- $e^- + h^+_{tr} \rightarrow$ recombination
- Organic dye + $[O_2^- \text{ or } OH^-] \rightarrow$ Degradation products

5. Conclusions

In the present study, pure and TiO$_2$:Ag nanoparticles have been synthesized by co-precipitation method, which falls under “bottom-up approach” for the synthesis of nanomaterials. The crystal structure of the resulting pure and Ag-TiO$_2$ nanoparticles were determined using XRD. Anatase phase was confirmed for pure nanoparticles whereas the doped nanoparticles were found to have a mixture of both anatase and rutile phases. The band gap of the nanoparticles was reduced with Ag doping. The photocatalytic activity of the nanoparticles was investigated by successful degradation of methylene blue dye. Further, the addition of Ag as dopant into TiO$_2$ crystal resulted in enhancing the photocatalytic degradation of MB dye which was directly related to duration of irradiation.

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