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Ag-Doped TiO₂: Synthesis, Characterization and Photodegradation of 4BS Dye

M.J. Pawar*, V.B. Nimbalkar, A.D. Khajone, S.B. Deshmukh

Laboratory of Materials Synthesis, Smt. Narsamma ACS College, Kiran Nagar, Amravati – 444 606, Maharashtra, India.

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ABSTRACT

Ag doped TiO₂ nanoparticles with different metallic content (0.0, 0.1, 0.15 and 0.2 wt.%) were prepared by using EDTA-Glycol method. For the sake of comparison blank TiO₂ sample is also prepared using same method. All the samples have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). X-ray diffraction technique revealed that Ag-doped TiO₂ has anatase structure and as the concentration of Ag increases the particle size will get decreases. The morphologies of TiO₂ samples are influenced by doping Ag as shown by SEM images. The present work is mainly focused on the enhancement of photocatalytic reactivity of as synthesized samples by the photodegradation of 4BS under visible light irradiation using a LED lamp of (15 W) as a light source. A 96.3% of photodegradation of 4BS dye was achieved by utilizing 1 g/L of Ag-doped TiO₂ at pH 6 for 100 min.

1. Introduction

Semiconductor based photocatalysis utilizes natural sun light or artificial light sources to initiate catalytically specific redox reactions under mild conditions, which finds wide applications in environmental remediation, photocatalytic water-splitting and CO₂ reduction [1]. The emergence of novel photocatalysts in recent years does not hinder researcher's enthusiasm on titanium dioxide (TiO₂), which is one of the most traditional yet promising semiconductors for photocatalytic applications because of its exceptional merits of biological friendliness, chemical inertness, low cost and earth-abundance [1–5]. The wide band gap (3.0–3.2 eV) and high charge recombination rate impose a fundamental restriction on the overall photocatalytic efficiency for TiO₂, which are the focus of numerous studies ever since Fujishima and Honda's pioneer work on TiO₂ photocatalysis [6].

Doping of TiO₂ with noble metal nanoparticles such as Pt [7], Ag [8], Pd [9] and Au [10–13] is an effective tactic to improve the photocatalytic activity. The noble metal nanoparticles contact closely with TiO₂ to form Schottky barriers, which drive photogenerated electrons from the *n*-type TiO₂ to the noble metals and enhance the charge separation rate and the photocatalytic activity. For TiO₂ doped with Au and Ag, there is an additional effect, the localized surface plasmon resonance (LSPR), which contributes to a strong absorption of the visible light and thus the photocatalytic performance under the visible light illumination [13–15]. The LSPR effect is affected readily by shape [16], size [17–19] and content [20] of Au nanoparticles, as well as characteristics of the TiO₂ supports [13, 18, 21, 22]. Among the noble metals, silver (Ag) is an attractive dopant due to its plasmonic properties in visible range along with extraordinary physicochemical properties and lower cost [23].

Wu et al. studied Ag-doped TiO₂ and reported the formation of metallic Ag, Ag₂O and AgO species on the surface of TiO₂ [24]. Liu et al. reported simultaneous deposition (or impregnation) and doping of Ag/Ag(I) on TiO₂. The formed Ag(I) contributes to the visible light absorption and the metallic Ag promotes the effective electron-hole separation [25]. Ortiz et al. reported the highest H₂ production from metallic Ag than Ag incorporated into the TiO₂ lattice [26]. Duan et al. investigated the role of Ag and oxygen vacancies in Ag-TiO₂ nanocomposites for promoting the effective e⁻/h⁺ separation [27]. Also, Nanaji et al. confirmed the combined effect of doped and metallic-Ag on TiO₂ for an enhanced photocatalytic activity [28]. Most of the Ag-doped TiO₂ photocatalysts were tested in the

application of photocatalytic dye degradation [29], antimicrobial activity [30], disinfection activity and nanofiltration membrane [31] etc.

In the present investigation, Ag doped TiO₂ was synthesized by EDTA-Glycol method in which ethylene glycol (EG) was used as a fuel. The effect of fuel on the morphology of Ag-doped TiO₂ was studied. The synthesized Ag doped TiO₂ catalysts were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and FTIR techniques. The photocatalytic activity of the synthesised catalyst has been investigated by studying the decomposition of methyl orange under sunlight exposure.

2. Experimental Methods

2.1 Synthesis of Ag-Doped TiO₂ Nanoparticles

The typical synthesis procedure for the preparation of Ag-doped TiO₂ nanoparticles with different Ag (0.0, 0.1, 0.15 and 0.2 wt.%) ratios prepared by the EDTA-Glycol method is as follows. Initially, 15 mL titanium (IV) isopropoxide was mixed with glacial acetic acid at 0 °C. To this aqueous medium, solution of EDTA was added drop wise under vigorous stirring for 1 h and the mixture was stirred further for 1 h. To the solution, calculated quantity of silver nitrate and 5 mL ethylene glycol (EG) was added and stirring was continued for further 4 h. The prepared solution was kept in the dark for 20 h for nucleation and aging. After that period, obtained mass was dried at 100 °C and calcined at 500 °C. Subsequently the product was crushed into fine powder for further characterization. To investigate the effect of fuel on morphology of synthesized material, volume of EG was doubled and Ag-doped TiO₂ material was prepared.

2.2 Characterization

The crystalline phase analysis of samples was performed via XRD-6100s X-ray diffractometer operating with a tube current of 40 mA, a tube voltage of 40 kV, and a scanning speed of 5°/min. The transmission electron microscopy (TEM) images were recorded on a JEM-3010 (JEOL, Japan). All Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Perkin-Elmer GX FTIR. Samples were recorded with KBr disc (1:10, sample/KBr) using 16 scans per sample at resolution of 4 cm⁻¹ over the range 4000–500 cm⁻¹. Infrared radiation interacts with chemical bonds to cause stretches, bends and other various atomic vibrations. A Perkin-Elmer Lambda 900 UV-vis spectrometer was used to record absorption spectra of the organic dyes under investigation for photodegradation studies. Spectra were recorded in the region 500–750 nm. The absorption at maximum wavelength (λ_{max}) of methylene blue (660 nm) was used to calculate degradation rates as a function of irradiation time.

*Corresponding Author: mjpa1809@gmail.com (M.J. Pawar)

Diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 900 UV-vis spectrometer. From the resulting diffuse reflectance spectra, the band gap of the semi-conductor sample could be recorded by placing the pellet into the reflection sphere where it reflects light directly from the source. The nitrogen adsorption-desorption isotherms of the synthesized photocatalysts were obtained to study the surface area and pore size volume of catalyst.

2.3 Photocatalytic Decolorization of 4BS

The photocatalytic reactivity of synthesized samples was evaluated by the decolorization of 4BS under visible light irradiation using a LED lamp of (15 W) as a light source for testing. Different amounts of the pure and Ag-doped TiO₂ powder were added into 25 mL of 20 mg/L 4BS solution. Before switch-on the LED light, the suspension was put in the reactor and stirred until dye adsorption was completed. After that, the LED light was turned on. The concentration of 4BS dye solution was evaluated at given time intervals of every 30 min by using UV-vis spectrophotometry at wavelength of 650 nm ($\lambda_{\max}$).

3. Results and Discussion

3.1 XRD Analysis

X-ray diffraction patterns (Fig. 1) of pure and Ag-doped TiO₂ samples evidenced that all the samples are composed of anatase nanocrystals with (101) plane as the preferential exposed face. For Ag(0.2)-TiO₂ sample, appearance of XRD peaks at $2\theta = 25.3^\circ, 37.8^\circ, 48.1^\circ, 53.9^\circ, 55.1^\circ, 62.7^\circ, 68.7^\circ, 70.3^\circ, 75.0^\circ$ and 82.6° corresponding to (101), (004), (200), (105), (211), (204), (116), (220), (215) and (224) planes of anatase phase confirmed the formation of pure Nanocrystalline anatase phase [JCPDS Card No.21-1272]. The XRD data obtained from the analysis confirm the decrease of the crystallite size when the Ag amount increases (Table 1), which is in agreement with the TEM images. This behavior is related to the occurrence of association defects due to the presence of the dopant, leading to distortions in the crystalline structure and smaller crystallites. The XRD data do not show any peaks related to Ag species, even for Ag(0.2)-TiO₂ sample, which is indicative of a high dispersion of the dopants in the TiO₂ samples.

Fig. 1 XRD patterns of the prepared pure and Ag-doped TiO₂ samples

Table 1 Physical properties of synthesized samples

Samples	Ag wt. %	Average crystallite size (nm)*	BET surface area (cm ² /g)	Average pore size (nm)	Pore volume (cm ³ /g)
TiO	0.0	22.21	112.862	3.658	0.342
Ag(0.1)-TiO ₂	0.10	14.54	154.421	4.753	0.395
Ag(0.15)-TiO ₂	0.15	11.22	182.213	4.956	0.412
Ag(0.2)-TiO ₂	0.20	7.65	242.550	5.439	0.475

*Average crystallite sizes were calculated by Debye Scherrer formula

3.2 SEM and TEM Analysis

The pure and Ag-doped TiO₂ samples with different concentrations of Ag addition were characterized by scanning electron microscopy. Fig. 2 demonstrates the SEM morphology of the synthesized Ag(0.2)-TiO₂ nanoparticles synthesized by the different volume of EG. SEM images depict the spherical surface morphology in the case of 5 mL EG, while nanorod-like particles can be observed when synthesized using double volume of EG. Because of their small size, the synthesized structures are uniform in nature, with little aggregation.

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The shape and size of pure and Ag-doped TiO₂ nanoparticles were analyzed by transmission electron microscopy. The particle sizes are found to be ≈ 5 –22 nm for the synthesized nanoparticles. Fig. 3 depicts the TEM images of sample Ag(0.2)-TiO₂ synthesized by using 10 mL of EG. Here, it was concluded that, the volume of EG is a crucial factor in decreasing the particle size of Ag(0.2)-TiO₂.

Fig. 2 SEM images Ag(0.2)-TiO₂ prepared using A) 5 mL of EG and B) 10 mL of EG

Fig. 3 TEM images Ag(0.2)-TiO₂ sample prepared by using 10 mL EG

3.3 Photocatalytic Degradation of 4BS

The initial concentration (C_0) and final concentration (C) of dye values were obtained from the absorbance spectra of intensity versus wavelength. Afterwards, the photocatalytic performance of pure and Ag-doped TiO₂ was evaluated through kinetics degradation; colorant concentration, as a function of exposure time under UV-visible radiation, was analyzed. The analyzed reaction pattern shows first order kinetics [32], as shown in Eq.(1).

$$\mu = \frac{dC}{dt} kC \quad (1)$$

k represents the exchange rate constant, obtained by integration of Eq.(1),

$$\ln \frac{C}{C_0} = -kt \quad (2)$$

Thus, the $\ln C/C_0$ graph versus t has a linear tendency with slope as k and thus C/C_0 values can be calculated.

3.3.1 Effect of Ag-Doping

The effect of Ag-doping on photocatalytic efficiency of TiO₂ was studied for the degradation of 4BS dye and shown in Fig. 4. The sample Ag(0.2)-TiO₂ with 0.2 wt.% Ag is the most photoactive of the doped samples; it showed significant photoactivity in 4BS. However, its response in the 4BS photodegradation is comparable to the response of pure TiO₂. The XRD study distinguishes particles of size minor for Ag(0.2)-TiO₂ as compared to the pure TiO₂, and Ag(0.1)-TiO₂ and Ag(0.15)-TiO₂ samples. Therefore, the Ag-doped TiO₂ photocatalytic performance strongly depends on reaching small particle size. In addition to the surface level, the sample Ag(0.2)-TiO₂ presents specific surface area and pore size values suitable for the process of 4BS photodegradation.

Fig. 4 Kinetic graphs of 4BS, for the pure sample and with the different percentages of the addition of Ag

Finally, the band gap energy value of this sample is lesser than the pure TiO_2 value. This indicates that the reduction of this parameter together with the morphological and surface properties of the $\text{Ag}(0.2)\text{-TiO}_2$ sample was a good photocatalyst to complete degradation of the 4BS. Due to high photoactivity, the sample $\text{Ag}(0.2)\text{-TiO}_2$ was only adopted for the further investigations.

Fig. 5 Effect of $\text{Ag}(0.2)\text{-TiO}_2$ dose on the photodegradation of 4BS

3.3.2 Effect of TiO_2 Dose

Fig. 5 indicates that the rate of photodegradation of 4BS under UV-light increases when the dose of catalyst is increased from 0.2 g/L to 1 g/L due to the increased surface area and hence greater number of active sites. However, further increase of TiO_2 concentration results in lower photocatalytic degradation which can be attributed to light scattering caused by the turbidity of the solution.

3.3.3 Effect of Initial Concentration of 4BS

Fig. 5 shows that the removal of 4BS decreases as the initial concentration of 4BS increased from 10 to 40 mg/L. The lower degradation efficiency at higher initial concentration of 4BS can be attributed to the fact that the higher 4BS concentrations could absorb more photons which reduces the available photons to activate the TiO_2 and these results in reduced degradation efficiency.

Fig. 6 Effect of initial concentration of 4BS on the photodegradation of 4BS [Catalyst dose = 1 g/L]

3.3.4 Effect of Initial pH

The influence of initial solution pH on the photodegradation of 4BS was examined in a pH range of 2–9. As shown in Fig. 7, the efficiency of 4BS degradation is strongly affected by the initial pH of the solution. Pure TiO_2 shows the highest photocatalytic activity at weakly alkaline medium (pH 8) due to greater concentration of $\bullet\text{OH}$ radical. However, the reaction rate constant is significantly decreased when the solution becomes more alkaline (pH 10), mainly due to the electrostatic repulsion between the negatively charged TiO_2 surface and the anionic form of 4BS molecules, which result in poor adsorption of the dye and decreased rate of photodegradation. For the sample $\text{Ag}(0.2)\text{-TiO}_2$, the highest 4BS removal is observed at pH 6.0 which can be attributed to the enhanced formation of the superoxide anion ($\text{O}_2^{\bullet-}$) and subsequent formation of $\bullet\text{OH}$.

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Fig. 7 Effect of initial pH of 4BS dye solution on photodegradation of 4BS over $\text{Ag}(0.2)\text{-TiO}_2$ sample [Catalyst dose = 1 g/L, 4BS concentration = 10 mg/L, Irradiation time = 100 min.]

3.3.5 Effect of Light Source

Fig. 8 shows the photocatalytic degradation of 4BS, normalized to light intensity, under different light sources, namely UV, simulated, and direct solar light. As clearly seen, 4BS degradation over the $\text{Ag}(0.2)\text{-TiO}_2$ photocatalyst under UV light is much higher than those with simulated and direct solar light. The observed photodegradation percentage of 4BS dye on 100 min irradiation was 96.3, 36.4 and 18.4 with UV simulated and direct solar light, respectively.

Fig. 8 Effect of light source on photodegradation of 4BS dye over $\text{Ag}(0.2)\text{-TiO}_2$ sample

Fig. 9 Effect of oxygen gas purging on the photocatalytic degradation of 4BS

3.3.6 Effect of Oxygen Purging

The effect of air and oxygen bubbling on the degradation of 4BS under simulated solar light is illustrated in Fig. 9. In this set of experiment, initial 4BS concentration, photocatalyst dosage, initial pH were constant at 10 mg/L, 1 g/L and 6 respectively. The gas flow rate was 2 L/min and the samples were withdrawn at regular time intervals. As exhibited in Fig. 9, the photocatalytic degradation of 4BS was enhanced with purging of oxygen gas in compare to that without purging of oxygen gas. The degradation rate with purging of oxygen gas increased from 37.30% to 93.42% by increasing time from 20 to 100 min, while it was ranged from 30.65 to 81.31% without purging of oxygen gas. This means that oxygen molecules play an important role in the photocatalysis, which will be

transformed to a superoxide radical anion ($O_2^{\cdot-}$) by grasping excited electrons in the conduction band of photocatalysts. Another reason for the enhanced photocatalytic degradation of dye with purging of oxygen gas is electron scavenging effect generated in conduction band may effectively react with dissolved oxygen and inhibit recombination between positive hole and electron.

4. Conclusion

This present research work reported the structural and photocatalytic properties of TiO_2 and Ag-doped TiO_2 synthesized by an EDTA-Glycol technique. The XRD pattern showed the co-existence of silver and anatase TiO_2 phases. Doping TiO_2 with silver has significant effect on the particle sizes. All type of Ag-doped TiO_2 exhibited larger absorption in the visible light region. The pore size distribution of pure TiO_2 is about 9–10 nm, while Ag-doped TiO_2 samples shown small about 7–9 nm diameter and the sample Ag(0.2)- TiO_2 is even smaller about 4–5 nm diameter. Compared with pure TiO_2 , Ag-doped TiO_2 had the larger specific surface area and pore size parameters, illustrating that Ag doping in TiO_2 affects the specific surface area and pore size. SEM images depict the spherical surface morphology in the case of 5 mL EG, while using double volume of EG, rod-like shape of the particles could be observed. The sample Ag(0.2)- TiO_2 with Ag 0.2 wt.% is the most significant photoactive among all the doped samples. The XRD study distinguishes particles of the smaller particle size and better photodegradation efficiency for Ag(0.2)- TiO_2 as compared to the pure TiO_2 . The rate of photodegradation of 4BS under UV-light increases as the dose of catalyst is increased from 0.2 g/L to 1 g/L at pH 6. Further studies are needed to improve photocatalytic efficiency of TiO_2 materials.

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