Visible Light Photocatalytic Property of Ag/TiO$_2$ Composite

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ABSTRACT. Ag/TiO$_2$ composite was synthesized by thermal decomposition method using tetraethyl orthotitanate, silver nitrate and hexamine as a surfactant. The synthesized materials were confirmed by X-ray diffraction. The morphology of the sample was investigated by field emission scanning electron microscope (FE-SEM). The morphology of the Ag/TiO$_2$ composite was found to be the cubic microstructure with complete decoration of Ag nanoparticles over the TiO$_2$ surface uniformly. The optical property of the photo catalyst was observed from UV-vis spectroscopy. The photocatalytic activity of the Ag/TiO$_2$ composite was investigated by the degradation of a methylene blue under visible light irradiation. The observed results showed that Ag incorporation enhance the visible-light adsorption and improved the photocatalytic efficiency of TiO$_2$ composite significantly under visible light.

Introduction. Recent years we are facing number of environmental issues related to the energy disaster, water pollutions, etc. To overcome this problem the semiconductor materials have been used as a photocatalyst for degradation of organic pollutants, hydrogen production from water splitting and dye sensitized solar cells. Among various semiconductor oxides titanium dioxide (TiO$_2$) is one of the well-known wide band gap n-type semiconductor materials. Since last decade, TiO$_2$ has been widely investigated for photocatalytic degradation of harmful organic pollutants from the waste water due to its nontoxicity, low cost and excellent chemical stability. Because of its limited visible-light absorption nature and low photocatalytic efficiency their practical application is limited and need to be improved. Consequently, the surface modification in TiO$_2$ lattice such as doping of various transition metals, noble metals and combine with narrow band gap semiconductor materials could make it as more sensitive to visible light and improve the photocatalytic efficiency. In general, the noble metals Pt, Pd, Rh, Au and Ag are having superior photocatalytic efficiency but their high cost limit their large scale applications. Recently, TiO$_2$ with noble metals combination have received more attention towards photodegradation. Among them the above noble metals Ag is the less expensive and can be used as visible sensitive material for photocatalytic activity. Since the surface loading of metallic Ag nanoparticles on different semiconductors would be an effective way to improve the photocatalytic activity [1, 2]. Hence, in this work the metallic Ag nanoparticle has been incorporated into TiO$_2$ matrix and used as visible photo catalyst material with improved degradation efficiency. Here, the Ag nanoparticles are readily available to accept photogenerated electrons from excited semiconductor which facilitates dioxygen reduction and thereby Ag/TiO$_2$ showed an enhanced UV-light photocatalytic activity for the decomposition of organic substances.
Materials. Analytical reagents of Tetraethyl orthotitanate, Silver nitrate and Hexamine were used as received without further purifications. Ethanol and double distilled water were used as the solvents. Ag/TiO$_2$ was synthesized by simple thermal decomposition method. Typically, 2.4 ml (0.01 M) of Tetraethyl orthotitanate was dissolved in 30 ml of ethanol and 0.01 M of silver nitrate dissolved in 50 ml of double distilled water and it was slowly added to reaction mixture. 2.5g of hexamine was added to the above mixture and the solution was stirred for 3h in 70 °C. The final product was centrifuged and washed with several times by water and ethanol. The synthesized materials was dried in room temperature and calcined at 450 °C.

Results and Discussion. The crystalline phase of Ag/TiO$_2$ composite are confirmed by XRD pattern as shown in Fig.1. (a). The observed XRD pattern clearly evidences the formation of mixed phase of face centered cubic Ag and rutile TiO$_2$. Typical 2θ˚ values at 38.1˚, 44.3˚, 64.4˚ corresponds to the metallic Ag in the face centered lattice and it is well matched with JCPDS card (No.65-2871). Similarly, the observed 2θ˚ values are 27.3˚ , 36.0˚, 41.1˚, 54.2˚, 56.5˚ and 68.8˚ corresponds to tetragonal phase and can be indexed to the JCPDS card (No. 77-0441). And no other secondary phase is observed in the XRD pattern which confirms that phase purity of the composite.

Fig. 1. (a) Shows the XRD pattern and (b) FTIR spectrum of Ag/TiO$_2$.

The FTIR spectrum of the prepared Ag/TiO$_2$ was shown in Fig.1 (b). The strong absorption band at 400 cm$^{-1}$ to 700cm$^{-1}$ corresponds to the Ti-O stretching vibrations [3]. The band appearing at 1610 cm$^{-1}$ is attributed to the bending vibrations of O-H. The broad absorption at 3464 cm$^{-1}$ corresponds to the O-H stretching vibrations due to absorption of water molecules from the moisture.

The optical properties of prepared sample were measured using UV-Vis Diffuse reflectance spectroscopy. Fig.2 (a) displays the UV-Vis spectrum of Ag/TiO$_2$ composite. The broad absorption in visible light is attributed to the surface plasmon resonance (SPR) confirming the formation of Ag nanoparticles [4]. The band gap energy can be estimated by following equation.

$$\alpha h\nu = A (h\nu - Eg)^{n/2}$$

where $\alpha$ represents the absorption coefficient, $\nu$ is the light frequency, $Eg$ is the band gap energy, $A$ is a constant and $n$ depends on the characteristics of the transition in a semiconductor.

The band gap plot of $(\alpha h\nu)^2$ vs $h\nu$ of Ag/TiO$_2$ shown in Fig. 2. (b), the calculated band gap value for Ag/TiO$_2$ is 2.8eV.
Fig. 2 (a) shows the DRS UV-Vis spectrum, (b) band gap plot of \((\alpha h\nu)^2\) vs \(h\nu\) of Ag/TiO\(_2\).

The surface morphology of the Ag/TiO\(_2\) composite is analyzed by field emission scanning electron microscope. As shown in (Fig. 3), the surface of the TiO\(_2\) is found to be cube like morphology and size of the cube is ~100 to 200nm. The small Ag nanoparticles uniformly dispersed on the surface of the TiO\(_2\) cubes. The size of the Ag nanoparticles is ~5nm to 10nm. The EDS spectrum confirms the presence of primary elements of Ti, Ag and O without any impurities.

Fig. 3. shows the FESEM images and Edax spectrum of Ag/TiO\(_2\).

**Photocatalytic activity.** The photocatalytic activity of the prepared materials was irradiated under visible light degradation of methylene blue. The photo chamber was designed with a 500 W xenon lamp. The photocatalytic degradation of methylene blue was examined by taking 100ml of reaction mixture containing 0.001M of methylene blue and 0.02g of Ag/TiO\(_2\). The prepared solutions were irradiated under visible light for 2 h. The concentration of the solution taken out from reaction mixture at different time intervals. The photocatalytic degradation solution was analyzed by UV-Vis spectroscopy. Fig. 4 shows the UV-Vis absorption spectrum of methylene blue under visible light irradiation time in presence of Ag/TiO\(_2\). As shown, the intensity of the methylene blue peak decreases with increasing the time, meantime the 85% of methylene blue degraded in 60 min under visible light degradation. Ag/TiO\(_2\) material can absorb and degrade the methylene blue solution in visible light degradation.
Ag nanoparticles are photoexcited due to the plasmon resonance. Consequently, the photoexcited electrons are migrated from the surface of the Ag nanoparticles to the conduction band of TiO$_2$. In meantime, due to crystallinity of the Ag nanoparticles, the electron migration is suppressed so as to reduce the recombination of e$^-$/h$^+$ pairs. The electrons which accumulate on the surface of TiO$_2$ are then scavenged by dissolved oxygen molecules in water to yield highly oxidative species such as the superoxide radical anion (O$_2^-$) and hydroxyl radical (OH), which can degrade the organic dyes effectively[1, 5, 6]. These oxidative species can easily diffuse out of the composite to attack the MB dye.

![UV-Vis absorption spectrum of methylene blue under visible light irradiation time](image)

Fig. 4 shows the UV-Vis absorption spectrum of methylene blue under visible light irradiation time in presence of Ag/TiO$_2$.

Summary. The Ag/TiO$_2$ material was synthesized by simple thermal decomposition method and investigated for MB photodegradation. The Ag/TiO$_2$ composite formation and microstructure was confirmed by XRD pattern and SEM analysis. It was observed that Ag decorated nano/micro cubes of TiO$_2$ microstructure. The estimated band gap value for prepared composite materials is about 2.8eV. The enhanced photocatalytic activity was observed for Ag/TiO$_2$ under visible light towards the degradation of methylene blue, which is mainly due to the surface plasmon resonance based recombination reaction between Ag and TiO$_2$. From this investigation, it can be concluded that Ag/TiO$_2$ composites could be better choice of photocatalyst material for MB degradation.

References


Cite the paper