

## Synthesis and Characterization of Ag/TiO<sub>2</sub> Nano Composite and its Application in Photo-Degradation of Methylene Blue

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**Abstract:** Nano composite of Ag/TiO<sub>2</sub> and nano crystalline TiO<sub>2</sub> were prepared by using TiCl<sub>4</sub> as a precursor in a simple sol-gel process. The prepared photo-catalysts were characterized by X-ray diffraction (XRD), scanning electron micrographs (SEM), energy dispersive X-ray microanalysis (EDX), transmission electron microscopy (TEM) and diffuse reflectance spectroscopy (DRS). A complete and effective photocatalytic degradation of a cationic aromatic dye, Methylene blue, in aqueous solutions has been carried out using nano composite of Ag/TiO<sub>2</sub> and nano crystalline TiO<sub>2</sub> under UV-C light irradiation. Experiments were conducted to compare the photocatalytic activities of nano composite Ag/TiO<sub>2</sub> with nano crystalline TiO<sub>2</sub>. The photoreactions were followed by monitoring the degradation of the dye as a function of irradiation time, in the presence of the nano photo-catalysts, by the visible/ultraviolet absorption spectroscopy. It has been found that the presence of silver in TiO<sub>2</sub> nano particles reduces the duration of complete photocatalytic degradation of Methylene blue by 20% due to the enhancement of electron-hole separation by the electron trapping of silver particles.

**Key words:** Silver doped titania nano particles • Cationic aromatic dye • Sol-gel process • Photo-catalytic degradation

### INTRODUCTION

Aromatic dyes are the most important class of synthetic organic dyes applying in the textile industry and are therefore common industrial pollutants. They are produced in large amounts and may enter the environment during the production and manufacturing process [1]. For the removal of recalcitrant organics, traditional methods like ultra filtration, extraction, air stripping, carbon adsorption, oxidation via ozonation or hydrogen peroxide and also biological treatment methods have been applied [2]. But these processes are non-destructive; and simply transfer the pollutant from one phase to another [3]. Recently heterogeneous photocatalysis has drawn much attention as an attractive technology for the complete destruction of undesirable contaminants. Titanium dioxide is one of the most promising photocatalyst for the environment polluted treatments [4]. However, this unique photocatalyst unavoidably facing

several demerits for its practical applications in photocatalytic reaction such as low photo-efficiency and photo-response in ultra-violet region which is not very practical for photocatalytic reaction in solar spectrum. Recently, attempts have been made to dope TiO<sub>2</sub> with suitable transitional metals, such as Cr, Mn, V, Fe, Co, Ni and Cu, in order to overcome the above mentioned problems and improve the photo-catalytic performances of TiO<sub>2</sub> [5]. The major doping methods include metal photo-depositing [6, 7], metal ion-implantation [8], plasma chemical vapor deposition [9, 10], sol-gel process [11], hydrothermal method [12, 13] and wet impregnation [14] and the photo catalytic activities were obviously enhanced in most cases [15-18].

In this research, unlike the common sol-gel methods which use organic precursors, a less expensive inorganic precursor (titanium tetrachloride (TiCl<sub>4</sub>)) has been used to prepare nano crystalline TiO<sub>2</sub> in a simple and efficient route. Ag/TiO<sub>2</sub> nano composite is synthesized via a wet

chemistry method. Decomposition of Methylene Blue was selected as a model reaction in order to evaluate the photo-catalytic activity of nano crystalline TiO<sub>2</sub> and also Ag/TiO<sub>2</sub> nano composite.

## MATERIALS AND METHODS

**Materials:** The reactants used in this study were liquid titanium tetrachloride (TiCl<sub>4</sub>) as a titania source, sodium hydroxide (NaOH), nitric acid (HNO<sub>3</sub>), silver nitrate (AgNO<sub>3</sub>), 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (Methylene Blue, C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S). All the chemicals were analytical grade and were purchased from Merck and used as received.

**Instruments:** All experiments were performed in a batch photo-reactor where a UV lamp (125W, UV-C,  $\lambda_{\text{max}}=254$  nm) as a radiation source was placed directly above the reactor. Water was circulated through the annulus to avoid heating during the reaction. The percent degradation of the dye was obtained by use of a SHIMADZU 1700 UV-Vis spectrophotometer. X-ray diffraction patterns were recorded using a D4-BRUKER diffractometer by Cu K $\alpha$  radiation at 30KV and 20mA. A Philips XL $\Phi$ -30 scanning electron microscope (SEM) was used to observe the morphology of nano-particles. JEOL JEM-200CX operated at 200 kV was used to carry out transmission electron microscopy (TEM) studies.

**Catalyst Preparation:** Stable sols of TiO<sub>2</sub> nano particles were synthesized by hydrolysis of TiCl<sub>4</sub> as a precursor. In a typical reaction sodium hydroxide was added to titanium tetrachloride until the pH of solution was reached to 7 at room temperature. White precipitate was removed by filtration and washed with deionized water until complete removal of chloride ions. Then white precipitate was suspended in deionized water and pH of slurry was adjusted to 1.5 using 1M nitric acid. Finally, the slurry was refluxed for 24 h and the resulting stable sol was collected by filtration. The sol was dried at 313 K and calcined at 673 K for 3 h to obtain titanium dioxide.

The nano composite of Ag/TiO<sub>2</sub> is synthesized by adding AgNO<sub>3</sub> solution to the stable sols of TiO<sub>2</sub> drop wise (6/94 weight percentage of Ag/Ti respectively). Then the slurry was dried at 313 K and calcined at 673 K for 3 h.

**Photo-Catalytic Decomposition of Methylene Blue:** In order to investigate the photo-catalytic activity of nano crystalline TiO<sub>2</sub> and nano composite of Ag/TiO<sub>2</sub> and their

applications to contaminant removal of triarylmethane dyes, a cationic basic dye such as Methylene Blue was utilize as a model compound without further purification. In separate experiments, 50 ml of Methylene Blue aqueous solutions with the initial concentrations of 10 ppm was mixed with the appropriate amounts of nano crystalline TiO<sub>2</sub> or nano composite of AgTiO<sub>2</sub> (1g/L) as photo-catalyst at pH=7. Prior to irradiation, the suspensions were stirred for 30 min in dark in order to establish the adsorption equilibrium and then irradiated for different duration of times. Finally, at the predetermined time intervals, 2 ml aliquots were removed from the system and centrifuged to remove the catalyst. Then the solutions were analyzed for degradation of Methylene blue under UV irradiation. Decreases in the concentration of Methylene blue in the solutions were investigated using the UV/Vis absorption spectrophotometer.

## RESULTS AND DISCUSSION

### Catalyst Characterization

**Powder X-Ray Diffraction Analysis (XRD):** The X-ray diffraction pattern of nano crystalline TiO<sub>2</sub> that prepared from preliminary sol is shown in Fig. 1a. As it can be seen the X-ray diffraction pattern indicates a quite good crystallization of the powder prepared by the sol-gel procedure. It can be seen than the peaks at 2theta of 25.28°, 38.08°, 47.92°, 53.32° and 62.66° are assigned to (101), (004), (200), (106) and (215) lattice planes of TiO<sub>2</sub> (ICCD card File No. 21-1272), which are attributed to the signals of anatase phase with more photocatalytic activity. The peak at 2 theta of 30.8 indicates the presence of brukite phase and no rutile phase was observed. The broad peaks in the XRD pattern strongly suggest very small size of the TiO<sub>2</sub> particles. From Scherrer equation [19] the size of the particles is estimated to about 10 nm. Fig. 1b shows the crystal phase composition for Ag/TiO<sub>2</sub> nano composite, prepared by the sol-gel process. The X-ray diffraction patterns of silver doped TiO<sub>2</sub> sample almost coincide with that of pure TiO<sub>2</sub> and show no diffraction peaks due to silver species, thus suggesting that the metal particles are well dispersed on the TiO<sub>2</sub> surface. Anatase type structure is kept in the Ag doped TiO<sub>2</sub> nano composite, indicating that the metal dopants are expected to be below the visibility limit of X-ray analysis and merely placed on the surface of the crystals without being covalently anchored into the crystal lattice [20].

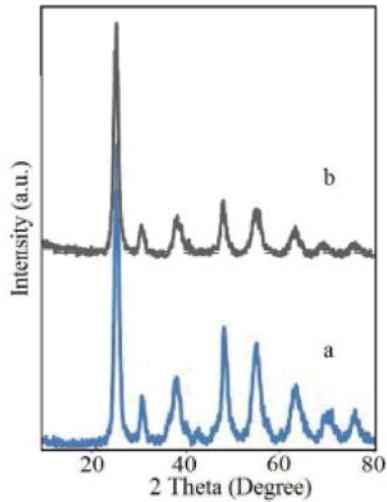


Fig. 1: XRD patterns of nanocrystalline TiO<sub>2</sub> (a) nano composite of Ag/TiO<sub>2</sub> (b)

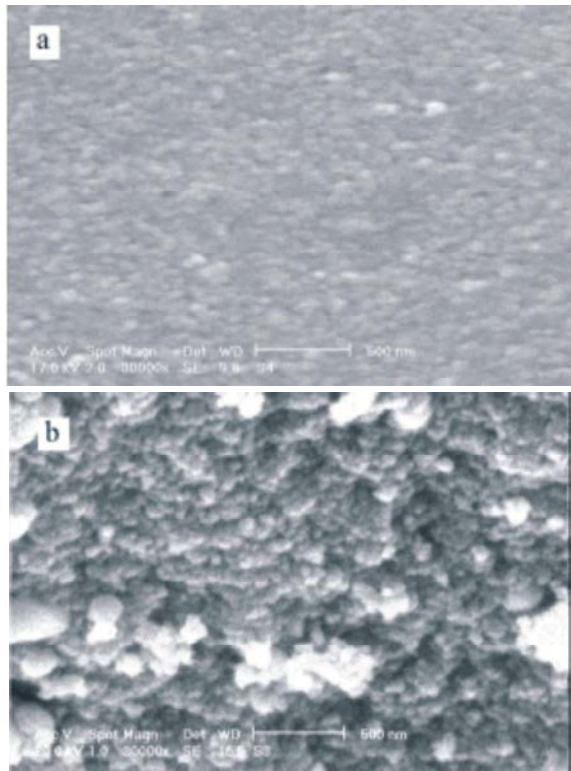


Fig. 2: SEM image of nano crystalline TiO<sub>2</sub> (a) and nano composite of Ag/TiO<sub>2</sub> (b)

**SEM-EDX Analysis:** The morphologies of particles were investigated by scanning electron micrographs (SEM). Fig. 2a and 2b show SEM images of nano crystalline TiO<sub>2</sub> and 6% silver doped sample, respectively, calcined at 673K for 3 h. The particle sizes in SEM micrographs are consistent to a good extent with the particle sizes

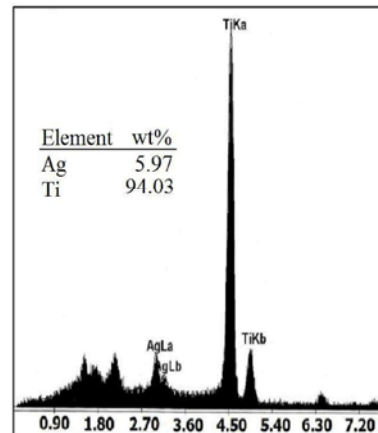


Fig. 3: EDX spectrum of nano composite of Ag/TiO<sub>2</sub>

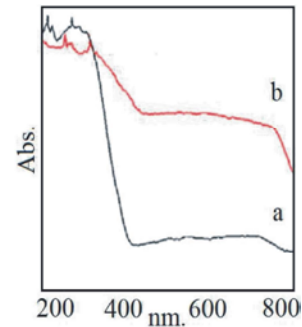


Fig. 4: Diffuse reflectance spectra of the catalysts, pure nano crystalline TiO<sub>2</sub> (a) nano composite of Ag/TiO<sub>2</sub> (b)

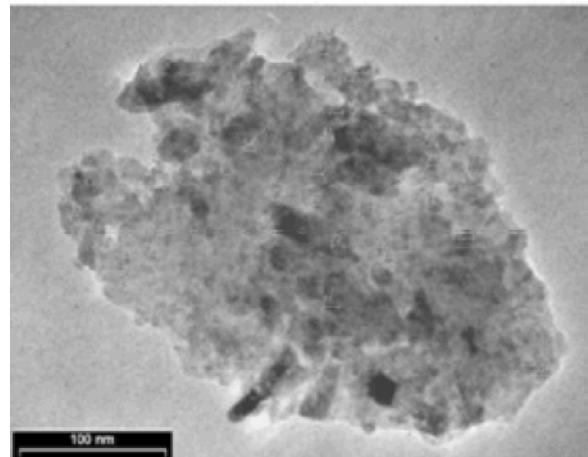


Fig. 5: TEM images of nano composite of Ag/TiO<sub>2</sub>

calculated from XRD peaks by using Sherrer (around 10nm). Furthermore, SEM images show that the synthesized nano particles are spherical and have homogenous morphology and it seems that doping of silver metal does not leave any change in the topology of the catalyst surface.

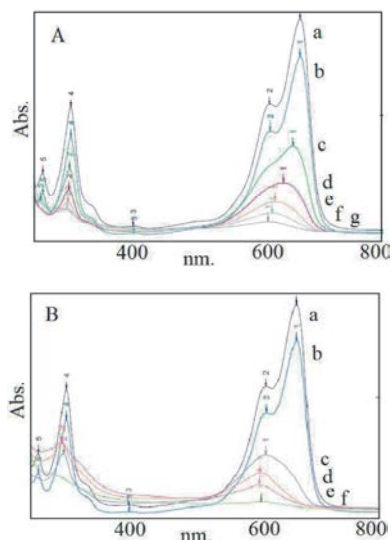


Fig. 6: Changes in the absorption spectra of Methylene Blue as a function of irradiation time; 0 min (a), 30 min in dark(b), 60 min(c), 120 min(d), 180 min(e), 240 min(f), 300 min(g) in the presence of synthesized nano crystalline  $\text{TiO}_2$  (A) and nano composite of  $\text{Ag/TiO}_2$  (B)

The result of energy dispersive X-ray microanalysis (EDX) shows that the mean weight percentage ratio of  $\text{Ag/Ti}$  in nano composite is equal to 6/94 (Fig. 3).

**UV-Visible Diffuse Reflectance Spectra:** A steep decrease of the absorption at a longer wavelength than 387 nm in UV-Vis diffuse reflectance spectrum of nano composite of  $\text{Ag/TiO}_2$  and nano crystalline  $\text{TiO}_2$  has been assigned to the intrinsic band gap absorption of anatase  $\text{TiO}_2$  (3.2 eV) (Fig. 4). Spectrum of silver doped  $\text{TiO}_2$  shows red shift in the band-gap transition (Fig. 4b). Red shift of this type can be attributed to the charge-transfer transition between silver electrons and the  $\text{TiO}_2$  conduction or valence band [21]. Apparently, doping  $\text{TiO}_2$  with  $\text{Ag}$  significantly increases the absorption of  $\text{TiO}_2$  photocatalysts in the visible region, leaving unaffected intrinsic band gap of anatase  $\text{TiO}_2$ .

**Transmission Electron Microscopy (TEM) Image:** The TEM images as shown in Fig. 5 confirm the distribution of silver in titania matrix in terms of bright and dark parts. The individual fine particles are observed with the average size of about 9.5 nm, in agreement with the SEM results.

#### Photo Catalytic Degradation of Methylene Blue Dye:

Fig. 6A and 6B show the changes in the UV/Vis absorption spectra of Methylene Blue due to the degradation by the nano crystalline  $\text{TiO}_2$  and nano composite of  $\text{Ag/TiO}_2$  at different duration of UV-Vis irradiation. The decrease in the intensity of absorption peak of Methylene Blue at  $\lambda=660$  nm indicates a rapid degradation of dye in this wavelength. To confirm the complete decomposition of Methylene blue by the photo-catalyst, the aqueous solution of these compounds were stirred for 30 min while maintaining in dark (Fig. 6B). This was done to ensure that adsorption would not be a cause for complete loss of the dye by nano crystalline  $\text{TiO}_2$ . Interestingly, a complete removal of the initial blue color under the UV-Vis irradiation was observed after 300 min for nano crystalline  $\text{TiO}_2$  and 240 min for nano composite of  $\text{Ag/TiO}_2$ . The photocatalytic mechanism involves the excitation of valence electrons to the conduction band by absorption the UV light, resulting in the formation of holes in the valence band. These electrons and holes can undergo subsequent reduction and oxidation before the recombination reaction. Silver can trap the excited electrons from  $\text{TiO}_2$ , leave the holes for the degradation reaction of organic species and suppress the electron-hole recombination. In other words since the Fermi level of  $\text{TiO}_2$  is higher than that of silver metal, electron transfer from conduction band of  $\text{TiO}_2$  to the metallic silver particles at the interface. This results in the formation of Schottky barrier at the  $\text{Ag-TiO}_2$  contact region and improves the photo-catalytic activity [22].

Due to the stability of the aromatic dye, most conventional methods, like biological treatments and common oxidations, are either not effective, or reduce the dye to potentially hazardous aromatic amines [23]. But degradation of Methylene blue by applying nano crystalline  $\text{TiO}_2$  and  $\text{Ag/TiO}_2$  nano composite successfully reduces the dye to mineral harmless and environmentally friend end products such as  $\text{CO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  [24].

#### CONCLUSIONS

Nano particles of titanium oxide (anatase) can be synthesized from inorganic precursor in a technically simple, solvent free and environmentally benign route. The photocatalytic performance of nano crystalline  $\text{TiO}_2$  can be improved by doping it with  $\text{Ag}$  in a wet-chemical route. Nano composite  $\text{Ag/TiO}_2$  enhance the

photocatalytic degradation of Methylene Blue to mineral harmless products under UV irradiation by 20% in comparison to nano crystalline TiO<sub>2</sub>. This treatment method is technically simple, environmentally friend, cost effective and highly time and energy efficient process for contaminant removal of Methylen Blue dye from industrial wastewaters.

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