



Photocatalytic Mineralization of Methylene Blue Aqueous Solutions by Ag/TiO₂ Nano Composite

Leila Torkian^{1,*}, Ehsan Amereh²

¹Department of Applied Chemistry, Islamic Azad University, South Tehran Branch, Tehran, Iran.

²Iranian Research and Development Center for Chemical Industries (ACECR), Karaj, Iran.

(Received 12 Apr. 2012; Final version received 14 Sep. 2012)

Abstract

Nanocomposite of Ag/TiO₂ and nanocrystalline TiO₂ were prepared by using TiCl₄ 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 nanocomposite of Ag/TiO₂ and nanocrystalline TiO₂ under UV-C light irradiation. Experiments were conducted to compare the photocatalytic activities of nanocomposite Ag/TiO₂ with nanocrystalline TiO₂. The photoreactions were followed by monitoring the degradation of the dye as a function of irradiation time, in the presence of the nanophoto-catalysts, by the visible/ultraviolet absorption spectroscopy. It has been found that the presence of silver in TiO₂ nanoparticles 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.

Keywords: Silver doped titaniananoparticles, 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 ultrafiltration, 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

*Corresponding author: Dr. Leila Torkian, Assistant Prof., Department of Applied Chemistry, Islamic Azad University, South Tehran Branch, P.O. Box: 11365/4435, Tehran, Iran. Email: ltorkian@azad.ac.ir

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_2 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_2 [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 photocatalytic 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_4)) has been used to prepare nanocrystalline TiO_2 in a simple and efficient route. Ag/TiO_2 nano composite is synthesized via a wet chemistry method. Decomposition of Methylene Blue was selected as a model reaction in order to evaluate the photocatalytic activity of nanocrystalline TiO_2 and also Ag/TiO_2 nanocomposite.

Experimental

Materials

The reactants used in this study were liquid titanium tetrachloride (TiCl_4) as a titania source, sodium hydroxide (NaOH), nitric acid (HNO_3), silver nitrate (AgNO_3), 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (Methylene Blue, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$). 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 $\text{Cu K}\alpha$ radiation at 30KV and 20mA. A Philips XLΦ-30 scanning electron microscope (SEM) was used to observe the morphology of nanoparticles. JEOLJEM-200CX operated at 200 kV was used to carry out transmission electron microscopy (TEM) studies.

Catalyst preparation

Stable sols of TiO_2 nano particles were synthesized by hydrolysis of TiCl_4 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 nanocomposite of Ag/TiO₂ is synthesized by adding AgNO₃ solution to the stable sols of TiO₂ 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 nanocrystalline TiO₂ and nanocomposite of Ag/TiO₂ and their applications to contaminant removal of triarylmethane dyes, a cationic basic dye such as Methylene Blue was utilized 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 nanocrystalline TiO₂ or nanocomposite of AgTiO₂ (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 nanocrystalline TiO₂ that prepared from preliminary sol is shown in Figure 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 that 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 TiO₂ (ICCD card File No. 21-1272), which are attributed to the signals of anatase phase with more photocatalytic activity. The peak at 2theta of 30.8 indicates the presence of brookite phase and no rutile phase was observed. The broad peaks in the XRD pattern strongly suggest very small size of the TiO₂ particles. From Scherrer equation [19] the size of the

particles is estimated to about 10 nm. Figure 1b shows the crystal phase composition for Ag/TiO₂ nanocomposite, prepared by the sol-gel process. The X-ray diffraction patterns of silver doped TiO₂ sample almost coincide with that of pure TiO₂ and show no diffraction peaks due to silver species, thus suggesting that the metal particles are well dispersed on

the TiO₂ surface. Anatase type structure is kept in the Ag doped TiO₂ 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].

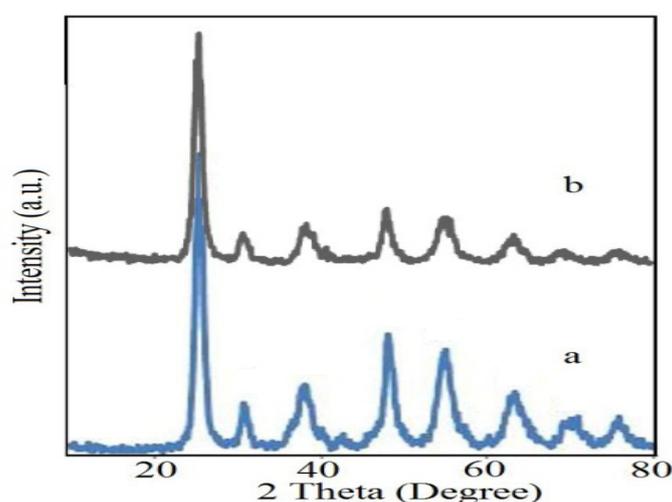


Figure 1. XRD patterns of nano crystalline TiO₂ (a) nanocomposite of Ag/TiO₂ (b).

SEM-EDX analysis

The morphologies of particles were investigated by scanning electron micrographs (SEM). Figure 2a and 2b show SEM images of nanocrystalline TiO₂ 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 calculated from XRD peaks by using Sherrer

(around 10nm). Furthermore, SEM images show that the synthesized nanoparticles 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. The result of energy dispersive X-ray microanalysis (EDX) shows that the mean weight percentage ratio of Ag/Ti in nanocomposite is equal to 6/94 (Figure 3).

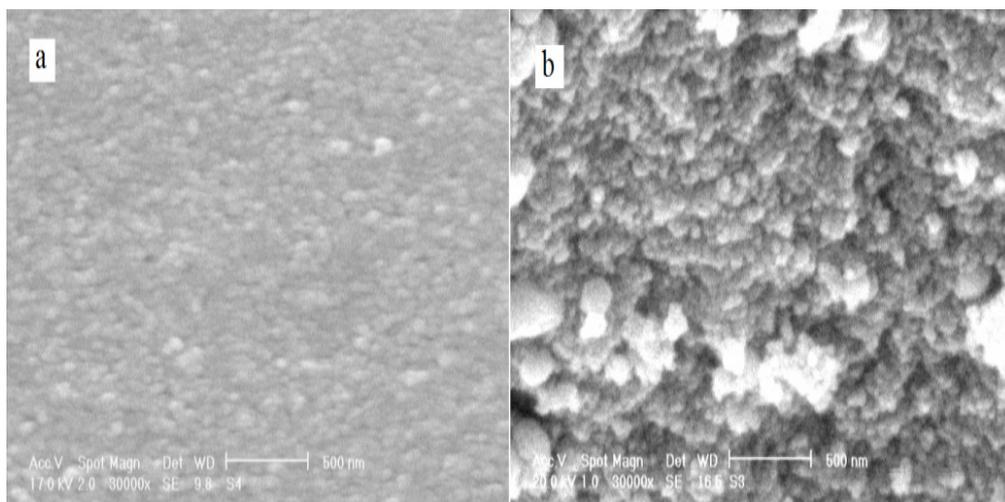


Figure 2. SEM image of nanocrystalline TiO_2 (a), and nanocomposite of Ag/TiO_2 (b).

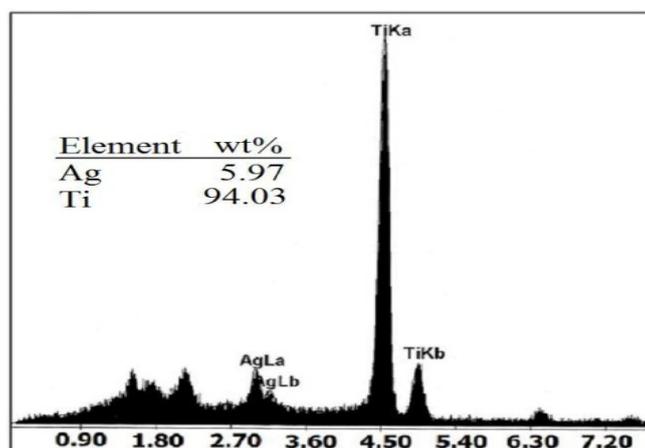


Figure 3. EDX spectrum of nanocomposite of Ag/TiO_2 .

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 nanocomposite of Ag/TiO_2 and nanocrystalline TiO_2 has been assigned to the intrinsic band gap absorption of anatase TiO_2 (3.2 eV) (Figure 4). Spectrum of silver doped TiO_2 shows red shift in the

band-gap transition (Figure 4b). Red shift of this type can be attributed to the charge-transfer transition between silver electrons and the TiO_2 conduction or valence band [21]. Apparently, doping TiO_2 with Ag significantly increases the absorption of TiO_2 photocatalysts in the visible region, leaving unaffected intrinsic band gap of anatase TiO_2 .

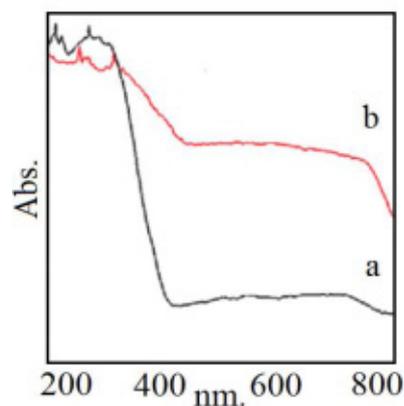


Figure 4. Diffuse reflectance spectra of the catalysts, pure nanocrystalline TiO_2 (a)nanocomposite of Ag/TiO_2 (b).

Transmission electron microscopy (TEM) image

The TEM images as shown in Figure 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.

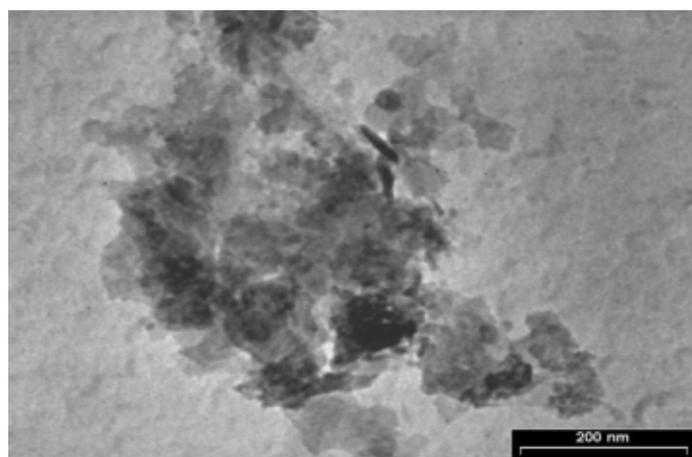


Figure 5. TEM images of nanocomposite of Ag/TiO_2 .

Photo catalytic degradation of Methylene Blue dye

Figure 6A and 6B show the changes in the UV/Vis absorption spectra of Methylene Blue due to the degradation by the nanocrystalline TiO_2 and nanocomposite of 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 (Figure 6B). This was done to ensure that adsorption would not be a cause for complete loss of the dye

by nanocrystalline TiO₂. Interestingly, a complete removal of the initial blue color under the UV-Vis irradiation was observed after 300 min for nanocrystalline TiO₂ and 240 min for nanocomposite of Ag/TiO₂. 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.

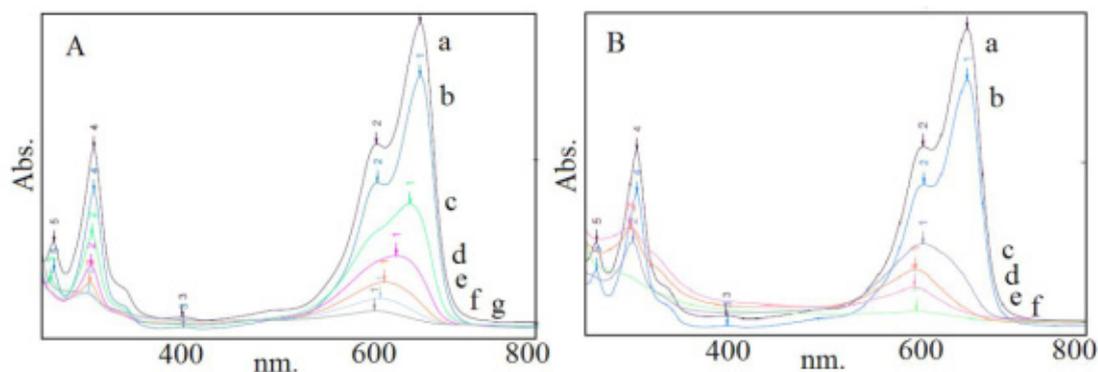


Figure 6. Changes in the absorption spectra of Methylene Blue as a function of irradiation time ;0 min (a),30 min in dark(b), 60 min(c), 120 min(d), 180 min(e), 240 min(f), 300 min(g) in the presence of synthesized nanocrystalline TiO₂(A) and nanocomposite of Ag/TiO₂(B).

Silver can trap the excited electrons from TiO₂, leave the holes for the degradation reaction of organic species and suppress the electron-hole recombination. In other words since the Fermi level of TiO₂ is higher than that of silver metal, electron transfer from conduction band of TiO₂ to the metallic silver particles at the interface. This results in the formation of Schottky barrier at the Ag- TiO₂ 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 nanocrystalline TiO₂ and Ag/

TiO₂ nanocomposite successfully reduces the dye to mineral harmless and environmentally friendly end products such as CO₂, SO₄²⁻, NH₄⁺ and NO₃⁻ [24].

Conclusion

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 nanocrystalline TiO₂ can be improved by doping it with Ag in a wet-chemical route. Nano composite Ag/ TiO₂ enhance the photocatalytic degradation of Methylene Blue to mineral harmless products under UV irradiation by 20% in comparison to nanocrystalline TiO₂. This treatment method is

technically simple, environmentally friend, cost effective and highly time and energy efficient process for contaminant removal of Methylene Blue dye from industrial wastewaters.

Acknowledgements

The authors thank the Office of the Vice-President for Research Affairs of South Tehran Branch of Islamic Azad University.

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