A novel approach for synthesis of visible-light-active nano-crystalline TiO₂ photocatalyst

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Abstract

Silver doped TiO₂ nanoparticles were prepared by combination of sol-gel and arc discharge methods in liquid. The Ag/TiO₂ nanoparticles were characterized by X-Ray diffraction (XRD), transmission electron microscopy (TEM) and ultra violet-visible absorption spectroscopy (UV-Vis). The visible light photocatalytic activities were successfully demonstrated for the degradation of Rhodamine B (Rh. B) as a standard organic compound under the irradiation of 90 W halogen light for 2 h. The results revealed that the Ag/TiO₂ nanoparticles extended the light absorption spectrum toward the visible region and significantly enhanced the Rh. B photodegradation under visible light irradiation. 0.05 gr Ag/TiO₂ nanoparticles exhibited highest photocatalytic efficiency. It has been confirmed that the Ag/TiO₂ nanoparticles could be excited by visible light (E<3.2 eV). The significant enhancement in the Ag/TiO₂ nanoparticles photocatalytic activity under visible light irradiation can be ascribed to the effect of doped noble metal Ag by acting as electron traps in TiO₂ band gap.

PACs: 81.16.-c; 52.80.Wq; 81.07.-b; 78.67.-n

Keywords: Silver doped TiO₂; Liquid arc discharge; Sol-gel.

1. Introduction

TiO₂ photocatalyst is an important functional semiconductor and possesses excellent activities and stabilities, but requires near-ultraviolet (UV) irradiation (about 4% of the solar spectrum) for effective photocatalysis, thereby severely limiting its practical application [1-4]. When photocatalyst titanium dioxide absorbs UV radiation from sunlight or illuminated light source such as fluorescent lamps, it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron to the conduction band of titanium dioxide, therefore creating the negative-electron (e⁻) and positive-hole (h⁺) pair. This stage is referred as the semiconductor’s photo-excitation state. The negative-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form superoxide anion. This cycle continues when light is available.

The activation equations can be written as:

\[ TiO₂ + h\nu (\lambda < 388 \text{ nm}) \rightarrow h_{vb}^+ + e_{cb}^- \quad (1) \]

\[ h_{vb}^+ + H_2O \rightarrow H^+ + \cdot OH \quad (2) \]

\[ \cdot e_{cb}^- + O_2 \rightarrow \cdot O_2^- \quad (3) \]

In this reaction, \( h_{vb}^+ \) and \( e_{cb}^- \) are powerful oxidizing and reducing agents, respectively. It is the hydroxyl radical (OH·), derived from the oxidation of adsorbed water or adsorbed OH·, that is the dominant strong oxidant and leads to decomposition of pollutants [5]. The problem is that the band edge of TiO₂ semiconductor lies in the UV region which makes it inactive under visible light irradiation. It is highly desirable to develop a photocatalyst that can use visible light in high efficiency under sunlight irradiation. Researchers have been interested in the modification of electronic and optical properties of this semiconductor for its efficient use in water and air purification under visible light irradiation.

In general, there are three ways to prepare the visible light TiO₂ photocatalyst: doping TiO₂ with transition metal ions such as V, Cr, Mn, Fe, Co, Ni; doping nitrogen into TiO₂ and Coupling of TiO₂ with a small band-gap semiconductor which extends light absorption into the visible region [6].

Lots of reports are available in nitrogen doped TiO₂ as an efficient visible photocatalyst [7-12]. Cong and co-workers reported on synthesis of N-doped TiO₂ visible photocatalyst using microemulsion and hydrothermal methods. They have reported that triethyamine as a nitrogen source show the highest photocatalytic activity for the decomposition of Rh. B in the visible light region [7]. In a similar work they have found that the co-operation of the nitrogen and Fe³⁺ ion leads to the much narrowing of the TiO₂ band gap and greatly improves the photocatalytic activity in the
visible light region. The photocatalyst co-doped nitrogen and 0.5% Fe$^{3+}$ showed the best photocatalytic activity and the degradation efficiency were improved 75% and 5% under both visible and ultraviolet irradiation, respectively, compared with the pure TiO$_2$ nanoparticles [10]. Yang and co-workers reported that on photocatalytic reactivities of multi-doped TiO$_2$ catalysts with B, C, S and N by degrading Rh. B in aqueous solution under visible-light irradiation ($\lambda > 420$ nm) [13]. It was found out that the reactivity was significantly enhanced and the catalyst doped with nitrogen, carbon, sulfur, and 0.3 wt% iron had the highest photocatalytic activity.

Also, many researches on synthesis of silver doped TiO$_2$ nanoparticles are going on as an appropriate alternative [14-19]. Most of the reported works were based on sol-gel [17, 19] or conventional chemical methods [14, 18]. Hamal and co-workers found that Ag/TiO$_2$ nanoparticles photocatalysts obtained by sol-gel route degrade the gaseous acetaldehyde 10 times faster than commercial Degussa P25–TiO$_2$ under visible light [17]. Ag/InVO$_4$-TiO$_2$ thin films were developed through sol-gel method from the TiO$_2$ sol containing Ag and InVO$_4$ by Ge and co-workers. It has been confirmed that the Ag/InVO$_4$-TiO$_2$ thin films could be excited by visible light ($E < 3.2$ eV). The significant enhancement in the Ag/InVO$_4$-TiO$_2$ photoactivity under visible light irradiation can be ascribed to the simultaneous effects of doped noble metal Ag by acting as electron traps and InVO$_4$ as narrow band gap sensitizer.

In this work, we have prepared visible Ag/TiO$_2$ photocatalyst based on sol-gel and arc discharge methods. We have studied the effect of arc current and duration on size distribution and the photocatalytic activity of the produced nanoparticles under visible light irradiation. Also the amount of silver doped TiO$_2$ on photocatalytic reactivity and decomposition of Rh.B was investigated.

2. Experimental

2.1. Synthesis of Ag/ TiO$_2$ nanoparticles

The schematic diagram of synthesis process which includes two parts is shown on Fig. 1. First of all the necessary liquid medium containing crystalline TiO$_2$ nanoparticles were prepared using sol-gel method. One mL TiCl$_4$ (Merck, 99%) was slowly added drop-wise into 10mL EtOH (Merck, 99.8%) under vigorous stirring at room temperature. A large amount of HCl gas was exhausted and a transparent yellowish solution was formed. The as prepared solution was dried at 100 °C for 24 hours leading to a white amorphp gel. The extracted powder was then annealed at 450 °C for 1 hour leading to white crystalline TiO$_2$ nanopowder.

![Fig. 1. Schematic diagram showing the procedure for synthesis of visible TiO$_2$ photocatalyst.](www.SID.ir)
0.1 g of obtained powder was dispersed in DI water serving as a liquid medium for arc discharge process. The arc discharge set up consists of a high current DC power supply and a reactor including anode, cathode and a micrometer which moves the anode towards the cathode, as we have reported in our previous works as a novel technique for synthesis of various nanostructures [20-24]. In discharge process a 10-20 A current was applied between two silver metallic electrodes. The voltage was dropped to about 2-3.5 V during the arc formation while the current was fixed to a desired amount. Both the anode and cathode were wire shaped, 1.5 mm in diameter and 99.2% purity (from Goodfellow). Initially, we bring the two electrodes into touch leading to a small contact cross section and thus to a high current density. Then we separate them from each other and as a result silver is ablated from the anode and then condensed in solution included dispersed TiO2 nanoparticles.

2.2. Characterization

Analysis of the crystalline structures was performed by XRD diffractometer (X'pert Philips) with wavelength of Cu Kα radiation in 2θ range from 10° to 80° by 0.05° sec⁻¹ steps. UV-Vis spectroscopy of the sam-

![Optical absorption spectroscopy of TiO2 and Ag/TiO2 nanoparticles at different silver concentrations.](image1)

![XRD pattern of pure TiO2, 0.05, 0.1 and 0.15 gr Ag doped TiO2 nanoparticles.](image2)
samples was taken out by a Lambda 950 spectrophotometer (Perkin Elmer) from 200 nm to 1100 nm wavelengths. TEM analysis was performed by a LEO 912 AB instrument at 200 keV accelerating energy by deposition of nanoparticles onto the copper grid at room temperature. Photocatalytic activity of the nanoparticles was measured by photodegradation of Rh. B with the initial concentration and volume of $10^{-5}$ M and 30 mL respectively at the presence of 30 mL Ag/TiO$_2$ solution. First the mixed Rh. B and Ag/TiO$_2$ solution was stirred in dark for 30 min to equilibrate the absorption/desorption between dye molecules and TiO$_2$ photocatalyst. Then it was irradiated at room temperature by a 90 W halogen lamp. The degradation rate was measured by UV–Vis spectrophotometer at the maximum absorption wavelength of Rh. B.

3. Results and discussion

3.1. UV/Vis spectroscopy

UV-Vis spectroscopy was taken out to find the optical properties of Ag/TiO$_2$ nanoparticles. Fig. 2 demonstrates optical absorption spectra of TiO$_2$ and Ag/TiO$_2$ nanoparticles. The absorption edge of pure TiO$_2$ nanoparticles is about 370 nm which shows a red shift in Ag/TiO$_2$ nanoparticles. This is due to decrease in band gap by introducing silver into TiO$_2$ as a noble metal. Absorption edge for 0.05, 0.1 and 0.15 gr Ag doped TiO$_2$ nanoparticles was 431, 464 and 488 nm, respectively. These values confirm decreasing in TiO$_2$ band gap. A 450 nm absorption edge was also reported by Hamal and co-workers in carbon and sulfur doped TiO$_2$ nanoparticles. They have found a maximum red shift on absorption edge for Ag/(C-S) TiO$_2$ nanoparticles annealed at 400 °C for 2 hours [17].

3.2. XRD analysis of the products

Crystalline phase and structure of the produced particles were found by XRD analysis. The results for pure TiO$_2$, 0.05, 0.1 and 0.15 gr Ag doped TiO$_2$ samples are illustrated in Fig. 3. There was no peak for as prepared TiO$_2$ sol in XRD pattern which confirms that the as prepared sol is amorph. As it is clear from the XRD pattern (Fig. 3a) by annealing the as prepared sol at 450 °C for 1 hour a white powder appears which is the crystalline TiO$_2$ in anatase phase. The obtained spectrum after heat treatment has the TiO$_2$ anatase phase peaks at $2\theta = 25.3, 37.7, 47.8, 54, 62.7$ and 75.2 degree with no impurity which is in agreement with 21-1272 standard card from JCPDS. Fig. 3b-d shows XRD results of the extracted powder of Ag/TiO$_2$ nanoparticles prepared by silver discharge in TiO$_2$ aqueous solution at 10 A arc current and different arc durations. Silver concentration in solution was successfully controlled by arc duration. In fact, by controlling the arc duration the amount of evaporated silver will be controlled in a desired amount of arc current. Silver concentration was measured by weighing the silver electrodes before and after the discharge process in a fixed amount of TiO$_2$ solution. These values were 0.05, 0.1 and 0.15 gr for 2, 3 and 5 seconds arc duration respectively. The peaks appeared at 27.8, 32.3, 38.1, 44.3, 46.2 and 64.4 are corresponded to formation of silver phase according to 04-0783 standard card from JCPDS. By increasing the arc duration more silver atoms evaporated from the anode and condensed in TiO$_2$ solution. The results show coexistence of silver and anatase TiO$_2$ phase in final products. The results are in close agreement with other works [18]. From the (101) peak of anatase TiO$_2$ at $2\theta = 25.3$ degree, the average size of crystallite was calculated using the Debye-Scherrer equation. The single crystalline domain size for TiO$_2$ nanoparticles was 16.8 nm.
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3.3. TEM analysis

The shape and size distribution of nanoparticles were characterized by TEM. The silver particles are too small to be observed by scanning electron microscope (SEM) but they are detected by transmission electron microscope (TEM) (dark dots in Fig. 4). The black dots in TiO$_2$ matrix which was also reported in other works should be attributed to the accumulation and the high electron density of Ag$^0$ nanoparticles [see for example 25-27]. They are uniformly dispersed in the TiO$_2$ matrix and exhibit a spherical shape and a small monodisperse size around 10–12 nm. Also the calculated average particles size in TEM analysis which is depicted in Fig. 4b is ~ 32 nm. This average particle size is bigger than the crystallite size obtained from XRD analysis which was expectable. In fact, this is the single crystalline domain size and should be smaller than the grain size which is available in microscopic analysis such as TEM.

3.4. Photocatalytic activity measurements

Changes in the absorption spectrum of Rh. B under visible illumination at different irradiation times for the samples prepared at 0.05, 0.1 and 0.15 gr Ag doped TiO$_2$ nanoparticles and one Rh. B sample as reference are illustrated in Fig. 6. No remarkable changes in the concentration of the Rh. B solution were observed in the absence of TiO$_2$, Ag and Ag/TiO$_2$ nanoparticles (Fig. 5a). Therefore, decomposition of Rh. B only depends on the photoexcitation of Ag/TiO$_2$ nanoparticles. It was observed that by increasing the irradiation time the maximum absorption peak decreases. This indicates that the concentration of Rh. B is decreasing at the presence of Ag/TiO$_2$ nanoparticles and visible light illumination, Fig. 5 (c-g). Also there are not significant changes in concentration of Rh. B at the presence of pure TiO$_2$ nanoparticles under visible light irradiation (Fig. 5b). By increasing the silver concentration from 0 to 0.05gr photodegra-
Photocatalytic reactions on Ag/TiO₂ surface can be expressed by the Langmuir–Hinshelwood model [28]. The reaction rate after the adsorption equilibrium can be expressed as

\[-\ln \left( \frac{C}{C_0} \right) = Kt\]

Where C and C₀ are the reactant concentration at time t = t and t = 0, respectively, K and t are the apparent reaction rate constant and time, respectively. A plot of \(-\ln \left( \frac{C}{C_0} \right)\) versus t will yield a slope of K (Fig. 6). The calculated reaction rate constant for the samples prepared at 0, 0.01, 0.03, 0.05, 0.1 and 0.15 gr Ag/TiO₂ nanoparticles were 13 × 10⁻⁴, 31 × 10⁻⁴, 36 × 10⁻⁴, 67 × 10⁻⁴, 35 × 10⁻⁴ and 26 × 10⁻⁴ min⁻¹, respectively.

Incorporation of a small amount of silver (0.01–0.15 gr) results in increased efficiency in photocatalysis under visible light irradiation. Silver has a Fermi level or electron accepting region at an energy just below the conduction band [6]. Therefore, after light absorption and charge separation, the electron in the conduction band can be effectively trapped by the silver, while the hole oxidizes water and forms hydroxyl radicals, without the threat of recombination [28]. There is an optimum amount of silver to rapidly trap electrons, but too much silver may cover the titanium dioxide and prevent light absorption. In addition, too much silver may mean that the silver acts as a recombination site itself and as a result a decrease in photocatalytic efficiency [29].

4. Conclusion

We have prepared Ag/TiO₂ nanoparticles by combination of the simple sol-gel and inexpensive arc discharge in liquid, methods. XRD results indicated coexistence of silver and TiO₂ phases. UV/Vis analysis revealed a red shift on absorption edge toward visible region in Ag/TiO₂ nanoparticles. Further, the photocatalytic activity of Ag/TiO₂ nanoparticles demonstrated that by increasing visible light illumination time, the maximum absorption peak and concentration of Rh. B decreases in the presence of Ag/TiO₂ nanoparticles. Decrease of concentration for the 0.05 gr Ag/TiO₂ nanoparticles was found to be more than the sample prepared at higher and less concentrations. In fact incorporation of silver nanoparticles facilitates longer charge separation by trapping photogenerated electrons and thus higher activity under visible light irradiation.

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