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Using electrical arc discharge method to prepare Ag-TiO_2 nanoparticles and study its photocatalytic activity

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A simple, inexpensive and one-step synthesis route of Ag-TiO_2 nanoparticles by arc discharge method has been reported. The resulting nanoparticles were characterized by using X-ray diffraction and scanning electron microscopy. X-ray diffraction patterns demonstrate dominance of rutile to anatase phase in TiO_2 and formation of silver metal onTiO_2 after arc discharge process. Scanning electron microscopy images exhibit the increase of reduced nanoparticles in 5 min arc duration as compared with 1 min arc duration. Photodegradation of methyl orange as a standard pollutant shows that the presence of silver in TiO_2 was found to enhance the photocatalytic activity. The high activity of silver doped TiO_2 is due to the enhancement of electron-hole separation by the electron trapping of silver particles.

Keywords: Ag-TiO_2 nanoparticles, Electrical arc discharge method, Photocatalytic activity

1 Introduction

Titanium dioxide (TiO_2) has attracted significant attention of researchers because of many interesting physical properties that make it suitable for a variety of applications[1,2]. When TiO_2 is exposed by photon when its energy is more than TiO_2's band gap, electron is excited from valance band to conduction band, then the electron-hole pair will be created[3,4].This phenomenon leads to hydrophilic and photocatalytic properties of TiO_2.Combination of these properties provides many applications such as solar cells[5,6], refinement of air and water[7,8], gas sensors[9], and self-cleaning surface [10,11]. Nevertheless multivarious studies were achieved; many researches are performed for improvement of properties. The only disadvantage of TiO_2 is that its band gap lies in the near-ultraviolet (UV) of electromagnetic spectrum: 3.2 electron volt (eV) and 3.0 eV for anatase and rutile, respectively. It is therefore, evident that any modification of the TiO_2-based photocatalysts, resulting in lowering of its band gap, is representing a breakthrough in the field[12,13]. Efforts have been made to extend the energy absorption range of TiO_2 from UV to visible light or to improve further the photocatalytic activity of TiO_2 by adding foreign metallic elements[14-16.] For instance, Ag can serve as electron trap aiding electron-hole separation and can also facilitate electron excitation by creating a local electric field. When Ag is deposited upon TiO_2, electron of electron-hole pair is trapped by silver. During radiation, then recombination rate is decreased[17,18]. In the present study, the photocatalytic degradation of the methyl orange (MO) in the aqueous suspensions of TiO_2 and Ag-deposited TiO_2 nanoparticles under UV light irradiation in order to evaluate and distinguish the various effects of Ag deposits on the TiO_2 photocatalytic activity, have been examined. The X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM) images of prepared materials were taken.

2 Experimental Details

2.1 Materials

TiO_2 powder was supplied from Gohsenol Company. The nano silver particles were made by electric arc discharge technique and then added to TiO_2 powder. The methyl orange, polyvinyl alcohol and *monoethanol amide stearate* were purchased from Merck Company.

2.2 Preparation of nanoparticles

The preparation system consists of two main parts: a high current *dc* power supply and a reactor including anode, cathode and a micrometer which causes movement of anode towards the cathode. The schematic diagram of the electrical arc discharge is shown in Fig. 1. A 50 ampere (A) arc current was applied between two silver electrodes. The voltage was dropped to about 20 volt (V) during the arc performance, while the current was fixed to desired

value. Both anode and cathode were disk shaped silver, 1 cm diameter and 2 mm thickness, and 99.99% purity. In this arc current, which was the threshold current for discharge between silver electrodes, discharge happens only between the electrodes and there is negligible erosion for silver electrodes. Two electrodes were connected to automatic electrical spark in suitable distance. Initially, we bring the two electrodes into touch, leading to a small contact cross-section and thus to a high current density. When argon passes through the path with 300 mbar pressure, Ar gas transits the based catalyst (titanium dioxide) to system's box. Hence, Ag metal is vaporized and embedded on based catalyst. External product was trapped in dish which consists of polyvinyl alcohol 10%, monoethanol amide stearate 2%, and the rest is deionization water. Collected products were annealed by heater at 120°C for 60 min. Also, products were calcined at 600°C for 60 min, and finally it was grinded.

2.3 Characterization

2.3.1 Measurements of photocatalytic activities

To investigate the effects of silver deposition on the photocatalytic activity of TiO_2, the photodegration of MO was carried out in the TiO_2, 0.1% Ag-$TiO_2$and 0.5% Ag-TiO_2nanosols under UV light irradiation, respectively. The molecular structure of MO is given in Scheme 1. A 100 ml pyrex beacker was used as a batch photoreactor. The TiO_2 or Ag-TiO_2 nanosol (50 ml) containing MO (10^{-5}M) was transferred into the photoreactor and aerated with stirring for 30 min in the dark. The MO/nanosol was then irradiated with the lamp located above the reactor at given irradiation time intervals. The light sources, purchased from Philips Company, were 30 W and working in 254 nm, A1 ml-aliquot was taken from the MO/nanosol and analyzed by UV-visible absorption spectroscopy (Perkin Elmer 55OES model) to monitor the degree of the MO photodegradation.

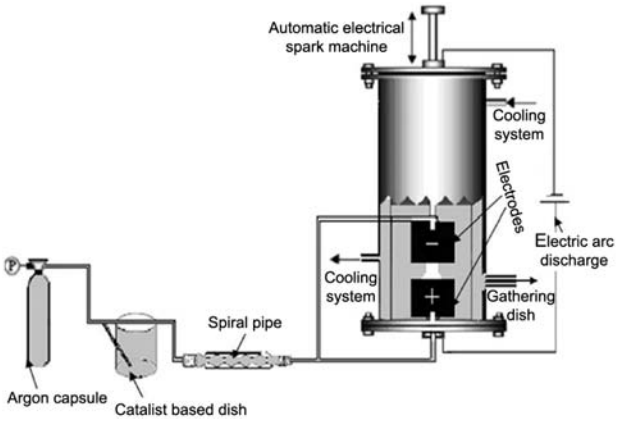
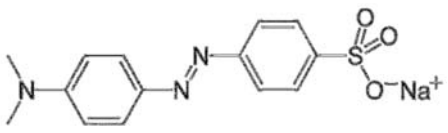


Fig. 1 — Schematic diagram showing the arc discharge process



Scheme 1 — Molecular structure of methyl orange

3 Results and Discussion

3.1 XRD analysis

The X-Ray Diffraction pattern of the powder samples synthesized in different concentration are taken by ADP2000 model from Ital structure Company and shown in Fig. 2. It can be seen that phase of titanium dioxide is completely rutile. After deposition of Ag on TiO_2, crystal peaks (111) and (200) of silver metal appear in 2θ = 38.15 and 44.34 degrees, respectively. By increasing the silver percentage, intensity of these peaks improves and then (220) and (311) crystal peaks of silver appear in 2θ = 64.5 and 77.47 degrees, respectively.

3.2 SEM analysis

Microscopic structure of the samples was observed by SEM images obtained by LEO 1455 VP model. Figure 3 (a and b) shows scanning electron microscopy images of Ag-TiO_2 nanoparticles prepared at 50A arc current with 1 and 5 min arc duration, respectively. The amount of reduced nanoparticles at

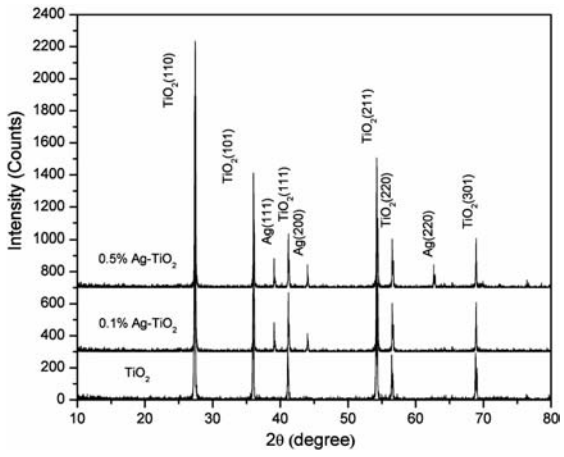


Fig. 2 — XRD pattern of TiO_2, at0.1% Ag–TiO_2 and at0.5% Ag-TiO_2synthesized powder

5 min arc duration is much higher than the reduced nanoparticles at 1 min arc duration. The obtained size is about 90 nm in 1 min duration and is about 70 nm for 5 min duration. The amount of electrons injected from discharge zone to the solution in 5 min arc duration, is more than the injected electrons in 1 min arc duration, which results in more reduced Ag nanoparticles. Although the reverse story is taken place for TiO_2 nanoparticles i.e. the more arc duration, the bigger TiO_2 nanoparticles. Their size change from 80 nm (1 min arc duration) to 100 nm (5 min arc duration) in sample 0.1 % Ag-TiO_2. It was

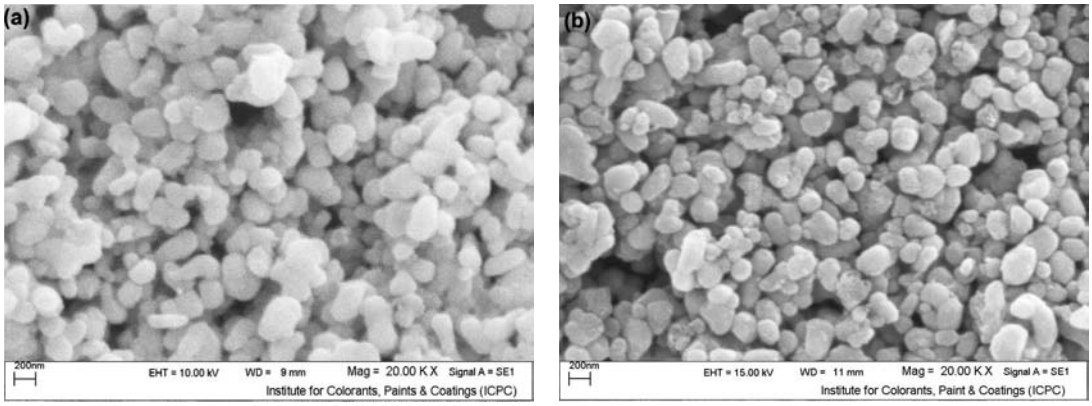


Fig. 3 — SEM images of (a) 0.1% Ag-TiO_2 nanoparticles with 1 and (b) 0.5% Ag-TiO_2 nanoparticles 5 minutes arc durations

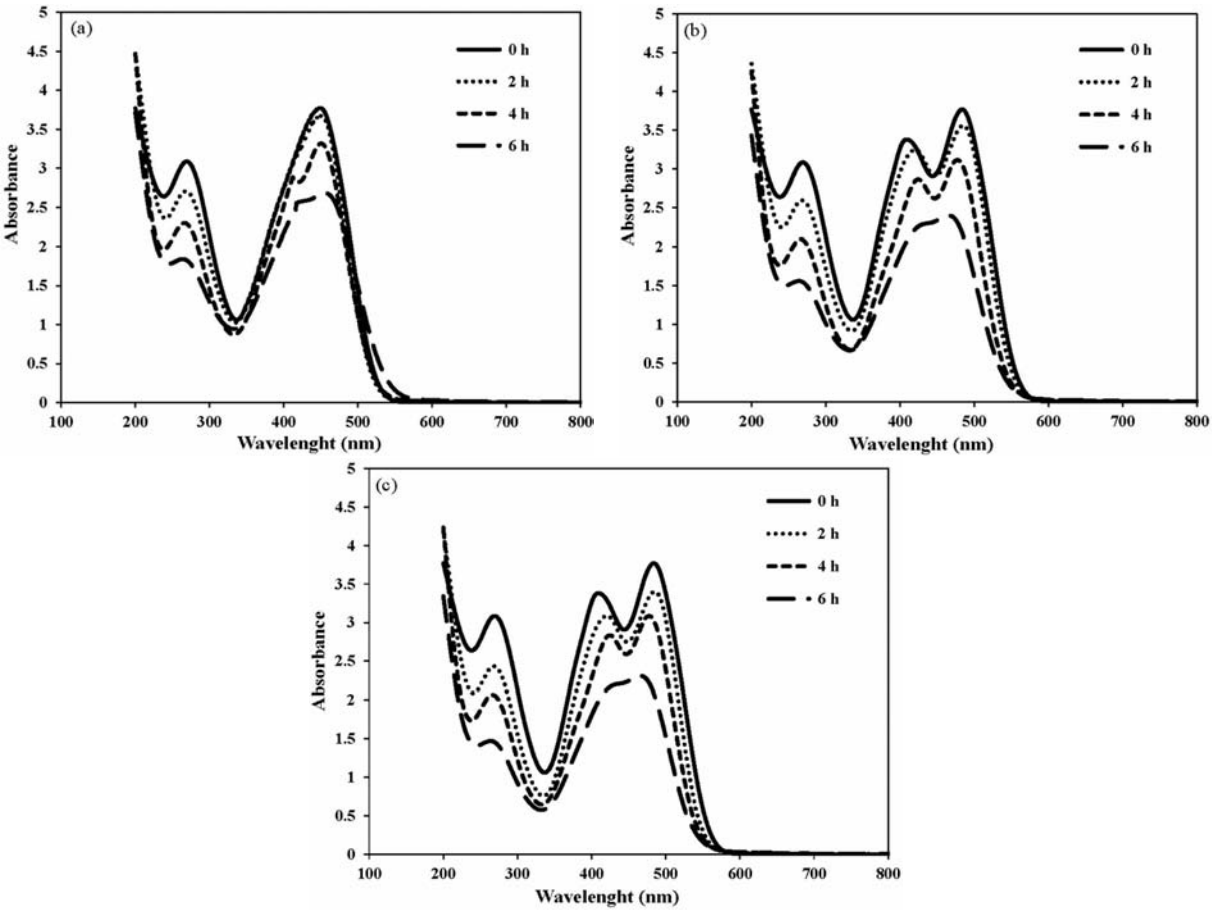


Fig. 4 — Absorption spectral changes of MO in the (a) TiO_2 nanosol and, (b) at 0.1.% Ag-TiO_2 nanosol, (c) at 0.5.% Ag-TiO_2 nanosol as a function of irradiation time (UV light). The initial concentration (C_0) of MO was 1×10^{-5}M, and the TiO_2 content was 0.4 % wt.

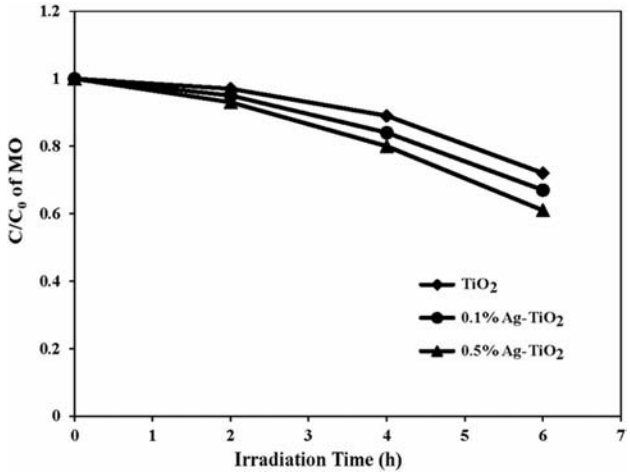


Fig. 5 — Comparison of the MO photodegradation in the TiO_2, at 0.1% Ag–TiO_2 and at 0.5% Ag–TiO_2 nanosols under UV light irradiation

observed that the particles are nanosized and spherical.

3.3 Photocatalytic activities

Photocatalytic reactions on Ag-TiO_2 surface can be expressed by the Langmuir-Hinshelwood model[19,20]. The reaction rate in the adsorption equilibrium process can be given as:

$$-\ln (C/C_0) = kt$$

where C and C_0 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 $\ln(C/C_0)$ versus t will yield a slope of k. Fig. 4 shows the spectral changes of MO in the TiO_2 nanosol, at 0.1.% Ag-TiO_2 nanosol and at 0.5% Ag-TiO_2 under UV-visible light irradiation. Compared to the pure TiO_2, the Ag–TiO_2nanosol exhibited a significant increase in the MO photodegradation rate as shown in Figs. 5. The calculated reaction rate constant for the samples prepared with TiO_2 nanosol, at 0.1% Ag-TiO_2 nanosol, and at 0.5 % Ag–TiO_2 were 0.0454, 0.0526, and 0.0625 h^{-1}, respectively. However, adding Ag to TiO_2 caused photocatalytic activity to be improved.

4 Conclusions

The Ag-TiO_2 nanoparticles by a high current electrical arc discharge of Ag electrodes have been prepared. XRD results confirm the formation of a mixture of nanocrystallineTiO_2 in rutile phase with silver metals. SEM images demonstrate that the size of Ag-TiO_2 nanoparticles at 5 min arc duration at 50A arc current, are smaller than1 min arc duration (only TiO_2 naoparticles can be observed). As the time for arc duration goes high, the removal of Ag from electrodes with small size will get order nicely. So, TiO_2 particles become larger, but the resultant particles become smaller in more arc duration. Therefore, the observed activities are improved. Photocatalytic activity of TiO_2 and Ag-TiO_2 nanoparticles was measured by photodegradation of MO under 2 mW/cm^2 UV irradiation. The results show that by increasing the irradiation time, both the maximum absorption peak and the concentration of MO decrease. Also, it is seen that the photonic efficiency increases with an increase in the metal loading up to an optimum level due to the decreasing of recombination effect of electron and hole.

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References

1 Yu J, Xiong J, Cheng B & Liu S, *Appl Catal B-Environ*, 60 (2005) 211.
2 Xing-Gang H, An-Dong L, Mei-Dong H, Bin L & Xiao-Ling W, *Chin Phys Lett,* 26 (2009) 771061.
3 Escobar-Alarco´n L, Arrieta A, Camps E, Muhl S, Rodil S & Vigueras-Santiago E, *Appl Surf Sci,* 254 (2007) 412.
4 Chang C C, Chen J Y, Hsu T L, Lin C K & Chan C C, *Thin Solid Films,* 516 (2008) 1743.
5 Wan L, Li J F, Feng J Y, Sun W & Mao Z Q, *Mater Sci Eng B-Solid,* 139 (2007) 216.
6 Mc Cormick J, Zhao B, Rykov S, Wang H & Chen J G, *J Phys Chem B,* 108 (2004) 17398.
7 Zan L, Tian L, Liu Z & Peng Z, *Appl Catal A-Gen,* 264 (2004) 237.
8 Xin B, Ren Z, Hu H, Zhang X, Dong C, Shi K, Jing L & Fu H, *Appl Surf Sci,* 252 (2005) 2050.
9 Ge L, Xu M & Fang H, *J Mol Catal A-Chem,* 258 (2006) 68.
10 Hemissi M, Amardjia-Adnani H & Plenet J, *Curr Appl Phys,* 9 (2009) 717.
11 SekharSamal S, Jeyaraman P & Vishwakarma V, *J Min Mater Char Eng,* 9 (2010) 519.
12 Nasr-Esfahani M & Habibi H, *Int J Photoenergy,* (2008) Article ID 628713.
13 Li C, Hsieh Y, Chiu W, Liu C & Kao C, *Sep Purif Technol,* 58 (2007) 148.
14 Lee M, Hong S & Mohseni M, *J Mol Catal A-Chem,* 242 (2005) 135.

15 Matos J, Laine J & Herrmann J, *Appl Catal B-Environ,* 18 (1998) 281.
16 Sena S, Mahanty S, Roy S, Heintz O, Bourgeois S & Chaumont D, *Thin Solid Films,* 474 (2005) 245.
17 Ren L, Zeng Y & Jiang D, *Catal Commun,* 10 (2009) 645.
18 Sung-Suh H, Choi J, Hah H, Koo S & Bae Y, *J Photochem Photobio A,* 163 (2004) 37.
19 Liao D, Badour C & Liao B, *J Photochem Photobiol A,* 194 (2008) 11.
20 Li Y, Li X, Li J & Yin J, *Water Res,* 40 (2006) 1119.