World Applied Sciences Journal 14 (Special Issue of Food and Environment): 54-59, 2011
ISSN 1818-4952

Effects of Operational Parameters on the TiO_2 and TiO_2/Ag Core-Shell Photocatalysis System for Decolorizing AR14

[1,2]Masood Hamadanian, [3]Mohsen Behpour, [4]Asra Sadat Razavian and [1]Vahid Jabbari

[1]Institute of Nanosciences and Nanotechnology, University of Kashan, Kashan, I.R. Iran
[2]Department of Physical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R. Iran
[3]Department of Chemistry, Faculty of Science, University of Kashan, Kashan, I.R. Iran
[4]Department of Analytical Chemistry, Faculty of Science, University of Kashan, Kashan, I.R. Iran

Abstract: In this work, nanostructured titanium dioxide (TiO_2) thin films have been prepared on glass substrates using a facile layer-by-layer dip-coating method. The nano-layer surface was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. It was observed that degradation of Acid Red 14 (AR14) depend on several parameters such as pH, the coting of silver and dipping times. In addition, TiO_2 from TiO_2/Ag demonstrated photocatalysis performance when irradiated and the Ag carrier further showed an electron-scavenging ability to mitigate electron-hole pair recombination, which can improve the photocatalytic efficacy. With the oxidization and electron-scavenging ability of Ag and the photocatalysis ability of TiO_2, TiO_2/Ag can decolor AR14 more efficiently than TiO_2.

Key words: Titanium dioxide · Silver · Electron-Scavenging · Photocatalysis · Decolorization

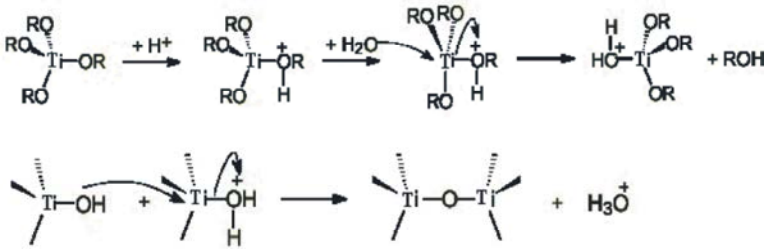
INTRODUCTION

With increasing environment protection awareness in recent years, environment pollution issues have become major concerns; among these issues, wastewater color is very important. Besides causing color contamination as well as affecting water body clarity and transmittance, some toxic dyes also pose hazards to organisms in water bodies [1]. Common dye wastewater treatment methods include biological (activated sludge) and chemical processes (the Fenton process and coagulation) [2,3]. Coagulation processes and the Fenton process have low equipment costs, but produce large amounts of sludge; thus, additional costs for sludge treatment are required. Using activated carbon to physically adsorb wastewater color showed a significant effect, but it requires frequent replacement and the treatment expense is so high that its application is not practical [4]. The above problems can be solved by using a titanium dioxide (TiO_2) plus ultraviolet (UV) photocatalysis method to remove dye color.

The anatase TiO_2 polymorph is the most important photocatalyst used today. Since the discovery of its photocatalytic activity by UV irradiationin 1972 [5], many studies have been developed with this material in the photodegradation of phenols [6], dyes [7], microorganisms [8], herbicides [9] and a variety of organic contaminants. Its band gap energy of 3.2eV provides the formation of electron-hole pairs which may be activated with wavelengths shorter than 380nm. Therefore, many efforts have been made to enhance the activation of TiO_2 at wavelengths closer to those of visible light. These efforts include methods such as doping of TiO_2 with transition metals, rare earths, metals, non-metallic anions, and surface modification (impregnation and deposition) with noble metals [10,11]. Regularly, surface modification consists of nanoparticles embedded or anchored to the surface of TiO_2, trapping of electrons being its main function, thereby decreasing the recombination of the electron-hole pairs. For noble metals, silver is one of the most suitable for industrial applications due to its low cost and ease of preparation. Nanoparticles of silver anchored to the surface of TiO_2 have proven to be highly efficient, favoring the activation of the titania under visible light irradiation [12,13].

The present study deals with an examination of photoadsorption, photoreduction and photodeposition of silver clusters on TiO_2 particles immobilized on the glass substrates. Experimental results have shown that the preparation of high transparent TiO_2 thin film by dip coating method needs to control pH, thickness of the film and Ag coating.

Corresponding Author: Masood Hamadanian, Institute of Nanosciences and Nanotechnology, University of Kashan, Kashan, I.R. Iran. Tel.: +98-361-5912382, Fax: +98-361-5552930.



Scheme 1: Mechanism of poly-condensation reactions of Ti(OBu)4 precursor in the acidic environment.

Experimental

TiO_2 Sol Preparing and Dip-Coating on the Glass Substrates: All the chemicals were purchased from Merck and were used without any further purification. Deionized water was obtained from ultra pure water system (type smart-2-pure made in TKA Company, Germany). 3.6 ml of Ti(OBu)4 was mixed well with 5 ml:2 ml ethanol:water, chilled in ice bath, then 0.03 M HNO3(aq) was added slowly into it with vigorous stirring. The mixture was stirred at ice bath for 4 h, kept in refrigerator for storage. For poly-condensation reactions of Ti(OBu)4 precursor, the process can be written as Scheme 1. The Ag-coated TiO_2 films were prepared by the incipient wet impregnation with 0.0004 M $AgNO_3$ on TiO_2 films.

Thin Films Characterization: The XRD patterns were recorded on a Philips X'pert Pro MPD model X-ray diffractometer using Cu $K\alpha$ radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 10-80°. The average crystallite size of anatase phase was determined according to the Scherrer equation. The morphology and size of nanoparticles was characterized using scanning electron microscope (SEM) (Philips XL-30ESM). The extent of AR14 degradation was monitored using UV-Vis spectrophotometer (Perkin Elmer Lambda 2S).

Evaluation of Photocatalytic Activity of the Samples: The experiments of the photocatalytic decomposition of AR14, with application of the immobilized catalyst bed were conducted in the laboratory scale apparatus. The UV source was 400W Osram lamps for experiments. The photocatalytic degradation was carried out with 100mL aqueous AR14 solution (10ppm). The degradation percentage of AR14 in the reaction process could be calculated by the following formula:

Where C_t is the concentration of AR14 after t min and C_0 is the initial concentration.

RESULTS AND DISCUSSION

XRD Analysis: The nanocrystalline anatase structure was confirmed by (101), (004), (200), (105) and (211) diffraction peaks [14] as shown in Figure 1. Typical peaks in XRD pattern are observed at 2θ values 25.28°, 38.08° and 47.92°, which assigned to 10 1, 004 and 200 planes, respectively, while the main peaks of rutile and brookite phases are at 2θ = 27.4° (110 plane) and 2θ = 30.8° (121 plane). Therefore, brookite phase has not been detected. In order to obtain photocatalytic activity, it is necessary to make proper anatase nanostructure, but it is evident that some rutile phase could improve the photocatalytic effect [15]. The average size of nanoparticles was estimated from the Scherrer equation was around 15-25 nm.

Characteristic of TiO_2 Films by SEM: We examined the quality of the TiO_2 thin films after dip-coating the glass beads into the TiO_2 suspension solution one (TiO_2-1) or five times (TiO_2-5). Figure 2(a), (b) denotes SEM micrographs of TiO_2 films fabricated on glass substrate, having different layers. As shown from microstructural observations, the thickness of film and surface defects increases in accordance with number of dipcoating. Cracking was less extensive in thinner films while very thick films which were produced using viscous solutions tended to peel off the substrate completely [16].

The second coating route was then carried out on the calcinated thin films to get a homogeneous and complete coated layer. SEM micrographs of the TiO_2 thin films calcinated at 550°C temperature, is shown in Figure 3.

The Figure 4 shows SEM images of the silver particles coated on the TiO_2-5 thin film surface. The aggregated phenomena by Ag on the TiO_2 may be due to the electrostatic attraction. Comparing bare TiO_2 (Figure 3) and TiO_2 coated electrode after Ag deposition, it can be seen that the Ag nano-clusters were formed and distributed at the films surface in a form of porous and sphere-like network of high roughness and complexity.

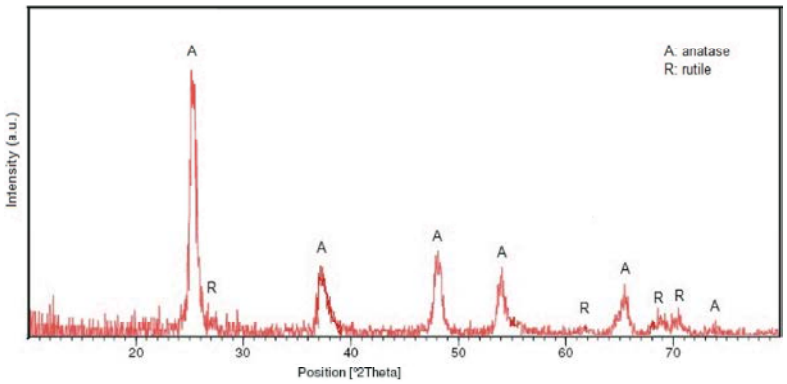


Fig. 1: The XRD Patterns of TiO2-5 thin film.

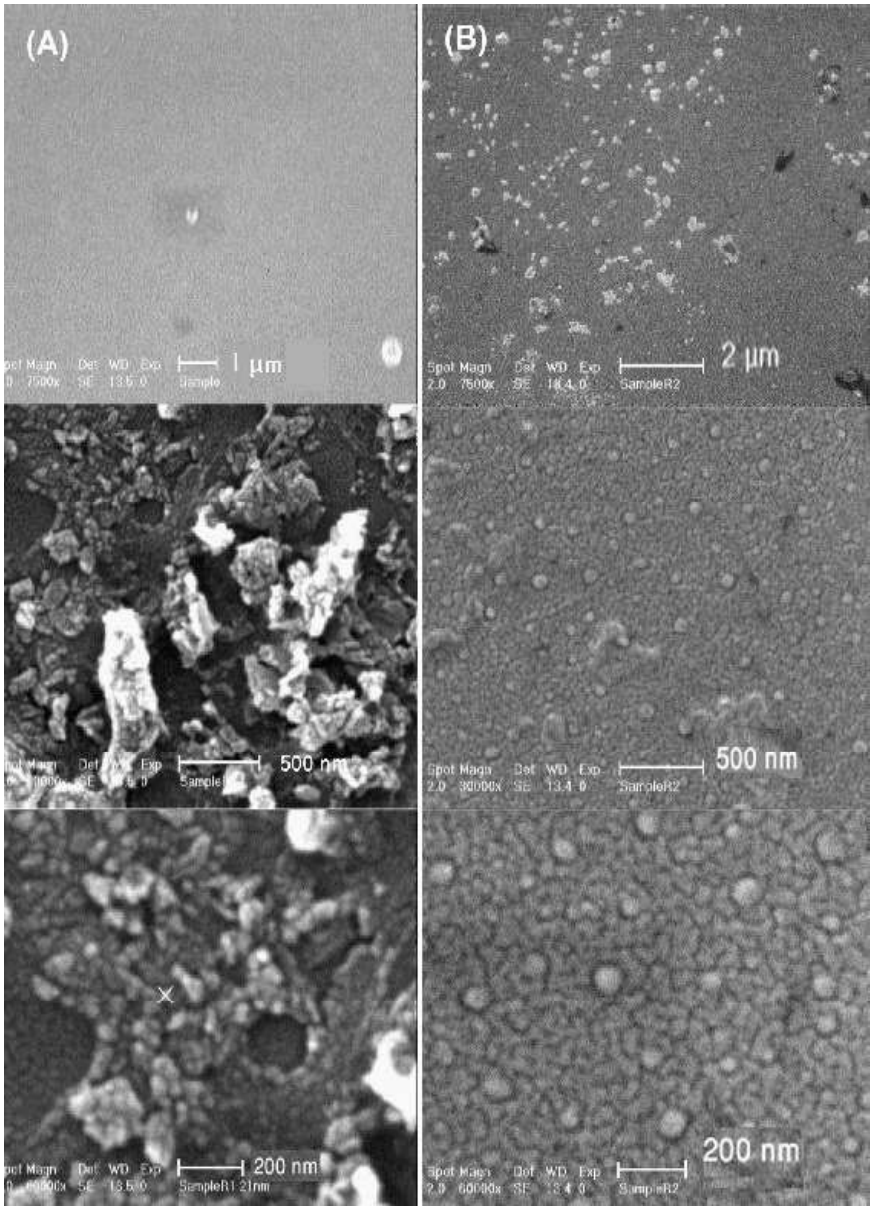


Fig. 2: The SEM images of TiO2 thin films dip-coated after one (a) and five times dip-coating (b).

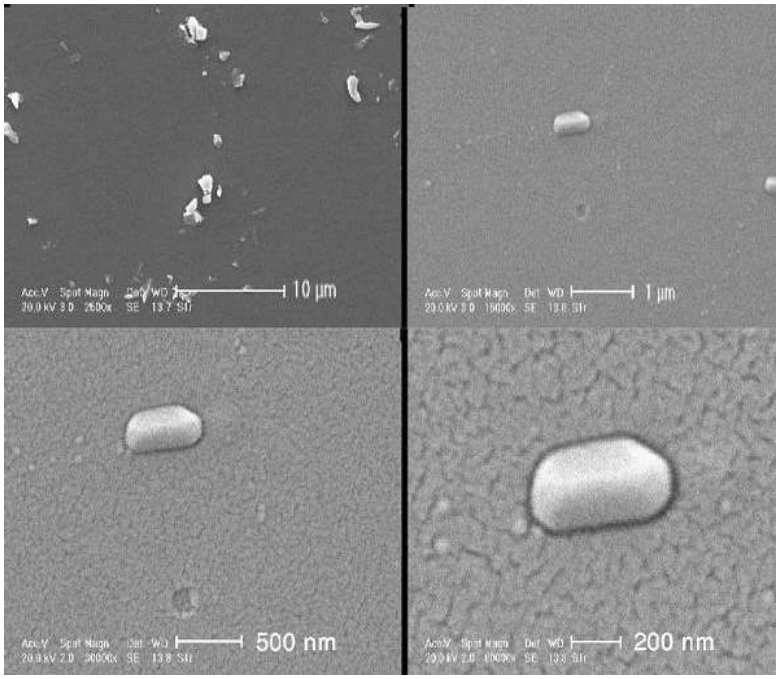


Fig. 3: The SEM images of TiO2 thin films dip-coated at one (a), and five times (b) calcinated in the 550 0C.

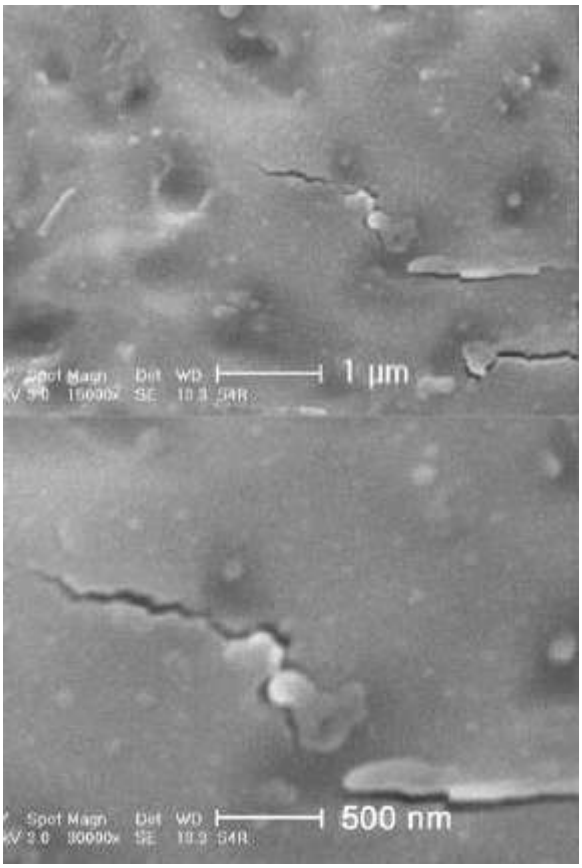
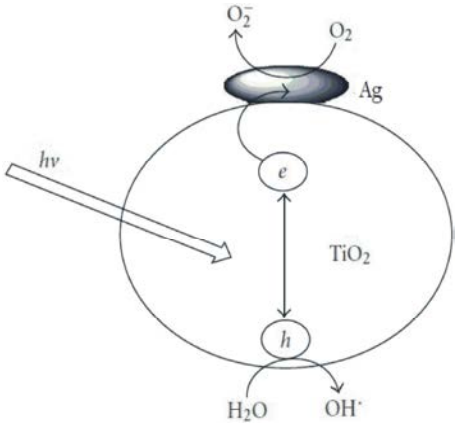


Fig. 4: The SEM images of Ag-coated TiO2-5 thin film. TiO2 film were immersed in 0.004M AgNO3 solution and irradiated by UV for 2.5 h.

Table 1: The photocatalytic effect on degradation of AR14 with TiO_2 thin films dip-coated in one (TiO_2-1), five times (TiO_2-5), and degradation of AR14 by Ag-coated TiO_2 (Ag-TiO_2-5).

	UV irradiation time (h)				
Sample Type	1	2	3	4	5
TiO_2-1	11	22	31	39	45
TiO_2-5	20	42	56	63	68
Ag-TiO_2-5	18	52	81	94	98



Scheme 2: Interfacial charge transfer process of silver-doped TiO_2 nanocomposites under the irradiation of UV light.

Photocatalytic Activity of TiO_2 and Ag-Coated TiO_2 Films: Table 1 presents the results obtained during photocatalytic decomposition of AR14 under UV light. The best decomposition results were obtained for Ag/TiO_2 removal was equal to 74%. In this case, TiO_2-5 was more active than TiO_2-1 catalyst. The differences in photocatalytic activity could be contributed from the differences in phases present, particle and surface morphology, and surface area [17].

As shown in Table 1, after modification by Ag, the catalytic activity of the TiO_2 layers were improved compared with the bare TiO_2 layer, because Ag coated TiO_2 itself has both photocatalysis and oxidization activities provided by TiO_2 and Ag, respectively, to decolorize dye. Furthermore, Ag in Ag-coated TiO_2 acted as an electron scavenger, and delayed electron-hole pair recombination derived from excitation of irradiated TiO_2, thus promoting photocatalytic decolonization. That means Ag^+ acts as a good electron trapper, therefore Ag- TiO_2 has a slowest electron-hole recombination rate and highest catalytic activity as shown in Scheme 2 [18].

CONCLUSION

The immobilization of Ag on the TiO_2 and deposition on glass sheets was achieved successfully by dip-coating processing. TiO_2 showed photocatalysis properties in the presence of UV irradiation and Ag from the TiO_2/Ag also played a role as an electron scavenger, delaying the combination of electron-hole pairs. In the photocatalytic process, part of the electrons excited from the irradiated TiO_2 transformed the oxidation state of Ag to metallic Ag, which revived the oxidation activity. Thus these described characteristics enhanced the photocatalytic activity of TiO_2/Ag on AR14 decolorization to a higher level than with commercial TiO_2. In addition, the heavier Ag carrier improved the solid-liquid separation of nano-TiO_2, thus contributing to TiO_2/Ag being more suitable for application in slurry systems for photocatalytic water treatment. In addition, preparation of the photocatalyst is very simple, and the cost is economical, too.

ACKNOWLEDGMENT

The authors gratefully acknowledged the financial support of Iran government grant for the financial support of this work which made the study possible.

REFERENCES

1. Kabil, A.S., 2000. Chlorotriazine reactive azo red 120 textile dye induces micronuclei in fish. Ecotox. Environ. Saf., 47: 149-155.
2. Lin, S.H. and M.L. Chen, 1997. Treatment of textile wastewater by chemical methods for reuse, Water Res., 31: 868-876.
3. Ahmad, A.L. and S.W. Puasa, 2007. Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process, Chem. Eng. J., 132: 257-265.
4. Ahmaruzzaman, M., 2008. Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface Sci., 143: 48-67.

5. Honda, K. and A. Fujishima, 1972. Nature, 238: 37-38.
6. Ding, Z., G.Q. Lu and P.F. Greenfield, 2000. J. Phys. Chem., B, 104: 4815.
7. Pekakis, P.A., N.P. Xekoukoulotakis and D. Mantzavinos, 2006. Water Res., 40: 1276.
8. Josset, S., J. Taranto, N. Keller, V. Keller, M.C. Lett, M.J. Ledoux, V. Bonnet and S. Rougeau, 2007. Catal. Today, 129: 215.
9. Konstantinou, I.K., V.A. Sakkas and T.A. Albanis, 2001. Appl. Catal., B, 34: 227.
10. Paola, A.D., G. Marci, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda and B. Ohtani, 2002. J. Phys. Chem., B, 106: 637.
11. Colón, G., J.M. Sánchez-Espa˜na, M.C. Hidalgo and J.A. Navío, 2006. J. Photochem. Photobiol., A, 179: 20.
12. VanGrieken, R., J. Marugán, C. Sordo, P. Martínez and C. Pablos, 2009. Appl. Catal., B, 93: 112.
13. Yang, X., F. Ma, K. Li, Y. Guo, J. Hu, W. Li, M. Huo and Y. Guo, 2010. J. Hazard. Mater., 175: 429.
14. Qamar, M., M. Saquib and M. Muneer, 2005. Dyes Pigm., 65: 1-9.
15. Takahashi, Y. and Y. Matsuoka, 1988. J. Mater. Sci., 23: 2259.
16. Subramanian, V., E.E. Wolf and P.V. Kamat, 2003. Langmuir, 19: 469-474.
17. Kim, D.J., S.H. Hahn, S.H. Oh and E.J. Kim, 2002. Materials Letters, 57: 355- 360.
18. Barati, N., M.A. Faghihi Sani, H. Ghasemi, Z. Sadeghian and S.M.M. Mirhoseini, 2009. Applied Surface Sci., 255: 8328-8333.