Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 131 (2008) 250–254

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of silver on the photocatalytic degradation of humic acid

Ankesh Bansal [a], S. Madhavi [b], Timothy Thatt Yang Tan [c,**], T.M. Lim [a,d,*]

[a] School of Civil and Environmental Engineering, Nanyang Technological University, Block N1, Nanyang Avenue, Singapore 639798
[b] School of Materials Science and Engineering, Nanyang Technological University, Block N4, 50 Nanyang Avenue, Singapore 639798
[c] School of Chemical and Biomedical Engineering, Nanyang Technological University, Block N1.2, 62 Nanyang Avenue, Singapore 637459
[d] Institute of Environmental Science and Engineering, Nanyang Technological University, Innovation Centre, Block 2,
Unit 237, 18 Nanyang Drive, Singapore 637723

Abstract

In this study, humic acid was mineralized and degraded photocatalytically in presence of bare TiO_2 and silver loaded TiO_2 (0.5–5.0 at.% Ag). X-ray diffraction (XRD) and inductive coupled plasma (ICP) analysis confirm the complete photodeposition of silver over TiO_2 by photodeposition method. X-ray photoemission spectroscopy (XPS) studies confirmed the presence of Ag^0 in all Ag–TiO_2 samples and the absence of Ag^+ ions. Silver loading over TiO_2 improved the rate of mineralization and degradation of humic acid with a maximum loading of 1.0 at.% Ag. Ninety percent carbon from humic acid was mineralized to CO_2 only after 60 min by using bare TiO_2 as a photocatalyst. However, this conversion was possible within 40 min by using 1.0 at.% Ag-loaded TiO_2. This observation verifies that coating of metals like silver over TiO_2 acts as an electron sink and can improve the redox reaction by preventing electron–hole recombination reaction. The optimum 1.0 at.% Ag loading in the current work is indicative that the blocking of the TiO_2 surface active sites by silver also plays an important role in the photocatalytic mineralization and degradation of humic acid. As the silver loading is increased, less number of active site are available over the surface of photocatalyst TiO_2 for redox reaction. This finding was supported by the TEM analysis of the photocatalyst samples.

Keywords: Humic acid; TiO_2; Silver; Photocatlysis; TEM; XPS; XRD

1. Introduction

Humic acid (HA) is the main constituent of the humic substances present in water that contributes to color and odor problems. Humic substances are also found to be the precursor of carcinogenic products like trihalomethanes (THMs.) [1–3]. It is hence necessary to remove the humic substances content in water below a safety threshold. Conventional coagulation and flocculation process followed by filtration methods are unable to remove TOC by more than 10–50% [4]. Maintenance of residual sludge containing high aluminum concentration generated by this coagulation/flocculation process poses additional concerns. Humic acid biodegradation [5,6] and surface activated carbon adsorption are relatively slow processes and hence inefficient. Heterogeneous photocatalysis is an effective alternative solution for elimination of HA from aqueous solution. TiO_2 [7–9] is a well-known photocatalyst that not only degrades the contaminants but also mineralizes them to CO_2, H_2O and mineral acids [2]. However, rapid combination of electron and hole pairs limits its photocatalytic efficiency [10,11]. Noble metal loading (Ag, Pt, Au) over TiO_2 has been prepared to improve its efficacy by suppressing the electron–hole recombination [12,13].

This paper hereby reports the photocatalytic degradation of humic acid in presence of Ag-loaded TiO_2. Optimum silver loading over TiO_2 for efficient photocatalytic degradation of humic acid was studied. Various amount of Ag was deposited onto TiO_2 (0.5, 1.0, 2.0 and 5.0 at.% Ag) by photodeposition. Extent of Ag loading was analyzed by X-ray diffraction (XRD) and inductive coupled plasma optical emission spectrophotometry (ICP-OES). X-ray photoemission spectra (XPS) of 1.0, 2.0 and 5.0 at.% Ag-loaded photocatalyst were studied to understand the role of electronic state of the Ag and Ti in a photocatalysis reaction. Size, morphology and distribution of Ag on TiO_2 were studied using transmission electron

---

* Corresponding author at: School of Civil and Environmental Engineering, Nanyang Technological University, Block N1, Nanyang Avenue, Singapore 639798.
** Corresponding author.
E-mail addresses: tytan@ntu.edu.sg (T.T.Y. Tan), tmlim@ntu.edu.sg (T.M. Lim).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.10.078

microscopy (TEM). Photocatalytic degradation of humic acid (8 mg/l) in the presence of bare TiO_2 and Ag deposited TiO_2 was compared. Extent of photodegradation and mineralization is measured by using UV–vis spectrometer and total organic carbon (TOC) analyzer, respectively.

2. Experimental

2.1. Materials and apparatus

Commercial Degussa P25 TiO_2 has been used in this study for all experiments. Water containing humid acid was obtained from Kranji Reservoir, Singapore. It was then post-treated to isolate humid acid from the water and made up to a final concentration of 90700 ppm humic acid stock solution. HPLC/GLC and UV–vis spectrophotometry analyses confirmed that the stock solution contained only humic acid and no other organic pollutant. Five hundred millilitres of 400 ppm humic acid prepared from the stock solution was then used in all the experiments. To prevent natural degradation of humic acid, this solution was stored under refrigeration (<4 °C) in a brown bottle covered by black card sheet and aluminium foil. $AgNO_3$ and methanol were used as silver precursor and electron scavenger, respectively for Ag photodeposition experiments. Ultra pure water obtained from Millipore Milli-Q system was used to prepare all solutions.

Photodeposition and humic acid degradation experiments were performed in a photoreactor described elsewhere [14]. A fluorescent black light blue lamp (20W NEC BLB with peak emission at $\lambda = 355$ nm) was used as the excitation source. Six hundred millilitres of the humic acid sample was circulated using peristaltic pump in the photoreactor from a reservoir, while a magnetic stirrer system was used to ensure proper mixing in the reservoir. Provisions have been given in reactor to measure the pH and extraction of samples at regular time intervals from reservoir for analysis. The photoreactor was covered by aluminium foil to prevent hazardous UV radiations to the user.

2.2. Preparation of photocatalyst

Silver deposited TiO_2 photocatalysts (0.5, 1.0, 2.0 and 5.0 at.% Ag) were prepared by using photodeposition method. A predetermined amount of TiO_2 was suspended in 250 ml Milli-Q water and sonicated for 30 min. This suspension was charged into the photoreactor and 350 ml Milli-Q water was added to make the solution 600 ml. It was then irradiated by UV light for 30 min to degrade the organic impurities adsorbed over TiO_2 surface. After 30 min, $AgNO_3$ of 0.1025N was added as per required composition of silver. pH of the solution was adjusted to 3 by injecting 0.7 M HNO_3. Five millilitres methanol was also added as an electron scavenger. Nitrogen gas at 100 ml/min was sparged in the system to prevent oxygen being dissolved in the solution as well as providing mixing. Samples were taken to analyze the Ag percentage in the solution through ICP-OES before starting and at the end of the experiment. Total time of photodeposition was set to 1 h in all four photodeposition experiments. The Ag–TiO_2 catalyst was subsequently recovered by centrifugation and washed repeatedly with Milli-Q water to remove any chemical impurities adsorbed over catalyst and dried in an oven and stored under vacuum in a desiccator.

2.3. Humic acid degradation and mineralization

0.06 g of photocatalyst was suspended in 588 ml Milli-Q water and was sonicated for 30 min. This suspension was circulated for 30 min in photoreactor while keeping air supply and UV light on to remove any organic impurities adsorbed over the photocatalyst surface. An aliquot of humic acid was added to this suspension to obtain final concentration of 0.1 g/l photocatalyst and 8 mg/l of humic acid. The pH of the solution

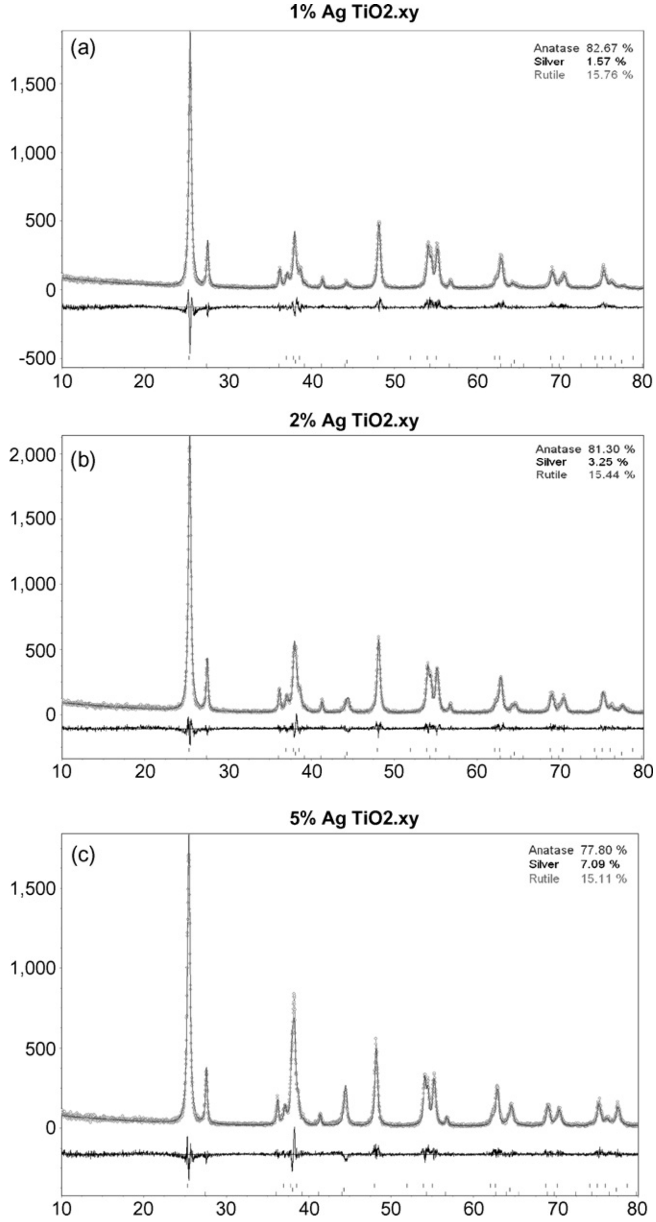

Fig. 1. Rietveld XRD phase analysis of (a) 1.0 at.% Ag–TiO_2 (b) 2.0 at.% Ag–TiO_2 and (c) 5.0 at.% Ag–TiO_2 photocatalyst.

was adjusted to 9 by addition of either sodium hydroxide or perchloric acid. Purified air was bubbled into the solution at the rate of 100 ml/min throughout the experiment. Samples were taken at regular interval and filtered through 0.45 μm PTFE membrane filter for analyses.

2.4. Analysis

Absorbance spectrophotometry (Jasco, V550) was used to determine the concentration of humic acid extracted at regular time intervals during the experiment at $\lambda_{max} = 254$ nm. The concentration of total dissolved organic carbon (TOC) in the solution was measured using a total organic carbon analyzer (Shimadzu, TOC-V_{CSH}) equipped with a non-dispersive infrared (NDIR) detector. The TOC was calculated as the difference between total carbon (TC) and inorganic carbon (IC). Dissolved Ag ions in solution samples were analyzed with a Perkin-Elmer Optima 2000DV ICP-OES. Transmission electron microscopy (JEOL JEM2100F) was employed to investigate the size and distribution of Ag deposits on the surface of TiO_2. The particles were dispersed in methanol by ultrasonic agitation and two droplets of the suspension were placed onto a carbon-coated copper grid. XRD analyses of photocatalysts were carried out using Shimadzu XRD 6000 at scanning rate of 1°/min to identify the phase of titanium dioxide present. Rietveld quantitative phase analysis was used to estimate the amount of Ag loadings. The oxidation states of Ag deposited on TiO_2 were analyzed using PHI 5600, X-ray photoelectron spectroscopy. Samples were loaded by dusting the sample powder on to a polymeric based adhesive tape stuck on the sample holder. All spectra were recorded using an X-ray source (Mg, $K\alpha_1$ radiation) with a scan range of 0–1000 eV binding energy. High-resolution spectra were recorded in selected energy range of Ag, C, O and Ti. The collected XPS spectra were analyzed using CASA (computer aided surface analysis) XPS software peak fitting program. Charge correction was done using ubiquitous carbon peak (C 1s = 284.71 eV).

3. Results and discussion

3.1. Photocatalyst characterization

Photodeposition of silver over TiO_2 was found to be almost complete with more than 99% Ag^+ photodeposited as Ag metal. The oxidation state of Ag is confirmed by XPS as Ag^0 (which will be discussed later) in all four photodeposition experiments (0.5, 1.0, 2.0 and 5.0 at.% Ag). These results were obtained from the ICP analysis of the aqueous samples taken before and after the photodeposition experiments. Fig. 1 shows the Rietveld phase analyzed XRD pattern for 1.0, 2.0 and

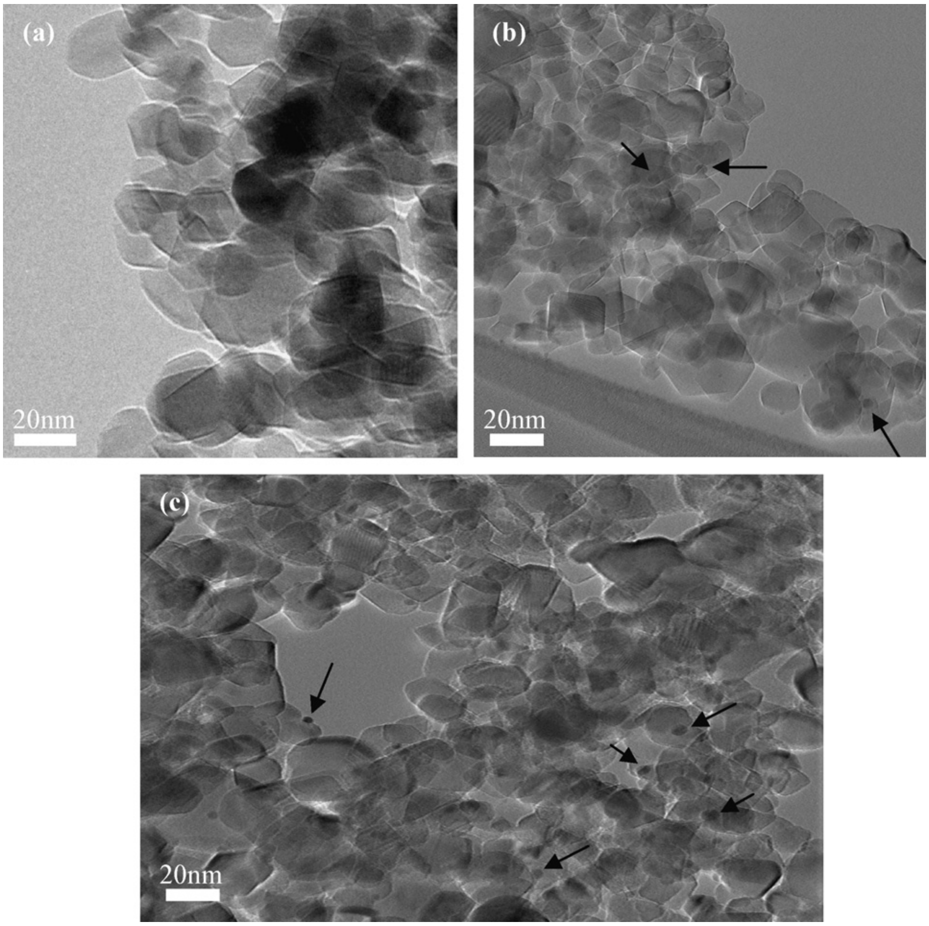

Fig. 2. Transmission electron micrograph (TEM) of bare and Ag-loaded TiO_2 photocatalyst. (a) Bare TiO_2, (b) 2.0 at.% Ag–TiO_2 and (c) 5.0 at.% Ag–TiO_2. → indicates Ag nanoparticles.

Table 1
Rietveld quantitative XRD phase analysis of Ag–TiO_2 photocatalyst

Ag-deposited (wt%) (calculated)	wt% from XRD		
	Ag	Anatase	Rutile
1.4	1.6	82.7	15.7
2.7	3.3	81.3	15.4
6.6	7.1	77.8	15.1

5.0 at.% Ag-loaded TiO_2. The wt% of the phases is summarized in Table 1. The wt% obtained from XRD phase analyses agreed well with the calculated amount of Ag corroborating with ICP analysis that photodeposition of Ag was almost complete. The wt% of anatase and rutile phases, as expected, did not change much with Ag deposition.

Fig. 2 shows the TEM micrographs of bare TiO_2, 2.0% and 5.0 at.% Ag-loaded TiO_2. Non-uniform agglomerates TiO_2 (average size around 50 nm) was seen for all samples (Fig. 2a). Particle shape and size did not change appreciably with Ag loading. Ag particles (black dots indicated) can be seen over the surface of Ag-loaded TiO_2 (Fig. 2b and c). Higher amounts of Ag loading results in increased coverage of TiO_2 surface (Fig. 2c). Silver nanoparticles were of the size range of 3–7 nm and were relatively well dispersed on the TiO_2 surface.

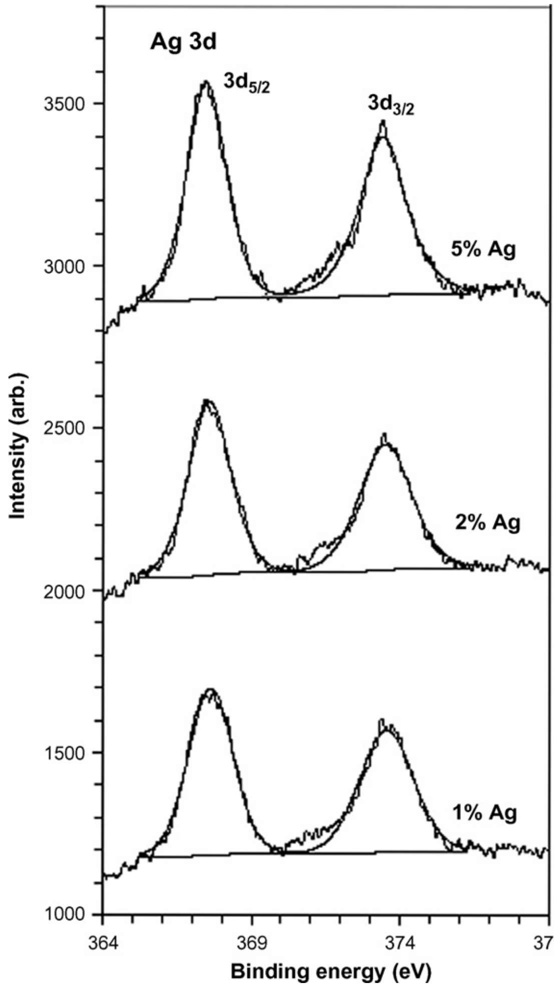

Fig. 3. High-resolution XPS spectrum of Ag 3d in (a) 1.0 at.% Ag–TiO_2, (b) 2.0 at.% Ag–TiO_2 and (c) 5.0 at.% Ag–TiO_2.

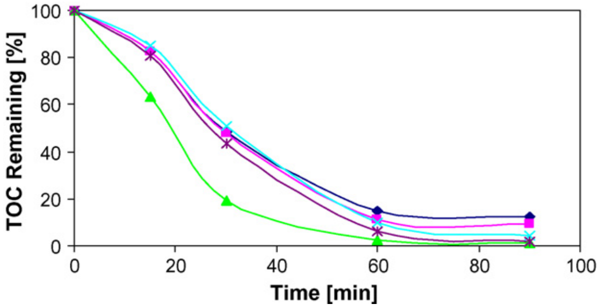

Fig. 4. Mineralization of humic acid by different photocatalysts: (◆) bare TiO_2, (■) 0.5 at.% Ag–TiO_2, (▲) 1.0 at.% Ag–TiO_2, (*) 2.0 at.% Ag–TiO_2, (×) 5.0 at.% Ag–TiO_2.

Valance state of silver in the Ag–TiO_2 samples was examined by XPS. Fig. 3 shows the deconvoluted Ag XPS spectrum of 1.0–5.0 at.% Ag–TiO_2. In all the samples, the characteristic Ag $3d_{5/2}$ and Ag $3d_{3/2}$ doublet peaks observed at binding energies (BE) 367.6 (±0.1) and 373.5 (±0.1) eV, respectively confirmed the presence of Ag^0 in all the samples. XPS peaks corresponding to Ag^+ ions were absent [15–17]. The BE of Ag does not change much with the amount of Ag doping on to TiO_2.

3.2. Mineralization and degradation

To determine the trend of mineralization, TOC value was measured for four samples collected at regular interval from each experiment and these results are plotted in Fig. 4. Fig. 4 shows that humic acid can be mineralized up to 85% in the presence of bare TiO_2 at 90 min. The presence of silver in TiO_2 particles enhanced the mineralization rate of humic acid. 1.0 at.% Ag–TiO_2 was found to be the optimum Ag loading with 99% mineralization of humic acid achieved in 90 min. This finding is consistent with other works, of which the deposited noble metal acts as an electron sink and prevent hole and electron recombination in the TiO_2, hence enhancing the photocatalytic activity [18]. It was also observed that as Ag loading increases, the photocatalytic efficiency did not improve proportionally. This can be attributed to the increased surface coverage with increased Ag loading, reducing the TiO_2 surface

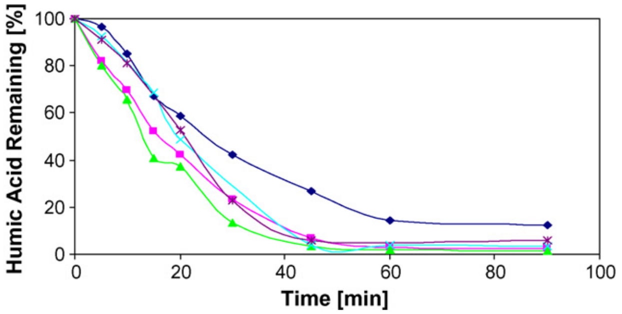

Fig. 5. Degradation of humic acid by different photocatalysts: (◆) bare TiO_2, (■) 0.5 at.% Ag–TiO_2, (▲) 1.0 at.% Ag–TiO_2, (*) 2.0 at.% Ag–TiO_2, (×) 5.0 at.% Ag–TiO_2.

active sites available for redox reaction. This inadvertently reduced the rate of mineralization.

Fig. 5 shows the result from photodegradation of humic acid for various TiO_2 photocatalyst. It can be observed that the rate of humic acid degradation was improved appreciably by using silver loaded TiO_2 instead of bare TiO_2. Though, again, it can be observed that the rate of degradation is not directly proportional to silver loading. It was found that the rate of degradation was maximum between 0.5 and 1.0 at.% Ag-loaded TiO_2.

4. Conclusion

Enhancement of mineralization and degradation rate of humic acid by Ag-loaded TiO_2 photocatalyst has been demonstrated. Mineralization and photodegradation rates of humic acid increased with increasing silver loading up to a maximum of 1.0 at.%, above which the rates started to decrease due to blocking of TiO_2 surface active sites as evidenced in TEM micrographs. Rietveld quantitative XRD phase analysis indicated that the obtained Ag at.% values agreed well with the calculated values, while the anatase and rutile phase composition remained almost constant. The size of the Ag nanoparticles was estimated to be 3–7 nm and they were relatively well distributed on the TiO_2 surface. XPS analysis indicates that silver is present in metal form in all Ag–TiO_2 photocatalyst samples.

Acknowledgements

We gratefully acknowledge Professor Tony Fane, Dr. Wang Rong and Dr. Wei Xie of Temasek Professorship Program ‘‘Membrane for Sustainable Water’’ for supplying the isolated humic acid stock solution.

References

[1] F.J. Stevenson, Humus Chemistry Genesis, Composition, Reactions, Willey Interscience, New York, 1982.
[2] B.R. Eggins, F. Palmer, A. Byrne, Water Res. 31 (1997) 1223–1226.
[3] N. Corin, P. Backlund, M. Kulovaara, Chemosphere 33 (1996) 245–255.
[4] G.S. Wang, S.T. Hsieh, C.S. Hong, Water Res. 34 (2000) 3882–3887.
[5] C. Hu, J.C. Yu, Z. Huo, P.K. Wong, Appl. Catal. B: Environ. 46 (2003) 35–47.
[6] Y. Wang, Water Res. 34 (2000) 990–994.
[7] M. Bekbolet, A.S. Suphandag, C.S. Uyguner, J. Photochem. Photobiol. A: Chem. 148 (2002) 121–128.
[8] C.S. Uyguner, M. Bekbolet, Int. J. Photoenergy 6 (2004) 73–80.
[9] D. Gonenc, M. Bekbolet, Water Sci. Technol. 44 (2001) 205–210.
[10] G. Rothenberger, J. Moser, M. Gratzel, N. Serpone, D.K. Sharma, J. Am. Chem. Soc. 107 (1985) 8054–8059.
[11] H. Tributsch, Photoelectrocatalysis, in: N. Serpone, E. Pelizzetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989, pp. 339–384.
[12] M. Sadeghi, W. Liu, T.G. Zhong, P. Stavropoulos, B. Levy, J. Phys. Chem. 100 (1996) 19466–19474.
[13] R.P.S. Suri, J. Liu, D.W. Hand, J.C. Crittenden, D.L. Perram, M.E. Mullins, Water Environ. Res. 65 (1993) 665–673.
[14] K. Chiang, T.M. Lim, L. Tsen, C.C. Lee, Appl. Catal. A: Gen. (2004) 225–237.
[15] M.S. Hyung, J.R. Choi, H.J. Hah, S.M. Koo, Y.C.J. Bae, Photochem. Photobiol. A: Chem. 163 (2004) 37–44.
[16] C. Wagner, W. Riggs, L. Davis, J. Moulder, in: G.E. Muilenberg (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer Corporation, Eden Prairie, Minnesota, 1979.
[17] C. Su, C.-H. Liao, J.-D. Wang, C.-M. Chiu, B.-J. Chen, Catal. Today 97 (2004) 71–79.
[18] T.T.Y. Tan, C.K. Yip, D. Beydoun, R. Amal, Effects of nano-Ag particles loading on TiO_2 photocatalytic reduction of selenate ions, Chem. Eng. J.: Environ. 95 (2003) 179–186.