Asian Journal of Chemistry Vol. 22, No. 2 (2010), 1619-1627

Effect of Nd^{3+}, Pectin and Poly(ethylene glycol) on the Photocatalytic Activity of TiO_2/SiO_2 Film

PARVIZ ABEROOMAND AZAR, SHAHRAM MORADI DEHAGHI†, SUSAN SAMADI*, SHABNAM KAMYAR† and MOHAMMAD SABER TEHRANI
Department of Chemistry, Islamic Azad University, Science and Research Branch, Tehran, Iran
Fax: 98) (21)44869761-2; Tel: (98) (21)44064818; (98)(912)6194057
E-mail: susansamadi@live.com

Titanium dioxide/silicon dioxide films were prepared by the sol-gel method without and with Nd^{3+} as a dopant, pectin and poly(ethylene glycol) as an additive. Scanning electron microscopy (SEM) has showed that the particle size of Nd-TiO_2/SiO_2 with pectin is smaller than poly(ethylene glycol) and the microstructure of the films have become loose with the addition of pectin. The influence of Nd^{3+}, pectin and poly(ethylene glycol) on the phase transformation of TiO_2/SiO_2 films from amorphous to anatase has been investigated by using X-ray diffraction. Films photocatalytic activities have been evaluated by a UV-exposure test. The results showed that the self-cleaning of nanocomposite Nd-TiO_2/SiO_2 was enhanced by organic polymer, especially pectin.

Key Words: Nanocomposite, Self-cleaning, Sol-gel, Organic polymer.

INTRODUCTION

The analysis of photocatalytic oxidation can be considered by two aspects. One is that it can be used to analysis some environmentally problematic compounds and the other is that a lot of analytical techniques should be properly developed and adopted to analysis (or monitor) the overall photocatalytic degradation concerned compounds process.

Recently, the photocatalytic oxidation technology has been applied to product with self-cleaning functions, such as antifouling and antibacterial. Titanium dioxide (TiO_2), a nontoxic material, has been taken as one of the popular photocatalysts because of its low cost. High photocatalytic activity of TiO_2 particles is depended on the structure and characteristic of the particles, such as crystallinity and prosity[1,2]. It is reported that anatase and nano-sized TiO_2 particles with porous structures, showed better photocatalytic activity[3,4].

Although, it's technological usage is limited by several factors. The most restrictive is concerned with the need for an UV excitation source, because TiO_2 is photoactive only under about an excitation wavelength of λ less than 385 nm because of

†Faculty of Chemistry, Islamic Azad University, Tehran North Branch, Tehran, Iran.

its large band gap (Ebg ≈ 3.2 eV). Thus the photocatalytic efficiency of TiO_2 is expected to be low under visible light irradiation because UV light is about less than 10 % of the overall intensity of solar[5,6].

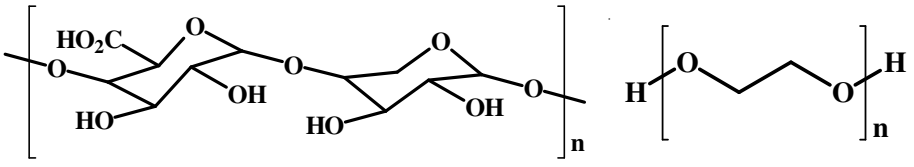
Because of improving the photoefficiency of the electronic process as well as the response into the visible part of the spectrum, TiO_2 doping with different elements. The effect of doping on the activity is depended on many factors, *e.g*., the method of doping and the type and the concentration of dopant[7,8]. Titania has been modified by doping with impurities such as various transition metals[7,9-12] inner transition metals[2,13-15] and non-metal atoms[16].

The nanoparticles are inclined to aggregation. This short detour is important in order to clarify the role of polymers as the most effective candidates for stabilizing dispersions of nanoparticles against aggregation and as solubilizing agents, providing a convenient tool for further manipulation of the dispersions for different applications[17]. Their unique electronic, optical and mechanical properties and hybrid polymer inorganic nanocomposite materials are responsible for different applications. Those were attracted the particular attention by researchers in recent decades[18].

Accordingly, it was observed that SiO_2 addition in TiO_2 films enables to increase intime the photo persistence induced super-hydrophilicity[19,20]. But more recently were showed that TiO_2-SiO_2 granular interfaces can also favour a natural and persistent super-hydrophilicity of sol-gel composite films without the need of any UV light[21,22]. In this research, we have been investigated the effect of Nd^{3+}, pectin and polyethylene glycol (PEG, 5000-7000) as a modifier for the size of TiO_2/ SiO_2 films, its monotonous and self-cleaning property.

EXPERIMENTAL

Titanium tetra isopropoxide (TTIP) and neodymium nitrate (both AR analytical grade, Merck Chemical Company) were used as titanium and neodymium sources for the preparation of the Nd-TiO_2 phtocatalysts. PEG, pectin (refer to Fig. 1), HNO_3, SiO_2 colloid solution and absolute ethanol, were purchased from Merck Chemical Company and deionized water.



(a) (b)

Fig. 1. Structure of (a) pectin, (b) PEG

Preparation of samples: The solution was almost prepared following Zhao *et al*.[23] But we added SiO_2 to this method. Four kinds of TiO_2/SiO_2 photocatalyst films were prepared by using the sol-gel method. Titanium tetra isopropoxide was dissolved in absolute ethanol, then additive was added (with molar ratio TTIP/ethanol/additive

= 1/125/4.5 × 10^{-3} g.g^{-1} sol.) and stirring until complete dissolution to this base solution (refer to Table-1). Then another mixture of absolute ethanol, HNO_3, deionized water, $Nd(NO_3)_3$ and SiO_2 (with molar ratio ethanol/HNO_3/H_2O/$Nd(NO_3)_3$/SiO_2 = 43/0.2/1/0.2 %/30) was added dropwise in to it, under vigorous stirring. The transparent colloidal suspension was stirred (45 min), then kept for 48 h to allow it to form as a gel. The tails, after pretreatment with fluoric acid, were coated with dip-coating method.

TABLE-1
FORMULATION OF SAMPLE SOLS

Sample	Amount of PEG in solution $g/g_{sol.}$	Amount of Pectin in solution $g/g_{sol.}$	Amount of Nd^{3+} (molar ratio)
1	–	–	–
2	–	–	0.2 %
3	4.5×10^{-3}	–	0.2 %
4	–	4.5×10^{-3}	0.2 %

Photocatalysis: The solution of methyl orange in deionized water (with a concentration of 5 mg L^{-1}) was chosen as the subject for photodegradation. This solution was set in the vicinity of tails under a 400 W high pressure mercury vapor lamp (Osram). An UV-VIS spectrometer model Varian was used to record the change concentration of the methylorange. Methyl orange solution was set in the vicinity of tails for 12 h in the darkness, with the purpose of eliminating the absorption effect of the solution in the catalyst.

Set up of photocatalytic reactor: The photocatalytic reduction studies of methyl orange were carried out using the photoreactor system was shown in Fig. 2, which consisted of a cubic borosilicate glass reactor vessel with an effective volume of 1000 mL, a cooling water jacket and a 400 W H-P mercury vapor lamp positioned above center of cubic, as an UV light source. The reaction temperature was kept at 25 ºC by means of cooling water.

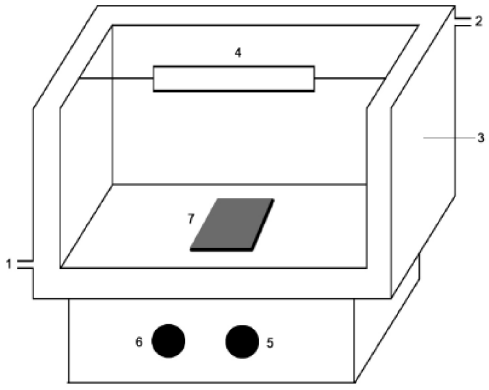


Fig. 2. Schematic diagram of the photoreactor system: 1-For entrance of water, 2-Water outlet, 3-Glass jacket, 4-UV lamp, 5-Stirrer, 6-Heater, 7-Tail

Characterizations: The phase composition of the powders was determined by a SCIFERT-3003 PTS X-ray diffractometer with CuK_α radiation. To identify phase of the powder, XRD was applied. The crystallite size can be determined by Scherrer formula:[24,25]

$$L = k\lambda/\beta\cos\theta$$

where L is the crystallite size, λ is the wavelength of X-ray radiation (CuK_α = 0.15418 nm), K is usually 0.89 and β the line width at half-maximum height. FT-IR analysis was carried out for the samples by Thermo Nicolet NEXUS-870. The microstructure of the film samples was observed with a SEM-XL30 scanning electron microscope.

The films photocatalytic properties were recognized by measuring the optical absorption spectra of a 5 ppm methylorange solution before and after the photodegrdation with catalysis of the film samples by means of Varian UV-Vis spectrometer. The photocatalytic activity was presented by the ratio of the absorption coefficients at the absorption peak (465 nm) before and after the photodegradation.

RESULTS AND DISCUSSION

Effect of Nd^{3+} and additives on the microstructure: FT-IR spectra of the TiO_2/SiO_2 gels, with and without Nd^{3+} and additives were represented in Fig. 3, in the wave number range from 4000 to 400 cm^{-1}. The wide absorptions band around 3700-3100 cm^{-1}, which can be assigned to the OH stretching vibration of surface hydroxyl group[2,23,26]. A great amount of propanol appears during the hydrolysis of TTIP, which leads to the appearance of hydroxyl bands (3700-3100 cm^{-1}). The intensity of bands in samples 1, 2 and 3, decrease in sample 4, because the association of hydroxyl is restrained by the steric effect of hydroxyl group[23]. The absorption band around 1632 cm^{-1} was stretching mode of physically adsorbed water and hydroxyl group[2,23,27]. This band observes in samples 1, 2 and 3, but any water and hydroxyl group is not absorbed by sample 4 with pectin and it can not be obsereved. The bands at 1115 cm^{-1} in samples 1, 2 and 3 can be assigned to asymmetric stretching vibration of the Ti-O bands[23,24] and the bands at 1070 cm^{-1} in samples 3 and 4 are the asymmetrical vibration of the Si-O-Si bands[22,28]. It has been suggested that the additives increase the formation Si-O-Si band. The peak at 604 cm^{-1} can be assigned to symmetric stretching vibration of the Ti–O–Ti group[23,27] and 1039 cm^{-1} which may correspond to Ti–O–C bending[27,29,30]. The Ti–O–C may result from the interaction between the Ti–O network and the organic polymers (pectin or PEG). So stable banding has existed[27] between the organic and inorganic components in samples 3 and 4. The peaks at 457 cm^{-1} in sample 2, 446 cm^{-1} in sample 3 and 436 cm^{-1} in sample 4 are due to the vibration modes of anatase skeletal O–Ti–O–Nd bands[2,31,32].

It was revealed that the kind and molecular weight of the polymer used greatly influences the average size of the nano particles, as well as their size distribution and stability against aggregation[33]. SEM images have been presented in Fig. 4. Sample 1 does not has any additive and Nd^{3+}. With high agglomeration, it has the

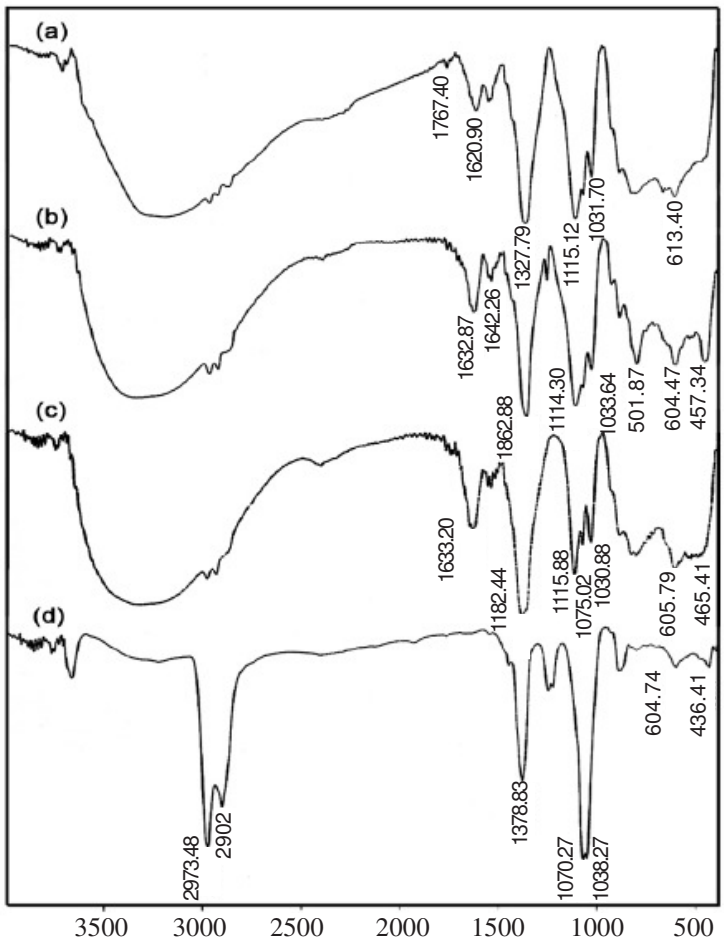


Fig. 3. FT-IR spectra of the sample sols. (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4

most range particle distribution and it is scattered. Nd^{3+} as a doping element was added to sample 2. Uniformity in sample 2 is better than sample 1, but worse than the others. When PEG or pectin was added, Nd-TiO_2/SiO_2 particle size decreases and distribution becomes narrow and coating monotonously. Sample 4 with pectin has the most uniform particle distribution with low agglomeration and porous microstructure.

Effect of Nd^{3+}, PEG and pectin on the anatase phase: Previous measurements of diffuse reflectance absorption spectra measured in the UV-VIS region only evidenced *f-f* transitions attributed to Nd^{3+} dopants. Strong bands indicative of the presence of Nd^{4+} ions were not observed. In this experiment, all the samples were sintered at 500 ºC for 2 h in Carbolite furnace. XRD patterns of four samples have been shown in Fig. 5. Anatase phase has not formed in sample 1. But this phase has formed

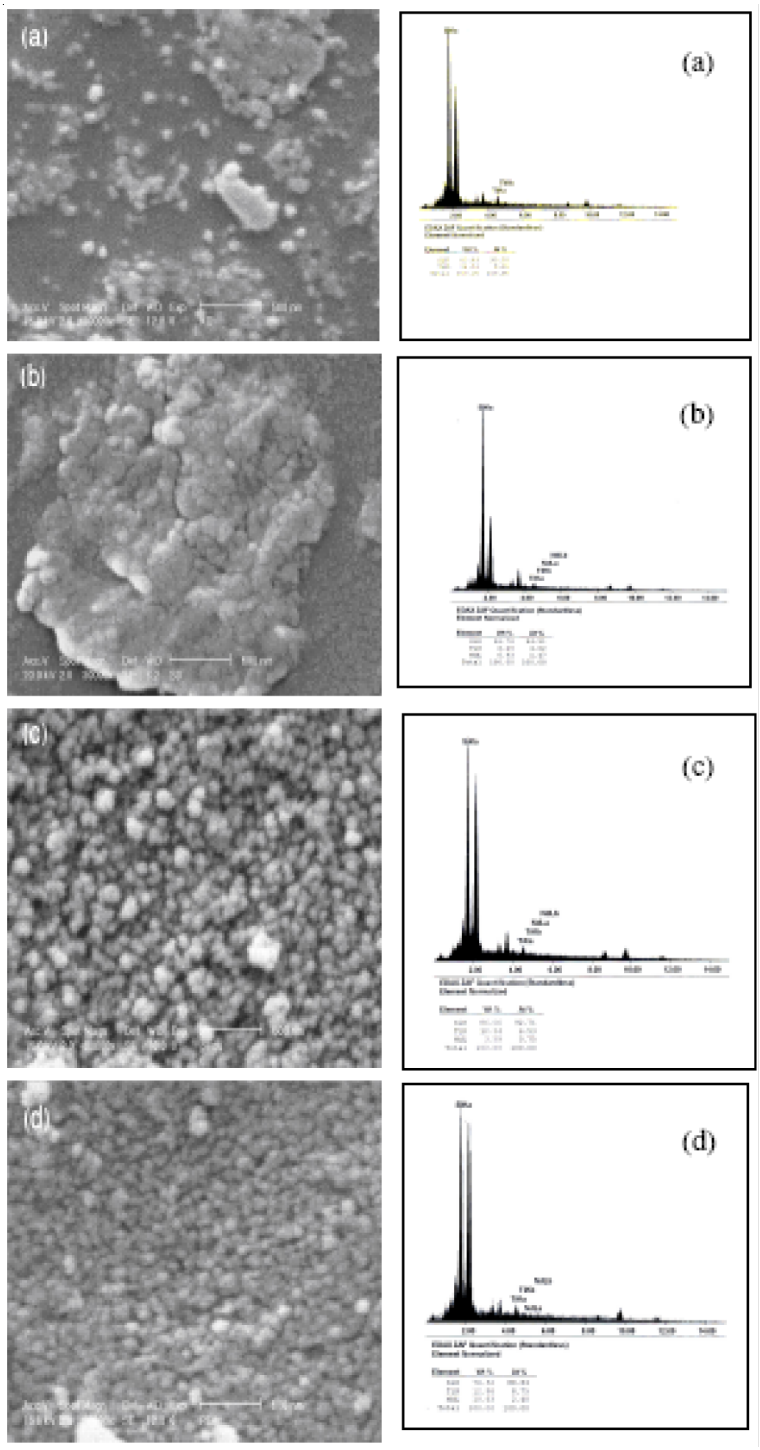


Fig. 4. SEM images for the sample films. (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4.

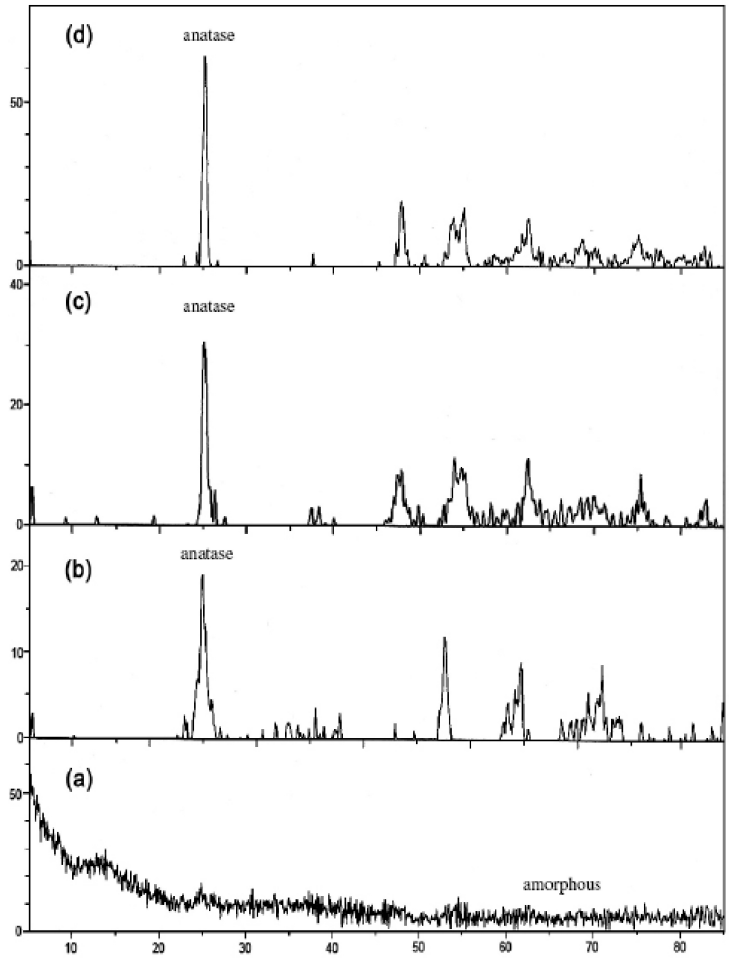


Fig. 5. XRD patterns of sol-gel synthesized TiO_2/SiO_2. (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4

when Nd^{3+} or additive is added. The XRD measurements have revealed that the samples possess an anatase structure and evidence of rutile and mixed phases have not been observed. It has been reported that sol-gel samples of TiO_2 undergo a phase transformation from anatase to rutile phase during heat treatment. Samples 2, 3 and 4 have presented different proportions of anatase phase. According to this graph, sample 4 is fully crystalline and is only in the anatase form and it is very good for self-cleaning ability.

According to the Scherre's equation, the crystallite size of Nd-TiO_2/SiO_2, was listed in Table-2. The optimum crystallite size for anatase because of getting the highest possible photoactivity is in range 8-10 nm. This range provides the best photoactivity for films. Crystalline size for anatase in Nd-TiO_2/SiO_2 with pectin is 11.7 nm and it's good for self-cleaning ability.

TABLE-2
CRYSTALLITE SIZE OF TiO_2/SiO_2 GEL SINTERED AT 500 ºC FOR 2 h

Sample	Crystallite size
1	–
2	4.30
3	11.0
4	11.7

Effects of Nd^{3+} and additives on the self-cleaning: The relationship between additives and photocatalytic activity has been shown in Fig. 6. The self- cleaning ability of films has increased with addition Nd^{3+} and additives. Doping with lanthanide metal ions, such as Nd^{3+} has been shown to increase photocatalytic efficiency for selected reactions.

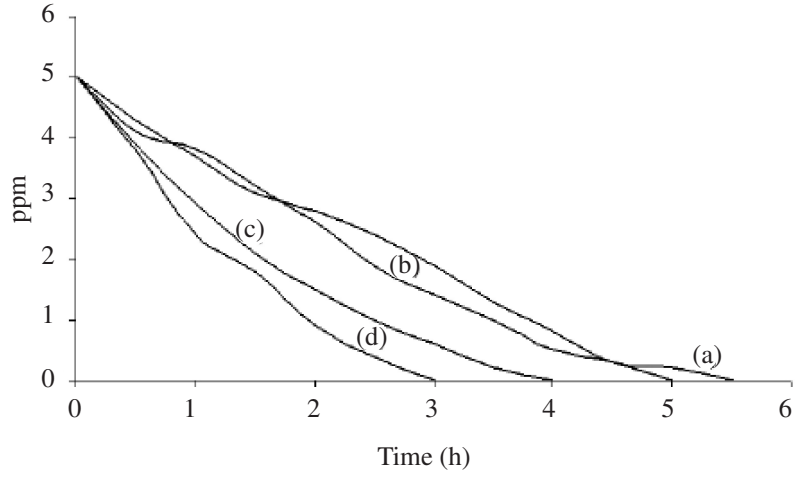


Fig. 6. Photodegradation rate of methyl orange solution under UV radiation. (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4

Organic polymer is used as a dispersant to prevent agglomeration of TiO_2 powder. According to Fig. 6, the self-cleaning ability with additives was better than other samples without additive. Therefore, a good self-cleaning ability of Sample 4 can be ascribed to the porous and less agglomerated microstructure.

Conclusions

The four kinds of TiO_2/SiO_2 photocatalyst films with and without Nd^{3+}, poly-(ethylene glycol) and pectin were prepared by using the sol-gel method. The results show that add Nd^{3+} and additives on the surface of TiO_2/SiO_2 colloid. The action between the additives decided the distribution of Nd-TiO_2/SiO_2 films. The photocatalytic activity and surface area of the films have been improved by pectin and poly(ethylene glycol). The best form is Nd-TiO_2/SiO_2 film with pectin as an additive.

REFERENCES

1. Z. Liu, X. Zhang, T. Murakami and A. Fujishima, *Sol. Energ. Mat. Sol. C*., **92**, 1434 (2008).
2. K.M. Parida and N. Sahu, *J. Mol. Catal. Chem. A*., **287**, 151 (2008).
3. S.S. Watson, D. Betdoun, J.A. Scott and R. Amal, *Chem. Eng. J*., **95**, 213 (2003).
4. N. Wetchakun and S. Phanichphant, *Curr. Appl. Phys*., **8**, 343 (2008).
5. J.O. Carneiro, V. Teixeira, A. Portinha, A. Magalh, P. Coutinho, C.J. Tavares and R. Newton, *Mater. Sci. Eng. B*, **138**, 144 (2007).
6. M.I. Litter, *Appl. Catal. B: Environ*., **23**, 89 (1999).
7. G. Colon, M. Maicu, M.C. Hidalgo and J.A. Navio, *Appl. Catal. B: Environ*., **67**, 41 (2006).
8. M. Anpo and M. Takeuchi, *J. Catal*., **216**, 505 (2003).
9. A. Kubacka, G. Colon and M. Fernandez-Garcia, *Catal. Today*, **143**, 286 (2009).
10. N. Serpone, D. Lawless, J. Disdier and J.M. Herrmann, *Langmuir*, **10**, 643 (1994).
11. M. Takeuchi, H. Yamashita, M. Matsuoka, M. Anpo, T. Hirao, N. Itoh and N. Iwamoto, *Catal. Lett*., **67**, 135 (2000).
12. A. Burns, G. Hayes, W. Li, J. Hirvonen, J.D. Demaree and S.I. Shah, *Mater. Sci. Eng. B*, **111**, 150 (2004).
13. P. Ghigna, A. Speghini and M. Bettinelli, *J. Solid State Chem*., **180**, 3296 (2007).
14. S. Rengaraj, S. Venkataraj, J.W. Yeon, Y. Kim, X.Z. Li and G.K.H. Pang, *Appl. Catal. B: Environ*., **77**, 157 (2007).
15. G. Colon, M.C. Hidalgo and J.A. Navio, *Appl. Catal. A: General*, **231**, 185 (2002).
16. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Sci.*, **293**, 269 (2001).
17. B.A. Rozenberg and R. Tenne, *Prog. Polym. Sci*., **33**, 40 (2008).
18. U. Schubert and N. Hüsing, Synthesis of Inorganic Materials, Revised and Updated Edition, Chap. 4, Wiley-Weinheim, edn. 2 (2005).
19. K. Guan, B. Lu and Y. Yin, *Surf. Coat. Tech*., **173**, 219 (2003).
20. K. Guan, *Surf. Coat. Tech*., **191**, 155 (2005).
21. S. Permpoon, G. Berthome, B. Baroux, J.C. Joud and M. Langlet, *J. Mater, Sci*., **41**, 7650 (2006).
22. M. Houmard, D. Riassett, F. Roussel, A. Bourgeois, G. Berthome, J.C. Joud and M. Langlet, *Appl. Surf. Sci*., **254**, 1405 (2007).
23. G. Zhao, Q. Tian, Q. Liu and G. Han, *Surf. Coat. Tech*., **198**, 55 (2005).
24. M.P. Zheng, M.Y. Gu, Y.P. Jin, H.H. Wang, P.F. Zu, P. Tao and J.B. He, *Mater. Sci. Eng. B*, **87**, 197 (2001).
25. L.D. Zhang and J.M. Mou, *Manometer Mater. Sci. Tech., Shenyang*, 95 (1994).
26. H. Thoms, M. Epple, M. Froba, J. Wong and A. Reller, *J. Mater. Chem*., **8**, 1447 (1998).
27. M.P. Zheng, M. Gu, Y. Jin and G. Jin, *Mater. Sci. Eng. B*, **77**, 55 (2000).
28. J. Jiao, Q. Xu and L. Li, *J. Colloid Inter. Sci*., **316**, 596 (2007).
29. K. Nakamoto, Infrred and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York (1986).
30. Department of Chemistry of Hangzhou University, Handbook of Analytical Chemistry, Chemical industry Press, Beijing (1983).
31. G. Soler-Illia, A. Louis and C. Sanchez, *Chem. Mater*., **14**, 750 (2002).
32. J. Yu, L. Zhang, Z. Zheng and J. Zhao, *Chem. Mater*., **15**, 2280 (2003).
33. G. Schmid, Nanoparticles, New York: Wiley-Interscience (2004).

(*Received*: 27 July 2009; *Accepted*: 3 November 2009) AJC-8025