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# Photocatalytic degradation of p-xylene over doped titania thin film

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## ABSTRACT

Doped titania thin film was made by deposition of nano $TiO_2$ doping with transitional metals (Fe, Cr and V) and non-metal (N) on glass reactor. The thin film was consisted of particles ranging from 15 nm to 20 nm uniformly dispersed on the surface and the thickness of thin film determined by Alpha-Step IQ was 286 nm. The thin film also was characterized by FE-SEM and AFM. To evaluate the photocatalytic activity of the thin film, photocatalytic degradation of p-xylene under UV and visible light irradiation was tested. It showed that doped titania thin film exhibited much higher photocatalytic activity as compared to that of non-doped titania thin film.

*Keywords:* Nano $TiO_2$ and doped $TiO_2$ thin film; Photocatalytic activity; p-xylene degradation

## 1. Introduction

In the past decades, $TiO_2$ has been the most widely used as photocatalyst because of its non toxicity, inexpensiveness, chemical stability and favorable opto-electronic properties. However, $TiO_2$ is active only under UV light irradiation (wave length < 388 nm) due to the wide band gap of 3.2 eV. More than 96% of solar light reaches earth surface is in the range of visible light (ca. 400–600 nm) since most UV is filtered by ozone layer. The modification with the goal of improving the optical absorption and photocatalytic performances, e.g. extending spectral response into visible region and enhancing photocatalytic activity, have received great interest [1–8]. $TiO_2$ modification approaches for achieving visible-light-driven photocatalysts by incorporating transition metal ions (e.g. $V^{5+}$, $Cr^{3+}$ or $Fe^{3+}$...) to narrowing the band gap has attracted much attention [5–7]. Other approaches such as doping nitrogen atoms into substitutional sites in the crystal structure of $TiO_2$ have been made [1,8–12]. Several practical problems arising from the use of powder during the photocatalytic process: a) separation of insoluble catalyst from suspension is difficult, (b) suspended particles tend to aggregate especially at high concentrations and (c) suspensions are difficult to apply on continuous flow syems. The $TiO_2$ immobilization as thin film form not only provides an advantage over the drawbacks encountered with powder suspensions but could also endow the surface with photoinduced hydrophilicity, with good uniformity, with properties closely related to the starting powder material [13–16]. Several methods have been employed to fabricate $TiO_2$ thin films, including e-beam evaporation [17], sputtering [18], chemical vapour deposition [19] dip-coating and sol–gel process [20–23].

To our best knowledge, in the most papers reported in the literature, they used dyes (methylene blue, red methyl, Rodamine B, etc…) as reactants to test

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photocatalytic activity of doped $TiO_2$ under visible light. Most studies demonstrated that doped $TiO_2$ photocatalysts exhibited much higher photocatalytic activities under visible light as compared to that of non-doped $TiO_2$ [5–8,12]. However, this confirmation is not quite "accurate" since dyes are visible light highly sensitive and they can improve a lot of photocatalytic activities of dyes degradation under visible light. Indeed, in the recent publication (Journal of Experimental Nanotechnology, 2011, in press ) we report photocatalytic degradation of 2-propanol (colourless compound) over non-doped $TiO_2$ and Fe-doped $TiO_2$ and it showed that non-doped $TiO_2$ sample was almost inactive whereas Fe-doped $TiO_2$ sample exhibited hight photocatalytic activity (conversion of 70%) under visible light. In this paper, we report the photocatalytic activities in the degradation of p-xylene over Fe-, Cr-, V- and N-doped $TiO_2$ photocatalysts under visible light.

## 2. Experimental

### 2.1. Synthesis of nano $TiO_2$ and $TiO_2$ doped thin film

Nano $TiO_2$ and doped $TiO_2$ were prepared by hydrothermal method (Fig. 1). An amount of commercial $TiO_2$ powder and isopropyl alcohol was dissolved in a hydrosulfuric acid solution to form clear mixture with the Ti-concentration of 0.25 M at room temperature. The precursor solution was transferred into a Teflon-lined stainless steel autoclave, heated to a temperature of 200°C for 10 h. The obtained products were filtered and washed by distilled water, dried at 100°C for 10 h and calcined at 500°C for 3 h.

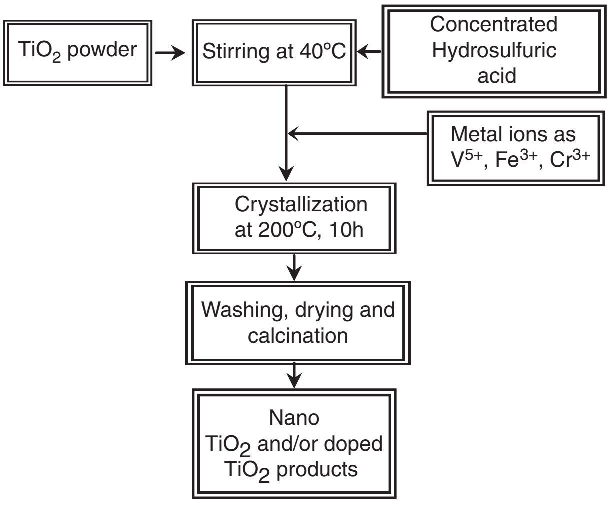

Fig. 1. Synthesis scheme of nano $TiO_2$ and doped $TiO_2$ by using hydrothermal method.

For non-metal-doping $TiO_2$, the aim of our research study is to use urea as a nitrogen source to synthesize N-doping $TiO_2$ powder by heating the mixture of urea and $TiO_2$. In N-doping $TiO_2$ process, urea and $TiO_2$ were mixed with various molar for a few minutes in agate mortar. The resulting mixture was calcined at 450–500°C for 3 h.

$TiO_2$ and doped $TiO_2$ thin film were prepared by dip-coating and depositing method. Firstly, 2 g of $TiO_2$ or doped $TiO_2$ was introduced into a beaker of 100 ml distillate water and stirred using magnetic stirrer for 30 min. Then the suspension containing in beaker was put into a ultrasonic batch for 30 min. Before dip-coating the reactor was cleaned and rough by treatment with the NaOH solution of 1M for two times and then dried at 100°C in an oven over night.

We chose the reactor made by quartz (not glass since glass can filter UV light) to deposit $TiO_2$ thin film. To make $TiO_2$ and doped $TiO_2$ thin film on quartz reactor, a certain amount of $TiO_2$ and/or doped $TiO_2$ suspension solution was introduced into a reactor and then the quartz reactor was rotated along to the horizontal direction. After that, the rest of suspension solution was evacuated and the reactor was put into an oven to dry at 100°C for 1 h. The process was repeated at least three times in order to get uniform thin film. The thickness of thin film could be adjusted by the times of dip-coating.

Before to photocatalytic test, the $TiO_2$ and doped $TiO_2$ thin film deposited on reactor were activated by heating in a furnace at 450°C–500°C for 3 h and cooled down at room temperature.

### 2.2. Characterization methods

Products were characterized by X-ray diffraction using CuKα radiation ($\lambda$=0.14045 nm) at 30 KV and 20 mA, 0.02° step size and 0.1 sec step time from 20° to 60° on a HUT-PCM-Bruker D8 Advance instrument. The size of crystallites was calculated from XRD data by applying the Scherer's equation and by measuring crystallite size from FE-SEM imagines of $TiO_2$ and doped $TiO_2$. The morphologies of $TiO_2$ and doped $TiO_2$ particles were investigated by field emission scanning electron microscopy (FE-SEM) using HITACHI S–4800 instrument operating at 10 kV and magnification of 80,000–100,000. The UV-Vis diffuse reflectance spectroscopy was performed in the wavelength range from 250 to 650 nm using a Shimadzu UV-Vis spectrophotometer.

The thickness and surface morphology of $TiO_2$ films were determined by a field emission scanning electron microscope (FESEM), an atomic force microscope (AFM, Multimode-VEECO-USA) and a surface profiler (Alpha-Step *IQ*, IQ KLA – CTENCOR).

### 2.3. Catalytic test

Photocatalytic activity was investigated in the gas-phase photocatalytic oxidation of p-xylene. The reactor was fixed along vertical direction and faced to three UV lamps (15 w, each) or mercury vapor lamps (125 w, each), which located around the reactor. The reaction condition are as follows: the gas-phase photocatalytic oxidation of p-xylene was carried out in the microflow reactor with the reaction parameters of (concentrations of reaction mixture of p-xylene (C° p-xylene), steam ($C°_{H_2O}$) and oxygen ($C°_{O_2}$) are 15.94; 11.5 and 285.7 mg/l, respectively. Gas-flow velocity was 6 l/h. Temperature is 400°C. The catalyst was coated on the surface of quartz tube with area of 68 $cm^2$ and the loading amount of $TiO_2$ was 30 mg. The analysis was carried out on GC Agilen 6890 Plus, detector FID, capillary column HP-1 methyl siloxane (30 m; 0.32 mm; 0.25 µm).

## 3. Results and disscusion

### 3.1. Characterization of samples

Fig. 2 shows the XRD patterns of $TiO_2$, V-, Cr-, Fe-doped $TiO_2$ and N-doped $TiO_2$ samples. The distinctive peaks at 2θ=25.3°, 37.8°, 47.7°, 54.0°, 62.4°, corresponding to the anatase crystal index are observed in all the samples. This indicated that after $TiO_2$ modification by doping transition metal ions such as V, Cr and Fe as well as doping non-metal (N), the crystalline structure of the anatase phase still remained. Moreover, the intensities of peaks were all most the same, indicating that their crystallites after doping did not change.

FE-SEM experiments were carried out to investigate the morphology of the samples. Fig. 3 presents the FE-SEM images of V-, Cr-, Fe- and N-doped $TiO_2$ samples. As seen in Fig. 3, no significant differences were observed when comparing the photographs of V-, Fe, Cr-doped $TiO_2$ and N-doped $TiO_2$, consisted of nearly spherical nanoparticles of 15–20 nm. The particle form and size of these samples were similar to those of non-doped $TiO_2$ sample. In the case of Cr-doped $TiO_2$. Particles tend to aggregate, forming bigger particles (20–30 nm).

UV-Vis absorption spectra of V-, Cr-, Fe-doped $TiO_2$ and N-doped $TiO_2$ samples are shown in Fig. 4. In the case of $TiO_2$, the fundamental absorption edge of $TiO_2$, appeared in the UV region at about 385 nm. In comparison to non doped $TiO_2$, the absorption edge of V-, Cr- and Fe- doped $TiO_2$ and N-doped $TiO_2$ was broaden and shifted to higher wavelength. The fundamental absorption edge of V-, Cr- and Fe- doped $TiO_2$ and N-doped $TiO_2$ appeared in the visible light region at about 500–600 nm. This indicated that UV-Vis absorption is closely related to doping metal ions and non-metal atoms.

Morphology of Fe doped $TiO_2$ was studied by using AFM (Fig. 5). From the top-view, it can observe that the particle size becomes bigger after depositing on the reactor surface and the surface is not smooth but rough. This indicates the formation of aggregates resulting from heating treatment.

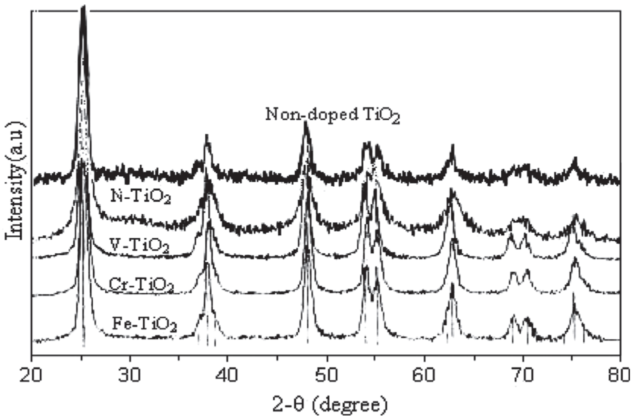

Fig. 2. XRD patterns of non-doped $TiO_2$ and V-, Cr-, Fe- and N- doped $TiO_2$.

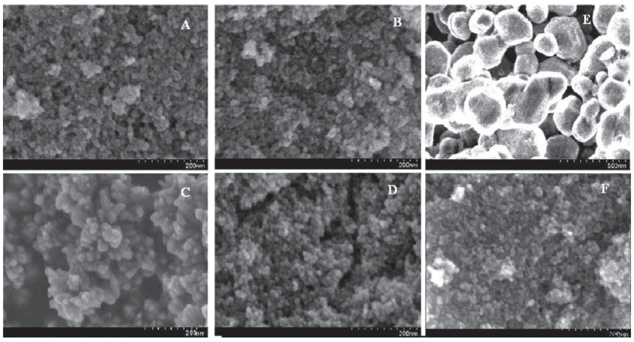

Fig. 3. FE-SEM image of: (A) Fe-doped $TiO_2$, (B) V-doped $TiO_2$, (C) Cr-doped $TiO_2$, (D) N-doped $TiO_2$, (E) $TiO_2$ powder (starting material) and (F) non-doped $TiO_2$.

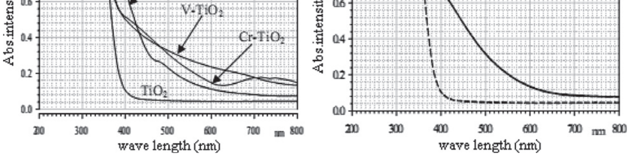

Fig. 4. UV-Vis diffuse reflectance spectra of V-, Cr-, Fe and N-doped $TiO_2$ samples.

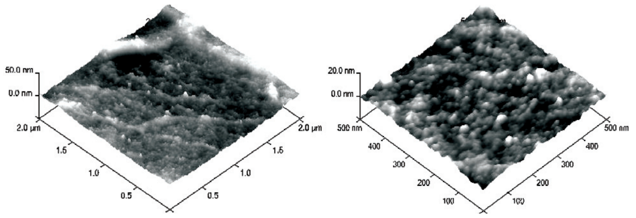

Fig. 5. AFM image (top-view) of Fe-doped $TiO_2$ thin film calcined at 460°C.

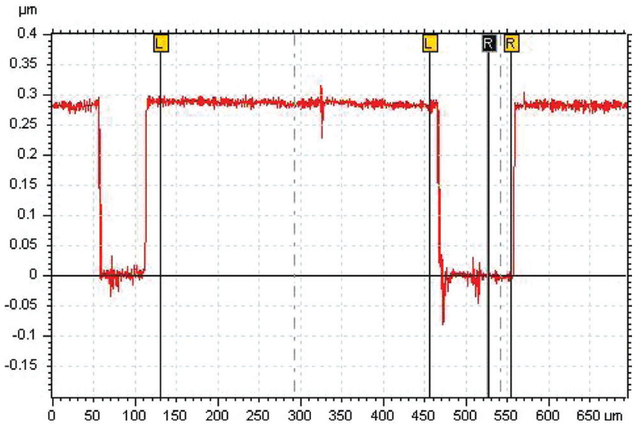

Fig. 6. Surface profile (Alpha-step IQ) of Fe-doped $TiO_2$ thin film (L: left side and R: right side) calcined at 460°C.

Thickness of the thin film was determined by Alpha-step IQ and the surface profile was presented in the Fig. 6. The determined value of thickness is 286 nm.

### 3.2. Photocatalysis

Photocatalytic decomposition of Volatile Organic Compounds (VOCs) has been received special interests. We have chosen p-xylene as model molecule to test photocatalytic activity. Here we define the yield conversion as gram of reactant completely converted to $CO_2$ per gram of photocatalyst.

Fig. 7, presents the yield conversion of p-xylene over 0.7 %wt. (V, Cr and Fe) loading $TiO_2$ catalysts using UV light (λ of 365 nm) and visible light (λ of 470 nm). As observed in Fig. 7, photocatalytic activity using UV light was lower than that using visible light for all doped $TiO_2$ samples. From these results, it could be concluded that doped $TiO_2$ samples are more suitable for use of visible light than that of UV light.

The dependence of the yield conversion on the amount of doped transition metal (Fe) is shown in the Fig. 8. As seen in the Fig. 8, the yield conversion increases with increasing Fe content in the range of 0–1% wt. Further increase of Fe content led to decrease the yield. It can be concluded that the content of 1% wt. of Fe loading is optimal.

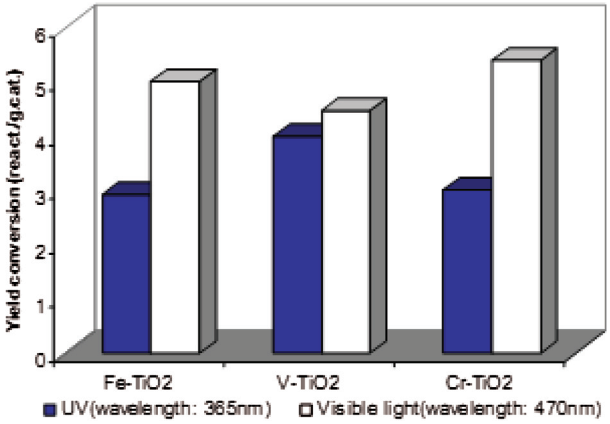

Fig. 7. Yield conversion of p-xylene over doped $TiO_2$ catalysts (0.7% wt. of Me loading) under UV and visible light irradiation.

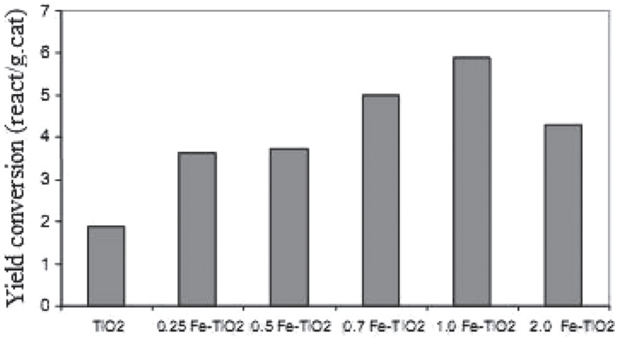

Fig. 8. Yield conversion of p-xylene over Fe-doped $TiO_2$ samples with different Fe loading under visible light irradiation.

Fig. 9 shows the yield conversion of p-xylene over non-doped $TiO_2$, Fe-, V-, Cr -doped a $TiO_2$ and N-doped $TiO_2$ using visible light with wavelength of 470 nm. As observed in Fig. 9, doped $TiO_2$ sample exhibited much higher yield conversion as compared to that of the non-doped $TiO_2$. Among doped $TiO_2$ samples, sample N-doped $TiO_2$ (N/Ti molar ratio of 1/1) showed the highest yield conversion. This indicated that non-metal doped $TiO_2$ was very effective photocatalyst, especially in visible light. To explain why the Fe-, Cr- and N-doped $TiO_2$ samples exhibited higher photocatalytic activity in p-xylene degradation as compared to that of non-doped $TiO_2$, we have done measurements by using different techniques like UV-vis, FT-IR, XPS, etc… and it revealed that by doping with these transition metals and non-metal, it leads to narrowing band gap ( higher absorption efficiency of visible light) as well as to create vacancies and defects (Ti-OH groups) acted as "active sites" (results to be published).

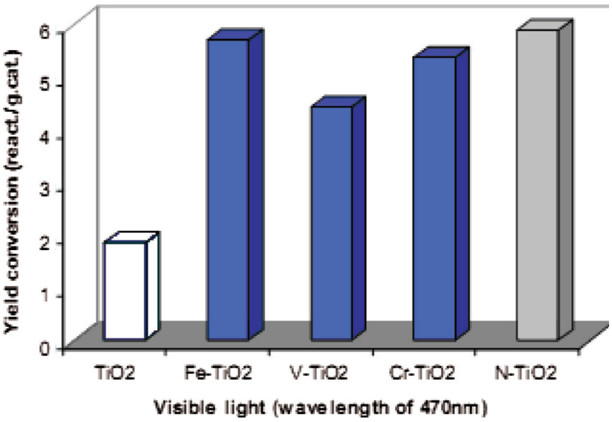

Fig. 9. Yield conversion of p-xylene over doped $TiO_2$ samples under visible light irradiation.

## 4. Conclusion

Nano $TiO_2$ was successful synthesized by hydrothermal treatment. The sample was modified by doping transition metal ions (V, Cr, Fe) and non- metal (N). Non-doped $TiO_2$ and doped $TiO_2$ samples were characterized by XRD, FE-SEM and UV-Vis. From the characterization results, it revealed that after doping, the structure (anatase phase) still remain and extending spectral response into visible region was noted. Photocatalytic activity in degradation of p-xylene (vapor phase) was investigated. The obtained results showed that in comparison to non-doped $TiO_2$, the doped $TiO_2$ samples exhibited much higher photocatalytic activity using visible light instead of UV.

## References

[1] D. Li and H. Haneda,"Enhancement of photocatalytic activity of sprayed nitrogen-containing ZnO powders by coupling with metal oxides during the acetaldehyde decomposition", Chemosphere, 54 (2004) 1099–1110.

[2] A.R. Khataeea and M.B. Kasiri, Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: Influence of the chemical structure of dyes, J. Mol. Catal. A: Chem., 328 (2010) 8–26.

[3] M. Anpo and M. Takeuchi, "The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation", J. Catal., 216 (2003) 505–516.

[4] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara and K. Takeuchi, "Role of oxygen vacancy in the plasma-treated $TiO_2$ photocatalyst with visible light activity for NO removal", J. Mol. Catal. A: Chem., 161 (2000) 205.

[5] A. Fuerte, M.D. Hernández-Alonso, A.J. Maira. A. Martínez-Arias, M. Fernández-García, J.C. Conesa and J.Soria, "Visible light – activated nanosized doped-$TiO_2$ photocatalyst", Chem. Commun., (2001) 2718–2719.

[6] Jeffrey C.-S. Wu and Chih-Hsien Chen, "A visible-light response vanadium-doped titania nanocatalyst by sol-gel method", J. Photochem. Photobiol. A: Chem., 163 (2004) 509–515.

[7] C. Adán, A. Bahamonde, M. Fennández- García and A. Martínnez-Arias. "Structure and activity of nanosized iron-doped anatase $TiO_2$ catalyst for phenol photocatalytic degration", Appl. Catal. B: Environ., 72 (2007) 11–17.

[8] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, "Visible-light photocatalysis in nitrogen-doped titanium oxides", Science, 293 (2001) 269–271.

[9] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto and S. Sugihara, "Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping" Appl.Catal. B: Environ., 42 (2003) 403–409.

[10] J.L. Gole, J.D. Stout, C. Burda, Y. Lou and Chen X, "Highly Efficient Formation of Visible Light Tunable $TiO_{2-x}N_x$ Photocatalysts and Their Transformation at the Nanoscale", J. Phys. Chem. B, 108 (2004) 1230–1240.

[11] H. Irie, Y. Watanaba and K. Hashimoto, "Nitrogen-Concentration Dependence on Photocatalytic Activity of $TiO_{2-x}N_x$ Powders", J. Phys. Chem. B, 107 (2003) 5483–5486.

[12] J. Yuan, M. Chen, J. Shi and W. Shangguan, "Preparations and photocatalytic hydrogen evolution of N-doped $TiO_2$ from urea and titanium tetrachloride", Int. J., Hydrogen Energy, 31 (2006) 1326–1331.

[13] C. Quinoneza, W. Vallejoa and G. Gordillo, Structural, optical and electrochemical properties of $TiO_2$ thin films grown by APCVD method, Appl. Surf. Sci., 256 (2010) 4065–4071.

[14] G. Triani, J.A. Campbell, P.J. Evans, J. Davis, B.A. Latella and R.P. Burford, Low temperature atomic layer deposition of titania thin films, Thin Solid Films, 518 (2010) 3182–3189.

[15] J. Xiong, S.N. Das, S. Kim, J. Lim, H. Choi and J.M. Myoung, Photo-induced hydrophilic properties of reactive RF magnetron sputtered $TiO_2$ thin films, Sur. Coat. Technol., 204 (2010) 3436–3442.

[16] N. Barati., M.A. Fagihi Sani, H. Ghasemi, Z. Sadeghian and S.M.M. Mirhoseini, Preparation of uniform $TiOh_2$ nanostructure film on 316L stainless steel by sol-gel dip coating, Appl. Sur. Sci., 255 (2009) 8328–8333.

[17] Y.L. Wang and K.Y. Zhang, Variation of the structural and optical properties of sol–gel TiO2 thin films with different treatment temperatures, J. Surf. Coat. Technol., 140 (2001) 155.

[18] S. Takeda, S. Suzuki, H. Odaka and H. Hosono, Photocatalytic $TiO_2$ thin filmnext term deposited onto glass by DC magnetron sputtering, J. Thin Solid Films, 392 (2001) 338.

[19] H.Y. Ha, S.W. Nam, T.H. Lim, I.H. Oh, S.A. Hong and Hong, Properties of the $TiO_2$ membranes prepared by CVD of titanium tetraisopropoxide, J. Membr. Sci., 111 (1996) 81.

[20] L. Hu, T. Yoko, H. Kozuka and S. Sakka, Effects of solvent on properties of sol–gel-derived $TiO_2$ coating filmsnext term, J. Thin Solid Films, 219 (1992) 18.

[21] C.J. Brinker and G.W. Scherer, Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing, Academic Press, Inc., New York (1990).

[22] B.H. Kim, J.H. Ahn, J.H. Jeong, Y.S. Jeon, K.O. Jeon and K.S. Hwang, Preparation of $TiO_2$ thin film on $SiO_2$ glass by a spin coating–pyrolysis process, J. Ceram. Int.,32 (2006) 223–225.

[23] Z. Zainal and C.Y. Lee, Properties and photoelectrocatalytic behavior of sol–gel derived $TiO_2$ thin films, J. Sol–Gel Sci. Technol., 37 (2006) 19–25.