Ceramics International 29 (2003) 851–856

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation and characterization of TiO_2–SiO_2 nano-composite thin films

Chul Han Kwon[a,b], Je Hun Kim[a], In Sun Jung[a], Hyunmin Shin[a,*], Ki Hyun Yoon[b]

[a] *Research Center, TIOZ Co. Ltd., 775-4 Wonsi-dong, Ansan, Kyunggi-Do, South Korea*
[b] *Department of Ceramic Engineering, Yonsei University, 134 Shinchon-dong, Seodaemoon-ku, Seoul 120-749, South Korea*

Received 17 December 2002; received in revised form 2 January 2003; accepted 2 June 2003

Abstract

TiO_2 nanocrystalline particles dispersed in SiO_2 have been prepared by the sol-gel method using titanium- and silicon-alkoxides as precursors. Nano-composite thin films were formed on the glass substrates by dip-coating technique and heat treated at temperatures up to 500 °C for 1 h. The size of the TiO_2 nanocrystalline particles in the TiO_2–SiO_2 solution ranged from 5 to 8 nm. The crystalline structure of TiO_2 powders was identified as the anatase phase. As the content of SiO_2 increased, the anatase phase tended to be stabilized to higher temperature. TEM results revealed the presence of spherical TiO_2 particles dispersed in a disk-shaped glassy matrix. Photocatalytic activity of the TiO_2–SiO_2 (1:1) thin films showed decomposition of ~95% of methylene blue solution in 2 h and a contact angle of ~10°. The photocatalytic decomposition of methylene blue increased and the contact angle decreased with the content of TiO_2 phase. TiO_2–SiO_2 with the molar ratio of 1:1 showed a reasonable combination of adhesion, film strength, and the photocatalytic activity.

Keywords: A. Sol–gel processes; B. Nanocomposites; D. TiO_2; D. SiO_2; Photocatalysts; Nanocrystals

1. Introduction

Titanium dioxide, among the transition metal oxide semiconductors widely used in photocatalysis, is the most suitable photocatalyst due to its high photocatalytic efficiency and chemical and physical stability under the reaction conditions. It has been acknowledged that TiO_2 attracted a great deal of attention as a photocatalytic semiconductor material for the past two decades. Titanium dioxide is a wide bandgap material ($E_g \sim 3.2$eV) exhibiting photocatalytic decomposition and super-hydrophilicity. Recently, photocatalysis based on titanium dioxide has attracted much attention in terms of environmental applications.

Since the photocatalytic activity was mostly confined to the surface of the photocatalytic material, its surface area must be increased to maximize the photocatalytic efficiency. One way to do this is synthesis of nano-sized TiO_2 particles to increase photocatalytic reaction sites on the surface. Also, the amount of anatase phase must be maximized among those crystalline phases such as anatase, rutile, brookite, because the anatase phase shows a higher photocatalytic activity. Also, to expand its applicability for various substrate materials, adhesion and hardness are needed to be enhanced by introducing a binder material such as silica.

TiO_2 films have been prepared by various vacuum techniques such as chemical vapor deposition [1], pulsed laser deposition [2], and sputtering [3,4]. The sol–gel technique has emerged as a promising processing route for synthesis of nano-sized particles and TiO_2 thin film fabrication because of the simplicity of sol–gel processing in addition to its high purity resulting from the availability of high purity chemicals as raw materials. For many technological applications, low processing temperature is highly desirable because it enables the use of certain substrate materials and/or prevents undesirable film-substrate interaction [5]. Unfortunately, the sol–gel processing involving metal alkoxide or other metal–organic precursors, in general, requires processing temperatures in excess of ~400 °C for the crystallization and removal of organics [6]. Besides, the sol–gel derived TiO_2 films possesses structures with low density as a whole, leading to lower refractive index [7]. Despite

---

[*] Corresponding author. Tel.: +82-2-2115-2154; fax: +82-2-2115-2155.

E-mail address: shin@tioz.co.kr (H. Shin).

0272-8842/03/$30.00 © 2003 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/S0272-8842(03)00019-1

the above-mentioned shortcomings, it is still possible to attain nanocrystalline TiO_2 via sol–gel process using appropriate process parameters, i.e., process temperature and time. Controlling the particle size, however, is not an easy task especially in the case of using other materials for any reason. It is widely accepted that as the particle size falls in the nanometer size range, the physical and chemical properties of the semiconductor are predominantly governed by the surface of the particle as compared with bulk semiconductor because the surface to volume ratio becomes more significant. Therefore, the photocatalytic characteristics of TiO_2 are strongly affected by its particle size and control of the particle size becomes one of the most important processing parameters.

From the literature, it becomes clear that TiO_2 in SiO_2 possesses a promising potential in that the composite material can be properly tailored to control and enhance the photocatalytic performance and its mechanical properties as well [8,9]. However, little attention has been paid to the investigation of the nature of the dispersed TiO_2 particles in SiO_2, which exhibited deviations from that of the bulk TiO_2 [10]. For instance, the addition of TiO_2 to SiO_2 induced higher acidic properties to a great extent than that for the bulk TiO_2 and the synthesized TiO_2/SiO_2 catalysts showed both structural and coordination changes due to the influence of processing parameters [11,12]. The nature and the oxidation states of titanium dioxide in the TiO_2/SiO_2 catalyst were also investigated [13]. However, the relationship between the photocatalytic properties of the TiO_2/SiO_2 system and the structural transformation of TiO_2 following its incorporation into silica has not yet been elucidated.

In this paper, the fabrication of TiO_2 nano-particles and TiO_2–SiO_2 nano-composite thin films at low temperatures via sol-gel processing and characterization of the crystal structure and their photocatalytic activities were investigated.

2. Experimental procedures

TiO_2 sols were synthesized via a sol-gel process. Titanium tetraisopropoxide (Dupont, USA) was used as the precursor for the sol-gel synthesis of anatase TiO_2 sol. A titanium tetra-isopropoxide solution was prepared by diluting with isopropyl alcohol. The solution was subsequently peptized by stirring in the presence of water and nitric acid as a catalyst. Thin films were coated on the glass substrates by dip-coating technique in a dry atmosphere at room temperature. A flow chart of the sol-gel process is provided in Fig. 1. TiO_2–SiO_2 thin films containing various amounts of TiO_2 were prepared in a similar manner. Silicon tetraethoxide in ethanol was hydrolyzed with water containing HNO_3 at 80 °C for 2 h. The hydrolyzed solution was diluted with ethanol before mixing with titanium solution. After Ti- and Si-solutions were mixed, the mixture was diluted further with ethanol to give an appropriate viscosity for a better wetting behavior upon coating.

The crystal structure, particle size, and surface area of the TiO_2 photocatalyst were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM). Surface morphology was examined using an atomic force microscopy (AFM). Photocatalytic activity was evaluated by measurement of the decomposition of methylene blue.

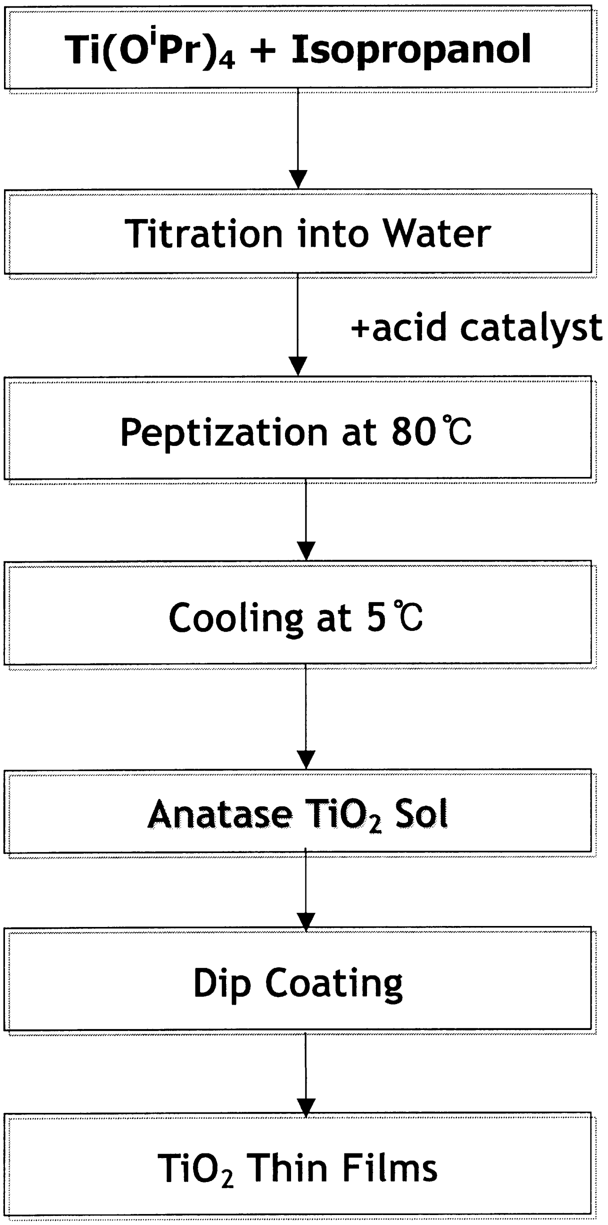

Fig. 1. Schematic diagram of sol-gel synthesis of the TiO_2 thin film.

3. Results and discussion

Fig. 2(a) shows the TEM image of TiO_2 nano-particles fabricated via a sol-gel processing. The average particle size of as-synthesized spherical particles was of about 5~8 nm in diameter. The nanocrystals were identified as anatase phase using X-ray diffraction.

In a sol–gel process of transition metal alkoxides, hydrolysis and condensation reactions occur very rapidly, so uniform and ultrafine products are difficult to obtain. With the use of bulky, branched alkoxy groups (i.e., isopropoxides), the hydrolysis and condensation rates can be reduced to favor the formation of small colloidal clusters, yielding a more uniform particle size [14]. It has been reported that high ratios of water to alkoxide were found to favor the formation of ultrafine particles of titania [15]. The molar ratio of water to alkoxide in this experiment was ~96%. A higher ratio of water to alkoxide in the reaction medium seems to ensure a more complete hydrolysis of alkoxides, favoring nucleation versus particle growth. Such conditions allowed an ultrafine crystallite size to be achieved.

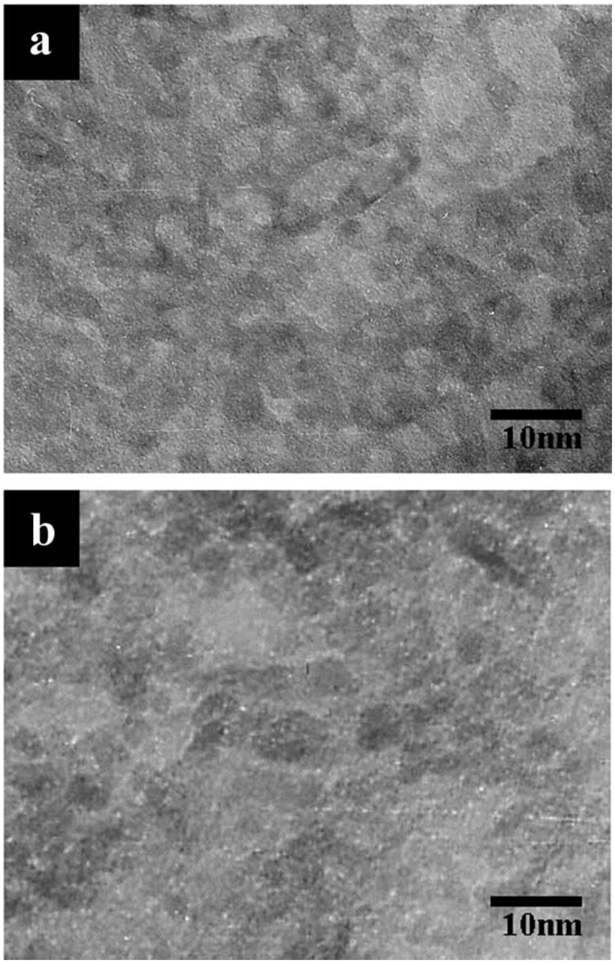

Fig. 2. TEM images of as-synthesized (a) TiO_2 particles and (b) TiO_2–SiO_2 nano-composite particles prepared by a sol-gel process.

On the other hand, TiO_2–SiO_2 (1:1 molar ratio) composite particles consisted of spherical anatase TiO_2 particles and disk-shaped glassy phase, which was believed to contain Si–O–Ti bonds, as shown in Fig. 2(b). Since the starting solutions were a partially hydrolyzed one, Si–O–Ti bondings may have formed via distribution of Ti atoms in O–Si–O chains. Similar observation was made by others [16].

Fig. 3 shows TiO_2 nanocrystallites homogeneously dispersed in the amorphous SiO_2 matrix. The lattice fringe of ~0.35 nm was also observed, which corresponds to the lattice spacing of (101) plane in the anatase phase.

Fig. 4 shows the XRD patterns of the TiO_2 powders heat-treated at various temperatures for 1 h. TiO_2 powder was obtained by drying the TiO_2 sol at 60 °C. In case of TiO_2 nanocrystals without the presence of SiO_2, the phase transition from anatase to rutile phase began to occur at 300 °C. A new peak at 27.4° began to appear

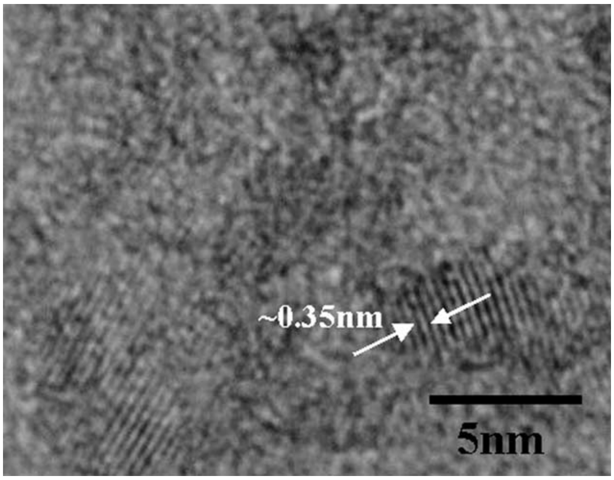

Fig. 3. High-resolution TEM image of as-synthesized TiO_2–SiO_2 nano-composite particles prepared by a sol-gel process.

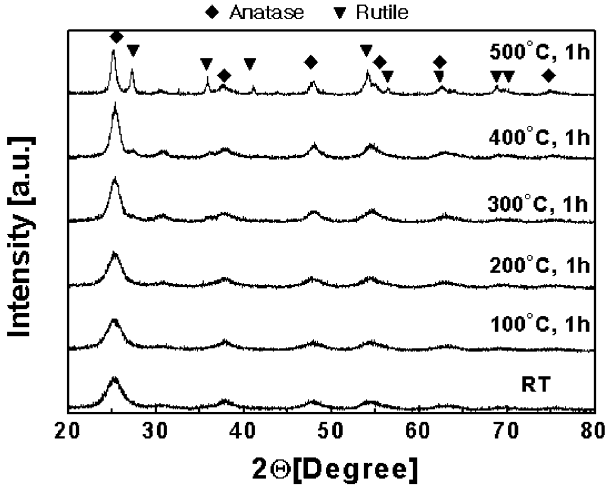

Fig. 4. X-ray diffraction patterns of TiO_2 thin films heat-treated at various temperatures for 1 h.

at 400 °C, which is characteristic (110) plane in the rutile phase. The average crystallite size was determined from the Scherrer's equation using the (101) reflections of the anatase phase assuming spherical particles. The nanocrystallite size of as prepared TiO_2 was ~4 nm and increased to 5.5, 6.5, and 13 nm for the samples heat-treated at 300, 400, and 500 °C, respectively. The broadening of the diffraction peaks decreased with increasing temperature and the grain size also increased with temperature. A minor brookite phase at 31 °C was observed for all the samples. The appearance of the brookite phase for titania derived from alkoxide hydrolysis precipitation, followed by hydrothermal treatment has also been reported by Wang et al. [15]. The mechanism by which the brookite phase coexists with the anatase is currently unknown.

For TiO_2–SiO_2 nano-composite films, the diffraction peaks were broad, showing that the crystal size was small. The phase transition from anatase to rutile was not observed up to 500 °C as shown in Fig. 5. Suppression of the anatase-rutile phase transformation for TiO_2–SiO_2 nano-composites may be due to dissolution of SiO_2 in anatase TiO_2 or vice-versa and diffusion barrier effect of SiO_2 in the TiO_2–SiO_2 interface. This phase stability in the presence of SiO_2 was reported by many other researchers [16,17]. Kumar et al. [18] reported that titania was in the form of rutile without the presence of silica at temperatures up to 1000 °C. However, the addition of 5–10% silica stabilized the anatase phase at these temperatures. While a mixture of rutile and anatase phase existed in case of 5% silica addition, 100% anatase phase could be obtained for 10% silica addition. Wang et al. [15] suggested that a critical size of 40–50nm is required for the phase transition from anatase to rutile. The crystal size of TiO_2 particles heat-treated at 500 °C was determined to be 13 nm by the Scherrer's equation using the (101) reflection, while the TiO_2 particle size in the TiO_2–SiO_2 nano-composite films remained to be ~6 nm. This implies that the addition of SiO_2 hinders the grain growth. Therefore, the anatase phase seemed to be stabilized to higher temperature, as the content of SiO_2 increased.

Thin films of TiO_2 and TiO_2–SiO_2 nano-composites have been deposited on the glass substrates by dip-coating technique. However, TiO_2 thin films did not show a good adhesion to the glass substrate. Two consecutive coatings led to the separation of the thin film from the glass substrate due to accumulation of the stress at the interface and hence, poor adhesion. It would require high temperature to ensure strong adhesion to the substrate. To improve the adhesion property of TiO_2 films, silica has been introduced as a binding material. Fig. 6 shows the TEM image of the cross-section of TiO_2–SiO_2 nano-composite thin films coated on the glass substrate by dip-coating techniques and heat treated at 100 °C for 1 h. A cross sectional TEM view of a 100 nm-thick film revealed a denser structure, and nanocrystals of TiO_2 were identified as the anatase phase using selected area diffraction technique as shown in the inset of Fig. 6, where Debye-Scherrer ring of (110) plane in anatase TiO_2 is shown.

As shown in Fig. 7, surface morphology of TiO_2 films with different amounts of SiO_2 heat treated at 100 °C for 1 h was investigated using atomic force microscopy. The atomic force microscopy indicated that the surface of the nano-composite film became curvier locally with increasing SiO_2 content as compared with that of pure TiO_2 films. Karthikeyan et al. [17] reported that the mean height of crystals on the surface of the TiO_2–SiO_2 glassy phase was found to increase with increasing temperature as the anatase TiO_2 crystal grew out of the glassy phase. In this study, however, as-synthesized particles obtained from the solution were already in the form of anatase TiO_2, not amorphous phase. Therefore,

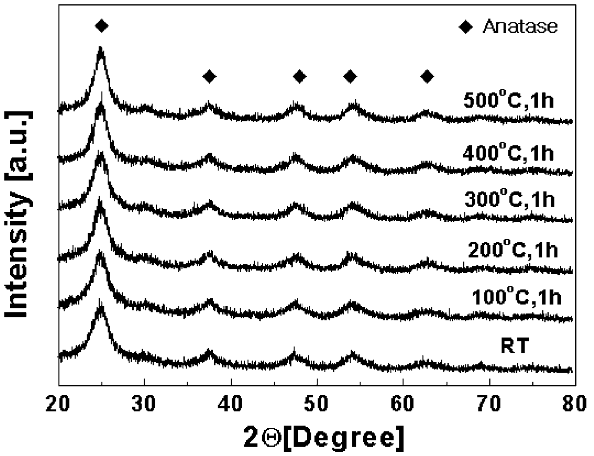

Fig. 5. X-ray diffraction patterns of TiO_2–SiO_2 nano-composite thin films heat-treated at various temperatures for 1 h.

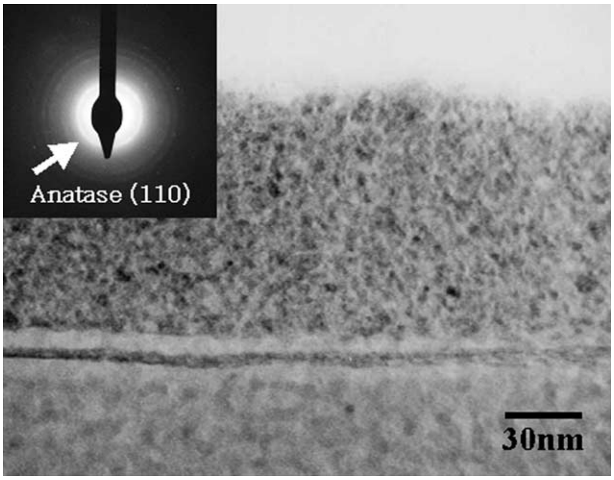

Fig. 6. TEM image of the cross-section of TiO_2–SiO_2 nano-composite thin films coated on a glass substrate by dip coating technique and the corresponding electron diffraction pattern (inset).

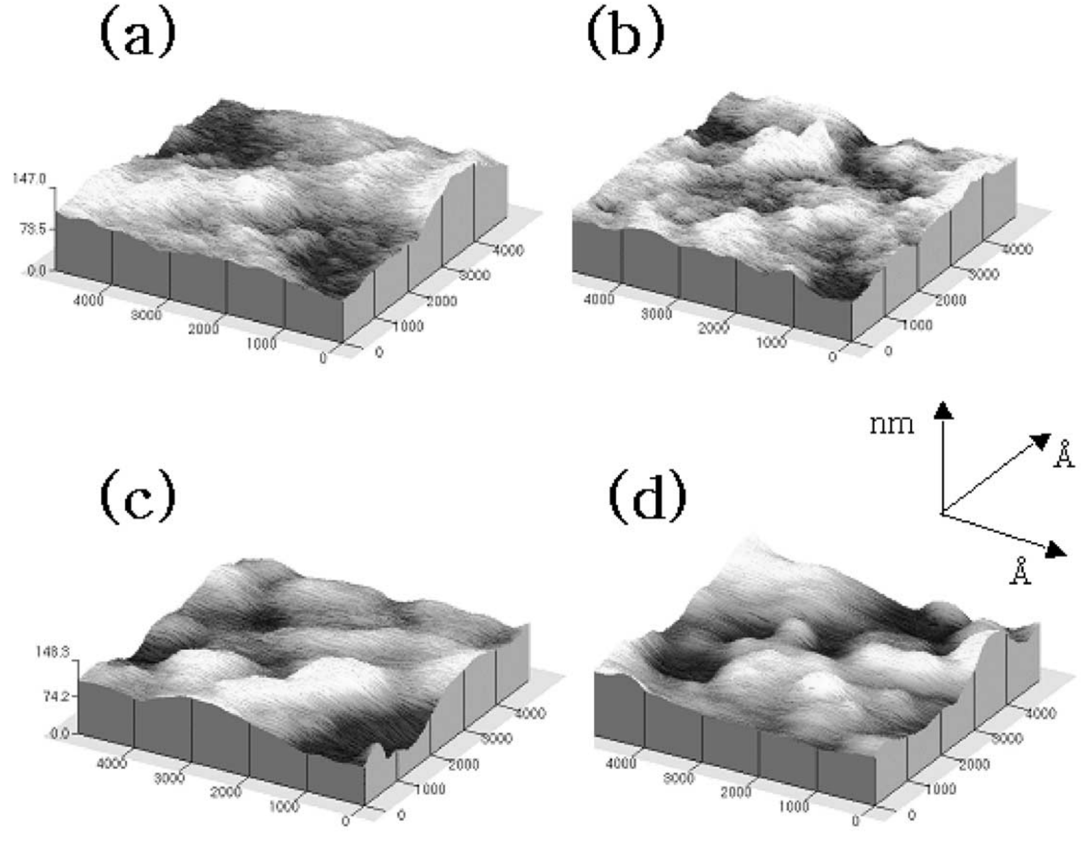

Fig. 7. AFM images of the thin films of (a) 100% TiO_2 (b) 70% TiO_2 + 30% SiO_2 (c) 50% TiO_2 + 50% SiO_2 and (d) 30% TiO_2 + 70%SiO_2 coated on glass substrates and heat treated at 100 °C for 1 h.

TiO_2–SiO_2 nano-composite thin films have surface morphologies that can be altered further if the samples were heat treated at higher temperatures. It can be concluded that the surface morphology, and thus the physical and chemical properties related to it can be tailored by adjusting the amount of SiO_2. The effect of the relative amount of TiO_2 and SiO_2 on the structural change of TiO_2–SiO_2 nanocomposite thin films heated-treated at 100 °C for 1 h was also investigated using X-ray diffraction. No structural transformation from anatase to rutile was observed over the range of 0–70% of SiO_2. The broadening of the (101) peak was only observed as the amount of SiO_2 increased due to the relative amount of TiO_2 and the glassy SiO_2.

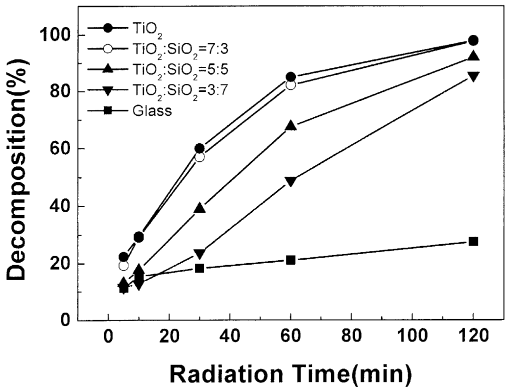

Fig. 8. Decomposition of methylene blue as a function of UV irradiation time for TiO_2 and TiO_2–SiO_2 nano-composite thin films with different SiO_2 content.

The photocatalytic activity of TiO_2–SiO_2 thin films was evaluated by the decomposition of methylene blue solution, as shown in Fig. 8. The photocatalytic activity of the TiO_2–SiO_2 thin films with the molar ratios greater than 1 showed decomposition of ~95% of methylene blue solution in 2 h. Even though the composite films with the molar ratio less than 1 showed better adhesion and strength of the film, their photocatalytic decomposing power for methylene blue was much inferior to those with the molar ratios greater than 1. The decomposing power of the TiO_2–SiO_2 composite thin film was not reduced to a great extent up to 50% of SiO_2. Since the adhesion property of the thin film was improved with an increasing amount of SiO_2, the composition of the composite should be adjusted in this range. Considering both the photocatalytic activity and the mechanical stability, the addition of 50% SiO_2 seems to be the best choice. The reason for ~20% of decomposition on the bare glass is due to the physical adsorption of methylene blue. For other cases, the decomposition of methylene blue is the combining effect of physical adsorption and decomposition of methylene on the surface. In addition, the TiO_2–SiO_2 thin films with the molar ratios greater than 1 showed a contact angle of $\sim 10^\circ$. The photocatalytic decomposition of methylene blue increased and the contact angle decreased with the content of TiO_2 phase.

4. Conclusion

Nanocrystalline TiO_2 ($\sim$5 nm) and TiO_2–SiO_2 nanocomposites have been prepared by a sol–gel process using titanium- and silicon-alkoxides as precursors. The crystalline structure of the as-synthesized TiO_2 powders was identified as anatase phase. For TiO_2–SiO_2 nanocomposites, TEM results revealed the presence of spherical TiO_2 particles ($\sim$5 nm) dispersed in a disk-shaped glassy matrix. The addition of SiO_2 suppressed the anatase–rutile phase transition at elevated temperatures. The TiO_2 photocatalyst showed high efficiency in decomposing methylene blue. Transparent TiO_2–SiO_2 (Ti/Si > 1) nanocomposite thin films with increased adhesion showed an excellent decomposing power for methylene blue.

References

[1] C. Byun, J.W. Jang, I.T. Kim, K.S. Hong, B.W. Lee, Anatase-to-rutile transition of titania films prepared by MOCVD, Mater. Res. Bull. 32 (4) (1997) 431.

[2] L. Escobar-Alarcon, E. Haro-Poniatowski, M.A. Chamacho-Lopez, Structural characterization of TiO_2 thin films obtained by pulsed laser deposition, Appl. Surf. Sci. 137 (1999) 38.

[3] G.H. Li, L. Yang, Y.X. Jin, L.D. Zhang, Structural and optical properties of TiO_2 thin films and TiO_2 + 2wt% $ZnFe_2O_4$ composite film prepared by r.f. sputtering, Thin Solid Films 368 (2000) 163.

[4] L.J. Meng, M.P. Santos, Investigations of titanium oxide films deposited by d.c. reactive magnetron sputtering in different sputtering pressures, Thin Solid Films 226 (1993) 22.

[5] K.M.S. Khalil, M.I. Zaki, Synthesis of high surface area titania powders via basic hydrolysis of titanium (IV) isopropoxide, Powder Technol. 92 (1997) 233.

[6] V.M. Gun Ko, F. Villieras, R. Leboda, M. Marciniak, B. Charmas, J. Skubiszewska-Zieba, Characterization of titania/silica gel by means of low-pressure nitrogen adsorption, J. Colloid Interface Sci. 230 (2000) 320.

[7] R. Leboda, V.M. Gun Ko, M. Marciniak, A. Malygin, A.A. Malkin, W. Grzegorczyk, et al., Structure of chemical vapor deposition titania/silica gel, J. Colloid Interface Sci. 218 (1999) 23.

[8] R. Burch, Z. Paal, P.G. Menon, Hydrogen effects in catalysis, Marcel Dekker, New York, 1988, p. 345.

[9] N. Economidis, R.F. Coil, P.G. Smirniotis, Catalytic performance of $Al_2O_3/SiO_2/TiO_2$ loaded with V_2O_5 for the selective catalytic reduction of NO_x with ammonia, Catal. Today 40 (1998) 17.

[10] G. Martra, Lewis acid and base sites at the surface of microcrystalline TiO_2 anatase: relationships between surface morphology and chemical behaviour, Appl. Catal. A: General 200 (2000) 275.

[11] C. Martin, I. Martin, C. Del Moral, V. Rives, FT-IR assessment through pyridine adsorption of the surface acidity of alkali-doped MoO_3/TiO_2, J. Catal. 146 (1994) 415.

[12] M.G. Reichmann, A.G. Bell, The influence of preparation chemistry on the phase distribution of silica-supported titania, Appl. Catal. 32 (1987) 316.

[13] Y. Xu, W. Zheng, W. Liu, Enhanced photocatalytic activity of supported TiO_2: dispersing effect of SiO_2, J. Photochem. Photobiol. A122 (1999) 57.

[14] C.J. Brinker, G.W. Scherer, The physics and chemistry of sol–gel processing, Academic Press, Inc, San Diego, CA, 1990.

[15] C.C. Wang, J.Y. Ying, Sol–gel synthesis and hydrothermal processing of anatase and rutile titania nonacrystals, Chem. Mater. 11 (1999) 3113.

[16] R.N. Viswanath, S. Ramasamy, Study of TiO_2 nanocrystallites in TiO_2–SiO_2 composites, Colloids and Surfaces A: Physicochemical and Engineering Aspects 133 (1998) 49.

[17] A. Karthikeyan, R.M. Almeida, Crystallization of SiO_2–TiO_2 glassy films studied by atomic force microscopy, J. Non-Cryst. Solids 274 (2000) 169.

[18] S.R. Kumar, C.S. Asha, K. Vasudevan, R. Suja, P. Mukundan, K.G.K. Warrier, Phase transformation in sol–gel titania containing silica, Mater. Lett. 38 (1999) 161.