Titania powder modified sol-gel process for photocatalytic applications

G. BALASUBRAMANIAN, D. D. DIONYSIOU*, M. T. SUIDAN*
Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221, USA
E-mail: dionysios.d.dionysiou@uc.edu; makram.suidan@uc.edu

V. SUBRAMANIAN
Formerly of Department of Material Science, University of Cincinnati, Cincinnati, OH 45221, USA

I. BAUDIN, J.-M. LAÎNÉ
Centre International de Recherche Sur l'Eau et l'Environnement (CIRSEE), ONDEO Services, 38 rue du Président Wilson, 78230 Le Pecq, France

Thick films of TiO_2 were prepared on glass and stainless steel substrates using an alkoxide sol-gel process modified by addition of Degussa P-25 powder. The prepared films were characterized by SEM, EDS, XRD and other methods. The TiO_2 films obtained from the powder modified sol were compared to films obtained from the alkoxide sol-gel without modification. The films obtained from the modified sol-gel were about ten times thicker for a single dip coating/heat treatment cycle than the films obtained from the sol without powder addition. The prepared thick films were smooth and free of macrocracking, fracture or flaking. The grain size of these films was uniform and in the range 100–150 nm and the films were a mixture of anatase and rutile TiO_2. The films obtained from the powder modified sol on the stainless steel substrate were also much harder compared to the films obtained from sols without modification and displayed excellent adhesion to the substrate. © 2003 Kluwer Academic Publishers

1. Introduction

Titanium dioxide (TiO_2) thin films have been utilized for a variety of applications including water purification [1, 2], air purification [3], gas sensors [4–6] and photovoltaic solar cells [7–10]. These TiO_2 thin films are synthesized by a variety of methods like sol-gel [11, 12], chemical vapor deposition (CVD) [13–15], electrodeposition [16] and electrophoresis [17, 18]. The sol-gel route of synthesis of TiO_2 films is advantageous in that no special equipment other than a furnace is needed and the film properties can be precisely determined by controlling sol preparation parameters such as concentration and nature of precursors [19], viscosity [11], dipping temperature [20], withdrawal speed [11, 21] and temperature and duration of heat treatment.

In this paper we report a modification of the alkoxide precursor sol-gel method described in detail elsewhere by Takahashi and Matsuoka [11]. Degussa P-25 powder was added to the sol prepared by the Takahashi and Matsuoka (TM) method. A number of different substrates were coated via dip coating and other methods. A very stable and viscous sol was formed and relatively thick films of TiO_2 were obtained and characterized by various methods. Subsequently these films were tested in a batch reactor for photocatalytic activity.

Films deposited by the alkoxide precursor sol-gel method tend to be dense, uniform and highly crystalline [22–26]. The photoactivity of the TiO_2 film depends on the porosity, grain size and phase of the crystallites, surface roughness and surface area. Many investigators have attempted to produce sol-gel films with higher photoactivity by adding both organic and inorganic modifiers to the sol-gel precursor solution. Kato *et al.* [12] reported that addition of polyethylene glycol (PEG) to the alkoxide precursor solution results in the production of thick TiO_2 films and that the thickness of the films obtained in a single dip coating cycle could be controlled by varying the molecular weight of the PEG. During the course of our current investigation, we could not produce stable titanium isopropoxide (TTIP) sols incorporating PEG. Upon the addition of PEG the sols tended to precipitate and even when they did not do so immediately, they precipitated after storage for a few days. The modified TM method used in the current investigation produced a sol that was stable indefinitely and could be used over a period of time.

---

*Authors to whom all correspondence should be addressed.
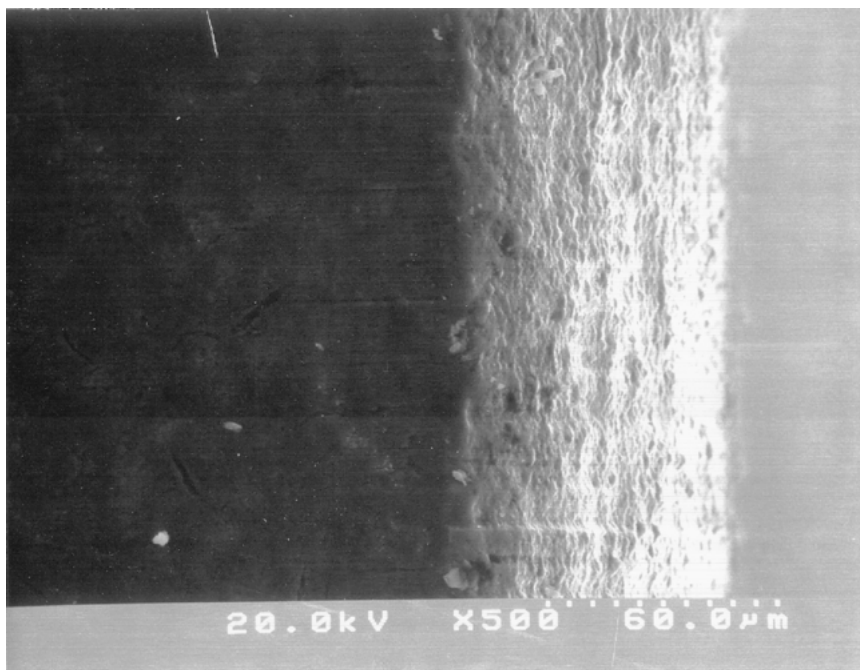
Figure 1 SEM micrograph of stainless steel coupon coated with modified TM sol-gel after 2 dip coating/heat treatment cycles at 600°C.

Imai and Hirashima [27] investigated the effects of addition of SiO_2 to the precursor solution to increase the photoactivity and reported that while mechanically strong films could be obtained, the photoactivity was decreased by the presence of silica in the crystal matrix. Some investigators have tried to increase the photocatalytic activity of the sol-gel derived TiO_2 film by controlling the crystal grain size and phase transformation. Ding *et al.* [28] and Kajihara and Yao [29] demonstrated that the crystal size of the TiO_2 films obtained via the alkoxide sol-gel route could be controlled by adjusting the amount of water available for hydrolysis. In the current investigation we did not attempt to study the effect of varying the amount of water available for hydrolysis, keeping it a constant across the experiments.

2. Experimental procedure

The detailed Takahashi and Matsuoka method has been described elsewhere [11]. Commercial extra pure titanium isopropoxide (TTIP) (Aldrich), isopropanol (iPrOH) (Fisher Scientific), Diethanolamine (DEA) (Fisher Scientific) and nanophase TiO_2 Degussa P-25 powder (50 m^2/g; 15–30% rutile + 85–70% anatase, mean diameter 30 nm) were used for the preparation of the sol. A 0.5 M solution of TTIP in iPrOH was prepared and subsequently a suitable amount of DEA was added to the solution. A molar ratio of DEA/ TTIP = 4 was used. The solution was stirred at room temperature for 2 hours. Subsequently water was added drop by drop under vigorous stirring. A molar ratio of H_2O/TTIP = 2 was used. A clear sol was obtained. This sol was stable at room temperature and no changes were observed even after storage for many months. The modified TM sol was prepared by addition of 30 grams/liter of Degussa P-25 TiO_2 powder. The powder was added slowly with vigorous stirring to prevent the formation of

agglomerates. A thick, white, viscous solution was obtained. This solution settled slowly over a period of two weeks. To prevent settling the modified sol was stirred constantly while in storage between experiments.

The stainless steel substrates to be coated were cleaned with ethanol and methyl ethyl ketone. Subsequently the substrates were dried at 125°C for 24 hours. A dip-coating apparatus, equipped with an adjustable motor to control the pull-out rate, was used to dip in and pull out the substrate at a constant rate of withdrawal. The pull-out rate used was 12.8 cm min^{-1}. To coat glass beads a different procedure was followed. Borosilicate glass beads (Fisher Scientific) of 6 mm diameter were placed in a beaker. The beaker with the coated beads was filled with the sol and allowed to stand for ten minutes. Subsequently, the sol was drained and the beaker was dried in air at room temperature for
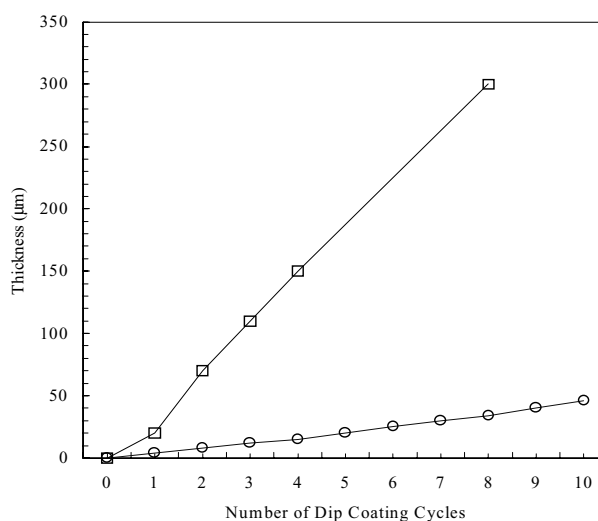

Figure 2 Relationship between number of dip coating cycles and thickness for (i) TM Sol [o] (ii) modified TM Sol [□].

24 hours and then heat-treated. After heat treatment and cooling, the beads were removed, mixed and put back in the beaker prior to coating again, to ensure the points of contact between the beads were not the same between coatings to prevent the occurrence of uncoated regions. Heat treatment for all samples was done using a multi-segment programmable furnace (Paragon Model HT-22-D, Thermcraft Inc., Winston-Salem, North Carolina). The furnace temperature was increased at a ramp rate of 3°C per minute until it reached 100°C and was held at 100°C for 1 hour. Subsequently, the temperature was increased at a ramp rate of 3°C to 600°C

and held for 1 hour. Finally the furnace was allowed to cool down naturally to room temperature. The cooling down period took approximately 12 hours.

A Hitachi S-4000 scanning electron microscope (SEM) was used to determine the thickness and morphology of TiO_2 layers on substrates. The same instrument was also used to perform electron diffraction spectroscopy (EDS) quantitative analysis of the TiO_2 films. It was not possible to prepare samples for SEM analysis by immobilizing them in acrylic resin as is conventionally done due to fluorescence effects. To eliminate this the acrylic cylinder was cut into two along a
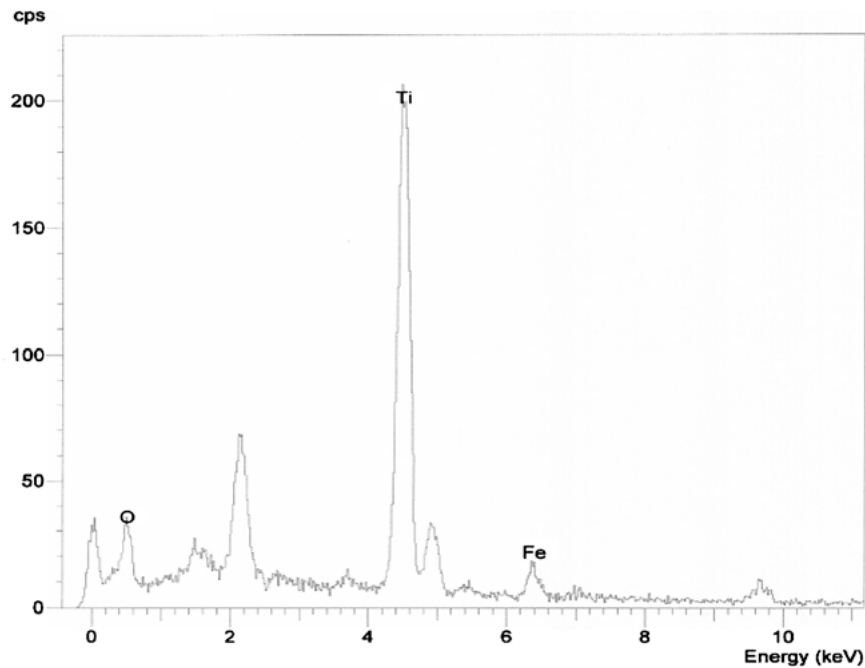

(a)
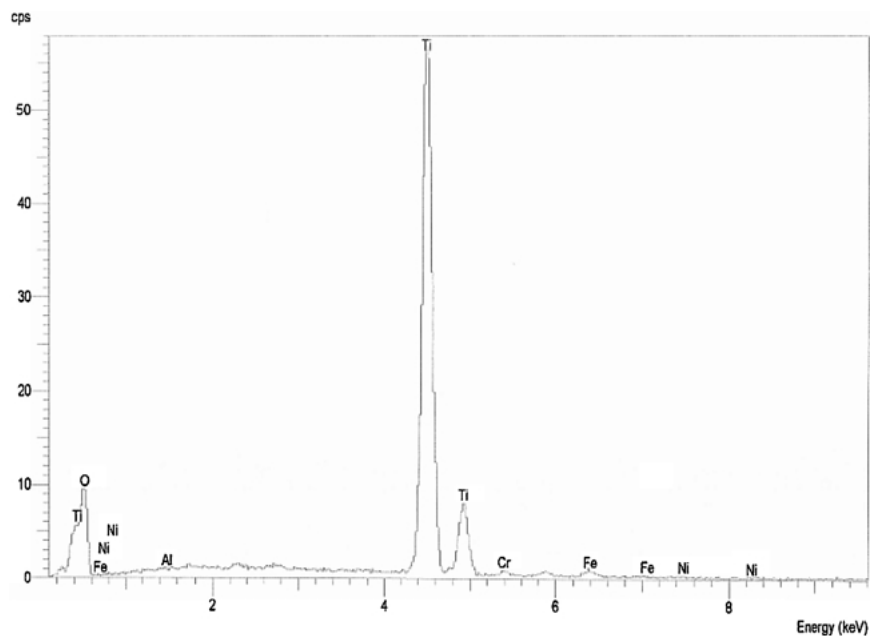
(b)

Figure 3 (a) EDS analysis of TiO_2 film on stainless steel substrate obtained from the TM sol after 8 dip coating/heat treatment cycles (b) EDS analysis of TiO_2 film on stainless steel substrate obtained from TM sol modified by addition of powder, after 8 dip coating/ heat treatment cycles (c) EDS analysis of TiO_2 film obtained on glass bead from modified TM sol after 8 coating/heat treatment cycles. (*Continued*)
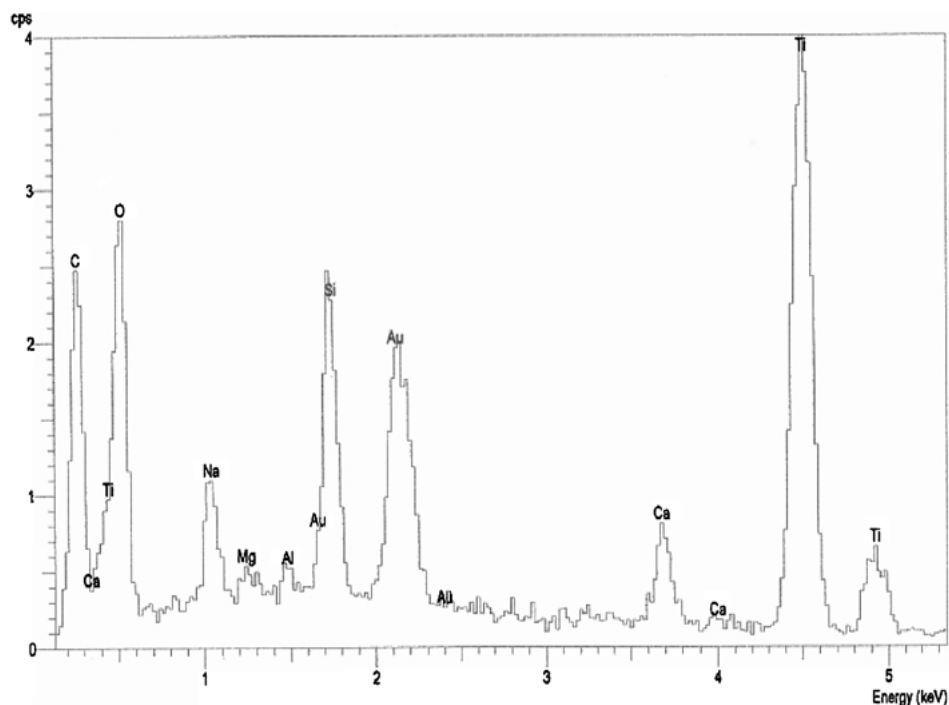
(c)

Figure 3 (*Continued*).

diameter and then clamped together to hold the samples for polishing. After polishing to a mirror finish the cylinder was unclamped and the samples were removed and then mounted upright on their unpolished edge using ceramic adhesives. The sample was then coated with gold using sputtering techniques prior to analysis

A Siemens Kristalloflex D500 diffractometer with Cu K_a radiation was used for the x-ray diffraction (XRD) experiments to determine the crystal structure of the TiO_2 catalyst. For each scan, 2θ was increased from 10.0 to 70.0 degrees with a step size of 0.040 and time to step ratio of 1.0. The hardness of the TiO_2 films was tested by Standard Test Method for Film Hardness by Pencil Test as per American Society for Testing and Materials (ASTM) Standard D 3363–92a [30].

3. Results and discussion

Fig. 1 shows the SEM micrograph of the TiO_2 coating on a stainless steel substrate after two dip coating/heat treatment cycles. Fig. 2 shows the relationship between thickness of the TiO_2 films and the number of dip coating/heat treatment cycles as observed from the SEM micrographs. The thickness increases fairly linearly for both the TM sol and the modified TM sol. The thickness of the film obtained per dip coating/heat treatment cycle from the TM sol is 3–4 μm while the thickness of the film obtained per dip coating/heat treatment cycle from the modified TM sol is between 30–40 μm. Thus the modified TM sol produces coatings that are about ten times thicker per cycle. The modified TM sol is more viscous than the unmodified TM sol and since the film thickness depends on the viscosity [11, 31], a thicker film is obtained per cycle with the modified TM sol. It is desirable to reduce the number

of dip coating/heating cycles required to form a thick layer of TiO_2 to reduce the time and costs associated with preparing TiO_2 film catalysts. The modified TM sol enables reduction in the number of dip coating cycles required by at least ten times when compared to the TM sol to form a TiO_2 film of equal thickness.

Several investigators [21, 31–33] have attributed the decrease in film thickness on heat treatment to the loss of the organic fraction of the film obtained by dip coating. The modified TM sol has less organic fraction than the TM sol due to the addition of the Degussa P-25 powder. The fraction of the dip-coated film lost during heat treatment is thus less for the modified TM sol than for the TM sol. It is also likely that the Degussa P-25 particles serve as nucleation sites and the particle growth occurs on the surface of the P-25 particles. Since the growth does not start *ab initio* as in the TM method, larger grains are formed for the modified TM method. Larger grains have been shown [28, 32, 34] to produce thicker films, and this is in agreement with our experimental results.

Fig. 3a and b show the EDS analysis of the film on stainless steel obtained from the TM sol and the modified TM sol respectively. The EDS analysis indicates the almost pure titania composition of both films. There are no peaks for carbon, indicating the absence of organic components. In Fig. 3a the peak at 2 keV is the peak for gold due to the gold sputtering of the sample. Fig. 3c shows the EDS analysis of the TiO_2 film obtained on a glass bead. The presence of a large peak for carbon indicates that organic components are present even after 8 heat treatment cycles. This may be possibly due to the lack of microcracks in the film and will be discussed in greater detail later in this paper in the discussion of the morphology of the film on glass beads.
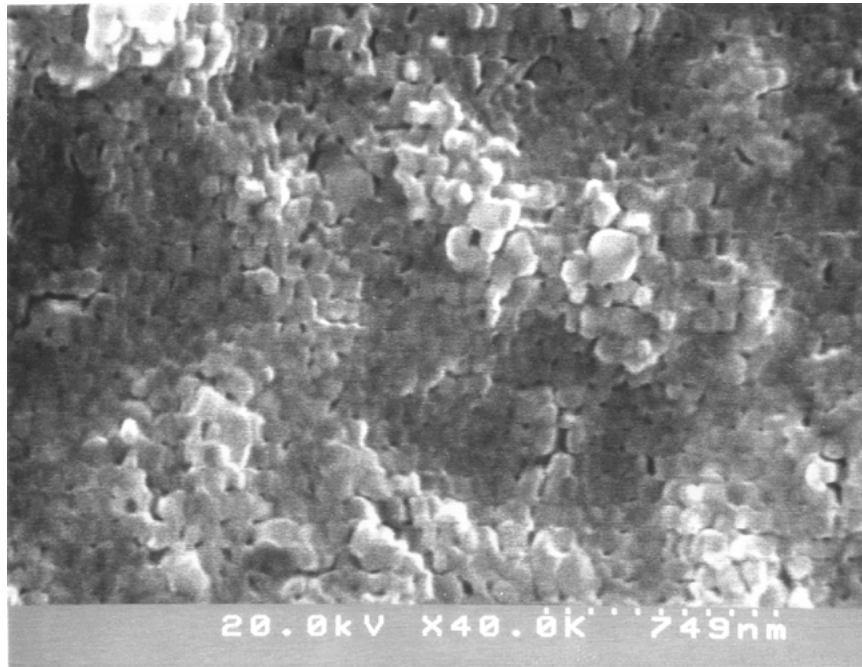
Figure 4 SEM micrograph showing the close packed crystal grains of the coating obtained from the modified TM sol.

Fig. 4. shows the grain structure of the TiO_2 coatings obtained from the modified TM sol on stainless steel substrates. The grains are uniformly sized between 100–150 nm. Ding *et al.* [32] report that grain growth rate is driven by surface energy which decreases with decreased surface area. In the modified TM process the grain growth is likely to occur on the surface of the P-25 particles. However as the grain grows larger, the surface area decreases and available surface energy decreases and grain growth tends to auto-inhibit. Thus the grain size increase tapers off. This phenomenon occurred between 100–150 nm under the experimental conditions of our study.

Fig. 5 shows the SEM micrograph of glass beads coated with the modified TM sol. The grain size is observed to be fairly uniform in the range of 100–150 nm consistent with the discussion above regarding the uniformity of the grain size. The presence of sub-grains on the surface of some of the grains suggests that secondary nucleation of purely sol derived TiO_2 crystal grains takes place on the surface of the larger grains derived from the P-25 particles.
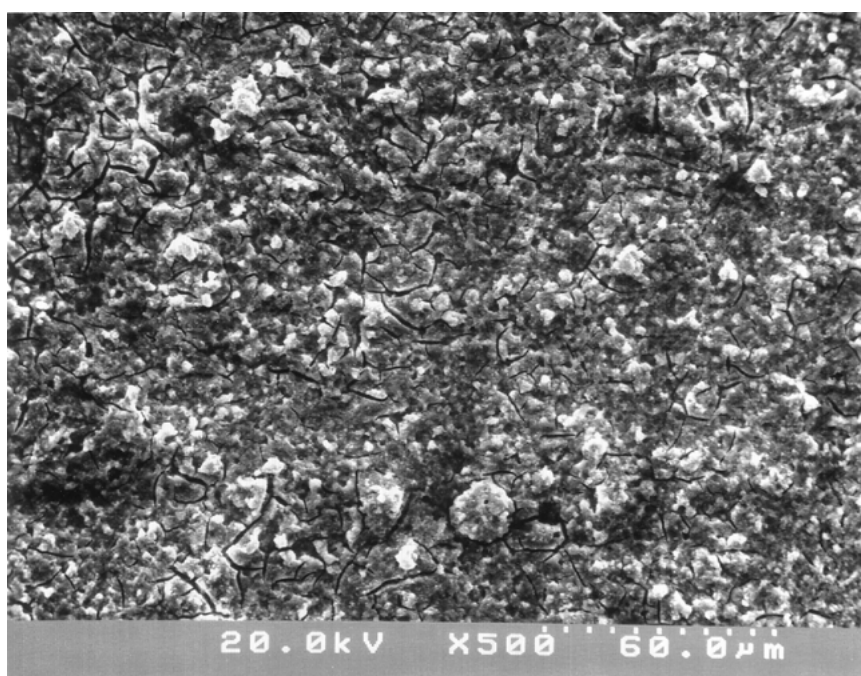
Fig. 6a and b show the morphology of the TiO_2 film obtained from the modified TM sol on the stainless steel substrates. The surface is rough but continuous. There are no macrocracks but microcracks are visible. The

Figure 5 SEM micrograph of TiO_2 coating on glass bead after eight coating/heat treatment cycles.
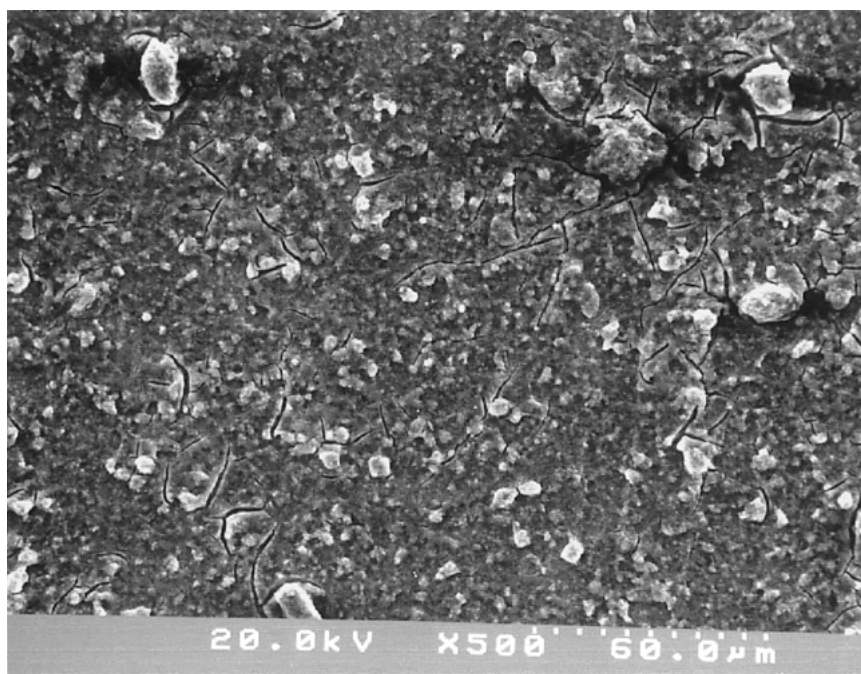
(a)

(b)

Figure 6 (a) SEM micrograph showing microcracks in the TiO$_2$ film obtained on stainless steel substrate from the modified TM sol after 4 dip coating/ heat treatment cycles (b) SEM micrograph showing microcracks in the TiO$_2$ film obtained on stainless steel substrate from the modified TM sol after 8 dip coating/heat treatment cycles.

extent and frequency of the microcracks increase with the number of dip coating/heat treatment cycles. The presence of microcracks suggests small residual compressive stresses [35]. Thick films of TiO$_2$ are prone to fracture and macro cracking due to the intrinsic film stresses that occur during the drying, crystallization, and densification processes. These stresses are caused by chemical reactions during drying, difference in thermal expansion coefficients between substrate and the TiO$_2$ film, grain interaction and grain size of the TiO$_2$ film [34, 35].

The observed absence of macrocracking may be explained by the competitive action of three stresses. When crystallization occurs, large compressive stresses are generated [25, 34, 35]. When grain growth and densification of the film occurs, the stresses are reduced [25, 32, 34, 36]. The densification that accompanies grain formation is directly proportional to grain size [32]. Since the Degussa P-25 particles provide an initial grain growth site ($\approx$30 nm), the growth takes place fairly quickly compared to *ab initio* grain growth and, consequently, the compressive stresses are reduced

quickly. Also the stainless steel substrate has a higher coefficient (17×10^{-6} °C) of linear thermal expansion than the TiO_2 film (2.1–2.8×10^{-6} °C) [37]. On cooling, the stainless steel substrate shrinks more than the TiO_2 film leading to further reduction of compressive stresses [34] and these reduced compressive stresses lead to the formation of small microcracks. Also in the preceding discussion in this paper, we have suggested that a larger fraction of titanium is present in the modified TM sol than in the TM sol, due to the addition of the Degussa P-25 powder. Que *et al.* [38] report that increase in titanium fraction in the film leads to less microcracking.

Fig. 7 shows the TiO_2 film formed on glass bead when coated with the modified TM sol. The film is free of any microcracks. When the glass beads are heated to 600°C during heat treatment, a slight softening of the glass bead takes place and compressive stress due to crystallization is reduced by creep of the softened glass substrate. This lack of microcracks has important implications for the composition of the film. Que *et al.* [38] have reported that TiO_2 films synthesized from organic precursors are purely inorganic after heat treatment at 500°C. However, with the addition of organically modified silanes, a glassy carbon-TiO_2 matrix was formed at very high heat treatment temperatures (>1000°C). They suggest the TiO_2 films densifies to the point that the carbon trapped in the matrix cannot escape even at very high temperatures. We suggest that a similar phenomenon takes place during heat treatment of the films on the glass beads. EDS analysis of film on glass beads (Fig. 3c) shows the presence of significant amounts of carbon, silicon, sodium, oxygen and titanium. The presence of silicon and sodium is possibly due to thermally assisted diffusion from the underlying glass substrate surface. The films obtained on the stainless steel substrates (Fig. 3a and b) are characterized by microcracks

and do not show the presence of carbon. Microcracks can facilitate the volatilization of carbon and the absence of microcracks in the TiO_2 film on glass due to the creep of the glass substrate tends to trap the carbon in the TiO_2 matrix. We have suggested earlier in this paper that the TiO_2 film obtained from the modified TM densifies fairly quickly due to the grain growth on the Degussa P-25 particles. As the film densifies upon heat treatment at 600°C due to crystallization, the trapped carbon forms a glassy carbon-TiO_2 matrix in the presence of Si. This could explain the peak for carbon observed in Fig. 3c.

Fig. 8 shows the X-ray diffractograms for stainless steel substrates coated with modified TM sol. As the number of coatings increases the amount of both anatase and rutile increases as is evident from the peaks. Both crystal phases are present in the Degussa P-25 powder (15–30% rutile + 85–70% anatase). The increasing amount of both can be explained by contributions from conversion of the amorphous TiO_2 synthesized from the TTIP precursor to the anatase phase and the increasing amounts of immobilized Degussa P-25 powder. Further analysis of the XRD peaks revealed that the amount of rutile increased from 40% in the first coating to 60% in the eighth coating.

The hardness of the films obtained from the TM sol and the modified TM sol by 8 dip coating/heat treatment cycles were estimated using the pencil hardness method [37]. The range of pencils were in the continuous order 6H, 5H, 4H, 3H, 2H, H, HB, B, 2B, 3B, 4B, 5B, 6B. The TiO_2 film on the stainless steel substrate obtained from the TM sol (without modification) was cut or scratched by all the pencils from 6H to the 4B pencil. The Gouge Hardness end point is 4B [30]. The 5B pencil produced a line and did not cut the film and the Scratch Hardness end point is 5B [30]. These
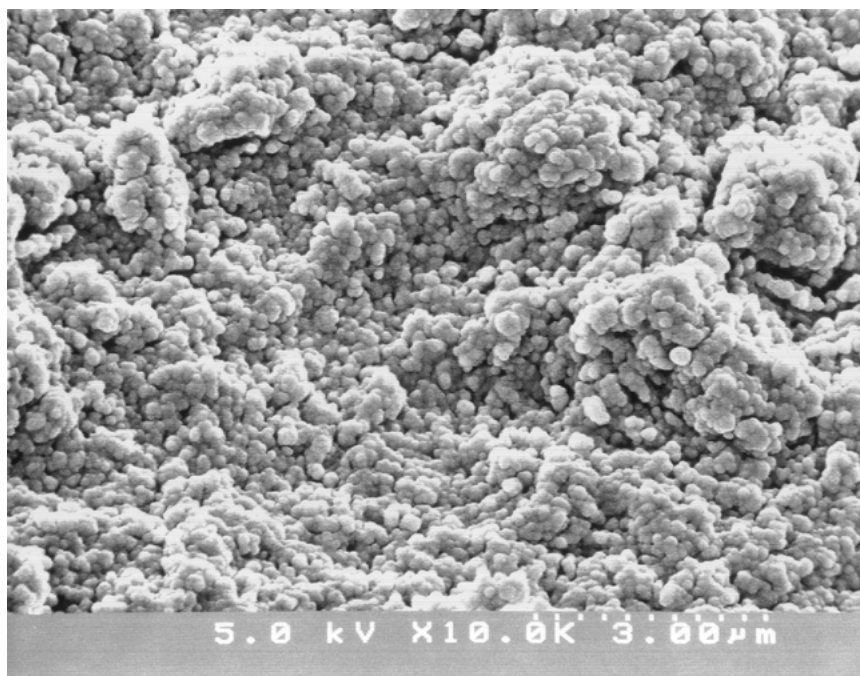

Figure 7 SEM micrograph of TiO_2 film on glass bead after 8 coating /heat treatment cycles showing the lack of any microcracks.
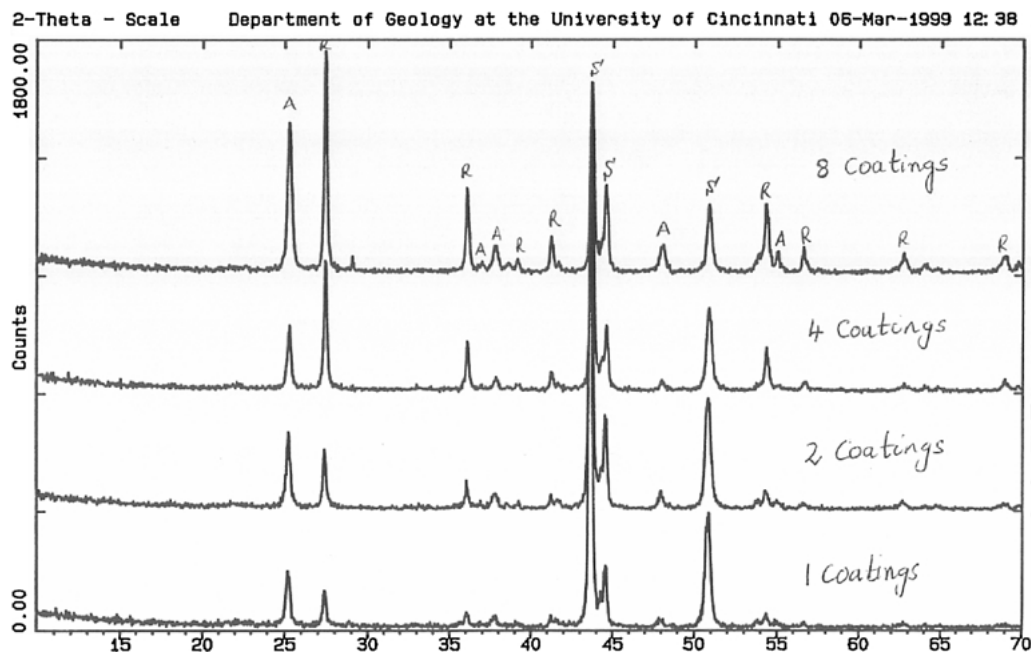
Figure 8 X-ray diffractogram for stainless steel substrates coated various number of times with modified TM sol and heat treated at 600°C. Notation: A: anatase; R: rutile; S: substrate.

results indicate that a relatively soft TiO_2 film is formed by coating with the TM sol without modification. The coating obtained from the modified TM sol was tested and a line was obtained with the 6H pencil indicating that the hardest pencil was unable to cut the film thus suggesting that the film obtained from the modified TM sol is extremely hard. The relatively large 100 nm grain size obtained from the modified TM sol coating indicates that a fairly dense film is obtained after heat treatment. The lack of pores or macrocracks observed in the SEM micrographs support this finding. Various investigators [11, 23, 32, 36] have suggested that increased grain size leads to greater densification and hardness of the film.

The adherence of the TiO_2 film obtained from the modified TM sol was tested using the tape stripping method. Extra strength transparent scotch tape (3M Corp.) strips were pressed to the 9 cm × 22 cm stainless steel substrate coated with TiO_2 film obtained from the modified TM sol. The tape was allowed to remain for 10 minutes and then pulled off both slowly and quickly. In either case, even after 30 applications and removal from the same area, no TiO_2 was observed on any of the strips nor was the film surface visibly disturbed in any way. The absence of any flaking off suggests that the film obtained from the modified TM sol-gel is extremely firmly bonded to the substrate and cannot be easily removed.

4. Conclusions

We modified the Takahashi and Matsuoka sol-gel method for preparing TiO_2 films by addition of Degussa P-25 powder. Extremely thick, uniform TiO_2 films were obtained on stainless steel substrates and glass beads. The per-dip-coating-cycle thickness for the powder modified sol was about ten times that of the unmodified TM sol, enabling the reduction of the number of dip coating cycles needed to produce a thick TiO_2 film on stainless steel substrate. The films were continuous except for localized microcracks and did not display porous structure. The grain size was uniform and in the range 100–150 nm for both the glass and the stainless steel substrate. The films obtained on the stainless steel substrates were very hard compared to the TiO_2 films obtained from the Takahashi and Matsuoka method without addition of powder. The films were very adherent to the stainless steel substrate despite their thickness and did not flake off or fracture. The films were a mixture of anatase and rutile, which was as expected due to phase transformation and presence of rutile phase in Degussa P-25 powder. We tested the photoactivity of the glass beads and the stainless steel substrates coated with powder modified TM sol in a batch reactor and in a continuous mode reactor. The samples coated with the modified TM sol display increased photocatalytic activity compared to substrates coated with TM sol without modification. Also, the continuous mode rotating disk reactor was run for six months without any visible catalyst attrition, confirming that very good adherence of the film was obtained from the modified TM sol. These results will be reported in a forthcoming publication.

References
1. I. M. BUTTERFIELD, P. A. CHRISTENSEN, T. P. CURTIS and J. GUNLAZUARDI, *Wat. Res.* **31** (1997) 675.
2. T. M. WANG, H. Y. WANG, P. XU, X. C. ZHAO, Y. L. LIU and S. CHAO, *Thin Solid Films* **334** (1998) 103.

3. W. CHOI, S. J. HONG, Y.-S. CHANG and Y. CHO, *Env. Sci. Tech.* **34** (2000) 4810.
4. H. E. HAGER and J. A. BELKO, *Sensors and Actuators* **8** (1985) 161.
5. J. HUUSKO, V. LANTTO and H. TOTVELA, *Sensors and Actuators B: Chemical* **16** (1993) 245.
6. V. DEMARNE, S. BALKANOVA, A. GRISEL, D. ROSENFELD and F. LEVY, *ibid.* **14** (1993) 497.
7. T. NAKADA and A. KUNIOKA, *Electronics & Communications in Japan, Part 2: Electronics* **69** (1986) 8.
8. B. O'REGAN and M. GRATZEL, *Nature* **353** (1991) 737.
9. Y. X. LI, J. HAGEN, W. SCHAFFRATH, P. OTSCHIK and D. HAARER, *Solar Energy Materials and Solar Cells* **56** (1999) 167.
10. G. PHANI, G. TULLOCH, D. VITTORIO and I. SKRYABIN, *Renewable Energy* **22** (2001) 303.
11. Y. TAKAHASHI and Y. MATSUOKA, *J. Mater. Sci.* **23** (1988) 2259.
12. K. KATO, A. TSUZUKI, Y. TORII, H. TAODA, T. KATO and Y. BUTSUGAN, *ibid.* **30** (1995) 837.
13. E. FREDRIKSSON and J.-O. CARLSSON, *Surface & Coatings Technology* **73** (1995) 160.
14. G. A. BATTISTON, R. GERBASI, A. GREGORI, M. PORCHIA, S. CATTARIN and G. A. RIZZI, *Thin Solid Films* **371** (2000) 126.
15. E. HALARY, G. BENVENUTI, F. WAGNER and P. HOFFMANN, *Applied Surface Science* **154** (2000) 146.
16. C. NATARAJAN and G. NOGAMI, *J. Electrochem. Soc.* **143** (1996) 1547.
17. D. MATTHEWS, A. KAY and M. GRATZEL, *Australian Journal of Chemistry* **47** (1994) 1869.
18. X. NIE, A. LEYLAND and A. MATTHEWS, *Surface and Coatings Technology* **125** (2000) 407.
19. K. KAJIHARA and T. YAO, *J. Sol-Gel Sci. & Tech.* **12** (1998) 193.
20. *Idem.*, *ibid.* **19** (2000) 219.
21. *Idem.*, *ibid.* **17** (2000) 173.
22. A. P. XAGAS, E. ANDROULAKI, A. HISKIA and P. FALARAS, *Thin Solid Films* **357** (1999) 173.
23. M. LAUBE, W. WAGNER, F. RAUCH, C. OTTERMANN, K. BANGE and H. NIEDERWALD, *Glass Sci. & Tech.* **67** (1994) 87.
24. N. NEGISHI, K. TAKEUCHI and T. IBUSUKI, *J. Mater. Sci.* **33** (1998) 5789.
25. C. R. OTTERMANN and K. BANGE, *Thin Solid Films* **286** (1996) 32.
26. W. W. SO, S. B. PARK and S. J. MOON, *J. Mater. Sci. Let.* **17** (1998) 1219.
27. H. IMAI and H. HIRASHIMA, *J. Amer. Ceram. Soc.* **82** (1999) 2301.
28. X. Z. DING, Z. Z. QI and Y. Z. HE, *J. Mater. Sci. Lett.* **14** (1995) 21.
29. K. KAJIHARA and T. YAO, *J. Sol-Gel Sci. & Tech.* **12** (1998) 185.
30. Standard Test Method for Film Hardness by Pencil Test, American Soc. of Testing and Materials, Standard Designation D 3363–92a (1992), p. 366.
31. L. L. HU, T. YOKO, H. KOZUKA and S. SAKKA, *Thin Solid Films* **219** (1992) 18.
32. X. Z. DING, X. H. LIU and Y. Z. HE, *J. Mater. Sci. Lett.* **15** (1996) 1789.
33. K. Y. JUNG and S. B. PARK, *Appl. Catal. B: Environ.* **25** (2000) 249.
34. D. H. J. TEEUW, M. DE HAAS and J. T. M. DE HOSSON, *J. Mater. Res.* **14** (1999) 1896.
35. G. J. EXARHOS and N. J. HESS, *Thin Solid Films* **220** (1992) 254.
36. B. A. MORALES, O. NOVARO, T. LOPEZ, E. SANCHEZ and R. GOMEZ, *J. Mater. Res.* **10** (1995) 2788.
37. M. L. SCOTT, *Nat. Bur. Stand. (US) Spec. Publ.* **688** (1985) 329.
38. W. X. QUE, Z. SUN, Y. ZHOU, Y. L. LAM, S. D. CHENG, Y. C. CHAN and C. H. KAM, *Mat. Let.* **42** (2000) 326.