Microscopy and Microanalysis Research
- The Journal of Microscopy Society of Thailand

Journal Home Page: www.mmres.org

Microsc. Microanal. Res.

Crystallinity Effect on the Photocatalytic Performance of TiO_2 Thin Films Prepared by CVD Process

Sumet Sakulsermsuk*, Saranyoo Chaiwichian, Pisith Singjai and Natda Wetchakun

Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

*Corresponding author's e-mail address: sumet.s@cmu.ac.th

ARTICLE INFO

Article history
Submitted: 23 Febuary 2017
Revised: 3 July 2017
Accepted: 10 July 2017
Available online: 28 July 2017

Keywords:
Titanium dioxide
Chemical vapor deposition
Photocatalyst
Thin films
Methylene blue

ABSTRACT

TiO_2 thin films were synthesized by using chemical vapor deposition (CVD) process at 530°C to examine the effect of CVD synthesis time on physical and optical properties, and photocatalytic activities. Thin films of nano-sized spherical TiO_2 particles were produced on borosilicate glass substrates by the CVD process for 60 min and 90 min. As the synthesizing time increased, the particle size of the TiO_2 films increased, but the thicknesses of the films decreased. The band gaps of the films prepared by deposition for 60 and 90 min were 3.51 and 3.25 eV, respectively. The photocatalytic activities of the TiO_2 thin films were monitored by studying the degradation of methylene blue under simulated solar light irradiation. The rate constant of methylene blue decomposition was found to increase from 4×10^{-4} to 6×10^{-4} min^{-1} when increasing the synthesis time from 60 min to 90 min. We proposed that the crystallinity of TiO_2 films is the main factor to enhance photocatalytic efficiency.

INTRODUCTION

Titanium dioxide (TiO_2) has unique physical and chemical properties, such as high refractive index, high chemical stability, excellent optical transmittance in the UV and visible regions, and high photocatalytic activity [1,2]. Recently, TiO_2 photocatalysts have been used for decontaminating the organic compounds in wastewater and for their antibacterial effects [3,4]. In many photocatalysis reactions, TiO_2 powders are used as photocatalysts for decomposing harmful pollutants. However, the powder form of TiO_2 causes two main problems, namely (1) difficulties in reusing the catalyst due to the waste of a large amount of water, and (2) agglomeration of catalyst particles in high concentration suspensions. To overcome these issues, the immobilization of TiO_2 on transparent substrates was developed to facilitate photocatalytic purification of water contamination. The coating by thin films of photocatalysts on glass substrates is one of solutions. Photocatalysts in the form of thin films are more reusable than those in the form of particles. Therefore, TiO_2 thin films are more suitable in long-term applications. It has been shown that TiO_2 thin films can be prepared by various methods, such as the sol-gel method [5,6], electrophoretic deposition [7,8], spin coating [9,10], sputtering [11,12], and chemical vapor deposition (CVD) [13,14]. Among these methods, CVD has advantages because it is able to prepare a catalyst coated on various substrates (*e.g.* Al_2O_3, glass slide, FTO, and ITO), with a high catalytic activity surface and low catalyst volume. Many studies on the preparation of TiO_2 thin films by CVD methods have been reported but most of them focused on the relations between CVD process conditions and physical, chemical, and electrical characteristics of the TiO_2 thin films [13-17], but studies on the effect of crystallinity on photocatalytic activity have been missing.

In this paper, we report on the synthesis and characterization of TiO_2 films prepared by using CVD for synthesis times of 60 min and 90 min. The physical and optical properties of the TiO_2 thin films were characterized by atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), UV-Vis spectrophotometry and Raman spectroscopy. The photocatalytic activities of the TiO_2 thin films were evaluated by examining the photodegradation reaction of methylene blue (MB) under simulated solar light irradiation. We observed that the rate of decomposition is higher for the film deposited for a synthesis time of 90 min than that deposited for 60 min.

METHODOLOGY

Preparation of TiO_2 films

The experimental setup of the CVD process for the synthesis of TiO_2 films on glass slides is shown in **Figure 1**. Firstly, titanium tetra isopropoxide (TTIP, Ti [OCH $(CH_3)_2]_4$, 97%, Sigma-Aldrich)

was used as the precursor for Ti. The 20 ml of TTIP was diluted in absolute ethanol (200 ml). Then, the TTIP was vaporized at 80 °C in a bubbler using argon gas. The volatilized TTIP solvent and the mixture of argon, oxygen and nitrogen gases were introduced into a quartz tube (100 cm length, I.D. = 4.4 mm), maintained at a constant temperature of 530°C for 60 or 90 min. The films synthesized for 60 and 90 min will be labeled as "60-min film" and "90-min film", respectively. The temperature and time used to produce the TiO_2 films are within the optimum to produce transparent films without contamination from residual carbon. The flow rate of O_2:N_2:Ar was 500:55:200 sccm. Ar was used as a gas carrier. N_2 was used as an additional gas carrier producing extra thrust for bubbling the ethanol solution. The presence of O_2 can lower activation energy of TIPP dissociation for TiO_2 formation by ultrasonication [16-17]. The glass slides used as the substrates were pre-treated in ethanol for 30 min prior to the deposition step. Then, the glass slide was placed on an alumina boat located 30 cm away from the side of the tube where the gases entered.

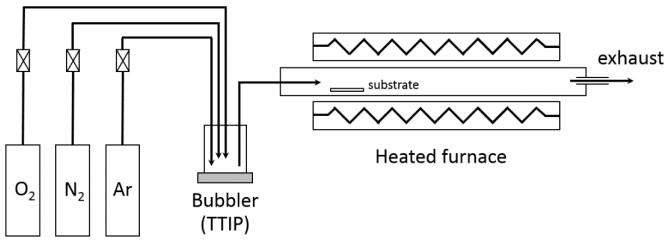

Figure 1 A schematic diagram of the CVD-coating of TiO_2

Characterization

The details of surface morphology and element composition were obtained using FE-SEM from JEOL JSM-6335F, EDS and AFM from a Nanoscope IIIa (Digital Instrument, USA). The transmittances and band gap of the two samples were obtained using a UV-vis spectrophotometer (Perkin Elmer Lambda 1050) at a wavelength of 300-700 nm. The crystalline phase of the TiO_2 thin film was determined using Raman spectroscopy with an excitation wavelength of 532 nm with a HORIBA Jobin-Yvon T64000 Raman spectrometer.

Photocatalytic degradation of methylene blue

The photocatalytic performances of the two samples were evaluated by the photodegradation of methylene blue as the model dye solution under simulated solar light irradiation. The 2 cm × 3 cm films of the photocatalyst were placed in a reactor with 100 mL of a 1.5×10^{-5} M aqueous MB solution for one hour to reach an adsorption-desorption equilibrium before being subjected to illumination. A simulated solar illumination lamp (Halogen lamp 50 W, Philips) was used as a light source. Then, the reactor system was irradiated for 6 h with periodic measurements of the remaining solution (15 minute intervals). This monitoring proceeded by collecting 3 mL of the solution. The absorbance spectrum was measured and the solution was returned to the reactor. The concentrations of MB were estimated based on the absorbance at 664 nm. The percentage of dye degradation was calculated from the following equation:

$$\%\text{Degradation}=\left(\frac{C_0-C_t}{C_0}\right)\times 100 \ ,$$

where C_0 is the initial concentration of dye and C_t is the concentration of dye after irradiation time t.

RESULTS AND DISCUSSION

Surface morphology

The surface tomography of the 60-min and 90-min films was investigated by AFM as shown in **Figure 2(a)** and **2(b)**. The surface roughness of the 60-min and 90-min films was measured to be 6.014 ± 0.575 and 2.192 ± 0.747 nm, respectively. The particle size of the 60-min film was 87.1 ± 18.6 nm. For the 90-min film, the AFM image can not distinguish particles in the film. The particle size for this film could not be determined. SEM morphological images of the TiO_2 films in **Figure 3(a) and 3(c)** display the agglomeration of TiO_2 nanoparticles, forming the thin film TiO_2. Estimated particle sizes of the 60-min and 90-min films are 87.1 ± 18.6 and 3.19 ± 0.15 nm, respectively. The cross section SEM images are also shown in **Figure 3**. The EDS line profiles are useful for distinguishing the region of the TiO_2 films from the glass substrates. The thicknesses of the 60-min and 90-min films were measured to be 3.19 ± 0.15 and 3.19 ± 0.15 μm, respectively. The particle size estimated from AFM is larger than that estimated from SEM because of the nature of tip movement during scanning.

Raman Spectroscopy

Raman spectroscopy was an important technique to examine the crystal phase of TiO_2 [18]. **Figure 4** shows the Raman spectra from

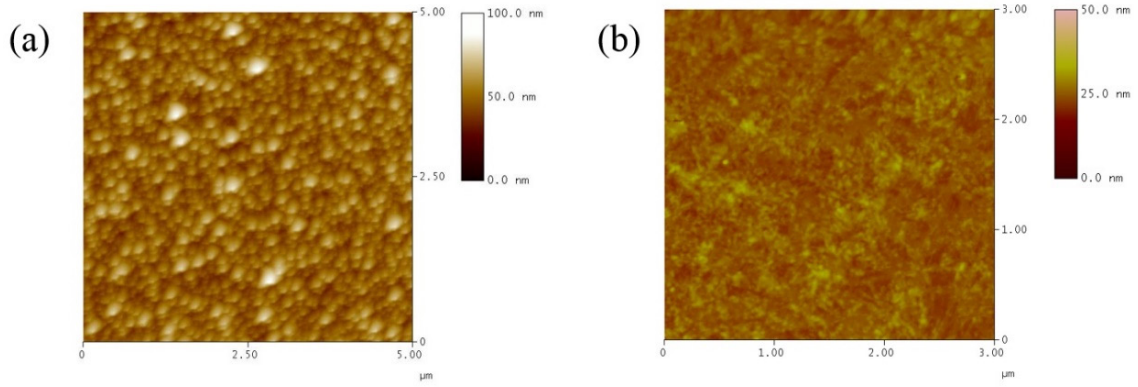

Figure 2 AFM images of TiO_2 thin films synthesized at 530°C for (a) 60 min and (b) 90 min.

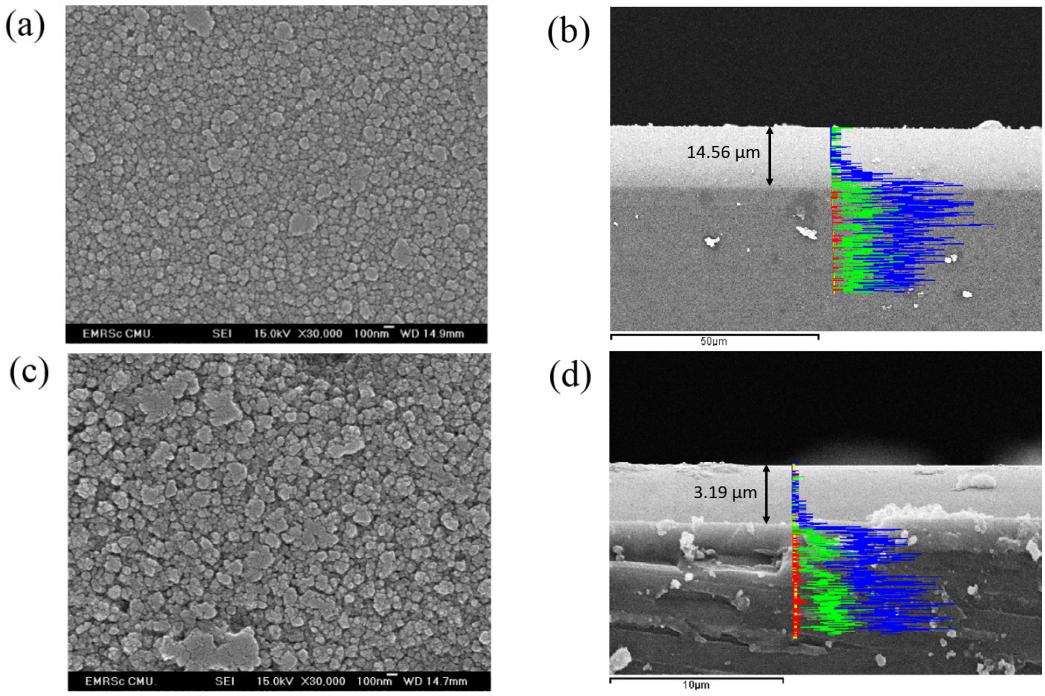

Figure 3 SEM images of the surface and the cross section of TiO_2 thin films synthesized at 530°C for 60 min (a, b) and for 90 min (c, d). EDS line profiles are shown in (c) and (d), where red is titanium, green is oxygen, and blue is silicon.

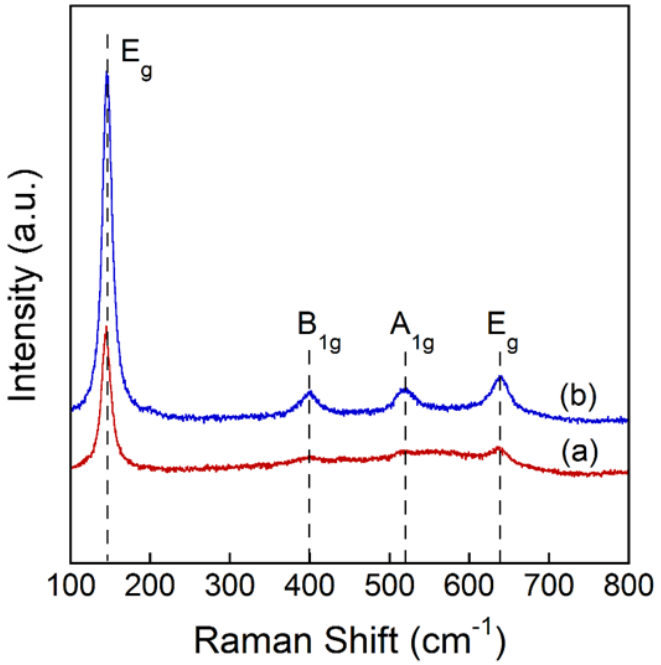

Figure 4 Raman spectra of TiO_2 thin films synthesized at 530°C for (a) 60 min and (b) 90 min.

the 60-min and 90-min films. The strong Raman peaks at around 145, 401, 521 and 640 cm^{-1} in **Figure 4(b)** can be assigned to anatase TiO_2 without rutile or brookite phases [19-20]. The weak-signal peaks in **Figure 4(a)** can be attributed to the non-well-crystallization of anatase TiO_2. The transmittance spectra of the 60-min and 90-min films are shown in **Figure 5(a)**. The absorption margins dramatically shift from 353 nm for the 60-min film to 382 nm for the 90-min film. The energy gap of TiO_2 films can be calculated from the relation,

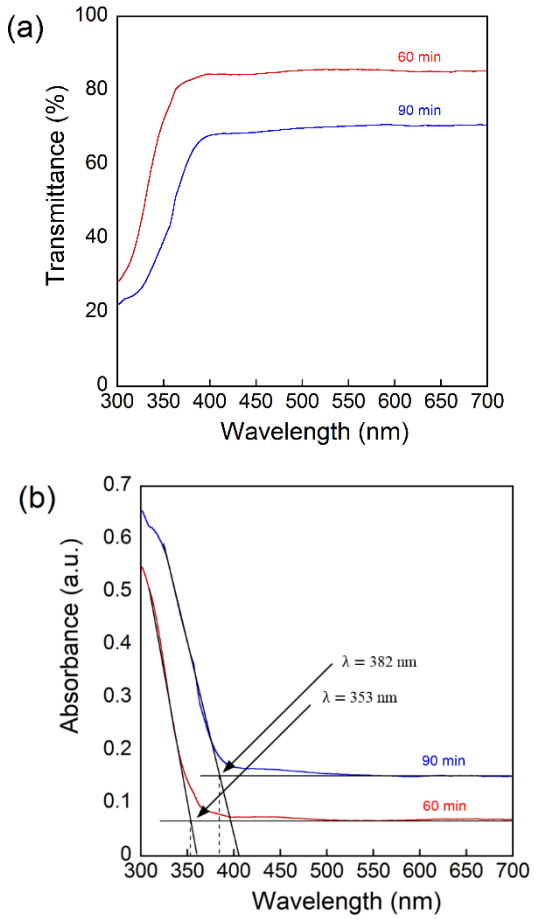

Figure 5 (a) Transmittance and (b) absorbance of TiO_2 thin films synthesized at 530°C for 60 and 90 min.

$E = hc/\lambda$ where h is the Planck constant, c is the speed of light, and λ is the cut-off wavelength in the plot of absorbance. The band gaps of the 60-min and 90-min films were calculated to be 3.51 eV and 3.25 eV, respectively.

Photocatalytic performances

The photodegradation of MB using the 60-min and 90-min films under simulated solar light irradiation is illustrated in **Figure 6(a)**. A slight decrease in MB concentration was observed in the presence of the 60-min and 90-min films. The methylene blue was degraded approximately 15% and 19% by the 60-min and 90-min films, respectively. It is notable that the 90-min film displays a better degradation effect than the 60-min film.

To quantitatively analyze the reaction kinetics of MB degradation, the experimental data in **Figure 6(a)** was fitted by the Langmuir–Hinshelwood model [21], as expressed by the following equation: $-dC/dt = k_{app}t$, where the C is the concentration and k_{app} is the apparent reaction rate constant. Integration of the above equation will lead to the concentration as a function of time: $-\ln(C/C_0) = k_{app}t$. Using such kinetic analysis, it is evident that the photocatalytic degradation of MB follows the pseudo-first order kinetic shown in **Figure 6(b)**. From the linear fitting curves of $-\ln(C/C_0)$ versus irradiation time, t, the MB degradation rate constants k_{app} were extracted to be 4.0×10^{-4} and 6.0×10^{-4} min^{-1} for the 60-min and 90 min films, respectively. The 90-min film exhibited the higher value of k_{app} than the 60-min film.

Discussion

The decrease of TiO_2 film thickness with increasing operating time likely attributes to the agglomeration of the particles in the TiO_2 films. In addition, the impurity atoms of Si and/or B from borosilicate glass might diffuse into TiO_2 films at the high temperature of 530°C. The amount of the impurity atoms in TiO_2 films are very small. Thus, their effect on optical and chemical properties of the films would be limited. Therefore, the quantum size effect and crystallinity of the TiO_2 films would mainly contribute to the deviation in band gap between 60-min TiO_2 and 90-min TiO_2 films. The large band gap in 60-min TiO_2 film can suppress the recombination rate for the photogenerated electron-hole pairs and enhance photocatalytic performance of the TiO_2 films. However, the 60-min film displayed less degradation of MB, reflected in a lower apparent reaction rate. This inconsistency can be explained by considering crystallinity of the film [18]. According to the results of Raman spectroscopy, the prominent peaks of the 90-min film have higher signal-to-noise ratios than the 60-min film. This indicates a better crystallinity in the film synthesized for the longer time. Furthermore, the anatase-phase TiO_2 is the most efficient phase of TiO_2 for MB degradation under simulated solar light irradiation [22-23]. We suggest that the effects of completeness are the main factors for the difference in photodegradation efficiency of MB solutions. From the SEM images, the thickness of the 60-min film is larger than that of the 90-min film. In contrast, the particle size of the 60-min film is smaller than that of the 90-min film. This can be understood by the agglomeration of particles at the longer synthesizing time. The contradiction of film thickness between the 60-min and 90-min films can be explained by the decrease of TTIP concentrations during the bubbling process. The amount of visible white vapor flowing into the quartz tube for the 90-min films was less than the initial deposition for the 60-min films. This could be a reason for the reduction of the

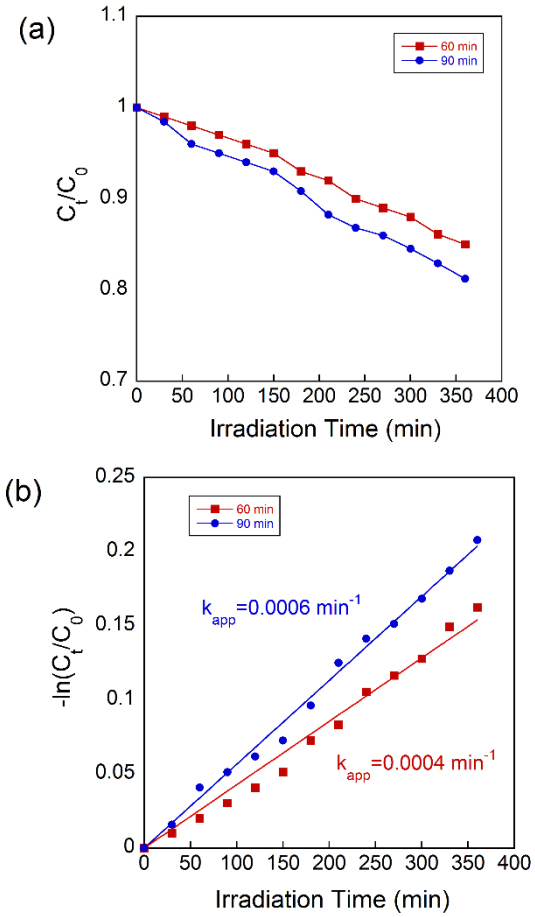

Figure 6 (a) Photodegradation efficiencies of MB solution as a function of irradiation time and (b) pseudo-first-order reaction kinetic ($-\ln(C_t/C_0)$) versus irradiation time in the presence of MB photolysis, TiO_2 (60 min, red square), and TiO_2 (90 min, blue circle) prepared by CVD process at 530°C.

90-min film thickness.

The thickness of the 60-min and 90-min films was 14.56 and 3.19 μm, respectively, while the energy band gap of these was 3.51 and 3.25 eV. The relation of an increase of band gap with a decrease of film thickness has not been reported in TiO_2 films prepared by sol-gel [5-6, 24] and dip-coating methods [25]. This inconsistency between band gap and film thickness may come from the different level of crystallinity of the TiO_2. The degradation levels of MB agree well with the band gap of TiO_2 films, in that the lower-band-gap 90-min films showed more MB degradation. Our result implies that the crystallinity of TiO_2 films should be considered for photocatalytic efficiency in water purification.

CONCLUSION

TiO_2 films were successfully synthesized on glass slides by chemical vapor deposition at the temperature of 530°C. The TiO_2 film synthesized for 90 min showed greater degradation of methylene blue than the one prepared for 60 min even with a smaller band gap. The measured band gaps of the films prepared for 60 and 90 min were 3.51 and 3.25 eV, respectively. The crystallinity of the films synthesized for 90 min is much better than that for 60 min. We propose that the

crystallinity of TiO_2 films is an important factor to consider in the photodegradation of methylene blue, not only their band gap.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the financial support from the Thailand Research Fund (TRF) (No. IRG5780013); the Materials Science Research Center, Faculty of Science and Graduate School, Chiang Mai University. Sumet Sakulsermsuk would like to thank Chiang Mai University for funding.

REFERENCES

1. O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.*, **2004**, 32, 42-90.
2. X. Li, W. Zheng, G. He, R. Zhao, D. Liu, Morphology control of TiO_2 nanoparticle in microemulsion and its photocatalytic property, *ACS Sustainable Chem. Eng.*, **2014**, 2, 288-295.
3. L. Ren, Y. Li, J. Hou, X. Zhao, C. Pan, Preparation and enhanced photocatalytic activity of TiO_2 nanocrystals with internal pores, *ACS Appl. Mater. Interfaces*, **2014**, 6, 1608-1615.
4. M. Krivec, K. Žagar, L. Suhadolnik, M. Čeh, G. Dražič, Highly efficient TiO_2 based microreactor for photocatalytic applications, *ACS Appl. Mater. Interfaces*, **2013**, 5, 9088-9094.
5. M. Covei, L. Predoana, P. Osiceanu, J.M.C. Moreno, M. Anastasescu, S. Preda, M. Nicolescu, M. Gartner, M. Zaharescu, Niobium/Vanadium doped TiO_2 multilayered sol-gel films: Structure, surface chemistry and optical properties, *Ceram. Int.*, **2016**, 42 13805-13811.
6. M. Dutaa, S. Simeonov, V. Teodorescu, L. Predoana, S. Preda, M. Nicolescu, A. Marin, D. Spasov, M. Gartner, M. Zaharescu, A. Szekeres, Structural and electrical properties of Nb doped TiO_2 films prepared by the sol–gel layer-by-layer technique, *Mater. Res. Bull.*, **2016**, 74, 15-20.
7. Y.-J. Liou, P.-T. Hsiao, L.-C. Chen, Y.-Y. Chu, H. Teng, Structure and electron-conducting ability of TiO_2 films from electrophoretic deposition and paste-coating for dye-sensitized solar cells, *J. Phys. Chem. C*, **2011**, 115, 25580-25589.
8. I. Gonzalo-Juan, A.J. Krejci, J.H. Dickerson, Toward dynamic control over TiO_2 nanocrystal monolayer by monolayer film formation by electrophoretic deposition in nonpolar solvents, *Langmuir*, **2012**, 28, 5295-5301.
9. M. Hashizume, T. Kunitake, Preparation of self-supporting ultrathin films of titania by spin coating, *Langmuir*, **2003**, 19, 10172-10178.
10. D.Y. Lee, J.-T. Kim, J.-H. Park, Y.-H. Kim, I.-K. Lee, M.-H. Lee, B.-Y. Kim, Effect of Er doping on optical band gap energy of TiO_2 thin films prepared by spin coating, *Curr. Appl. Phys.*, **2013**, 13, 1301-1305.
11. V. Bukauskas, S. Kaciulis, A. Mezzi, A. Mironas, G. Niaura, M. Rudzikas, I. Šimkienė, A. Šetkus, Effect of substrate temperature on the arrangement of ultra-thin TiO_2 films grown by a dc-magnetron sputtering deposition, *Thin Solid Films*, **2015**, 585, 5–12.
12. S. Peng, Y. Yang, G. Li, J. Jiang, K. Jin, T.T. Yao, K. Zhang, X. Cao, Y. Wang, G. Xu, Effect of N_2 flow rate on the properties of N doped TiO_2 films deposited by DC coupled RF magnetron sputtering, *J. Alloy Compd.* **2016**, 678, 355-359.
13. M.Y. Song, S. Chin, J. Jurng, Y.-K. Park, One step simultaneous synthesis of modified-CVD-made V_2O_5/TiO_2 nanocomposite particles, *Ceram. Int.*, **2012**, 38, 2613–2618.
14. S. Chaudhary, A. R. Head, R. Sanchez-de-Armas, H. Tissot, G. Olivieri, F. Bournel, L. Montelius, L. Ye, F. Rochet, J.-J. Gallet, B. Brena, J. Schnadt, Real-time study of CVD growth of silicon oxide on rutile TiO_2(110) using tetraethyl orthosilicate, *J. Phys. Chem. C.*, **2015**, 119, 19149-19161.
15. H. Lee, M.Y. Song, J. Jurng, Y.-K. Park, The synthesis and coating process of TiO_2 nanoparticles using CVD process, *Powder Technol.*, **2011**, 214, 64-68.
16. S. Yamauchi, Y. Imai, Plasma-assisted chemical vapor deposition of TiO_2 thin films for highly hydrophilic performance, *Cryst. Struct. Theory Appl.*, **2013**, 2, 1-7.
17. K.-H. Ahn, Y.-B. Park, D.-W. Park, Kinetic and mechanistic study on the chemical vapor deposition of titanium dioxide thin films by in situ FT-IR using TTIP, *Surf. Coat. Technol.*, **2003**, 171, 198-204.
18. Z. Wang, S. Elouatik, G.P. Demopoulos, Understanding the phase formation kinetics of non-crystalline kesterite deposited on mesoscopic scaffolds via in situ multi-wavelength Raman-monitored annealing, *Phys. Chem. Chem. Phys.*, **2016**, 18, 29435-29446.
19. W. Thongsuwan, T. Kumpika, P. Singjai, Photocatalytic property of colloidal TiO_2 nanoparticles prepared by sparking process, *Curr. Appl. Phys.*, **2008**, 8, 563-568.
20. I.O. Mazali, A.G. Souza Filho, B.C. Viana, J. Mendes Filho, O.L.J. Alves, Size-controllable synthesis of nanosized-TiO_2 anatase using porous Vycor glass as template, *Nanopart. Res.*, **2006**, 8, 141.
21. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B: Environ.*, **2001**, 31, 145-157.
22. D.P. Macwan, P.N. Dave, S. Chaturvedi, A review on nano-TiO_2 sol-gel type syntheses and its applications, *J. Mater. Sci.*, **2011**, 46, 3669-3686.
23. A. Fujishima, X. Zhang, Titanium dioxide photocatalysis: present situation and future approaches, *C. R. Chimie*, **2006**, 9, 750-760.
24. P. Chrysicopoulou, D. Davazoglou, Chr. Trapalis, G. Kordas, G. Optical properties of very thin (<100 nm) sol-gel TiO_2 films, *Thin Solid Films*, **1998**, 323, 188-193 (1998).
25. M. Sreemany, S. Sen, A simple spectrophotometric method for determination of the optical constants and band gap energy of multiple layer TiO_2 thin films, *Mater. Chem. Phys.*, **2004**, 83, 169-177.