THE INFLUENCE OF ETHANOL ON THE MORPHOLOGY, PHASE AND CRYSTAL SIZE OF THE SOL-GEL DIP COATING TiO_2 THIN FILMS

S.A. Yazid[1], Z.M. Rosli[2], J.M. Juoi[1] and T. Moriga[3]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Mechanical and Manufacturing Engineering Technology,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.

[3]Tokushima-UTeM Academic Centre,
Tokushima University, 2-1 Minami-Josanjima,
770-8506, Tokushima, Japan.

Corresponding Author's Email: [2]zmr@utem.edu.my

Article History: Received 20 September 2018; Revised 10 July 2019; Accepted 2 October 2020

ABSTRACT: The effect of ethanol and its concentration on the characteristic of a sol-gel TiO_2 thin film was investigated. Three concentrations (M) of 0 M (without solvent), 3 M and 5 M were prepared by varying ethanol to water ratio in a sol of titanium (IV) isopropoxide as a precursor. A glass slide substrate was dipped into the sol for ten times to produce layers of TiO_2 films before finally heated at 500°C for 1-hour. Analysis on the TiO_2 surface morphology was obtained using Scanning Electron Microscope (SEM). Phases and crystal size of the TiO_2 films were analyzed using X-ray diffraction (XRD) and reinforce with Raman Spectroscopy (RS). SEM result showed that surface cracks observed for all deposited TiO_2 film. At 5M of ethanol, the cracks produced were more severe causing films delamination. Mixture of anatase, brookite and rutile phases were identified only with TiO_2 thin film of 0M of ethanol. The effect of ethanol on crystal size, however, was insignificant due to similar crystallite size (~17.29 nm) obtained at 3 M and 5 M. Hence, the development of TiO_2 phases without the use of solvent is emboldening to explore as an attempt toward producing ecological photocatalytic materials via green process.

KEYWORDS: *TiO_2 Thin Film;, Sol-Gel; Dip Coating; Solvent Free*

1.0 INTRODUCTION

TiO_2 is the most exploited photocatalytic materials in many industrial applications because of its low-cost process, high efficiency, nontoxicity as well as chemically and biologically stable [1–3]. Fabricating TiO_2 thin films is amenable due to surface contamination and has been the subject of study for many years [4]. Sol-gel technique is one of the many exemplars and the most established and functional methods in synthesizing TiO_2 because it offers many advantage such as low temperature processing, easy to produce large coating area, provides high surface homogeneity and most importantly has a low cost [5].

Yet, there are few other critical factors that must be considered during synthesizing sol-gel TiO_2 film such as the choice of precursor, type of solvent, the role of acid and water to produce the desired coating's quality and characteristic [6–8]. For example, the effect of solvent on TiO_2 thin films fracture formation has been the focus of study by Bockmeyer and Löbmann [9]. An image processing software were used to evaluate the extent of crack damage and crack time formation that develop when different solvents were used. They had confirmed that film crack due to tensile stress can develop during the thermal treatment. These cracks will always appear if the tensile stress and cooling exceeds the stability or the inner coherence of the materials. The nature of solvent is also testified can influence the rate of hydrolysis and condensation. Larger particles with rough surface films had deposited as the reaction rates of hydrolysis and condensation increases whereas lower reaction rate tend to form columnar particles with a smooth surface [10].

TiO_2 phases were also reported can be influenced depending on the choice of solvent used. In the work of Edusi et al. [11], they used aerosol-assisted CVD technique to deposit TiO_2 phases and attained that solvents like ethanol or propanol will lead to anatase phases while rutile phase preferred when methanol was used. They concluded that, the use of dissimilar solvents can have a direct effect in governing the TiO_2 phases when deposited as a film [11]. Using ethanol as solvent was also claimed can retard the anatase phase formation [12]. Meanwhile, Tryba et al. [13] found that the solubility of ethanol as an organic solvent is low when an alkoxide precursor was used. As a result, it can hinder the development of important TiO_2 phases and even lead to agglomeration in nanoparticles scale [13]. However, high amount of solvent can impact serious risk to the environment and health [14]. Hence, in this paper, the role of solvent becomes the considered subject to seek for optimum solvent concentration in promoting TiO_2 phases and crystal size in sustaining green process.

2.0 METHODOLOGY

Figure 1 shows process flow for preparing the sol-gel dip coating TiO_2 thin film. Deionized water,Titanium (IV) isopropoxide (TTiP) (Sigma Aldrich Co.), hydrochloric acid (HCl) and ethanol (95%), used as a hydrolysis medium precursor, catalyst and solvent respectively. The TiO_2 sols were prepared from two different solutions at room temperature and labelled as Sol A and Sol B. For the Sol A, a mixture of ethanol and deionized water was stirred for 30 minutes, followed by dropping 0.4 ml of HCl. Simultaneously, TTiP and ethanol were stirred briskly for 30 minutes to produce Sol B. Then, mixed both solutions and stirred constantly for 3 hours before kept for 48 hours. Varied of ethanol concentrations for preparing the TiO_2 sol shown in Table 1.

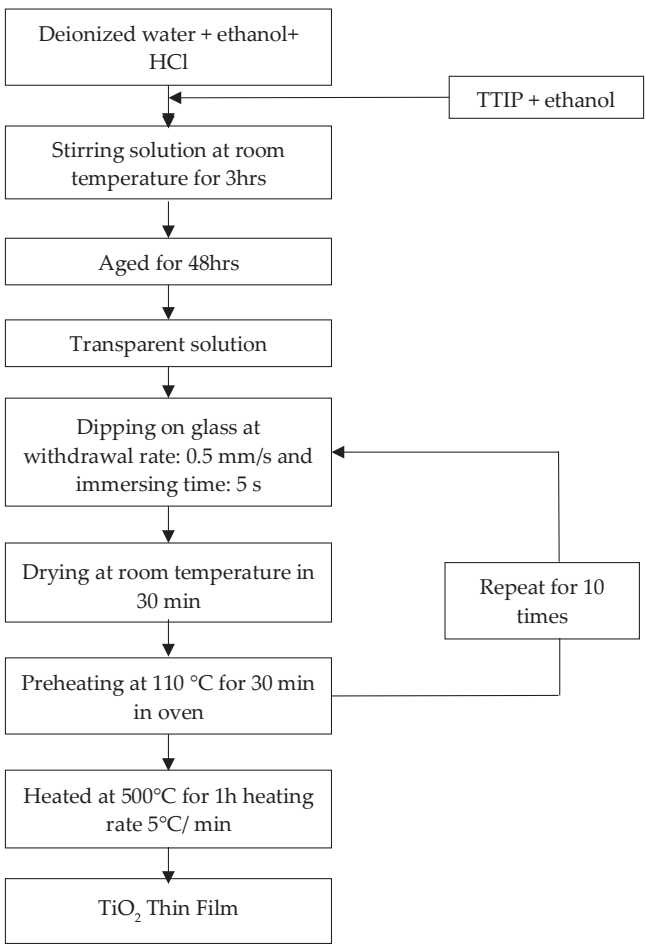


Figure 1: Process flow for preparing the sol-gel dip coating TiO_2 thin film

Table 1: Varied of ethanol concentrations for preparing the TiO_2 sol

Sol	Volume (ml)			Ethanol (M)
	DI	TTiP	HCl	
1	32	2	0.4	0
2	32	2	0.4	3
3	32	2	0.4	5

Dip coater was used during dipping process between glass substrates and TiO_2 sols with a dipping speed of 30 mm/min and 5s of dwelling time. Then, coated glass was left to dry for 30 minutes followed by oven dried at 110°C for another 30 minutes. Annealing process was carried out at 500°C for one hour in a furnace with a heating rate of 5 °C/min. Then, dipping layers were set for ten times to obtained desired TiO_2 thin film [15]. Surface morphologies of the deposited TiO_2 thin film were analyzed using SEM (Carl Zeiss EVO 50). TiO_2 phases were detected with X-ray diffraction techniques of an X'Pert Pro model with Cu K-Alpha of 1.54060 Aº with generator settings at 30 mA and 40 kV in the range of 10-90° respectively. The crystallite size of the TiO_2 thin films was calculated from the XRD line broadening using Debye-Scherrer's formula such as

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

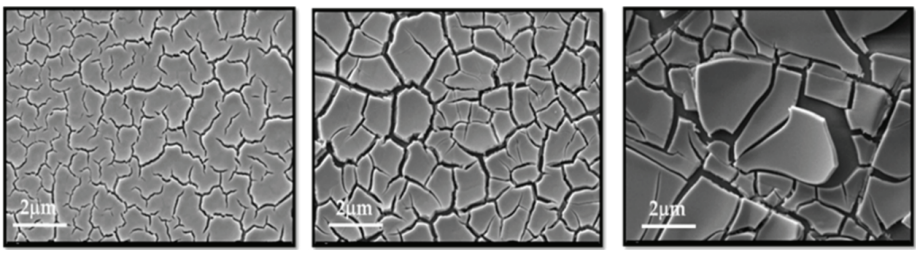
where D is the crystallite size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; and β is the line width at half-maximum height. Affirmation of the TiO_2 phases were confirmed by Raman spectroscopy (UniRAM-3500) with laser excitation of λ= 532 nm wavelength.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology

Comparison on the surface morphology of the deposited TiO_2 thin film against ethanol dilutions were shown in Figure 2. As seen in the figure, cracks were visible for all deposited TiO_2 film. At 5M of ethanol, cracks produced were more severe causing films delamination and thus, forming island of TiO_2 film flakes. These cracks were resulted from film shrinkage and tensile stress due to excessive water and rapid solvent loss during the drying process [16].

As the ethanol concentration increase, the amount of solvent trapped or associated in the films were also increased. Upon thermal treatment, vast amount of solvent was forced to evaporate rapidly. Therefore, the TiO_2 films produced at higher solvent concentration produced more severe cracks with delaminated films than the TiO_2 film produced at low solvent concentration.



(a) (b) (c)

Figure 2: SEM surface morphology of the deposited TiO_2 thin films corresponding to ethanol concentrations corresponding to (a) 0M of Ethanol, (b) 3M of Ethanol and (c) 5M of Ethanol

3.2 The Deposited TiO_2 Phases

Figure 3 shows the XRD spectrum of the TiO_2 thin films against various ethanol concentrations after annealed at 500°C for 1h. Obviously, each of the TiO_2 thin films produced from 0M, 3M and 5M of ethanol exposed anatase (1 0 1) as the dominant phase detected especially at an angle of $\theta = 25°$. Rutile phase (110) was also identified to co-exist with anatase but only when ethanol was not used as a solvent.

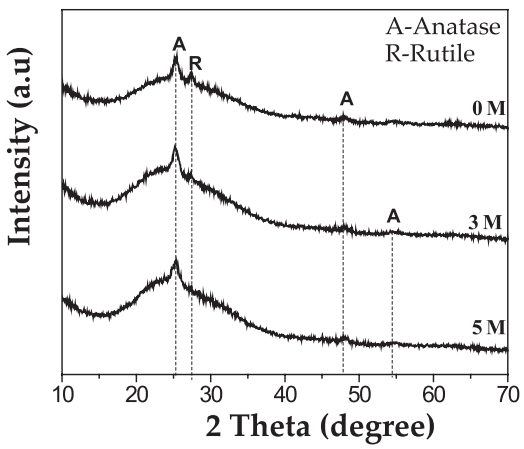


Figure 3: XRD pattern of the deposited TiO_2 thin films against ethanol concentrations

As the solvent concentration increased, rutile's intensity was found to gradually disappear. Solvent is known for its capability to slow down the rate of hydrolysis and condensation [17]. Thus, increasing ethanol concentration will further reduce the hydrolysis and condensation rate and thus, can lead to the disappearance of crystalline phases and produced amorphous TiO_2. This performance is caused by the stearic hindrance attained by the ethanol when it is adsorbed on the surface of titania particles, thus restraining the hydrolysis of the alkoxide and further crystallization [18]. In the case of 0M of ethanol, steric hindrance will not occur. Therefore, a stronger nucleophilic of H2O and alkoxide molecules have more chance to react causing more alkoxyl group from the alkoxide to be substituted by the hydroxyl group from water. This could explain the reason of an easy establishment of phases such as anatase and rutile during the absence of ethanol as solvent.

3.3 Raman Spectrum and Analysis

Figure 4 shows the Raman spectrum of the deposited TiO_2 thin films. General, there are six features of active bands for the Raman spectrum of anatase which are ($A_{1g} + 2B_{1g} + 3E_g$). Brookite has thirty-six active bands of ($9A_{1g} + 9B_{1g} + 9B_{2g} + 9B_{3g}$) and rutile have four Raman actives bands of ($A_{1g} + B_{1g} + B_{2g} + E_g$) [19]. Thus, for all TiO_2 thin film samples, Raman bands emerged at 144, 196, 397, 514, and 638 cm^{-1} are very distinctive and can be allocated to anatase phase. For the 0M of ethanol, the Raman bands emerged at 432 cm^{-1} can be assigned to rutile phase but then gradually disappeared as increasing the ethanol concentration. There are also others Raman bands noticeable at 248 and 322 cm^{-1} especially for the 0 M of ethanol which can be allocated to the brookite phases. However, the intensities of the Raman spectrum for the brookite and rutile are negligible and slowly disappeared as increasing the ethanol concentrations. The same pattern also observed for the XRD when analyzing the rutile phase. Unlike XRD, Raman spectroscopy have been proved can work best for most of crystalline oxide and even amorphous oxide that have a wide range of bond angles, broadening peaks and featureless signal [20]. Therefore, the brookites phases were distinguishable with Raman as compare to XRD. The main reason of the undetected brookites phases with the XRD is not really clear now but could be related to the very small grain produced (such as < 5 nanometer) [21]. Furthermore, the disappearance of brookite phase as the ethanol concentration increased can also be related to the stearic hindrance exerted by the ethanol as explained before.

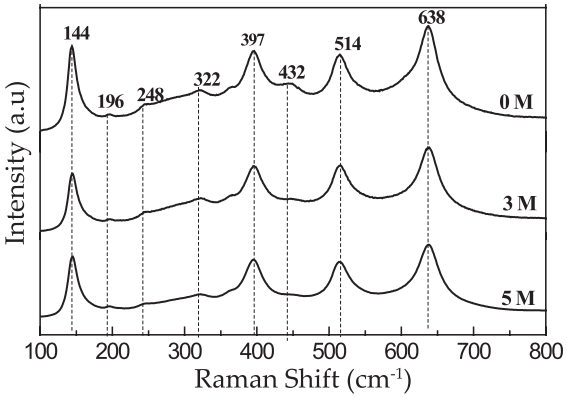


Figure 4: Raman spectrum of the deposited TiO_2 thin films against ethanol concentrations

3.4 Crystal Size

Figure 5 shows the crystal size of the deposited TiO_2 thin films produced against ethanol concentrations calculated using Debye-Scherrer's equation. Only anatase existed at angle of $\theta = 25°$ and rutile existed at an angle $\theta = 27°$ were reckoned in this work. For the TiO_2 thin films deposited with 0M of ethanol, the crystal size of anatase and rutile phases were found to be 12.35 nm and 21.71 nm respectively. Meanwhile, the TiO_2 thin films deposited with 3M and 5M of ethanol, the anatase phases increased to a crystal size of 17. 29 nm for both respectively. Rutile phase was not detected and negligible at these ethanol concentrations. The effect of annealing temperatures on crystal size has been study by several researchers such as in the work of Sayilkan et al. [22]. They found that the crystal size increased as a function of annealing temperature. According to Zhang and Banfield [23], anatase is the most thermodinamically stable if the crystall size produced is less than 11 nm. Brookite is most stable if the crystall size produced is between 11 nm and 35 nm. Above 35 nm, rutile is the most stable. Since, a persistent temperature of 500°C was used throughout all ethanol concentrations, therefore, an extreme change in the crystal size was not observed in this work. Thus, the effect of solvent on crystal size in this work is insignificant.

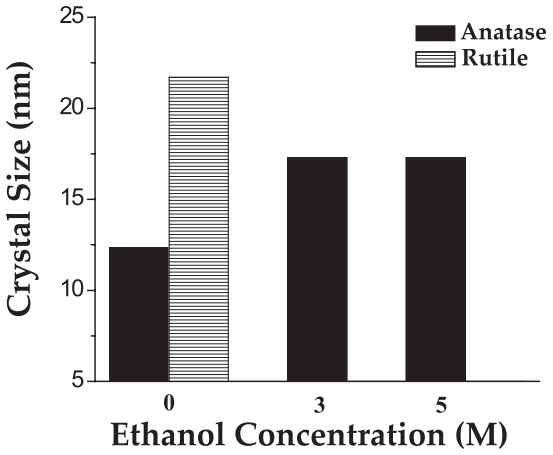


Figure 5: Bar chart of TiO_2 phases and its crystal size against ethanol concentrations

4.0 CONCLUSION

TiO_2 thin films were successfully deposited on glass slide substrate from three ethanol concentrations of 0M, 3M and 5M via sol gel dip coating technique. SEM results showed that cracks were visible for all deposited TiO_2 film. At 5M of ethanol, cracks produced were more severe causing films delamination. Anatase was the main phases emerged during all TiO_2 thin films. Rutile and brookite phases were found to presence only with 0M of ethanol. Even though brookite was not detected with XRD, Raman spectrum confirmed its existence. The crystal size of anatase increase to 17.29 nm but the crystal size of rutile and brookite diminished as the ethanol concentration increased. These observations lead to a suggestion that the use of ethanol as a solvent should be considered and controlled in designing the desired TiO_2 thin film phases. Depositing TiO_2 thin film with minimizes solvent or solvent free is believed to be industrially useful for supporting green process and green environment.

ACKNOWLEDGMENTS

The authors would like to thank the financial support given by the Ministry of Higher Education Malaysia and Universiti Teknikal Malaysia Melaka (UTeM) through Grant FRGS/1/2016/ TK05/FKP-AMC/F00319 and all SM4GT group members under Advanced Manufacturing Centre for the support given throughout this research.

REFERENCES

[1] M. Sahdan, M. Alias, J. Lias, M. Abdulmalek and N. Nayan, "Influence of different solvents on the formation of uniform titanium dioxide (TiO_2) thin film by sol-gel", *Applied Mechanics and Materials*, vol. 773-774, pp. 667–671 , 2015.

[2] O. Wiranwetchayan, S. Promnopas, T. Thongtem, A. Chaipanich and S. Thongtem, "Effect of alcohol solvents on TiO_2 films prepared by sol–gel method", *Surface and Coatings Technology: Part A*, vol. 326, pp. 310–315, 2017.

[3] C. Xu, G.P. Rangaiah and X.S. Zhao, "Photocatalytic Degradation of Methylene Blue by Titanium Dioxide: Experimental and Modeling Study", *Industrial and Engineering Chemistry Research*, vol. 53, no. 38, pp. 14641–14649, 2014.

[4] M.A. Musa, J.M. Juoi, M.R. Zulkifli, N.D. Johari and T. Moriga, " Effect of Degussa P25 content on the deposition of TiO_2 coating on ceramic substrate", *Journal of Advanced Manufacturing Technology*, vol. 12, no. 1(3), pp. 111-124, 2018.

[5] N. Fagnern, R. Leotphayakkarat, C. Chawengkijwanich, M.P. Gleeson, N. Koonsaeng and S. Sanguanruang, "Effect of titanium-tetraisopropoxide concentration on the photocatalytic efficiency of nanocrystalline thin films TiO_2 used for the photodegradation of textile dyes", *Journal of Physics and Chemistry of Solids*, vol. 73, no. 12, pp. 1483–1486, 2012.

[6] M.E. Simonsen and E.G. Søgaard, "Sol-gel reactions of titanium alkoxides and water: Influence of pH and alkoxy group on cluster formation and properties of the resulting products", *Journal of Sol-Gel Science and Technology*, vol. 53, no. 3, pp. 485-497, 2010.

[7] D.L. Marchisio, F. Omegna, A.A. Barresi and P. Bowen, "Effect of mixing and other operating parameters in sol - gel processes", *Journal of Sol-Gel Science and Technology*, vol. 47, no. 19, pp. 7202-7210, 2008.

[8] D.A.H. Hanaor and C.C. Sorrell, "Review of the anatase to rutile phase transformation", *Journal of Materials Science*, vol. 46, no. 4, pp. 855–874 , 2011.

[9] M. Bockmeyer and P. Löbmann, "Crack formation in TiO_2 films prepared by sol-gel processing: Quantification and characterization", *Thin Solid Films*, vol. 515, no. 13, pp. 5212–5219, 2007.

[10] L. Hu, T. Yoko, H. Kozuka and S. Sakka, "Effects of solvent on properties of sol-gel-derived TiO_2 coating films", *Thin Solid Films*, vol. 219, no. 1-2, pp. 18-23, 1992.

[11] C. Edusi, G. Sankar and I.P. Parkin, "The effect of solvent on the phase of titanium dioxide deposited by aerosol-assisted CVD", *Chemical Vapor Deposition*, vol. 18, no. 4-6, pp. 126–132, 2012.

[12] M. Alzamani and E. Eghdam, "Sol–gel synthesis of TiO 2 nanostructured film on SiO 2 pre-coated glass with a comparative study of solvent effect on the film properties", *Journal of Sol-Gel Science and Technology*, vol. 80, no. 1, pp. 19-29, 2016.

[13] B. Tryba, M. Tygielska, C. Colbeau-Justin, E. Kusiak-Nejman, J. Kapica-Kozar, R. Wrobel, G. Zolnierkiewicz and N. Guskos, "Influence of pH of sol-gel solution on phase composition and photocatalytic activity of TiO_2 under UV and visible light", *Materials Research Bulletin*, vol. 84, pp. 152–161, 2016.

[14] N.D. Johari, M.R. Zulkifli, J.M. Juoi and S.A. Yazid, "Comparison on the TiO_2 crystalline phases deposited via dip and spin coating using green sol–gel route", *Journal of Materials Research and Technology*, vol. 8, no. 2, pp. 2350-2358, 2019.

[15] A.R. Nurhamizah, M.R. Zulkifli, J.M. Juoi and M.A. Musa, "Effect of dipping numbers on the crystalline phase and microstructure of Ag-TiO_2 coating", *Key Engineering Materials*, vol. 694, pp. 133-137, 2016.

[16] M.A. Musa, J. M. Juoi, M. R. Zulkifli and N. Masrom, "Influence of HCl content and ageing time on TiO_2 coating formation in acidic sol-gel solutions", *Key Engineering Materials*, vol. 694, pp. 138–142 , 2016.

[17] V. Loryuenyong, K. Angamnuaysiri, J. Sukcharoenpong and A. Suwannasri, "Sol-gel template synthesis and photocatalytic behaviour of anatase titania nanoparticles", *ScienceAsia*, vol. 38, no. 3, pp. 301-306, 2012.

[18] J.C. Yu, J. Yu, L. Zhang and W. Ho, "Enhancing effects of water content and ultrasonic irradiation on the photocatalytic activity of nano-sized TiO_2 powders", *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 148, no. 1-3, pp. 263–271, 2002.

[19] M. Rezaee, S.M.M. Khoie and K.H. Liu, "The role of brookite in mechanical activation of anatase-to-rutile transformation of nanocrystalline TiO_2: An XRD and Raman spectroscopy investigation", *CrystEngComm*, vol. 13, no. 16, pp. 5055–5061, 2011.

[20] L.Z hao, Y. Yu, L. Song, X. Hu and A. Larbot, "Synthesis and characterization of nanostructured titania film for photocatalysis", *Applied Surface Science*, vol. 239, no. 3-4, pp. 285–291, 2005.

[21] K. Eufinger, D. Poelman, H. Poelman, R. De Gryse and G.B. Marin, *Thin solids films: Process and Applications*. Kerala: Transworld Research Network, 2009.

[22] F. Sayilkan, M. Asilturk, H. Sayilkan, Y. Onal, M. Akarsu and E. Arpac, "Characterization of TiO_2 synthesized in alcohol by a sol-gel process: The effects of annealing temperature and acid catalyst", *Turkish Journal of Chemistry*, vol. 29, no. 6, pp. 697–706, 2005.

[23] H. Zhang and J.F. Banfield, "Understanding polymorphic phase transformation behavior during growth of nanocrystalline aggregates: Insights from TiO_2", *Journal of Physical Chemistry B*, vol. 104, no. 15, pp. 3481–3487, 2000.