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Controlling the particle size of nanobrookite TiO_2 thin films

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ABSTRACT

In this study, pure nanobrookite TiO_2 thin films were successfully deposited on glass substrates with the spin-coating method using titanium butoxide and acetic acid. The particle size of TiO_2 films was controlled by the water:AcAc volume ratio. This study shows that it is possible to obtain single oriented pure brookite films. The structural and optical properties of the nanobrookite TiO_2 thin films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), ultraviolet–visible spectroscopy (UV–vis), scanning electron microscopy (SEM), spectrophotometer (NKD), and Fourier transform infrared spectrometer (FTIR).

1. Introduction

TiO_2 (titania), which is used in many researches, is a semiconductor material that has a wide band gap, high refractive index and high dielectric constant [1,2]. Nanostructured TiO_2 films have a number of applications in electronic devices such as solar cells, sensing applications, electrochromic devices, hydrogen storage and photocatalytic systems [3,4].

Many methods have been used to prepare nanostructured TiO_2 such as magnetron sputtering deposition, sol–gel deposition, and chemical vapor deposition (CVD) [4].

TiO_2 has three crystalline forms: brookite, anatase and rutile. The crystal system of brookite structures is orthorhombic. On the other hand, rutile and anatase structures are tetragonal. These crystal structures are composed of TiO_6 (octahedra) by edges and corners. In the structure of anatase, each octahedron is linked with 8 neighbor octahedrons (four sharing an edge and four sharing a corner) [5]. In rutile, each octahedron linked with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) [5]. The structure of brookite is framed by sharing three edges and corners of the TiO_6 (octahedron) [6]. Brookite phase of TiO_2 is difficult to produce purely [6,7]. Many methods have been used to prepare brookite TiO_2 structure such as hydrothermal method, sol–gel deposition, chemical vapor deposition (CVD), pulsed laser deposition (PLD) [7,8]. Brookite TiO_2 nanostructures are produced as particles, films, nanorods and nanoflowers [7–10]. Generally, brookite phase of nanocrystalline TiO_2 are synthesized by thermohydrolysis of $TiCl_4$ (tetrachloride) in HCl or NaCl solutions [11,12]. Brookite phase is also obtained using titanium tetraisopropoxide and butoxide with HCl acid [13,14]. Particle size is a very important parameter for systems, because the smaller the particle size is, the larger surface area and bandgap energy it generates. Sol–gel deposition process allows to control nanostructures of thin films. Nano TiO_2 structures are prepared by sol–gel method with different preparation conditions such as heat treatment temperature and with different precursor parameters such as water, acid and alcohol contents in literature. The influence of preparation conditions and precursor parameters on particle sizes of TiO_2 nanostructures with anatase and rutile phases was studied in details [15–18].

The particle size of nanostructured TiO_2 which was controlled by molar ratios of water, acid and alcohol during sol–gel deposition process was measured using XRD. The particle size of nanocrystal TiO_2 structures with different molar ratios of alkoxide:alcohol:water (with a fixed alkoxide:alcohol) resulted in the range of 8.6 and 12 nm, and the ones with different molar ratios of water:alkoxide:acid were measured in 10 and 60 nm range [15,16]. The results indicate that particle size of nano TiO_2 structures decrease with the increasing water and acid quantities due to the increasing rates of hydrolysis reaction. In another study, particle size increases as the water amount increases due to the use of different amounts of precursors such as alkoxide, water, ethanol, etc., and the use of different heat treatment temperature.

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The particle size of nanocrystal TiO_2 structures with different molar ratios of water:alkoxide and different heat treatment temperatures were measured in 27 and 106 nm range, and the ones with different water contents were measured in 5.3 and 10.6 nm range [17,18].

The results indicate that particle size of nano TiO_2 structures increase with the increasing amount of water due to the agglomeration. Heat treatment causes a phase transformation from amorphous phase to anatase, rutile or brookite phase. The particle size of nanostructured TiO_2 was increased with temperature [15]. Anatase and rutile phases of TiO_2 which are easily obtained in pure form are used widely in researches. Anatase structures are efficient as photocatalyst and rutile is rarely photocatalytic active [19]. The photocatalytic activity of titania depends on several factors such as crystal phase, particle size, band gap and surface area. Recently, nanostructured TiO_2 in brookite phase is used for photocatalytic and solar cell applications [20–23]. Here are some examples from studies conducted on brookite structures in literature. The brookite TiO_2 particles consisted of a single crystal suggesting that the brookite TiO_2 particles have high crystallinity, which is important for photocatalytic activity [23]. Brookite-rich structures, especially films, exhibit higher visible light photocatalytic activity than anatase and rutile structures [24,25]. The brookite phase of TiO_2 is also superior photocatalytically to other TiO_2 phases under UV [25]. However, the brookite-rich TiO_2 film is more sensitive in photoinduced hydrophilicity than the anatase one especially under weak UV light irradiation [26].

We synthesized pure brookite phase of nanostructured TiO_2 film, which is difficult to produce, using titanium butoxide, ethanol and acetic acid. In this experiment, we did not study hydrophilicity and photocatalytic activity. The purpose of our research is to control the particle size of thin films. The effect of volume ratios of water:AcAc on the particle size of nanobrookite TiO_2 film was investigated. XRD analysis shows that the particle size of the film was approximately 7.9 nm. We found that particle size can be controlled by volume ratios of water:AcAc in nanobrookite thin films.

2. Experimental

2.1. Preparation of nanobrookite TiO_2 films

Nanobrookite TiO_2 thin films were prepared using sol–gel method. The sol was prepared by dissolving titanium butoxide ($Ti(OC_4H_9)_4$) in ethanol. Acetic acid (AcAc) was added dropwise in the solution under continuous stirring. Water was added for hydrolysis and polycondensation. As a precursor solution of $Ti(OC_4H_9)_4$:ethanol:water:AcAc a volume ratio of 0.4:4:0.1:0.2 was used. Titanium butoxide, ethanol and acetic acid concentrations were held fixed, and particle size was controlled only by changing the water:AcAc volume ratio, e.g., to 0.25, 0.5, 1, and 2. These sols were mixed using magnetic stirring for 3 h at 25 °C.

Nanobrookite TiO_2 films were deposited on Corning 2947 glass substrates with a spin-coating technique with a spin speed of 1000 rpm in the room temperature (21 °C). After coating, TiO_2 films were immediately placed in an oven which was already heated at 450 °C. The films were taken out of the oven and were left at the room temperature at the end of 1 h.

These samples were heat-treated at 450 °C for 1 h. The thickness of nanobrookite TiO_2 films was measured approximately 80 nm.

2.2. Sample characterization

Structures of produced films deposited on glass substrates were characterized by X-ray diffractometer (GBC-MMA, Cu-Kα radiation). The surface morphology was characterized by atomic force microscopy (Shimadzu scanning probe microscope SPM-9500J3) and scanning electron microscopy (S-3100H, Hitachi Ltd.). Optical transmittances and reflectances of films were determined by a spectrophotometer (Aquialla Inst., nkd7000, UK) which is a device that is designed to measure transmittance and reflectance. Spectroscopic analysis of TiO_2 films was performed using UV visible spectrophotometer (Agilent 8453). Fourier transform infrared (FTIR) spectrums of films in the transmission mode have been recorded in the wave number range of 600–4000 cm^{-1} on a Perkin Elmer Spectrum FTIR Spectrometer.

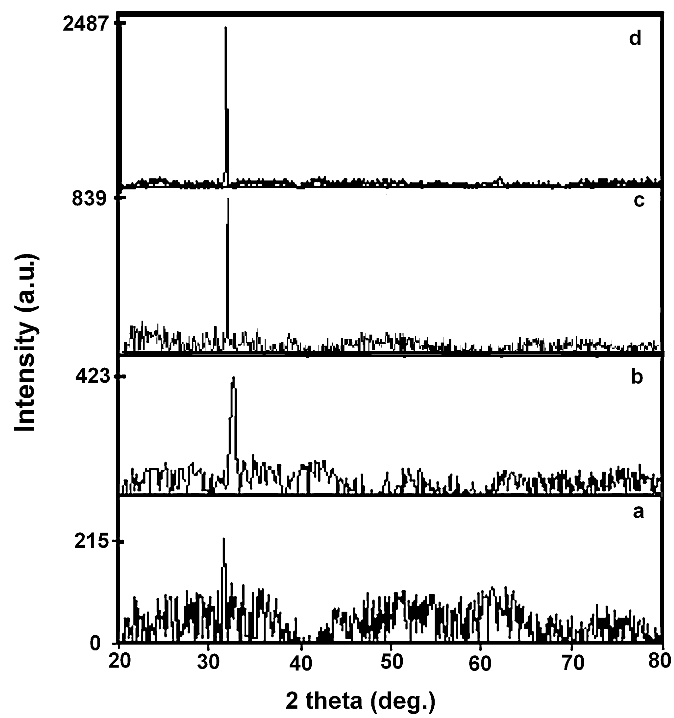

Fig. 1. X-ray diffraction patterns of nanobrookite TiO_2 thin films for different water:AcAc volume ratios: (a) 0.25, (b) 0.5, (c) 1, (d), 2.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the diffraction patterns of nano TiO_2 films which were prepared with different water:AcAc volume ratios. The results of X-ray diffraction indicate that TiO_2 films contain only brookite phase peaks. The heat treatment provides the crystallization of the TiO_2 film.

The amorphous phase of the TiO_2 film transformed into the brookite (orthorhombic crystal system) phase due to the heat treatment. The peak of brookite is present according to JCPDF card no. 75-1582. Because of the very thin structure of the thin films, the brookite phase of the TiO_2 films was demonstrated (2 1 1) as a single peak [27,28].

The crystalline size of TiO_2 film is calculated with the Scherrer equation, according to the XRD results:

$$d = \frac{k\lambda}{b\cos(\theta)} \quad (1)$$

where k is a constant (shape factor, k = 0.89), λ is the wavelength of the incident light, θ (theta) is half of the diffraction angle (rad), and b is the full width at half-maximum (FWHM) of the diffraction line [29]. Based on the XRD results, Table 1 shows average particle sizes of TiO_2 films which are prepared with different water:AcAc volume ratios.

Table 1
Average particle sizes of nanobrookite TiO_2 films for different water:AcAc volume ratios.

Data	Ti(IV) (ml)	Ethanol (ml)	Water:acid	FWHM	Particle size (nm)
a	0.4	4	0.25	0.35	4.1
b	0.4	4	0.5	0.24	5.9
c	0.4	4	1	0.18	7.9
d	0.4	4	2	0.12	11.9

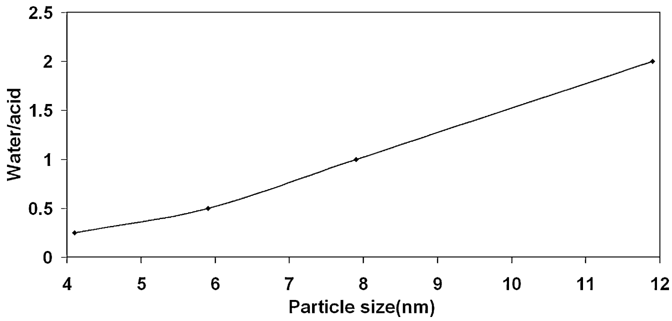

Fig. 2. Particle size values for different water:AcAc volume ratios.

Fig. 2 shows that the particle sizes of nano TiO_2 films decrease with the decreasing water:AcAc volume ratio [30]. The influence of the water:AcAc volume ratio on the crystallinity of nanobrookite film was investigated. When titanium butoxide, ethanol and acetic acid concentrations were held fixed, particle size was decreased by decreasing the water:AcAc volume ratio. The increase in the amount of water promotes the crystallization of the amorphous structure of TiO_2. During sol–gel synthesis of TiO_2, the hydrolysis rates are low for less amount of water in the solution, and excess titanium alkoxide in the solvent favors the development of Ti–O–Ti chains through alcoxolation [30]. The increase in the amount of water causes the agglomeration, which led to the increase in the particle size of the obtained TiO_2 [17,31,42].

3.2. SEM analysis

SEM images of nanobrookite TiO_2 films are shown in Fig. 3. It reveals the highly porous nature of films in which the water:AcAc volume ratios are equal to 0.25 and 0.5.

We also observed particles as homogeneous and spherical. We observed that the particle size decreased with the decrease in the water:AcAc volume ratios in Fig. 3, and it is supported by XRD results.

3.3. AFM analysis

Atomic force microscope was used to characterize the surface morphology of the nanobrookite TiO_2 film.

We compared the roughness of nanobrookite TiO_2 films for various water:AcAc volume ratios. Surface roughness of nanobrookite TiO_2 films were determined Rms: 2.25, 2.78, 3.13, 3.40 nm for 0.25, 0.5, 1, 2 water:AcAc volume ratios using afm. The Roughness of the films decreased with an decrease in the water:AcAc volume ratio. We observed that particle size decreased with the decrease in water:AcAc volume ratios in Fig. 4, and it is supported by SEM and XRD results. The Roughness also decreased with the decreasing particle size.

3.4. FTIR analysis

FTIR spectra of nanobrookite TiO_2 films are shown in Fig. 5. FTIR spectrum is used to investigate the presence of functional

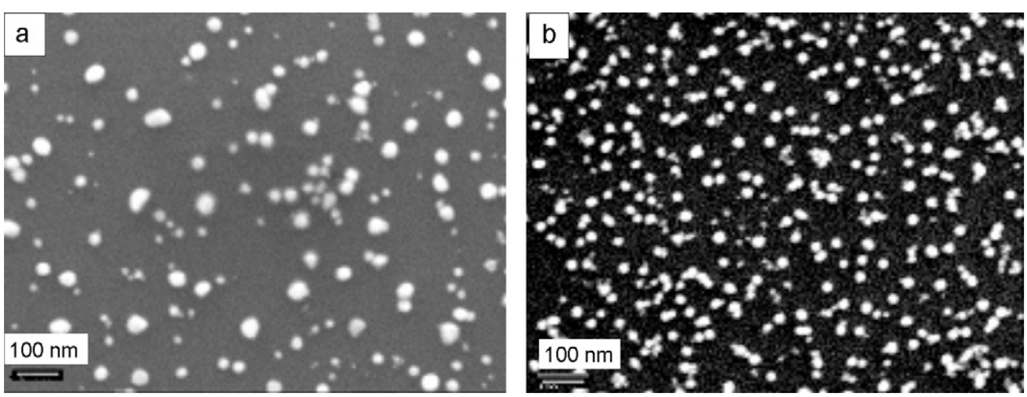

Fig. 3. SEM images of nanobrookite TiO_2 films for different water:AcAc volume ratios: (a) 0.5, (b) 0.25.

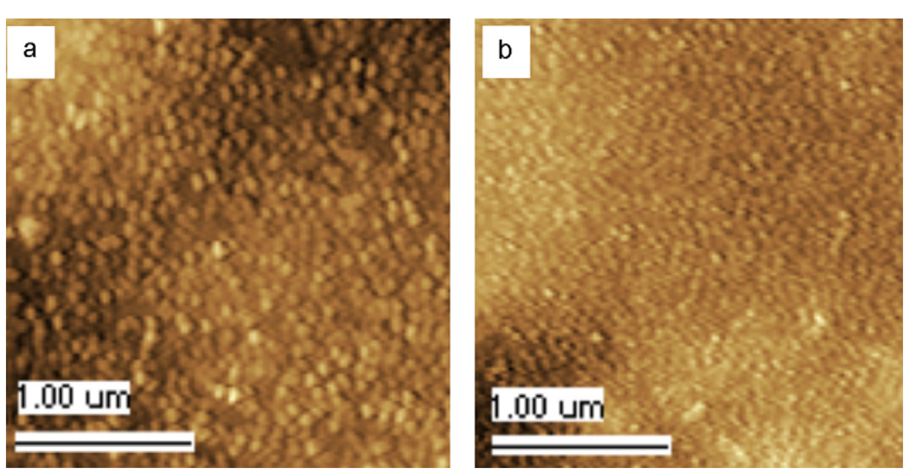

Fig. 4. AFM images of nanobrookite TiO_2 films for different water:AcAc volume ratios: (a) 0.5, (b) 0.25.

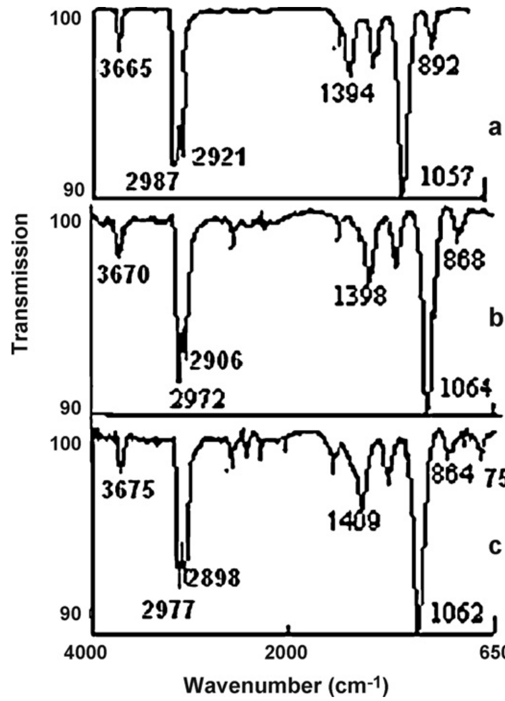

Fig. 5. FT-IR spectra of nanobrookite TiO_2 films for different water:AcAc volume ratios: (a) 1, (b) 0.5, (c) 0.25.

groups in compounds. In this study, we compared FTIR spectra of nanobrookite TiO_2 films for various water:AcAc volume ratios.

This spectra shows hydroxyl groups (OH stretching frequencies) of nanobrookite TiO_2 films around 3665 and 3675 cm^{-1}. The IR band around 2987 and 2977 cm^{-1} indicates the C–H stretching vibration. The IR band of the nanobrookite TiO_2 films around 1057 and 1064 cm^{-1} indicates the stretching vibration of the O–C–C bands of the alkoxide groups.

The IR band of the nanobrookite TiO_2 films around 892 and 864 cm^{-1} indicates the Ti–O–Ti bond of titania films [32–36]. These results showed that when water:AcAc volume ratios were decreased, hydroxyl groups and Ti–O–Ti bond of titania films shifted to a smaller wavelength.

3.5. Optical properties

Absorption spectra of nanobrookite TiO_2 films was analyzed using UV–vis spectrophotometer as shown in Fig. 6. The quantum size effect of nano-particles was confirmed by the band gap energy shift using ultraviolet–visible spectroscopy (UV–vis).

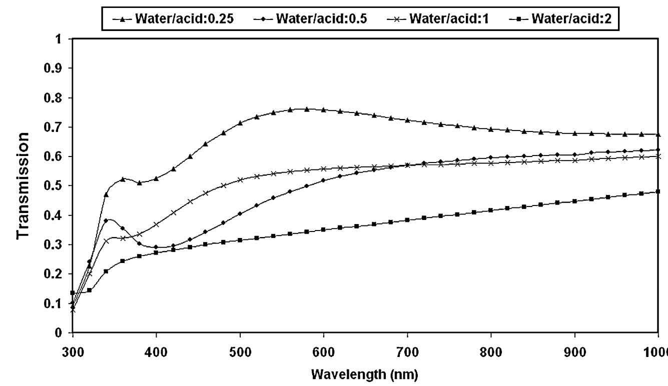

Fig. 7. Transmission spectra of nanobrookite TiO_2 films for different water:AcAc volume ratios.

Quantum size effects occur for TiO_2 particles in the order of 1–10 nm in size [37–41].

The UV–vis absorption spectra shows that absorption edge shifts to a shorter wavelength with the decreasing particle size due to a quantum size effect. The increase in the amount of water also produce a red shift in the absorption spectrum of nanobrookite TiO_2 films [31,42]. This has been attributed to interaction between water and surface Ti^{3+} centers caused by oxygen vacancy defect sites [42]. This result showed that the absorption spectrum can be sensitive to surface characteristics of the nanobrookite TiO_2 films.

Transmission and reflection of the film was investigated at the wavelength range from 300 nm to 1000 nm as shown in Figs. 7 and 8 using NKD. There are two regions in the spectrum; an increasing region and a region of stable transmittance.

When water concentration of the nanobrookite TiO_2 solution was increased, we observed that color of the solution was whiter than before. When water:acid volume ratios of the nanobrookite TiO_2 film were increased, transmittance of the film decreased. We determined that the reflectance of the nanobrookite film decreased with the increasing water:acid volume ratios. Interference effects were observed in the reflectance spectra.

We determined that transmittance and reflectance of the nanobrookite film decreased with the increasing particle size.

The optical band gap (E_g) of the TiO_2 thin film was determined using Eq. (2) where α is linear portion of absorption coefficient, $h\nu$ is the photon energy and A is a constant [43].

$$(\alpha h\nu) = A(h\nu - E_g)^n \tag{2}$$

Strong linearity was observed for different n values at $n = 2$ (indirect allowed transition) versus $(\alpha h\nu)^{1/2}$, which was found to give the best fit for pure nanobrookite TiO_2 thin films.

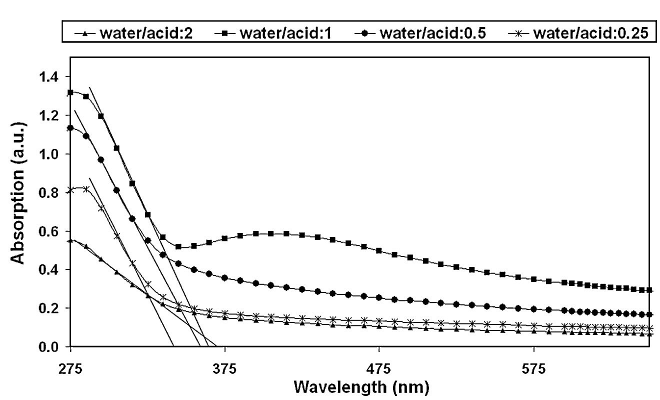

Fig. 6. Absorption spectra of nanobrookite TiO_2 films for different water:AcAc volume ratios.

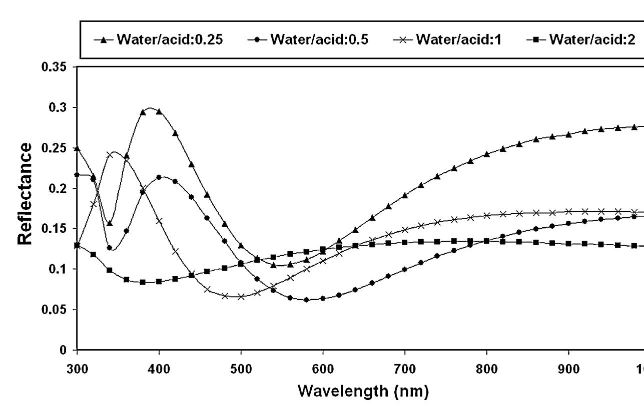

Fig. 8. Reflection spectra of nanobrookite TiO_2 films for different water:AcAc volume ratios.

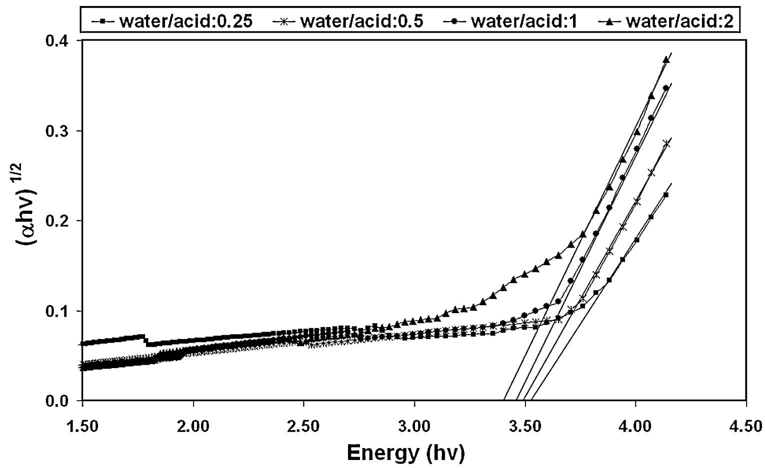

Fig. 9. $\alpha h\nu^{1/2}$–$h\nu$ graphs of nanobrookite TiO_2 films for different water:AcAc volume ratios.

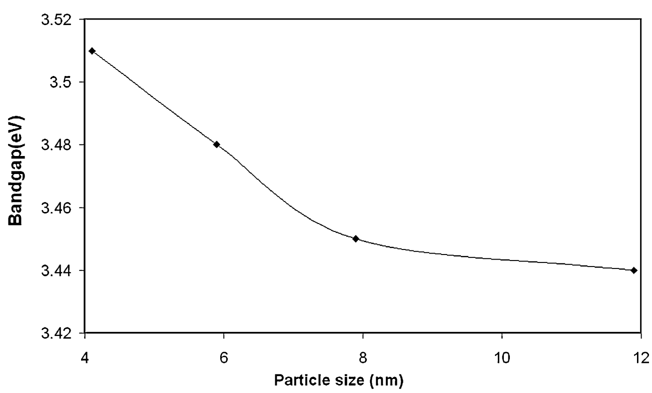

Fig. 10. Band gap energy–average particle size (using XRD results) graphs for different water:AcAc volume ratios.

The graph shown in Fig. 9 shows that band gap energies of TiO_2 films were determined between 3.44 and 3.51 eV for different water:AcAc ratios respectively as an indirect transition energy. When particle size is decreased, nanobrookite TiO_2 films exhibit absorption in the shorter wavelength region, and thus the increase in the band gap in nanobrookite films can contribute towards the higher photocatalytic activity of the films in the UV range [44].

Particle size of TiO_2 thin films (Table 1) changed with the band gap energy values as shown in Fig. 10. We observed that particle size of pure nanobrookite TiO_2 films decreased with the increasing band-gap energy.

4. Conclusions

In this study, we report on the preparation and structural characterization of pure nanobrookite TiO_2 films. This work has shown that pure nanobrookite TiO_2 thin films are obtained as single orientation (2 1 1) at 450 °C heat treatment temperature. It is found that particle size can be controlled by changing water:AcAc volume ratios (with a fixed $Ti(OC_4H_9)_4$:ethanol:AcAc volume ratio). The results indicate that an increase in the water:AcAc volume ratio leads to the increase in the particle size of TiO_2 films due to the agglomeration. The roughness of pure nanobrookite TiO_2 films increases with the increasing particle size. Transmittance and reflectance values of the nanobrookite film decrease with the increasing particle size.

It has been found that the spectrum red-shifts with increasing water concentration. When particle size is decreased, nanobrookite TiO_2 films exhibit absorption in the shorter wavelength region, which consequently increases the band gap values of the films. As a result of this, nanobrookite films have larger surface areas. Due to these characteristics, single oriented pure nanobrookite TiO_2 thin film which has a large surface area with a particle size of 4.1–11.9 nm can be used in electronic and optical applications such as photocatalytic, and hydrophilic applications.

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References

[1] R. Mechiakh, F. Meriche, R. Kremer, R. Bensaha, B. Boudine, A. Boudrioua, Opt. Mater. 30 (2007) 645–651.
[2] D.S. Hinczewski, M. Hinczewski, F.Z. Tepehan, G.G. Tepehan, Sol. Energy Mater. Sol. Cells 87 (2005) 181–196.
[3] E.D. Şam, M. Ürgen, F.Z. Tepehan, V. Günay, Key Eng. Mater. 264–268 (2004) 407–410.
[4] X. Chen, S.S. Mao, Chem. Rev. 107 (2007) 2891–2959.
[5] A.L. Linsebigler, G. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735–758.
[6] R.C. Bhave, B.I. Lee, Mater. Sci. Eng. A 467 (2007) 146–149.
[7] J.H. Lee, Y.S. Yang, J. Mater. Sci. 41 (2006) 557–559.
[8] Y. Djaoued, R. Brüning, D. Bersanic, P.P. Lottici, S. Badilescu, Mater. Lett. 58 (2004) 2618–2622.
[9] B. Zhao, F. Chen, Q. Huang, J. Zhang, Chem. Commun. 34 (2009) 5115–5117.
[10] A.A. Ismail, T.A. Kandiel, D.W. Bahnemann, J. Photochem. Photobiol. A: Chem. (2010) 1–29.
[11] A.D. Paola, M. Addamo, M. Bellardita, E. Cazzanelli, L. Palmisano, Thin Solid Films 515 (2007) 3527–3529.
[12] A.D. Paola, G. Cufalo, M. Addamo, M. Bellardita, R. Campostrini, M. Ischia, R. Ceccato, L. Palmisano, Colloids Surf. A: Physicochem. Eng. Aspects 317 (2008) 366–376.
[13] A. Garcia-Ruiz, A. Morales, X. Bokhimi, J. Alloys Compd. 495 (2010) 583–587.
[14] D. Reyes-Coronado, G. Rodriguez-Gattorno, M.E. Espinosa-Pesqueira, C. Cab, R. de Coss, G. Oskam, Nanotechnology 19 (2008) 145605 (10 pp.).
[15] N. Venkatachalam, M. Palanichamy, V. Murugesan, Mater. Chem. Phys. 104 (2007) 454–459.
[16] K. Juengsuwattananon, A. Jaroenworaluck, T. Panyathanmaporn, S. Jinawath, S. Supothina, Phys. Stat. Sol. A 204 (2007) 1751–1756.
[17] S. Mahshid, M. Askari, M.S. Ghamsari, N. Afshar, S. Lahuti, J. Alloys Compd. 478 (2009) 586–589.
[18] R. Inaba, T. Fukahori, M. Hamamoto, T. Ohno, J. Mol. Catal. A: Chem. 260 (2006) 247–254.
[19] A.M. Luis, M.C. Neves, M.H. Mendonça, O.C. Monteiro, Mater. Chem. Phys. 125 (2011) 20–25.
[20] E.L. Beltran, P. Prene, C. Boscher, P. Belleville, P. Buvat, S. Lambert, F. Guillet, C. Marcel, C. Sanchez, Eur. J. Inorg. Chem. (2008) 903–910.
[21] K. Jiang, T. Kitamura, H. Yin, S. Ito, S. Yanagida, Chem. Lett. 31 (2002) 872–873.
[22] D. Lee, J. Park, J.C. Kyoung, H. Choi, D. Kim, Eur. J. Inorg. Chem. 6 (2008) 878–882.
[23] N. Murakami, T. Kamai, T. Tsubota, T. Ohno, Catal. Commun. 10 (2009) 963–966.
[24] H. Pan, X. Qiu, I.N. Ivanov, H.M. Meyer, W. Wang, W. Zhu, M.P. Paranthaman, Z. Zhang, G. Eres, B. Gu, Appl. Catal. B: Environ. 93 (2009) 90–95.
[25] B.I. Lee, S. Kaewgun, W. Kim, W. Choi, J.S. Lee, E. Kim, J. Renew. Sustain. Energy 1 (2009) 023101 (7 pp.).

[26] T. Shibata, H. Irie, M. Ohmori, A. Nakajima, T. Watanabe, K. Hashimoto, Phys. Chem. Chem. Phys. 6 (2004) 1359–1362.
[27] S. Kim, K. Lee, J.H. Kim, N. Lee, S. Kim, Mater. Lett. 60 (2006) 364–367.
[28] I.N. Kuznetsova, V. Blaskov, I. Stambolova, L. Znaidi, A. Kanaev, Mater. Lett. 59 (2005) 3820–3823.
[29] K.P. Biju, M.K. Jain, Thin Solid Films 516 (2008) 2175–2180.
[30] Y. Bessekhouad, D. Robert, J.V. Weber, J. Photochem. Photobiol. A: Chem. 157 (2003) 47–53.
[31] I. Martini, J.H. Hodak, G.V. Hartland, J. Phys. Chem. B 102 (1998) 607–614.
[32] M. Sabzi, S.M. Mirabedini, J. Zohuriaan-Mehr, M. Atai, Prog. Org. Coat. 65 (2009) 222–228.
[33] J. Sabataityte, I. Oja, F. Lenzmann, Comptes Rendus Chimie 9 (2006) 708–712.
[34] A. Verma, S.B. Samanta, A.K. Bakhshi, S.A. Agnihotrya, Sol. Energy Mater. Sol. Cells 88 (2005) 47–64.
[35] K.M.K. Srivatsa, M. Bera, A. Basu, Thin Solid Films 516 (2008) 7443–7446.
[36] M. Sasani Ghamsari, A.R. Bahramian, Mater. Lett. 62 (2008) 361–364.
[37] C.S.S.R. Kumar, Nanomaterials: Toxicity, Health and Environmental Issues, Wiley-VCH, Weinheim, 2006, pp. 220–221.
[38] L. Ge, M. Xu, M. Sun, H. Fang, Mater. Res. Bull. 41 (2006) 1596–1603.
[39] Q. Zhang, L. Gao, J. Guo, Appl. Catal. B: Environ. 26 (2000) 207–215.
[40] Y. Chen, S. Zhou, G. Gu, L. Wu, Polymer 47 (2006) 1640–1648.
[41] L. Zhao, Y. Yu, L. Song, X. Hu, A. Larbot, Appl. Surf. Sci. 239 (2005) 285–291.
[42] J.Z. Zhang, in: J.Z. Zhang (Ed.), Optical Properties and Spectroscopy of Nanomaterials, World Scientific Company, UK, 2009, ISBN 9812836659, pp. 184–185.
[43] Y. Djaoued, M. Thibodeau, J. Robichaud, S. Balaji, S. Priya, N. Tchoukanova, S.S. Bates, J. Photochem. Photobiol. A: Chem. 193 (2008) 271–283.
[44] P. Periyat, K.V. Baiju, P. Mukundan, P.K. Pillai, K.G.K. Warrier, Appl. Catal. A: Gen. 349 (2008) 13–19.