SYNTHESIS OF MESOPOROUS TITANIA BY POTATO STARCH TEMPLATED SOL-GEL REACTIONS AND ITS CHARACTERIZATION

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Received December 16, 2009; Accepted January 14, 2010

ABSTRACT

Mesoporous titania powders with high-order crystalline building blocks had been synthesized through the sol-gel process using potato starch gel template. Internal spongelike pore structure of starch gel template was generated by heating the starch granules at 95 °C in water solution and freezing the starch gel at -15 °C. The synthesis routes were performed by immersing the starch gel template for 4 days into the white colloidal solution of TiO_2 *nanoparticles, which were prepared by hydrolyzing titanium (IV) tetraisopropoxide (TTIP) in ethanol at pH 1. Mesoporous* TiO_2 *powders were obtained by two different ways of template removal, performed by calcination of the* TiO_2*-starch composites at 600 °C for 4 h or combination of extraction with ethanol-HCl (2:1) at 80 °C and calcination at 500 °C for 4 h. Fourier Transform Infra Red (FT-IR) spectra shows both of template removal methods result in decreasing of characteristic vibrational band of the starch hydrocarbon on the resulted* TiO_2 *powders. The X-Ray Diffraction (XRD) pattern imply that the concentrations of starch gel template influence the anatase crystallite peaks intensity of the synthesized* TiO_2 *powders.* TiO_2 *templated by 20% of starch sponges gel has highest intensity of anatase crystallite. Scherrer calculation inidicated that anatase particle size has nanoscale dimmension up to 12.96 nm. The nano-architecture feature of mesoporous* TiO_2 *scaffolds was also evaluated by the Scanning Electron Microscope (SEM). It is shown that mesoporous* TiO_2 *framework consist of nanocrystalline* TiO_2 *particles as buiding blocks. The* N_2 *adsorption-desorption isotherm curves assign that* TiO_2 *powder resulted from extraction-calcination route has higher mesoporosity than that of only calcinated. The synthesized mesoporous* TiO_2 *powder exhibits high Brunauer-Emmet-Teller (BET) specific surface area up to 65.65* m^2*/g.*

Keywords: *mesoporous* TiO_2*, potato starch, template*

INTRODUCTION

Porous materials with high-order regulated of pore size distribution and specific surface area have been widely synthesized and attract much interest because of its prospective applications. As one of the most important porous material, mesoporous titania has shown significant role in some application field such as photocatalyst [1-2], photoelectrode in dye sensitized solar cell (DSSC) system [3], sensor device [4]. In such applications, mesoporous titania could show high photocatalytic activity for their porosity and crystallinity. It has been widely known that photocatalytic activity of titania may depend on its phase structure, crystallite size, the specific surface area, and pore structure. Many studies have confirmed that the anatase phase of titania shows highest photocatalytic performance [5-6]. Therefore, it is interesting to control the crystallite phase and size, also the surface structure of mesoporous titania in order to enhance the photocatalytic activity.

Many works have been reported and considered to the preparation of mesoporous titania with highly photocatalytic activity and the improvement of photocatalyst performance. Various routes of mesoporous titania synthesis such as sol-gel process, hydrothermal, direct deposition from aqueous solution even aerosol process have been implemented. Amongst, the sol-gel process has been widely applied as a synthetic route for the preparation of new material, providing very homogenous sample, even at low synthesis temperature. It has also been shown that TiO_2 in the anatase phase can be synthesized at room temperature without any previous or further thermal or hydrothermal treatment [7].

Recently, synthetic routes are directed using various kind of template agents such as ionic surfactant [8], neutral surfactant [9] and also non-surfactant template [10-11] to generate the formation of mesoporous titania. Among which non-surfactant template is prefered for its low cost and environmental friendly. It also have been succesfully employed as template based on hydrogen bonding interactions [11]. Polymer of starch sponge gel with internal sponge-like structure has been used to produce hierarchical

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architectures in the form of macroporous titania monolith with meso-/macroporosity [12]. As potato starch is readily available, inexpensive, and easy to handle, so the synthetic process performs some advantages of being facile, low cost, environmentally benign, and amenable to scale-up.

In this paper, we employ potato starch gel template in the synthesis of mesoporous titania through the sol-gel reaction. The influence of potato starch gel templates concentration to the resulted TiO_2 crystallinity is investigated. We also describe a modification of template removal technique through the combination of ethanol-acids extraction/calcination and its effect on crystallinity and porosity of the resulted TiO_2.

EXPERIMENTAL SECTION

Materials

Titanium(IV) tetraisopropoxide ($Ti(OC_3H_7)_4$, 97%) used as a titanium source was supplied from Aldrich. Commercial potato starch 'Deoni' was used as starting material on sponges gel template preparation. Whereas, absolute ethanol (C_2H_5OH, 99.9%) and chloride acid (HCl, 37%) for wet chemical process were purchased from Merck.

Instrumentation

The FT-IR spectra of the synthesized TiO_2 powders from two different template removal pathways were measured on a Shimadzu 8201 PC FT-IR Spectrophotometer to confirm the complete removal of the starch molecule. The crystallite phase of TiO_2 powder was evaluated by powder X-ray diffractometer (XRD, Philips) with Cu Kα radiation (λ = 1.5406 Å), and the average particle size of anatase crystallite (D) was estimated by Scherrer's formula [13]:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is the Scherrer constant (0.9), λ is the wavelenght of Cu Kα radiation, β is the full-width at half-maximum (FWHM) intensity of the anatase (d_{101}) peak, and θ is the Bragg reflection angle. Weight per cent compotition of anatase and rutile phases were determined by Spurr and Myers equation [14]:

$$X_R = \frac{1}{1 + 0.8 I_A / I_R}$$

where x_R is the weight fraction of rutile, I_A and I_R are relative intensities of the primary peaks corresponding to anatase (d_{101}) peak at 2θ = 25.4° and rutile (d_{110}) peak at 2θ = 27.5° respectively.

The porosity of TiO_2 powders was examined using N_2 adsorption-desorption measurement at 77 K with gas sorption analyzer (NOVA 1200, Quantachrome) and the specific surface area was calculated using multi-point BET method of NovaWin2 version 2.2. The surface morphology of synthesized mesoporous TiO_2 powders was examined using scanning electron microscope (SEM) JEOL JSM-6360 LA.

Procedure

Potato starch gel template preparation

Starch gel sponges were prepared as discribed previously [12], with a modification of template removal as follow. Spongelike template was prepared into different starch concentrations 9-20% (w/v), by diluting 4.5-10 g of starch granules to 50 mL of deionized water under stirring at room temperature. The swelling granules could be obtained by heating the starch slurry at 95 °C, then manual stirring was performed until gelatinization occurred. The gelatinized starch paste was kept at 95 °C for 10 min without stirring. It was mold to the 2 cm x 2 cm x 2 cm dimension and left to age at room temperature for 15 h, then freeze dried at -15 °C for 3 days to initiate spongy gel template formation.

Synthesis of mesoporous TiO_2 by potato starch gel template

Typical mesoporous TiO_2 was then fabricated by the following method: The previous frozen starch gel then was dried for 2 days at room temperature and subsequently immersed in the TiO_2 colloidal solution (pH 1) and shaken gently for 4 days. TiO_2 colloidal was prepared through hydrolyzing 20 mL of TTIP (Aldrich 97%) in 140 mL of ethanol absolute under addition of 7 mL of 1 M HCl. The TiO_2-loaded template (TiO_2-starch composite) was then removed from the colloidal solution, washed with deionized water and dried in air for 30 min. The starch template was removed by two different pathways: calcination of TiO_2-starch at 600 °C for 4 h and extraction of TiO_2-starch composite in ethanol-HCl solution then subsequently calcined at 500 °C for 4 h to obtain mesoporous powders. The extraction process was taken place for 5 h at 80 °C.

RESULT AND DISCUSSION

Templated sol-gel reaction through the hydrolysis of titania precursor (TTIP) for mesoporous titania synthesis has been generated using potato starch sponges gel. Internal pore structure of starch sponges gel provided as template for mesoporous titania formation. By this method, an eco-environmentally synthetic route on high-order crystallite mesoporous titania is envisaged.

Potato starch sponges gel and TiO_2-starch composite

Potato starch sponges gel templates were prepared by adding starch granules into the water solvent under controlled stirring at room temperature. Starch is insoluble in cold water because of its crystalline structure. Free access of water is probably prevented owing to the hydrogen interactions and formation of oxygen bridges between the nearly parallel crystals. Starch swells when treated with cold water and shrinks to its original size when dried to its previous water-content. Raising the water temperature up to 95 °C could break the hydrogen bonds of the starch polymer so the water molecules absorbed into the starch granules and resulted in highly swollen starch, then start gelatinizing to form paste of starch [15]. Freezing the starch paste is the most important steps for preparing internal porous (macroporous) starch because the dehydration of water absorbed could take place during freezing to form three dimensional starch skeletons [12].

SEM image of Fig 1a shows that potato starch gel frameworks have sponge-like appearance. It is consisted of intact 3-D continuous macroporous network with various pore sizes that were controlled by starch concentration as depicted on Fig 1b. Based on SEM estimation, it remains that starch gel morphology prepared with 9 wt% of starch concentration has approximately 8-150 µm pore size with 1-3 µm of wall thicknesses. By this sponges gel structure, it is possible to incorporate various TiO_2 nanoparticles in the pores of potato starch gel.

Composites of TiO_2-starch were prepared by immersing 3-D skeleton of starch sponges gel into the white colloidal TiO_2 dispersions at pH 1. TiO_2 nanoparticles were precipitated onto the surface of the starch framework to produce an intact composite. The TiO_2 loading are probably facilitated by electrostatic interactions between positive charge of TiO_2 nanoparticles at pH 1 and hydrated amylose of 3-D porous network. This interaction prevents the initial deposition of nanoparticles onto the external surface or in the near-surface regions of the pores, so that the colloids may penetrate deeply into the bio-polymeric architecture [12].

SEM image of Fig 2a shows that TiO_2 loading and precipitating on the starch gel surface. This phenomenon causes smaller opening and thicker wall of TiO_2-starch composite compare to the initial porous starch sponges gel. During the drying step, the increased ionic strength associate with evaporation of the solvent gives rise to particles aggregation and the formation of continuous TiO_2 layers on the internal surface of the starch sponges gel [12]. It reveals that tightly TiO_2 layers have been attached on the starch surface.

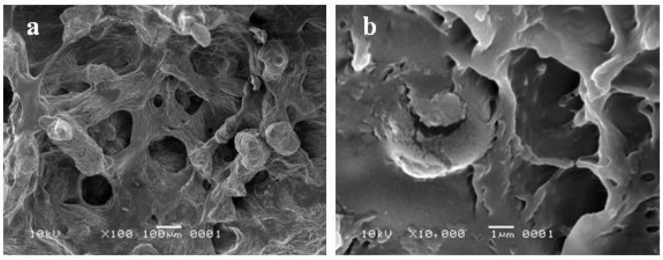

Fig 1. SEM images of potato starch sponge gel 9 wt% at (a) 100x magnification (scale bar 100 µm) and (b) 10,000x magnification (scale bar 1µm)

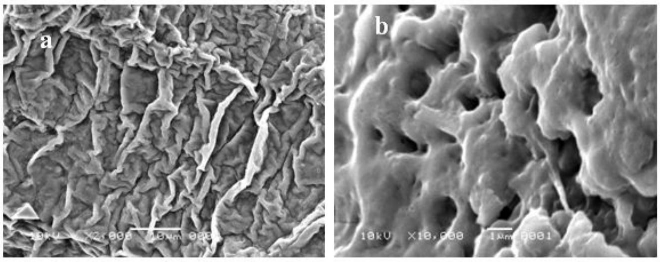

Fig 2. SEM images of TiO_2-starch composite 9% of starch at (a) 2,000x magnification (scale bar 10 µm) and (b) 10,000x magnification (scale bar 1 µm)

Potato starch templated-mesoporous TiO_2

Mesoporous TiO_2 with nanocrystalline scaffolds was obtained by starch gel template removal, through combination of ethanol-HCl extraction at 80 °C for 5 h and calcinations at 500 °C for 4 h. Template removal was also taken place by calcinations at 600 °C for 4 h for comparison.

Direct evidence for the starch gel template removal from the TiO_2 scaffolds was obtained by FT-IR spectroscopy. Fig 3a reveals a broad peak from 3600 to 3300 cm^{-1} assigns the hydrogen bonded of –OH stretching of starch monomer, Ti-OH on the titania surface and water molecules which were adsorbed physically through the hydrogen interactions onto the TiO_2 surface. Asymmetric stretching vibration of $-CH_2-$ from the starch compartment was observed at wave number of 2924.09 cm^{-1}. In addition, the peaks at 1635.64 and 1404.18 cm^{-1} were corresponding to the water molecule and in-plane –OH bending modes, respectively [4]. Further confirmation shows that the broad peak of Ti-O-Ti vibration at 900 to 400 cm^{-1} which was attributed as basic scaffolds of TiO_2 framework has not appeared regularly yet. On the other hand, this characteristic vibration mode for TiO_2 framework is clearly depicted in Fig 3b and 3c. In both of that figures, the peaks intensity of $-CH_2-$ asymmetric vibration appeared to decrease, while in-plane –OH bending mode disappeared after calcinations treatment. It remains that starch template molecule removal could

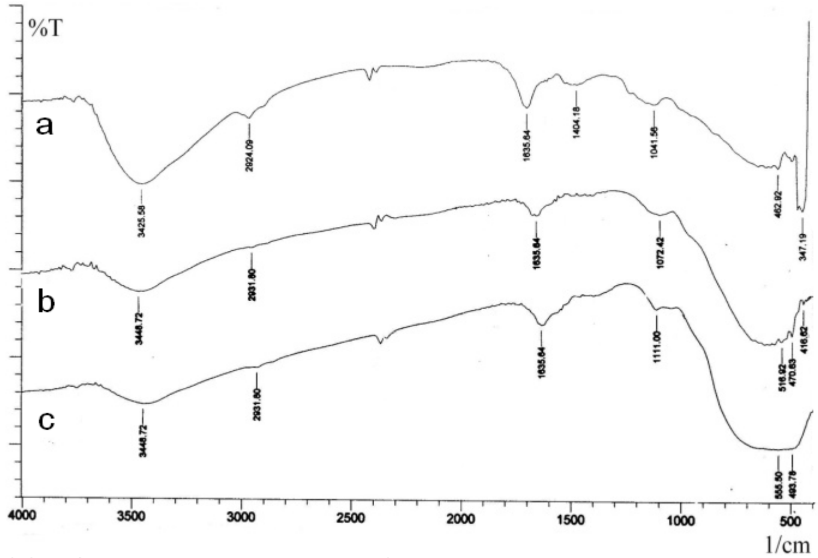

Fig 3. FT-IR spectra of (a) TiO_2-starch gel composite after ethanol-acid extraction treatment; (b) TiO_2 powder from combined template removal, and (c) TiO_2 powder resulted by calcinations at 600 °C for 4h

Table 1 Crystallite of mesoporous TiO_2 powders resulted from various starch gel template concentration

Sampel	Anatase (d_{101})			Rutile (d_{110})			X_R (%)
	2θ (deg)	d (Å)	D (nm)	2θ (deg)	d (Å)	D (nm)	
JCPDS data*		3,5200			3,2470		
non-templated TiO_2	25,2721	3,5200	67,8797	27,4772	3,2434	24,9724	4.0077
TiO_2 with 9 wt%	25,2317	3,5270	24,8573	-	-	-	-
TiO_2 with 15wt%	25,2948	3,5182	22,1065	27,5545	3,2345	20,3343	3.3933
TiO_2 with 20 wt%	25,4524	3,4966	19,4732	27,5396	3,2365	34,0963	8.8319

**Joint Committe on Powder Diffraction Standars*

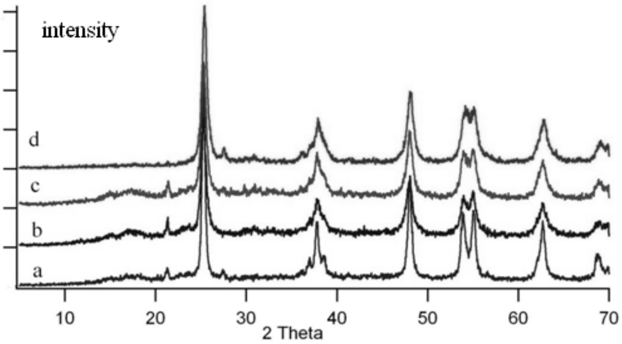

Fig 4. XR-D pattern of (a) non-templated-TiO_2, (b) mesoporous TiO_2 with 9%, (c) 15% and (d) 20% percentage of starch gel template calcined at 600 °C for 4 h

be taken place either by extraction-calcinations or only calcination methods.

The effect of starch gel concentration on the mesoporous TiO_2 crystallite (crystal phase and size) was investigated by X-rays diffraction method. Fig 4 compared diffraction pattern of TiO_2 powders with various weight percentage of starch gel templates which were calcined at 600 °C for 4 h. It reveals that template removal process by this technique provides dominantly yield of anatase phase crystallite formation. It shows that higher concentration of starch gel template makes the increasing of anatase peaks intensity and the FWHM magnitude appears to be narrower. It remains that the resulted TiO_2 powders consisted of high-order crystallite size of anatase phase. This phenomenon could be happened because the starch gel template provided internal pores space that could limit the crystal growth of anatase phase. However, further confirmation of crystallite phase by Spurr and Myers calculation indicated the increasing of rutile compositions along the starch concentration rising, which were resumed at Table 1.

SEM images in Fig 5 show the morphology of mesoporous TiO_2 powder synthesized by our starch gel template method after the template removal using combined extraction and calcinations technique. This nano-architecture involves the chemical based construction and self assembly of organic-inorganic moieties with high-order structure controlled by starch gel templating. Hierarchically internal pores of resulted mesoporous TiO_2 is revealed on Fig 5a. Image at higher magnification (Fig 5b) shows that nanocrystalline TiO_2 particles perform as building blocks in the mesoporous structures of TiO_2 framework.

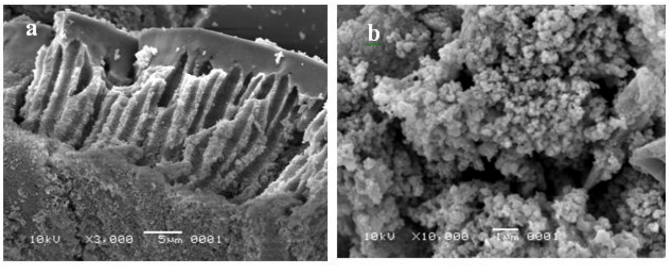

Fig 5. SEM images of mesoporous TiO_2 nanocrystalline at (a) 3,000x magnification and (b) 10,000x magnification

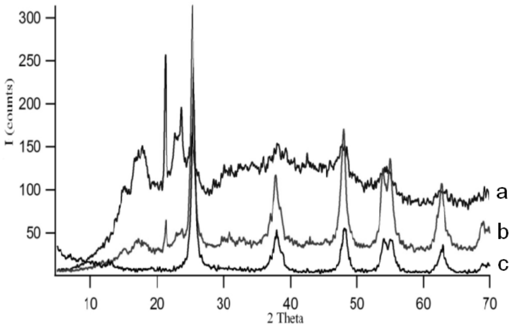

Fig 6. XRD pattern of (a) TiO_2-starch composite after extraction treatment, (b) TiO_2 after extraction-calcination, and (c) calcined TiO_2 at 600 °C for 4 h

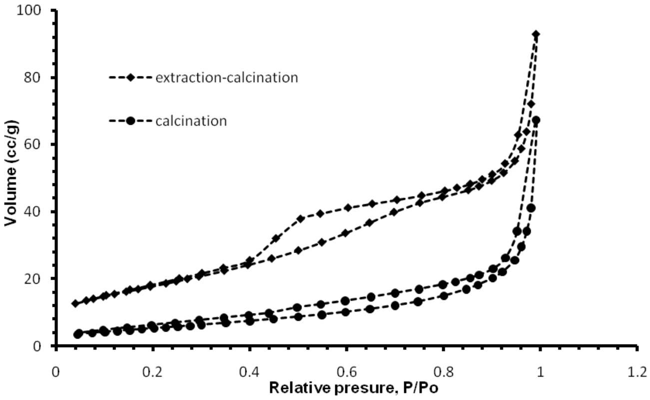

Fig 7. N_2 adsorption-desorption isotherms of the mesoporous TiO_2

Template removal influences on the resulted mesoporous TiO_2 crystallite were investigated by XRD method. It showed that, TiO_2-starch composite particles are amorphous when only extracted in ethanol-HCl without calcination as indicated in Fig 6a. Broad peaks on the 2θ 17.95°; 21.33° are related to the crystallite lattice of starch polymer, and 2θ of 25.22° corresponds to primarily anatase phase lattice of TiO_2. Calcination treatment at 500 °C could improve the anatase crystallinity of mesoporous TiO_2 powders as depicted at Fig 4b. However, Fig 4c implicated that TiO_2 powders treated by calcination at 600 °C without ethanol-acid extraction treatment have lower anatase crystalline intensity. It proved that extraction treatment could increase the anatase cryastallinity because re-hydrolysis process could be directed to break the unhydrolyzed alkyls in the TiO_2 gel [16]. Based on Scherrer estimation, the crystallite size of TiO_2 particles after extraction and calcination is around ~13 nm, which is smaller than both the resulted TiO_2 by calcination only (~24.86 nm) and the nontemplated-TiO_2 (~67.88 nm). It is clear that starch gel template may possibly limit the TiO_2 crystal growth.

Nitrogen adsorption-desorption isotherms curves of resulted mesoporous TiO_2 powders were depicted on Fig 7. Isotherm curve of mesoporous TiO_2 prepared by starch gel 9 wt% indicates a type-IV with an H2 hysteresis loop according to IUPAC classification [17], indicating mesoporous structure of the TiO_2 powders. From BET analysis, the mesoporous TiO_2 from extraction-calcination treatment has specific surface area up to 65.65 m^2/g higher than TiO_2 with only calcination treatment (20.36 m^2/g). It means that extraction treatment has played significant roles in stabilizing the constructed pore by potato starch over gradually template removal steps. In our previous work, it was proven that the mesoporous TiO_2 powder resulted from combined template removal had highest photocatalytic activity on the triiodide formation from iodide species under UV light irradiation compared to P-25 Degussa and only calcinated TiO_2, owing to its crystallinity and high specific surface area [18].

CONCLUSION

Highly porous and crystalline TiO_2 had been synthesized through potato starch templated method. Higher concentration of starch gel template directed to the crystallinity improvement of anatase phase. It is also observed that template removal through the ethanol-acid extraction technique played important role in stabilizing the created pores. In addition, mesoporous TiO_2 synthesized through that combined template removal showed higher-order of crystallinity and porosity than that of only calcinated TiO_2 powders.

ACKNOWLEDGEMENT

The authors acknowledge financial support from Directorate of Higher Degree Education Indonesia under Competency Research Grant 2008-2009.

REFERENCES

1. Victor, F., Stone, J., and Davis, R.J., 1998, *Chem. Mater.*, 10, 1468-1474.

2. Negishi, N.,Takeuchi, K., and Ibusuki, T.,1997, *Appl. Surf. Sci*., 121-122, 417-420.
3. O'Regan, B. and Gratzel, M.,1991, *Nature*, 353, 737-740.
4. Yang, D., Takahara, N., Lee, S., and Kunikate, T., 2008, *Sens. Actuators, B*, 130, 379-385.
5. Hoffmann, M.R., Martin, S.T., Choi, W., and Bahnemann, D.W., 1995, *Chem. Rev*., 95, 1, 69-96.
6. Fujishima, A., Rao, T.N., and Tryk, D.A., 2000, *J. Photochem. Photobiol., C,* 1, 1-21.
7. Rao, C.N.R., and Gopalakrishnan, J., 1997, *New Direction in Solid State Chemistry*, 2nd ed., Cambridge University press, Cambridge.
8. Yusuf, M.M., Imai, H., and Hirashima, H., 2003, *J. Sol-Gel Sci. Technol*., 28, 1, 97-104.
9. Yang, P., Zhao, D., Margolese, D.I., Chmelka, B.F., and Stucky, G.D., 1999, *Chem. Mater*., 11, 2814.
10. Zheng, J.Y., Pang, J.B., Qiu, K.Y., and Wey, Y., 2001, *Microporous Mesoporous Mater.,* 49, 1, 189-195.
11. Takenaka, S., Takahashi, R., Sato, S., and Sodesawa, T., 2000, *J. Sol-Gel Sci. Technol.*, 19, 1-3, 711-714.
12. Iwasaki, M., Davis, S.A., and Mann, S., 2002, *J. Sol-Gel Sci. Technol.,* 32, 101-102.
13. Zhang, H. and Banfield, J.F., 2002, *Chem. Mater*., 14, 4146.
14. Spurr, R.A. and Myers, H., 1957, *Anal. Chem*., 29, 760.
15. Bean, M.M. and Yamazaki, W.T., 1978, *J. Cereal Chem.,* **55,** 937.
16. Yu, J.,Yu, J.C., Ho, W., Leung, M.K., Cheng, B., Zhang, G., and Zhao, X., 2003, *Appl. Catal., A*, 255, 313.
17. Rouquerol, F., Rouquerol, J., and Sing, K., 1999, *Adsorption by Powders and Porous Solids: Principles, Methodology, and Applications*, Academic Press, San Diego.
18. Budi, C.S., and Kartini, I., 2009, *Synthesis of Mesoporous TiO_2 Nanocrystalline with Potato Starch as Pore Template and Its Photocatalytic Activity*, The 2009 International Conference on Chemistry, Biological and Environmental Engineering CBEE, Singapore, 9-11 October 2009.