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Glucose Templated Hydrothermal Synthesis of Porous Nanocrystalline Anatase TiO_2

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Synthesis of porous nanocrystalline anatase TiO_2 was performed hydrothermally employing glucose as the pore-forming agent. It was found that at low concentration, glucose has played dual actions of pore generating agent and anatase crystalline phase stabilizer. It is supposed that the presence of open chain aldehyde as isomeric structure of glucose acting as the oxygen supplying agent in inducing the anatase crystalline phase. The resultant porous TiO_2 powders were composed of highly uniform rounded rectangular shape particles generating surface area as high as 74.9 m^2/g with Barrett-Joyner-Halenda (BJH) pore diameter of 12.9 nm, indicative of mesoporosity. Photosensitized TiO_2 film by dye extract of mangosteen fruit pericarps has generated reasonable photocurrent with an open circuit voltage of 0.35 V.

Key Words: Glucose, TiO_2, Hydrothermal, Natural dye, Mangosteen.

INTRODUCTION

There has been great interest in the use of TiO_2 nanoparticles as sensors, for the detection of O_2, NO_2 and organic molecules[1], photocatalyst[2,3] and solar cells[4-6]. These increase interest in nanostructured materials calls for the development of preparation techniques that allow for tailoring specific pores on nanometer size. One method for engineering such structures involves the chemical manipulation of nano-building blocks *via* templating sol-gel method[7]. Sol-gel processing can be used to make nanometer sized TiO_2 by a chemical reaction in solution starting with metal alkoxides as a precursor at room temperature. Hydrolysis and polycondensation reactions occur simultaneously when titanium(IV) tetra isopropoxide mixes with water. Then, polymerization takes place to form higher molecular weight products (nuclei and subsequently particles) and the crystals grow. Sol-gel processing brings advantage of possibility to obtain large amount of powders with a high level of chemical purity[8]. However, it lacks of reproducibility and tends to produce low crystallinity powders[9]. Therefore, hydrothermal step is necessary to compensate those drawbacks. Template and pore directing agents are then applied to obtain highly uniform porous materials with tunable pore size[10-13].

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Recently, porous SiO_2 powders have been synthesized by using glucose template[14]. This approach is envisaged to be a biotemplate porous material synthesis which is reproducible, environmentally benign and enable producing high quality powders. It was obtained that as the glucose concentration increased in the synthesis, these pore parameters generally increased and the N_2 sorption isotherms gradually transform from reversible type I to type IV-like isotherms with H_2 hysteresis. At low glucose concentrations (< 36 wt %), both micropores and mesopores contribute to the porosity of the materials. However, at high glucose concentrations (36-64 wt %), mesopores are dominant. The aggregation or assembly of the aggregates of the glucose molecules and their hydrogen-bonding interactions with the silicate species might direct the mesophase formation. However, the role of glucose on pore generation as well as TiO_2 crystal growth has not been explored yet.

It is believed that the use of glucose as pore-generating agent for the synthesis of nanocrystalline mesoporous anatase TiO_2 by hydrothermal method is first reported in present communication. The reaction conditions such as hydrothermal time and temperature, as well as the glucose concentration were studied over their role on TiO_2 crystallinity, an important characteristic for solar cells and photocatalysts. It was found that at low concentration (< 4 wt %), glucose acts both as pore-generating and anatase TiO_2 crystalline phase stabilizer. The presence of short-time aldehyde moieties is supposed responsible for these glucose dual actions. The performance of TiO_2 powders obtained at optimum reaction condition was evaluated as photoanode in natural dye-sensitized solar cell employing crude extract of mangosteen fruit pericarps usually used as Batik (Indonesia traditional clothes) dyes as the sensitizer.

EXPERIMENTAL

Titanium(IV) tetra isopropoxide, α-D-glucose and Triton X-100 were purchased from Aldrich. HNO_3, ethanol, acetone, sodium iodide, iodine and ethylene glycol were supplied by Merck. All chemicals were used as received. F-doped tin oxide (FTO) glass was from Pilkington, USA. Typically, glucose-templated TiO_2 were prepared by the following procedures. One gram of glucose was dissolved in 20 mL of distilled water and heated for 15 min at 80 ºC, under vigorous stirring. In separate beaker, 0.73 g of titanium tetra isopropoxide was dissolved in 5 mL of ethanol. Then, the two solutions were mixed and stirred for another 15 min before subsequently transferred into a tightly capped Teflon jar for hydrothermal treatment at 180 ºC for alternated hydrothermal time. The as-synthesized mixture was recovered by vacuum filtration and washed with ethanol and distilled water. The resultant powders were vacuum-dried at 60 ºC for 4 h and calcined at 450 ºC for 4 h. The hydrothermal treatment was varied at temperature of 100-260 ºC for 4-20 h. The glucose concentration was varied at 0.2-7.0 wt %.

XRD analysis of the calcined powders was carried out on the Shimadzu XRD-6000 using CuK_α radiation at 40 kV and 30 mA. The microphotographs of the calcined TiO_2 powders were obtained using Jeol JSM-6360 LA scanning electron

microscope. Porosity of calcined TiO_2 powders were evaluated by N_2 gas sorption analyzer NOVA 1000 (Quantachrome). UV-vis spectra of the dye solution and the dye attached on TiO_2 films on the glass substrate were measured with a λ Bio-20 (Perkin-Elmer) spectrophotometer equipped with diffuse-reflectance integrating sphere.

Preparation of sensitized TiO_2 layers on F-doped tin oxide glass for photoanode of natural dye-sensitized solar cells: TiO_2 layers were deposited on F-doped tin oxide glass (1.5 cm × 2 cm, sheet resistance of 15 Ω^{-1}) by simple *doctor-blading* technique[4]. It was carried out by dropped the slurries on one edge of the glass substrate and then sheared a glass rod across. The slurries were made of the composition of 1 g TiO_2 powder, 1.25 mL HNO_3 pH 4 and few drops of Triton-X-100. Desired viscosity was adjusted by varying the drops of Triton X-100. As-sheared films were dried at room temperature and calcined at 450 ºC for 5 min. The as-sintered films were subsequently stored in desiccator until use. Dried pericarps of mangosteen fruit (*Garcinia mangostana* L.) were crushed and macerated with ethanol (1:4 w/v) for 24 h to extract the colour substance. The remaining powders were separated by vacuum filtration.

Solar cell assembling and testing: TiO_2 films on conducting glass were used as photoanodes. Prior to dye adsorption, the electrodes were heated at 450 ºC for 15 min and cooled to 80-100 ºC. Then the electrodes were directly immersed into the crude extract of dye solution overnight. Au was vapour deposited by using Jeol evaporator Vacuum JEE-4X on a pre-cleaned conducting glass to be used as counter electrode. The working electrodes were sandwiched onto the counter electrodes. The electrolyte (0.83 g KI and 0.127 g I_2 in 10 mL ethylene glycol) was then dropped and allowed to spread capillary forming interface between electrodes. Electrical contacts to the cells were provided by using alligator clips. The photocurrent-voltage (I-V) curves were determined under illumination with a halogen lamp (lamp intensity of 100 mW/cm^2).

RESULTS AND DISCUSSION

Porous nanocrystalline TiO_2 synthesis: Glucose has shown interesting template properties in mesoporous material synthesis of silica[14]. In this study, aqueous solutions of α-D-glucose were used to interact with ethanolic solution of $Ti(OiPr)_4$ in order to obtain well-directed pore structure. The mixtures were then heated hydrothermally at various hydrothermal temperature of 100-260 ºC for varied hydrothermal time (4-20 h). Fig. 1 shows the effect of alternating glucose concentrations on crystallinity and crystalline phases of TiO_2 powders resulted from hydrothermal treatment for 4 h at 180 ºC.

It can be seen that increasing glucose concentration resulted in the formation of predominantly anatase crystalline phase (2θ *ca.* 2.5º) with highest crystallinity obtained at 4 % by weight glucose. This inferred that glucose concentration as high as 4 % by weight stabilize the anatase seeds, hindering further agglomeration and

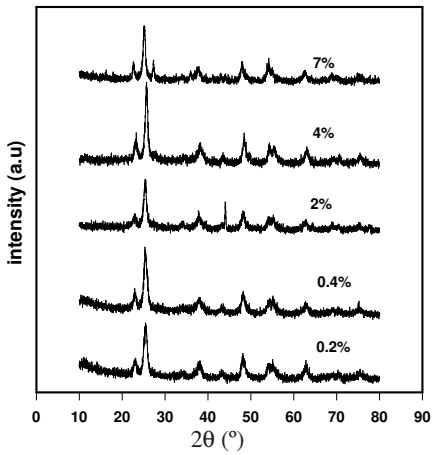

Fig. 1. Wide-angle XRD patterns of the calcined TiO_2 synthesized hydrothermally with alternated glucose concentration at 180 ºC for 4 h

thus the crystal growth into rutile (2θ *ca.* 2.7º). As the rutile grows (at 7 % wt glucose), anatase crystallinity decreases to compensate the growth of the other polymorph. We have shown previously that higher glucose concentration leads to the formation of porous TiO_2 with higher porosity due to the formation of open chain aldehyde structure of glucose orienting the O-Ti-O chains to form bigger porous structure[15]. It has also been shown that glucose may act as oxygen-supplying agent for crystalline anatase growth similar as observed by Garnweitner *et al.*[16] anatase crystallinity reached highest crystallinity at higher glucose concentration. However, excess glucose concentration (> 4 % wt) induces the transformation of anatase to rutile crystalline phase. Thus, it is suggested to perform the synthesis of porous anatase TiO_2 hydrothermally by employing glucose as pore-forming agent as high as 4 % by weight. Instead of inducing anatase to rutile phase transformation, high concentration glucose (> 4 % by weight) tend to decrease the porosity of the resulted TiO_2, as depicted in Table-1.

TABLE-1
THE TEXTURE PARAMETERS OF CALCINED TiO_2 POWDERS SYNTHESIZED HYDROTHERMALLY

Sample	S_{BET} (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
At 180 ºC, 4 % wt glucose	54.76	4.70	0.06
At 100 ºC, no glucose	71.51	7.40	0.26
At 100 ºC, 0.4 % wt glucose	74.93	12.90	0.48
At 100 ºC, 2 % wt glucose	44.68	16.50	0.37
At 100 ºC, 4 % wt glucose	27.12	14.51	0.20
At 100 ºC, 7 % wt glucose	34.88	12.01	0.20

The role of hydrothermal temperature on the crystallinity of TiO_2 is then investigated, since the transformation of anatase to rutile crystalline phases of TiO_2 is

accelerated at high temperature[9,17]. Fig. 2 displayed the XRD patterns of the resultant TiO_2 powders at various hydrothermal temperature of 100-260 ºC. It can be seen that the highest TiO_2 crystallinity was obtained at hydrothermal temperature of 180 ºC. Minor rutile phase was readily observed at hydrothermal temperature above 140 ºC. This may be caused by increased energy as a consequence of increasing hydrothermal temperature that may be readily used for crystal growth. Instead, there could be also oxygen depletion at higher hydrothermal time, which is expected to accelerate the transformation through the formation of anion vacancies[17]. It can be seen that the lack of oxygen supply at higher hydrothermal temperature (260 ºC) resulted in significantly low crystallinity of TiO_2.

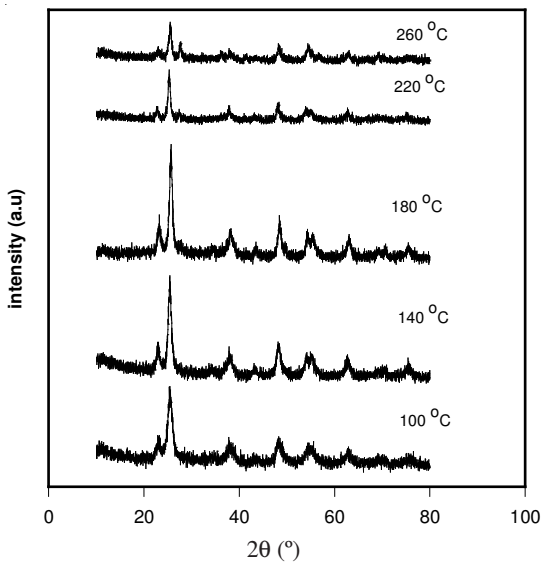

Fig. 2. Wide-angle XRD patterns of the calcined TiO_2 synthesized hydrothermally with 4 % wt glucose at alternated hydrothermal temperatures for 4 h

Fig. 3 showed the XRD patterns of TiO_2 powders synthesized at 180 ºC for varied hydrothermal time. It is observed that hydrothermal time influences the powder crystallinity fluctuatively. Transformation of anatase to rutile tends to occur at longer hydrothermal time. It is reasonable since rutile is crystalline phase of TiO_2 which is more thermodynamically stable than anatase[9].

The N_2 adsorption-desorption isotherm and pore size distribution of calcined hydrothermally synthesized titania are shown in Fig. 4. Combination of type II-IV isotherms with 54.76 m^2/g BET-specific surface area and average pore diameter of 4.70 nm is observed. It is generally accepted that this type of isotherm will only appear in a solid possessing pores ranging from large micropores to mesopores[18]. The monolayer adsorption is not complete until reaching relative pressure of 0.15, where the loop opens, indicating an existence of pores between micro and mesopores.

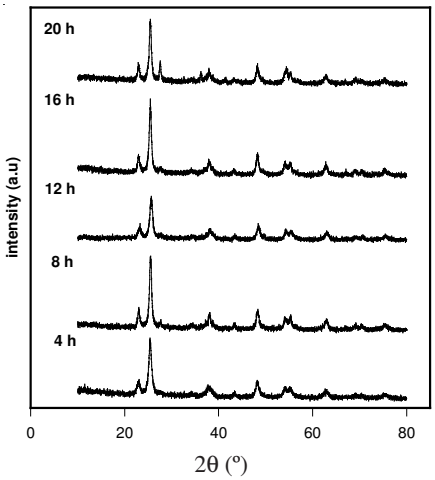

Fig. 3. Wide-angle XRD patterns of the calcined TiO_2 synthesized hydrothermally with 4 wt % glucose at 180 ºC for varied hydrothermal times

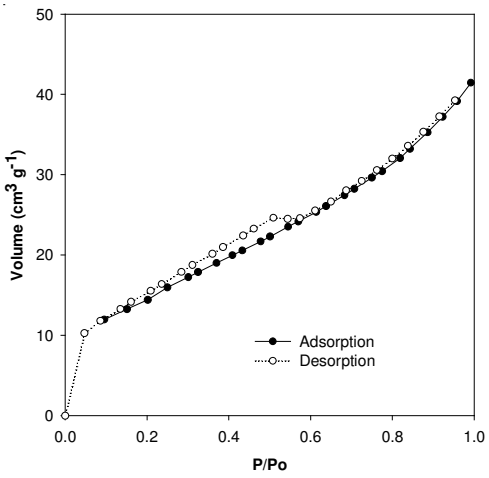

Fig. 4. The N_2 adsorption-desorption isotherm of calcined hydrothermally synthesized of glucose-templated TiO_2 powders at 4 wt % glucose for 4 h at 180 ºC

A tailing upward at higher relative pressure close to P/Po = 1 shows the macroporosity. The large hysteresis loop of type H_2 is characteristic of capillary condensation taking place in mesoporous materials containing cylindrical pores with bottlenecks[18]. A wide hysteresis loop indicates quite broad pore size distribution of the resultant porous TiO_2 (Fig. 5).

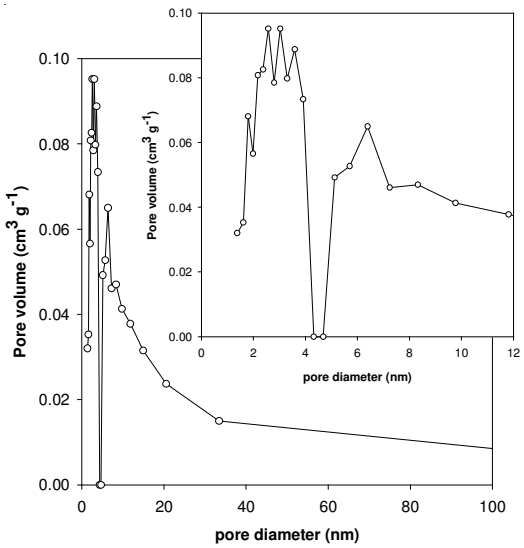

Fig. 5. Barrett-Joyner-Halenda (BJH) pore size distribution derived from desorption branch of calcined hydrothermally synthesized of glucose-templated TiO_2 powders at 4 % wt glucose for 4 h at 180 ºC

Fig. 6 displayed SEM image of calcined TiO_2 powders synthesized hydrothermally at 180 ºC for 4 h at 4 wt % glucose template. The image reveals the presence of homogeneous spherical grains morphology which are less aggregated with porous surface. The grain dimension is around 0.126 μm. Such porous structure is similar as colloidal TiO_2 usually used for photoanodes on dye-sensitized solar cells[4,19].

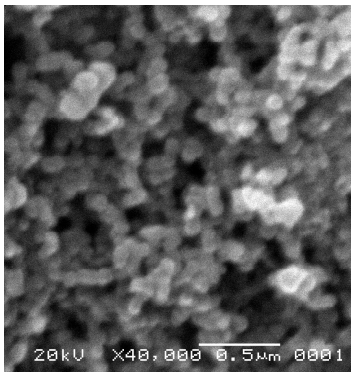

Fig. 6. Scanning electron micrograph of calcined hydrothermally synthesized of glucose-templated TiO_2 powders at 4 % wt glucose for 4 h at 180 ºC

Natural dye-sensitization of TiO_2 films: The dye-sensitized solar cell is an attractive candidate for a new renewable energy source because of the low-cost materials and the facile manufacturing used in its production. The construction consists of TiO_2 film on conducting glass substrate and the dye-sensitizer adsorbed on it as the working electrode (photoanode), Au-coated conducting glass as the counter electrode and the redox couple I^-/I_3^- as the electrolyte injected between the sandwiched-electrodes. Glucose-templated TiO_2 has shown characteristics ideal to be used as dye-substrate for the working electrode. The use of a natural dye, obtained from the dried-pericarps of mangosteen fruit extract, as the molecular sensitizer of nanostructured TiO_2 films results in reddish-brown colored photoanodes. The electronic spectrum of the ethanolic dye solution and the corresponding adsorbed dye on TiO_2 film are shown in Fig. 7.

The broad absorption bands of the crude extract of the dried pericarps of mangosteen fruit is advantageous for light harvesting. The bands were predicted as a results of π-π^* electronic transition of the conjugation systems present in the dye. The dye component of the mangosteen fruit pericarps may be ascribed as anthocyanins. The anthocyanins, a special class of flavonoids, are responsible for bright and often intense, red to blue colours in a variety of flowers, leaves and fruits[20]. As adsorbed on TiO_2 film, the wavelength of the absorption peak (λ_{max} = 549 nm) was significantly shifted to the longer wavelength (red-shifted) compared to that in ethanol (λ_{max} = 539 nm) indicating the presence of chemical interaction between the dye structure in their monomeric structure and TiO_2 surface[21,22]. No blue-shifting observed indicates that there is no tendency of the dye components in this crude extract to

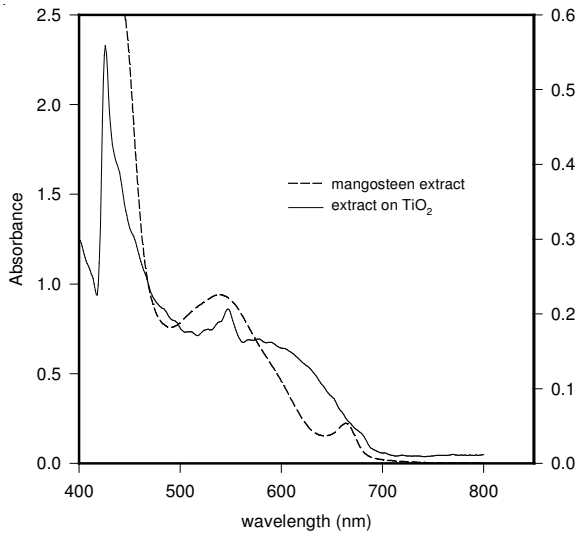

Fig. 7. Absorption spectra of ethanolic crude mangosteen fruit pericarps extract and as adsorbed on TiO_2 film

form H-dye aggregates[22]. However, the second absorption peak of the dye extract was overlapped with the first broad band and slightly red-shifted. This may indicate the formation of *J-dye aggregates*[22,23]. Actually, the formation of dye-aggregation does not always necessary to be suppressed. The formation of *H-aggregates* has shown good sensitization and solar cell efficiency[22,23]. But, disorder stacking of *J-aggregates* hardly showed good sensitization[23]. In the wavelength regions of 400-680 nm, the dye showed efficient absorption on TiO_2. Therefore, the TiO_2 electrode adsorbed with this natural dye had a sufficient absorption in whole visible light region ensuring efficient light harvesting. Since the anatase crystalline phase is preferred for dye-sensitized solar cell[24] attempts to incorporate TiO_2 powders synthesized hydrothermally at 180 ºC for 4 h at 4 % wt glucose template which has anatase phase dominantly into a dye-sensitized solar cell construction was carried out. A one coat slip-cast electrode was assembled with Au-deposited counter electrodes. The photovoltaic performance of this natural-dye sensitized solar cell is shown in Fig. 8 under dark and light measurement.

Sensitizing effects of the crude extract of mangosteen fruit pericarps natural dyes indicated by evaluation of their corresponding absorption spectra are confirmed quantitatively by their respective I-V curves. The solar cell parameters derived from the curves are J_{SC} of 0.057 mA/cm^2, V_{OC} of 0.38 V, the fill factor (FF) of 22.61 % and the global efficiency (η) of 0.02 %. It can be seen that the constructed cells possess sloppy I-V curves. It is concluded that the disorder of the chromophore arrangement on TiO_2 surface and the dye-aggregate formation as indicated by the absorption spectra cause the low conversion of solar energy into electricity due to the self-quenching between neighboring dyes.

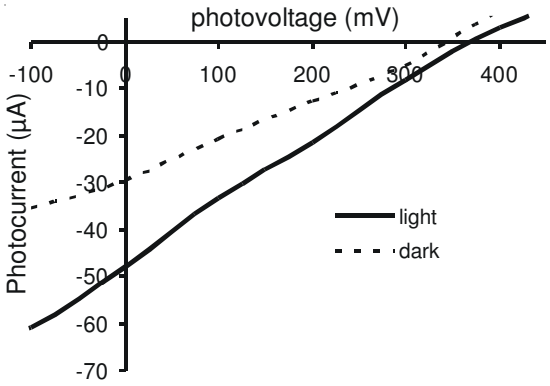

Fig. 8. The I-V curve of mangosteen fruit pericarps extract sensitized solar cell of glucose-templated TiO_2

Conclusion

It has been shown that glucose-templated porous TiO_2 synthesis hydrothermally produced anatase crystalline phase as major polymorph. It is also observed that glucose induced the formation of anatase phase up to certain concentration. Rutile crystalline phase was just starting to appear at higher content of glucose (> 4 % wt), for prolonged hydrothermal time (> 12 h) and at higher hydrothermal temperature (> 180 ºC). This simple synthesis route has also been developed for starch as the neutral pore-generating agent. From the solar cell testing of the resultant TiO_2 powder, it is suggested that the alignment of the dye on the TiO_2 surface and the circumstances around the dye affected the sensitization efficiency. It is suggested to suppress the formation of the J-like aggregates and promote covalent linkage between the dye structure and the TiO_2 surface. This may promote the global solar cell efficiency. The use of a natural product also enables a faster, simpler and environmentally friendly solar cell production without the requirement of all steps involved in the preparation and purification of synthetic dyes.

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REFERENCES

1. T. Trindade, P. O'Brien and N.L. Pickett, *Chem. Mater*., **13**, 3843 (2001).
2. A.L. Linsebigler, G. Lu and J.T. Yates, *Chem. Rev*., **95**, 735 (1995).
3. A. Fujishima, T.N. Rao and D.A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev*., **1**, 1 (2000).
4. B. O'Regan and M. Gratzel, *Nature*, **353**, 737 (1991).
5. K. Tennakone, G.K.R. Senadeera, V.P.S. Perera, I.R.M. Kottegoda and L.A.A. de Silva, *Chem. Mater*., **11**, 2474 (1999).

6. M.K.I. Senevirathna, P.K.D.D.P. Pitigala, V.P.S. Perera and K. Tennakone, *Langmuir*, **21**, 2997 (2005).
7. J.D. MacKenzie and E.P. Bescher, *Acc. Chem. Res*., **40**, 810 (2007).
8. J. Yu, J.C. Yu, W. Ho, M.K.-P. Leung, B. Cheng, G. Zhang and X. Zhao, *Appl. Catal. A: General*, **255**, 309 (2003).
9. K. Yanagisawa and J. Ovenstone, *J. Phys. Chem. B*, **103**, 7781 (1999).
10. Y. Yue and Z. Gao, *Chem. Commun*., 1755 (2000).
11. L. Wang, S. Tomura, M. Maeda, F. Ohashi, K. Inukai and M. Suzuki, *Chem. Lett*., 1414 (2000).
12. G. Soler-Illia, C. Sancez and C.G.A. Louis, *Chem. Mater*., **14**, 750 (2002).
13. B. Tian, X. Liu, B. Tu, C. Yu, J. Fan, L. Wang, S. Xie, G.D. Stucky and D. Zhao, *Nature Mater*., **2**, 160 (2003).
14. Y. Wei, J. Xu, H. Dong, J.H. Dong, K. Qiu and S.A. Jansen-Varnum, *Chem. Mater*., **11**, 2023 (1999).
15. I. Kartini, S. Wahyuningsih, T.D. Wahyuningsih and Sutarno, Proceeding of National Conference on Chemistry and Chemistry Education, Universitas Gadjah Mada, Indonesia, p. C3 (2007).
16. G. Garnweitner, M. Antonietti and M. Niederberger, *Chem. Commun*., 397 (2005).
17. J. Ragai and W. Lotfi, *Colloid. Surf*., **61**, 97 (1991).
18. S.J. Gregg and K.S.W. Sing, Adsorption, Surface area and Porosity, Academic Press, London, edn. 1, p. 67 (1967).
19. R. Durrant, J. Nelson and D.R. Klug, *Mater. Sci. Technol*., **16**, 1345 (2000).
20. O.M. Andersen and G.W. Francis, in Plant Pigments and their Manipulation, ed. by K.M. Davies, Blackwell Publishing Ltd. CRC Press LLC, Boca Raton, p. 293 (2004)
21. C.G. Garcia, S.A. Polo and N.M. Iha, *An. Acad. Bras. Cienc*., **75**, 163 (2003).
22. A. Ehret, L. Stuhl and M.T. Spitler, *J. Phys. Chem. B*, **105**, 9960 (2001).
23. K. Sayama, S. Tsukagoshi, T. Mori, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga and H. Arakawa, *Sol. Energy Mater. Sol. Cells*, **80**, 47 (2003).
24. I. Kartini, D. Menzies, D. Blake, P. Meredith, J.C.D. da Costa and G.Q. Lu, *J. Mater. Chem*., **14**, 2917 (2004).

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