

Concentration and Temperature Effect on Controlling Pore Size and Surface Area of Mesoporous Titania by Using Template of F-68 and F-127 Co-Polymer in the Sol–Gel Process

Nitin A. Jadhav¹, Chang Woo Kim¹, Umapada Pal²,
Jinheung Kim³, and Young Soo Kang^{1,*}

¹Department of Chemistry, Sogang University, Seoul 121-741, Korea

²Department of Physics, Instituto de Fisica, Universidad Autonoma de Puebla, Puebla 72570, Mexico

³Department of Chemistry and Nano Science, Ewha Womans University, Seoul, 120-750, Korea

Mesoporous titania with crystalline pore walls and controlled pore sizes was fabricated through triblock copolymer (pluronic series) templated sol–gel process by changing the copolymer concentration and by adjusting their calcination temperature. Compared with mesoporous silicate, the synthetic condition of mesoporous titania would be sensitive to calcination temperature. Their pore arrangement and pore size depend strongly on the concentration of copolymer used as a template. Their arrangement of pores and specific surface area increases with the increase of calcination temperature up to critical limit, 320 °C. Beyond the critical temperature, the orderness of pores and specific surface area decreases due to the collapse of the pore walls. The specific surface area, pore size and pore orderness can be controlled by optimizing calcination temperature as well as polymer concentration. We demonstrate the mechanism of pore formation and their collapse in the sol–gel synthesis of mesoporous titania.

Keywords: Mesoporous Materials, Titania, Crystallization.

1. INTRODUCTION

Recently, mesoporous metal oxides with large pore size, high specific surface area, and ordered pore network have been attracted much attention due to their potential applications in catalysis,¹ photocatalysis,² photovoltaic,^{3–5} energy storage, and gas sensing devices.⁶ Crystalline mesoporous metal oxides like Co₃O₄, NiO, MnO₂,^{7,8} have been fabricated using hard templates like mesoporous silica⁹ or mesoporous carbon.¹⁰ Crystalline TiO₂ materials have attracted great interest due to the enhanced photo-induced electron transfer ability of anatase phase, and resistance to photo-corrosion. The mesoporous TiO₂ structures are one of the efficient photocatalysts because of their highly ordered porous structure and ultrahigh photoactive surface area. It also has high oxygen production efficiency by water splitting in UV region.¹¹ However, very few works have been reported on the synthesis of crystalline titania (TiO₂) using either soft or hard templates.

Very recently Yue et al.¹² have fabricated highly crystalline mesoporous TiO₂ using hard templates such as SBA-15 and KIT-6. Shibata et al.^{13,14} have fabricated mesoporous TiO₂ particles with crystalline walls through sol–gel reaction of TiOSO₄ in the presence of cetyltrimethylammonium bromide (C₁₆TAB) without using high temperature calcinations process. Pan and Lee¹⁵ could control the cubic and hexagonal phase of mesoporous titania just by varying the speed of spinning in spin coating process. The reaction was done with the acidic titanium precursor and Pluronic F-127 as template. Though the pore size of the silica-based mesostructures could be varied in between 3 and 15.0 nm using Pluronic P-123 as structure directing agent, the average pore size and specific surface area in most of the reported works on mesoporous titania could be varied from 1.5 to 10 nm, and from 16 to 283 m²/g, respectively.^{16–18}

Mesoporous metal oxides prepared using polymer templates such as Pluronic P-123 and F-127 are generally of poor crystallinity because the soft templates cannot tolerate high temperature required for their crystallization.

*Author to whom correspondence should be addressed.

The optimum catalytic activity of mesoporous titania has been observed to be dependent strongly on the crystallinity, pore size, pore size distribution, number of pores and specific surface area. It is essential to control these parameters for the efficient photocatalytic activity and other applications of mesoporous titania.

In the present work, we report on the fabrication of ordered mesoporous TiO₂ with wide range of average pore size (2.6–4.8 nm) and specific surface area (216–348 m²/g) using soft templates such as Pluronic F-68 and F-127. Structural effect of copolymer, their concentration, and calcination temperature on the porosity have been studied. Cubic mesoporous phase is observed at relatively lower template concentration. However, the hexagonal mesoporous phase is observed as template concentration increases. Moreover, hexagonal phase has lower thermal stability compared with cubic mesoporous phase. Considering this point of view, disordered TiO₂ mesoporous structures were observed at comparatively higher template concentration.¹⁵ Recipes for controlling such parameters in mesoporous TiO₂ through triblock copolymer templated sol-gel process have been proposed.

2. EXPERIMENTAL DETAILS

2.1. Reagent and Chemicals

Titanium (IV) butoxide ((Ti(OC₄H₉)₄), 97.0%, Aldrich) used as titanium precursors, tri-block copolymers EO106PO70EO106 (Pluronic F127, Sigma Aldrich) and EO80PO30EO80 (Pluronic F68, Sigma Aldrich) as structure directing agent, ethyl alcohol ((C₂H₅OH), 94.0%, Samchun Chemicals), and hydrochloric acid (35~37%, Samchun Chemicals) used as solvent and pH controlling agent were used as received, without further purification.

2.2. Synthesis of Mesoporous TiO₂

The synthesis of mesoporous TiO₂ were carried out through triblock copolymer-templated sol-gel method via an evaporation-induced self-assembly (EISA) process. For preparing Ti-sol, 2.7 mL (0.38 M) of titanium tetrabutoxide was dissolved and stabilized in 2.9 mL of 35% HCl solution, under vigorous stirring for 3 hrs. Ethanol solutions either of Pluronic F-68 or of Pluronic F-127 were prepared by adding different amounts of either of the copolymers in 15.2 mL of ethanol (94%) under vigorous stirring for 3 hrs. The amounts of the Pluronics were varied to make the concentration of final solution as 0.001 M, 0.0025 M, 0.005 M, and 0.01 M. The previously prepared yellowish Ti-sol was then added to the Pluronic solutions by dropwise under stirring. The stirring process was continued for 12 hrs until the mixture become colorless and transparent. The resulting mixtures were then poured onto glass Petri-dish and the solvent was allowed to evaporate under atmospheric conditions for 13–15 days.

The obtained white films were then calcinated at 315 °C for 12 hrs at 1 °C/min heating rate. The effect of calcination temperature was studied by calcining the sample F-127 (0.001 M) and F-68 (0.005 M) at 260 °C, 280 °C, 300 °C and 315 °C for 12 hrs using the same heating rate.

2.3. Characterizations

The shape and orderness of pores were examined using JEOL, JEM-2010 and JEOL JEM 2100F transmission electron microscopes operating at 200 kV. For the TEM analysis small amount of sample was dispersed into 95% ethanol. For the structural determination, powder X-ray diffraction patterns were recorded with Rigaku X-ray diffractometer using the CuK α radiation ($\lambda = 1.5405 \text{ \AA}$). Surface area, pore volume, pore size distribution and pore diameter were measured by BET Quantachrome Autosorb AS1win instrument. Before analyzing the pore structure, the sample was outgased at 300 °C for 7 hrs. The mesophase of mesoporous material was observed by Rigaku D'Max 2500 18 K Small Angle X-ray Scattering system. To examine the dissociation temperature of pluronic triblock co-polymer the thermogravimetric analysis were performed on T.G.A 2050 Thermogravimetric Analyzer. Measurements were taken with a heating rate of 10 °C/min from 30 °C to 800 °C.

3. RESULTS AND DISCUSSION

3.1. TEM Measurement

Figures 1 and 2 shows the typical TEM images of the porous titania prepared using different concentrations of pluronic F-127 and F-68, and annealed at 315 °C for 12 hrs. The calcinations temperature of 315 °C was chosen as the temperature for both Pluronic F-127 and Pluronic F-68 to be dissociated as evidence from the thermogravimetric analysis. Formation of ordered porous structures can be clearly observed for the sample prepared with 0.001 M concentration of the copolymer template. With the increase of copolymer concentration, the pore orderness of the formed structures decreases and finally they become disordered as can be seen from the micrograph of Figure 1(d). The TEM images of the titania samples prepared with different concentration of pluronic F-68 are shown in Figure 2. In Figure 2, the pore orderness increases with the increase of pluronic concentration up to 0.005 M, and then the structures become disordered. As in the case of the previous set of samples prepared with pluronic F-127, the pore walls in these samples are also crystalline in anatase phase. To study the effect of calcination temperatures, the samples prepared with each copolymer at their optimum concentrations were calcinated at different temperatures. The typical TEM micrographs of the samples prepared with pluronic F-127, which was calcinated at various temperatures, are presented in Figure 3. As can be seen in

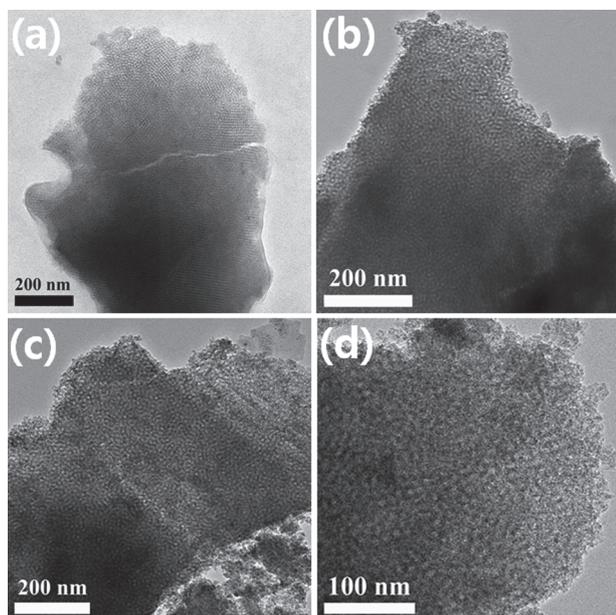


Fig. 1. Typical TEM images of the mesoporous TiO_2 samples synthesized using different concentrations of F-127: (a) 0.001 M, (b) 0.0025 M, (c) 0.005 M and (d) 0.01 M. All samples were calcinated at 315 °C for 12 hrs.

Figure 3, the most ordered porous structures are formed when the samples was calcinated at 315 °C. The pore wall crystallinity of the samples also increased with the increase of annealing temperature. The samples calcinated above 320 °C produced disordered and collapsed pores. Apart from the disordered pores, more fraction of the pores

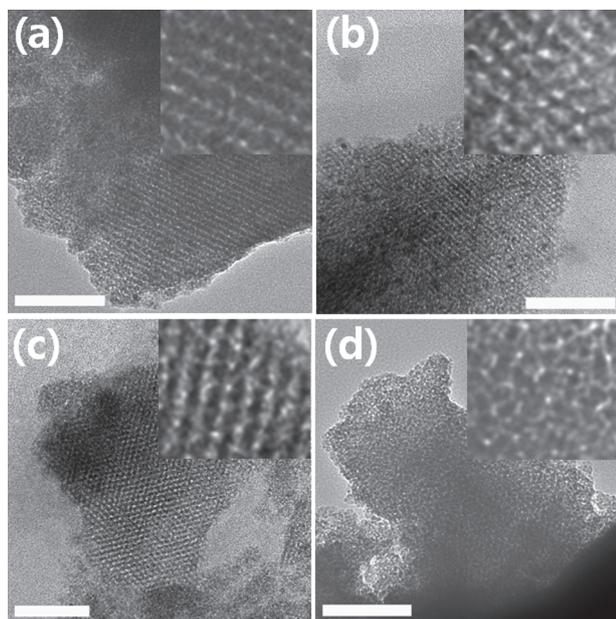


Fig. 2. Typical TEM images of the mesoporous TiO_2 samples synthesized using different concentrations of F-68: (a) 0.001 M, (b) 0.0025 M, (c) 0.005 M and (d) 0.01 M. All samples were calcinated at 315 °C for 12 hrs (white bar, 100 nm).

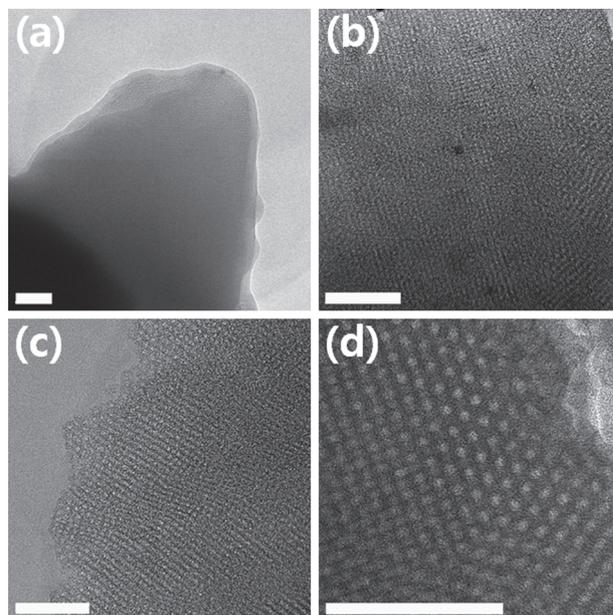


Fig. 3. Typical TEM images of the mesoporous TiO_2 samples synthesized using 0.001 M concentration of F-127 and calcinated at: (a) 260 °C, (b) 280 °C, (c) 300 °C and (d) 315 °C for 12 hrs (white bar, 100 nm).

remained blocked with the carbon remained after thermal dissociation of the copolymer template in the samples calcinated at lower temperature. It results in reducing their specific surface area and average pore size as would be seen from their nitrogen adsorption/desorption results presented later. Similar results were also observed for the samples prepared with Pluronic F-68 as shown in Figure 4.

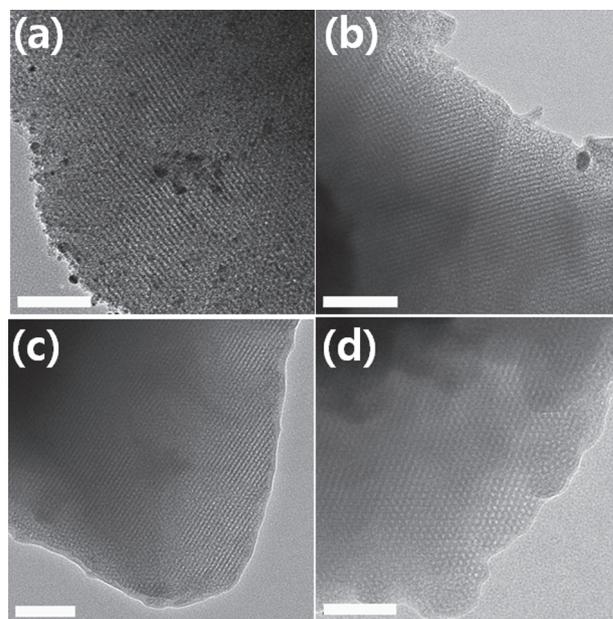


Fig. 4. Typical TEM images of the mesoporous TiO_2 samples synthesized using 0.005 M concentration of F-68 and calcinated at: (a) 260 °C, (b) 280 °C, (c) 300 °C and (d) 315 °C for 12 hrs (white bar, 100 nm).

The results indicate that the concentration of copolymer template is vital for maintaining the pores in ordered state. For each copolymer, there seems to be an optimum concentration for which we can obtain well-ordered porous titania structures. This is schematically shown in Figure 5. As both F-68 (EO80PO30EO80) and F-127 (EO106PO70EO106) are triblock copolymers with $(\text{PEO})_n-(\text{PPO})_m-(\text{PEO})_n$ blocks with different n and m values, they form micelles in aqueous environments keeping the hydrophilic (PEO) parts outwards. The concentration of these micelles in the reaction solution depends on the molar concentration of the copolymers. At very low concentration, the copolymer produces very few micelles scattered in the reaction solution. The copolymer produces a very large number of micelles with no sufficient space in between to form ordered network at very high concentration. At the optimum concentration of the copolymer, a moderate number of micelles are formed having enough space between them for ordered network.

3.2. WAXD and SAXS Measurement

The wide angle XRD patterns in Figure 6 of the samples revealed the crystallinity of the porous walls to be anatase phase (JCPDS #211227). The small angle X-ray diffraction patterns as shown in Figures 7(a) and (b) shows the first peak around 0.1–0.4 degree having high intensity and there are shoulder peaks around 0.5–1.3 degree having low intensity. This indicates long range ordering in the structure because the first strong peak and second weak peaks were found in the ordered mesoporous structure. And as we already discussed in TEM analysis, the cubic mesoporous phase is generally observed at relatively lower template concentration. However, the hexagonal mesoporous phase is observed as template concentration

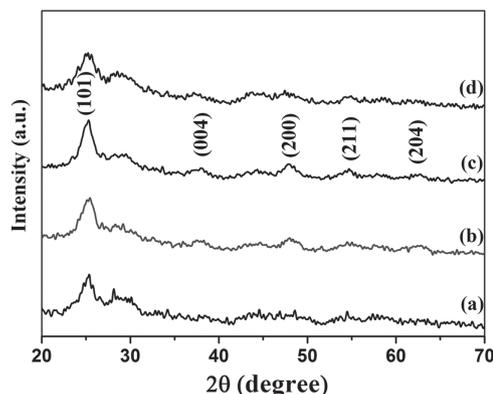


Fig. 6. XRD spectra of the mesoporous TiO_2 samples synthesized using different concentration of F-127: (a) 0.001 M, (b) 0.0025 M, (c) 0.005 M and (d) 0.01 M. All samples were calcinated at 315 °C for 12 hrs. The diffraction peaks are identified using the standard JCPDS #211227 data.

increases. This indicates that the (100) peak position is going to be shifted toward relatively higher 2theta value as template concentration increases. This can be clearly seen in high molecular weight template like pluronic F-127. The cubic mesophases is going to be converted into the hexagonal mesophases as the concentration of template increases and the high intensity of (100) peak is going to be shifted at higher 2theta value around 0.12–0.36 degree. Finally the peak position reached 0.48 degree when template concentration increases from 0.0025 M to 0.01 M. But this trend is less effective when pluronic F-68 is used as template due to its low molecular weight.

3.3. N_2 Adsorption/Desorption Isotherms

The nitrogen adsorption/desorption isotherms of the samples prepared with different concentrations of Pluronic

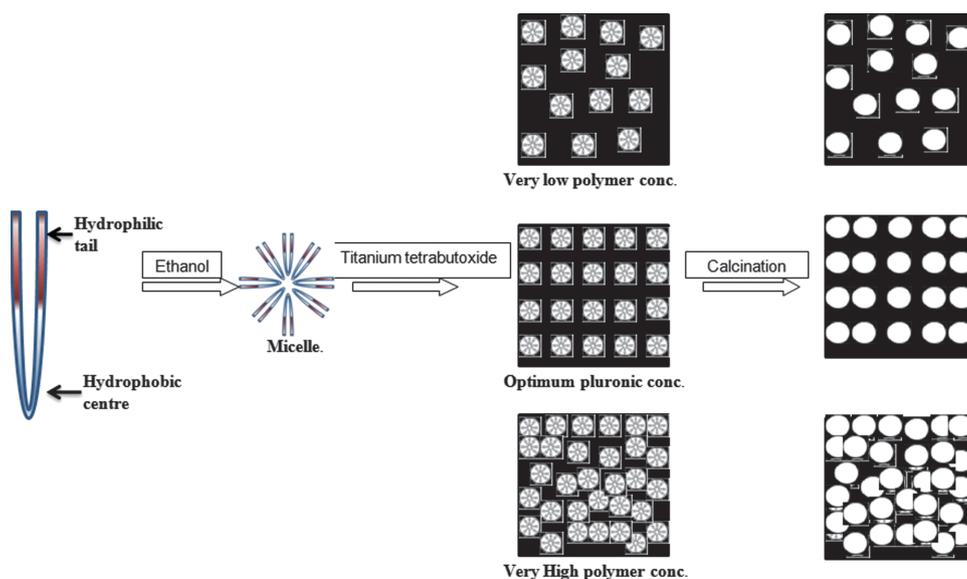


Fig. 5. Schematic drawing for formation of ordered and disordered porous structure of TiO_2 at different pluronic concentrations.

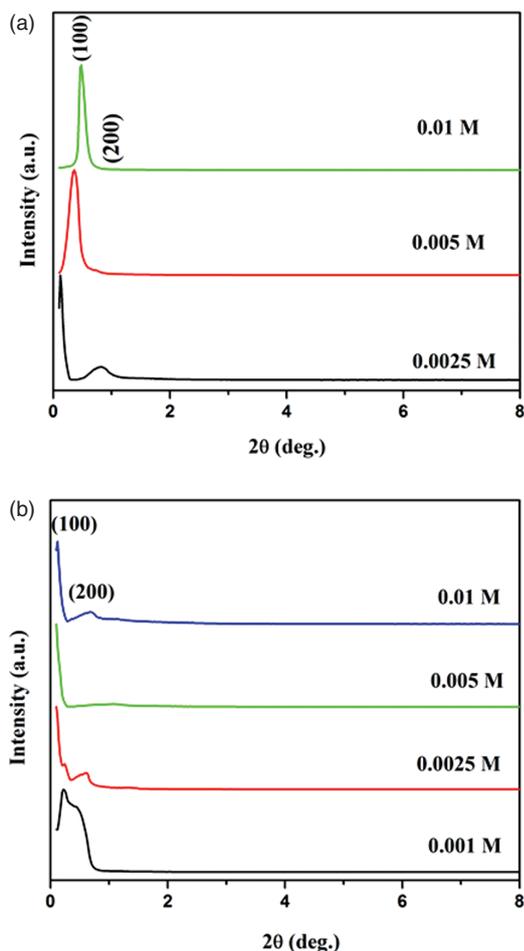


Fig. 7. Low angle XRD of mesoporous TiO_2 synthesized at different polymer concentration of (a) pluronic F-127 and (b) pluronic F-68.

F-127 are presented in Figure 8(a). As can be noticed, all the samples revealed similar and type-IV isotherms (IUPAC classification),¹⁹ which is associated to mesopores of high degree of pore size uniformity¹⁵ with a sharp desorption at about $P/P_0 = 0.45$. It indicates a sudden evaporation of adsorbate from cylindrical shaped pores. Similar results were observed for the samples prepared with pluronic F-68. Figure 8(b) shows that the variation of average pore size and specific surface area of the samples are compared with different concentrations. The variations of average pore size are similar for both of the pluronics. However, the pore size is higher for the Pluronic F-127 than Pluronic F-68 due to its higher chain length, which leads formation of bigger micelles. The average pore size in both cases is optimum for a certain concentration of the Pluronic, and then it decreases. The decrease of pore size at high copolymer concentration is due to the steric hindrance occurred when number of micelles is large in solution due to high concentration of pluronic. However, the specific surface area of the porous structures increased with the increase of the concentrations of the copolymers in Figure 8(c).

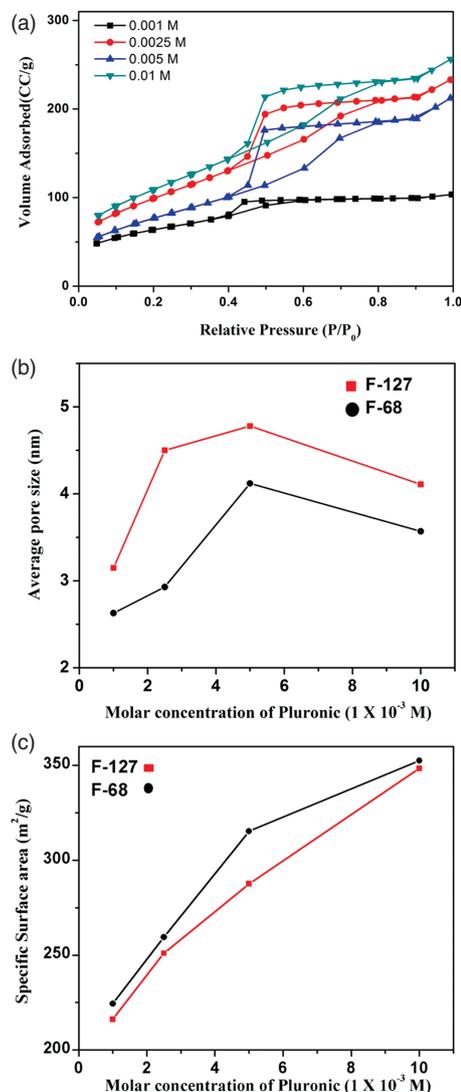


Fig. 8. (a) Nitrogen adsorption/desorption isotherms for the mesoporous TiO_2 samples synthesized using different concentration of F-127 (from 0.001 M to 0.01 M). All samples were calcinated at 315 °C for 12 hrs. The variation of (b) average pore size, and (c) specific surface area versus the various copolymer concentration.

To study the effect of calcination temperature on the specific surface area, the samples were synthesized using pluronic F-127 and pluronic F-68 at their optimized concentrations 0.001 M and 0.005 M, respectively, and calcinated at different calcination temperatures as 260 °C, 280 °C, 300 °C and 315 °C. Figure 9(a) shows typical nitrogen adsorption/desorption isotherm of the sample prepared with different calcination temperature. As the calcination temperature was increased, the specific surface area was also increased, which can be seen in Figure 9(b). The reason for this is already discussed in above TEM results. At lower calcination temperature due to thermal dissociations of polymer template the carbon residue formed, which remaining present inside the pores. Hence their pores blocked due to presence of carbon residue. It results in the decrease in the specific surface area and orderness

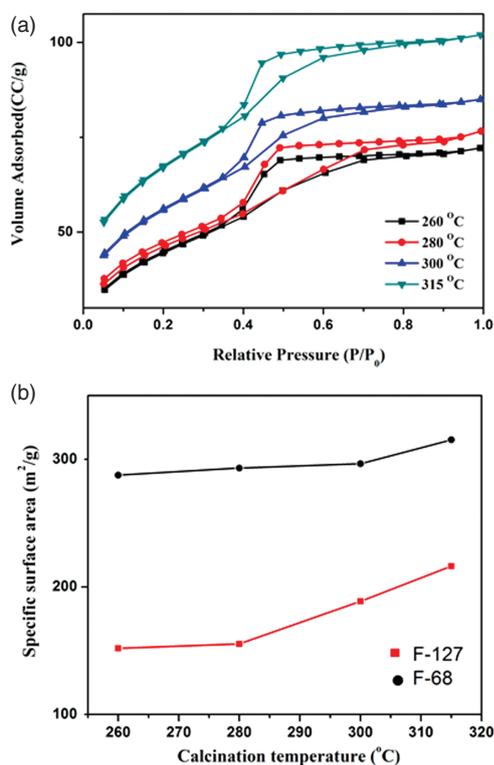


Fig. 9. (a) Nitrogen adsorption/desorption isotherms for the mesoporous TiO₂ sample synthesized using 0.001 M conc. of F-127 and calcinated at from 260 °C to 315 °C for 12 hrs. (b) The variation of specific surface area versus the calcination temperature.

of pores. While on calcinating at higher calcination temperature, 315 °C, the template was removed completely from inner part of pores, and results in clean pores. Due to this, most ordered porous structure is formed with high specific surface area.

4. CONCLUSIONS

The synthesis strategy of mesoporous TiO₂ powder in bulk amount through triblock copolymer-templated sol-gel method via an EISA process has been reported. We also expose some focus on the optimization of template concentration to obtain ordered mesostructure, effect of increasing template concentration on surface area and pore size because both of these factors play an important role in the efficiency of photocatalysis. And we also demonstrated

shortly the thermal stability of pore wall and effect of calcination temperature on surface area and orderness of mesoporous structure.

Acknowledgments: This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded from the Ministry of Education, Science and Technology (MEST) of Korea for the Center for Next Generation Dye-sensitized Solar Cells (No. 2011-0001055).

References and Notes

1. D. Carta, M. F. Casula, A. Corrias, A. Falqui, Á. Dombovári, A. Gálós, and Z. Kónya, *J. Nanosci. Nanotechnol.* 11, 6735 (2011).
2. H. Wang, Y. Teng, L. Radhakrishnan, Y. Nemoto, M. Imura, Y. Shimakawa, and Y. Yamauchi, *J. Nanosci. Nanotechnol.* 11, 3843 (2011).
3. M.-K. Seo and S.-J. Park, *J. Nanosci. Nanotechnol.* 11, 4633 (2011).
4. G. Xiao, C. Xian, H. Li, and L. Chen, *J. Nanosci. Nanotechnol.* 11, 1923 (2011).
5. S. Ameen, Y.-B. Im, G. C. Jo, Y. S. Kim, and H.-S. Shin, *J. Nanosci. Nanotechnol.* 11, 541 (2011).
6. H. F. Lu, F. Li, G. Liu, Z.-G. Chen, D.-W. Wang, H.-T. Fang, G. Q. Lu, Z. H. Jiang and H.-M. Cheng, *Nanotechnology* 19, 405504 (2008).
7. C. Dickinson, W. Z. Zhou, R. P. Hodgkins, Y. F. Shi, D. Y. Zhao, and H. Y. He, *Chem. Mater.* 18, 3088 (2006).
8. F. Jiao, A. Harrison, J. C. Jumas, A. V. Chadwick, W. Kockelmann, and P. G. Bruce, *J. Am. Chem. Soc.* 128, 5468 (2006).
9. D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.* 120, 6024 (1998).
10. S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, and O. J. Terasaki, *J. Am. Chem. Soc.* 122, 10712 (2000).
11. H. Kato and A. Kudo, *J. Phys. Chem. B* 106, 5029 (2002).
12. W. Yue, A. Xu, J. T. S. Irvine, P. S. Attidekou, C. Liu, H. He, D. Zhao, and W. Zhou, *Chem. Mater.* 21, 2540 (2009).
13. H. Shibata, T. Ogura, T. Mukai, T. Ohkubo, H. Sakai, and M. Abe, *J. Am. Chem. Soc.* 127, 16396 (2005).
14. H. Shibata, H. Mihara, T. Mukai, T. Ogura, H. Kohno, T. Ohkubo, H. Sakai, and M. Abe, *Chem. Mater.* 18, 2256 (2006).
15. J. H. Pan and W. I. Lee, *New J. Chem.* 29, 841 (2005).
16. K. Liu, H. Fu, K. Shi, F. Xiao, L. Jing, and B. Xin, *J. Phys. Chem. B* 109, 18719 (2005).
17. D. Fattakhova-Rohlfing, M. Wark, T. Brazesinski, B. M. Smarsly, and J. Rathousky, *Adv. Funct. Mater.* 17, 123 (2007).
18. J.-Y. Zheng, J.-B. Pang, K. Y. Qiu, and Y. Wei, *J. Mater. Chem.* 11, 3367 (2001).
19. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.* 114, 10834 (1992).

Received: 31 July 2011. Accepted: 23 December 2011.