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Fabrication of Mesoporous Titanium Dioxide Assisted by Resorcinol/Formaldehyde Gel

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Mesoporous structures of materials have attracted considerable attention recently because of their potential in a variety of applications. In this work, resorcinol/formaldehyde (RF) gel was used as a template for the synthesis of mesoporous titania, which is in great interest in catalysis, photocatalysis, gas sensor and photovoltaic applications. RF-gel was prepared by the sol-gel polycondensation of resorcinol (R) and formaldehyde (F). Titanium tetraisopropoxide (TTIP) was used as precursor for titania. However, direct incorporation of TTIP into RF-gel was limited by a spontaneous reaction between TTIP and RF gel, which consequently resulted in rapid solidification of the gel. Titania sol was firstly prepared from TTIP via sol-gel process. After certain period of aging time, the titania sol was added into RF mixture, which had been aged for predetermined period of time as well. After that, the mixture was further aged for another 36 hours before being dried at 80°C. Finally, the dried gel was calcined at 500°C for 4 hours to remove the RF template. The obtained titania powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurement via nitrogen adsorption, and Fourier transform infrared spectroscopy (FTIR). The specific surface area of the samples was in the range of 30-33 m^2/g. and the average diameter of about 8.8-37.7 nm. It was found that the rate of addition for titania sol into the RF-gel had influence on the phase of the final product. The increased rate favored the formation of titania in rutile phase.

Keyword: Mesoporous, Titania, Resorcinol/formaldehyde gel

INTRODUCTION

Porous ceramics are essential for many industries where high permeability, high surface area, or insulating characteristics is required [1]. Nanocrystalline titanium dioxide (TiO_2 or titania), as one of the most important oxide semiconductor materials, has been extensively researched during recent years for its superior physical and chemical properties (e.g., catalytic and photocatalytic activity, good stability toward adverse environment, sensitivity to humidity, dielectric characteristic, photo-electrochemical conversion, nonlinear optics, and photoluminescence) [2, 3]. Furthermore, strong oxidizing power of photogenerated holes, chemical inertness, and non-toxicity of TiO_2 have also made it a superior photocatalyst [4]. Titanium dioxide is also a fascinating material from a surface science point of view [5].

Nanostructured titania has attracted lots of attention in the past decade because of its large effective surface area which enhances surface reactions that lead to many industrial applications as gas sensors and solar cells [5]. Many techniques have been developed to prepare nanostructured titanium dioxide with unique properties, such as liquid processes (e.g., sol–gel, solvothermal and hydrothermal techniques), solid state processing routes (mechanical alloying, milling, mechano-chemical), radio-frequency or thermal-plasma deposition and other routes such as laser ablation [6-10]. Yet, most of the synthesized products are either non-porous nanoparticles or nanostructures that contain micro-pores, which might not be able to accommodate reaction of relatively large compound.

In this work, mesoporous titanium dioxide was prepared using resorcinol-formaldehyde (RF) gel as a template. RF gel is a product from polymerization of resorcinol (R) and formaldehyde (F). RF gel has a capability to be further processed into carbon aerogel with many special characteristics such as a tortuous open-cell structure, ultrafine pore size (< 50 nm) and high surface area (400-1000 m^2g^{-1}) [11]. The main objective of the present work is to study effects of various factors, including rate of addition for titania precursor into RF gel, the R-to-F molar ratio in the preparation of RF gel, the molar ratio between RF gel and titania sol, and aging time for both RF gel and titania sol, on pore structure and surface area of the product.

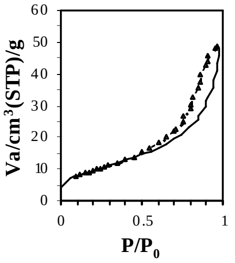
EXPERIMENTAL

RF solution was firstly prepared by dissolving resorcinol (99%, Fluka) in ethanol under magnetic stirring, with the addition acetic acid. After dissolution, formaldehyde solution (37% in water, stabilized by 10-15% wt. methanol, Ajax Finechem) that was previously mixed with titanium tetraisopropoxide (TTIP 99%, Aldrich) in ethanol was added to the solution. The molar ratio of TTIP-to-ethanol-to-acetic acid was 1:9:0.1. The mixture was stirred for another 15 min at room temperature. Then, it was poured into a cup and aged at room temperature for 36 hours in a closed system to obtain RF/TiO_2 hydrogels. After that, the obtained gel was dried for 3 hours at 80°C. The dried sample was calcined at 500°C for 4 hours in a box furnace to remove residual organic compound as well as RF gel from titania. The obtained products were characterized by various techniques. X-ray diffraction (XRD) analysis was conducted for phase identification and average crystallite size. The microstructures were investigated by scanning electron microscopy (SEM). The specific surface area was determined from BET analysis. Fourier transform infrared spectroscopy (FTIR) was used for identification of functional group in the products.

RESULTS AND DISCUSSION

General characteristics of the product

For the titania product synthesized by adding the titania precursor (i.e, TTIP solution) into RF gel that was prepared using R/F molar ratio of 0.5 and then calcined at 500°C, the BET analysis revealed type IV adsorption isotherm (see Figure 1a), which suggested the presence of mesopores within the product. By comparing with the adsorption isotherm obtained from the calcined titania sol (i.e., the product formed without the assistance of RF gel), it was clearly indicated that the use of RF gel could introduce mesoporosity into titania. The specific surface area of titania formed using RF gel template, in this case, was found to be 33 m^2/g, which was significantly higher than that of the calcined titania sol, as shown in Table 1.



(a) (b)

Figure 1. N_2 adsorption/desorption isotherm of titania synthesized with (a) and without (b) the assistance of RF gel

Table 1. Surface area and average pore diameter of products formed with and without the use of RF gel.

Condition	Surface area (m^2/g)	Average pore diameter (nm)
TiO_2	18.5	3.1
RF/TiO_2	33.5	8.9

Figure 2 shows FTIR spectra of the RF/TiO_2 composite prior to the calcination, comparing with those of dried titania sol and neat RF gel. It should be noted that the RF gel employed was aged for 36 h and the R/Ti molar ratio in the RF/TiO_2 composite was 0.35. All samples showed the absorption bands at 1375, 1090, 1045, 880 and 800 cm^{-1}, which are results from residual ethanol within the samples [12]. The RF/TiO_2 composite showed similar IR absorption bands as that of the neat RF gel, e.g., at wavenumber of 1612, 1473 and 1443 cm^{-1} for aromatic ether bonds; at 1508 cm^{-1} for C=C in aromatic rings; and at 1218 and 1220 cm^{-1} for C-C-O asymmetric stretching [13]. However, the intensity of some bands were changed. Moreover, besides the broad band at 500-600 cm^{-1} corresponding to Ti-O-Ti bonds, additional signals such as the bands at 1070, 1040, 930 and 880 cm^{-1}, which are corresponding to titanium ethoxide functional groups [12], were also observed. These results suggested the interaction between TTIP and RF network. The fact that the signals for aromatic ether bonds at 1473 and 1443 cm^{-1} [13] significantly increased also suggested the increased network of resorcinol/formaldehyde assisted by TTIP.

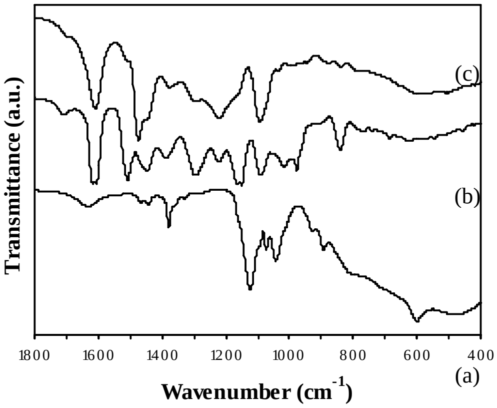


Figure 2. FTIR spectra of titania sol (a), neat RF gel (b) and RF/TiO_2 composite before being calcined (c)

Effect of addition rate of TTIP into RF gel

In addition to the evidence of interaction between TTIP and RF gel as discussed earlier, it should also be noted that the reaction between TTIP and RF gel could also be witnessed visually. Color of the RF mixture changed right after TTIP was dropped into, which confirmed spontaneous reaction between TTIP and RF gel. Furthermore, for RF gel prepared with some specific conditions, the reaction resulted in rapid solidification of the gel. Therefore, the addition rate for TTIP into RF gel would significantly affect the porosity of the final product.

Figure 3 shows XRD patterns of RF/titania composite after being calcined at 500°C. The samples were prepared using different preparation details. The first sample, i.e., T001, was prepared by slowly adding 4.5 ml TTIP solution into RF solution. It took 2 min to complete the addition process. The second sample (T002) was prepared in similar manner to that of T001, but the TTIP solution was added to the RF solution within 5 second. For the last sample (T003), TTIP was poured into RF solution within 5 second as well, but no acetic acid was used in the preparation of RF gel. The XRD results show that T001 and T003 samples were titania in anatase phase, while T002 was mainly rutile. The result clearly indicated that the rate of TTIP addition significantly influenced the phase of the final product. The increased TTIP addition rate favored the formation of titania in rutile phase. On the other hand, the presence of acetic acid in RF gel did not affect phase formation of titania.

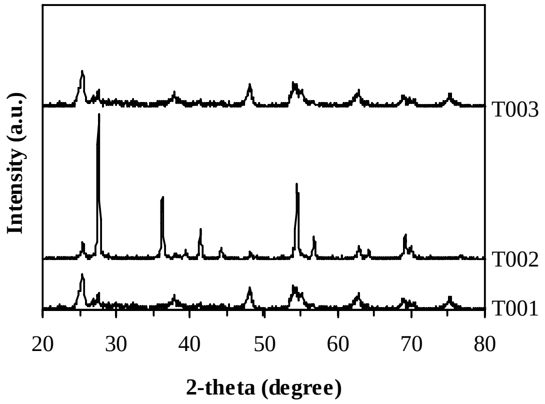


Figure 3. XRD patterns of titania powders prepared by using different rate of TTIP addition

Effect of R/F ratio

Figure 4 compares FTIR spectra of precalcined RF/TiO_2 composites that were prepared using RF gel with R/F molar ratio of 0.5 and 1.0, respectively. The R/Ti molar ratio was fixed at 0.35.

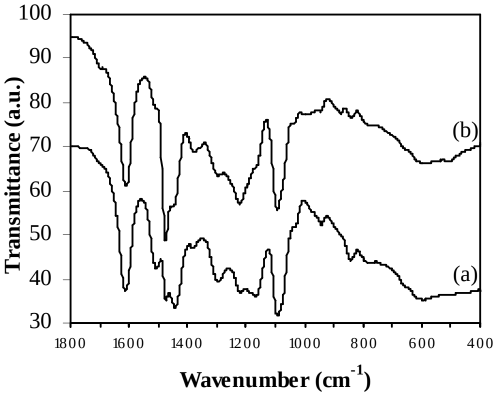


Figure 4. FTIR spectra of precalcined RF/TiO_2 composites that were prepared with R/F molar ratio of 1.0 (a) and 0.5 (b)

The composite with higher fraction of formaldehyde (i.e., lower R/F ratio) would resulted in greater extent of condensation of resorcinol to form RF network, as witnessed from the increase in intensity of the absorption bands at 1612, 1473 and 1443 cm^{-1}, which are corresponding to aromatic ether bonds. The signals for C-C-O asymmetric stretching at 1218 and 1220 cm^{-1} as well as those for in plane OH vibration at 1381 and 1377 cm^{-1} [13] were also increased. As the results, it made the RF gel to be less reactive to TTIP, which agreed with the observation that the intensity of the signal for Ti-O-C bonding at wavenumber of 1091 and 1093 cm^{-1} [12, 14] in the sample with R/F ratio of 0.5 was lower than that of the sample prepared with higher R/F ratio.

SEM micrographs of titania products obtained after calcination of RF/TiO_2 composites are shown in Figure 5. The composites were prepared with various R/F ratios. It could be seen that the particles were, in fact, aggregates of nanosized particles.

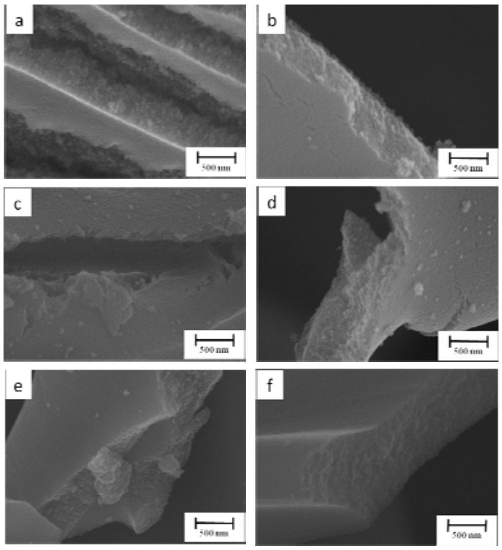


Figure 5. SEM images of titania products obtained from the calcination of RF/TiO_2 composites that were prepared using R/F ratio of 0.5 (a-b), 1.0 (c-d) and 1.5 (e-f)

Effect of aging time for RF gel

It has been recognized that prolonged aging of the RF gel results in further condensation of the gel. The aging process also affects pore distribution within the RF gel. In this section, RF gel was prepared and aged prior to the addition of TTIP into the gel. The duration of the aging time was varied in order to observe its effect on the reactivity of RF gel with TTIP.

FTIR spectrum of the RF/TiO_2 composites prepared by using RF gel that was aged for 0-2 days are shown in Figure 6. All samples were prepared with R/F and R/Ti molar ratio of 0.5 and 0.35, respectively. It was found that all spectrums were very similar. Nevertheless, the intensity of the signal for Ti-O-C bonding was highest in the sample prepared using RF aging time of 1 day. The absorption bands corresponding to aliphatic hydroxyl group (at 1000 and 998 cm^{-1}) was also minimum for this sample. These results indicated that the RF aging time of 1 day is optimum for the reaction with TTIP. Prolonged period of aging time might result in the highly condensed gel that became less reactive. As the result, titania product obtained from the calcination of the RF/TiO_2 that was prepared with RF gel aged for 1 day was found to have the highest surface area, as shown in Table 2.

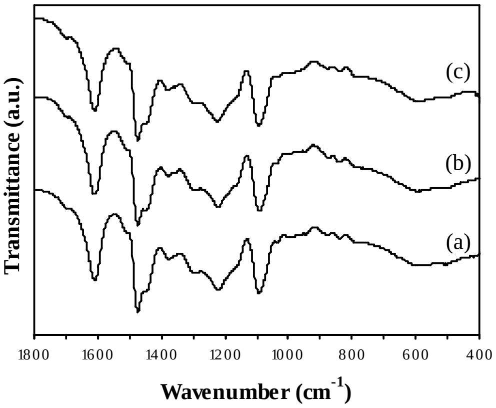


Figure 6. FTIR spectra of precalcined RF/TiO_2 composites that were prepared from RF gel aged for 0 (a), 1 (b) and 2 days (c)

Table 2: Surface area and average pore diameter of titania formed from calcination of RF/TiO_2 composite prepared by using RF gel aged for various period of time.

RF aging time (day)	Surface area (m^2/g)	Average pore diameter (nm)
0	31.9	4.4
1	36.1	4.3
2	23.1	4.2

Effect of aging time for titania precursor

In this section, effect of titania aging time was investigated. Instead of adding titania precursor (i.e., TTIP solution) directly into RF gel, the titania precursor was aged for 6 h to allow the formation of titania sol prior to the addition to RF gel. It should be noted that the RF gel used in this section was not aged. The R/F molar ratio was fixed at 0.5.

It was observed from the FTIR spectra in Figure 7 that the aging time for titania precursor lowered its reactivity, which subsequently affected the bonding structure of RF network in the RF/TiO_2 composite, especially for aromatic ether and C-C-O bonding. The aging of TTIP solution also allowed titania nanoparticles to form and grow before being added into RF mixture. As the result, grains within the product obtained after calcination became larger, which could be clearly observed from SEM images shown in Figure 8.

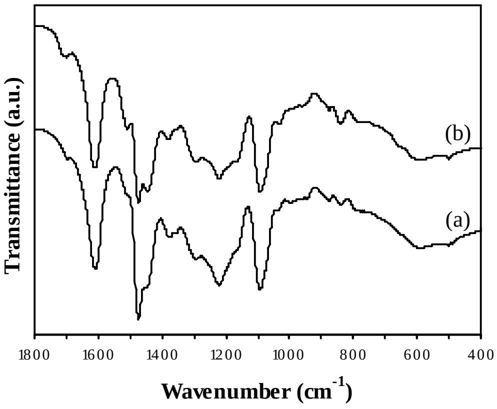


Figure 7. FTIR spectra of precalcined RF/TiO_2 composites that were prepared by using TTIP solution aged for 0 (a) and 6 h (b)

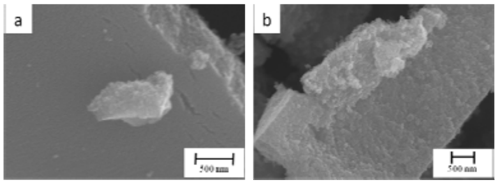


Figure 8. SEM images of titania products obtained from the calcination of RF/TiO_2 composites that were prepared using TTIP solution aged for 0 (a) and 6 h (b)

CONCLUSION

In the present contribution, mesoporous titania was synthesized by the aid of RF gel. Reaction between TTIP and RF network was confirmed and found to be an important factor affecting porosity of the final product. Several factors, including rate of addition for titania precursor, R/F molar ratio and aging time for both RF gel and titania precursor, were found to have influence toward the TTIP/RF reaction.

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REFERENCES

1) W. Zhang, H. Wang and Z. Jin: Materials Letters **59** (2005) 250.
2) C. Wang, Z.-X. Deng and Y. Li: Inorganic Chemistry **40** (2001) 5210.
3) S. Mahshid, M. Askari and M.S. Ghamsari: Journal of Materials Processing Technology **189** (2007) 296.
4) M. Miyauchi, A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe: Chemistry of Materials **12** (1999) 3.
5) S.K. Hazra, S.R. Tripathy, I. Alessandri, L.E. Depero and S. Basu: Materials Science and Engineering: B **131** (2006) 135.
6) C.-S. Kim, B.K. Moon, J.-H. Park, B.-C. Choi and H.-J. Seo: Journal of Crystal Growth **257** (2003) 309.
7) A.M. Ruiz, G. Sakai, A. Cornet, K. Shimanoe, J.R. Morante and N. Yamazoe: Sensors and Actuators B: Chemical **103** (2004) 312.

8) D.H. Kim, H.S. Hong, S.J. Kim, J.S. Song and K.S. Lee: Journal of Alloys and Compounds **375** (2004) 259.
9) S.-M. Oh and T. Ishigaki: Thin Solid Films **457** (2004) 186.
10) T.Y. Masakazu Matsubara, Hisayoshi Itoh, Hiroaki Abe and Keisuke Asai: Jpn. J.Appl. Phys **42** (2003) L479.
11) B. Babic, B. Kaluₒerovic, L. Vracar and N. Krstajic: Carbon **42** (2004) 2617.
12) M. Burgos and M. Langlet: Thin Solid Films **349** (1999) 19.
13) I. Poljansek and M. Krajnc: Scientific paper **52** (2005) 238.
14) W.L. Guo, Z.M. Lin, X.K. Wang and G.Z. Song: Microelectronic Engineering **66** (2003) 95.