

# Thermal Effect of Carbamates Based Polymer on the TiO<sub>2</sub> Growth

Jong Wook Shin,<sup>1</sup> Soo Young Kim<sup>2</sup>

<sup>1</sup>Department of Internal Medicine, Chung-Ang University College of Medicine, Dongjak-gu, Seoul 156-756, Korea

<sup>2</sup>School of Chemical Engineering and Materials Science, Chung-Ang University, Dongjak-gu, Seoul 156-756, Korea

Received 10 June 2011; accepted 4 September 2011

DOI 10.1002/app.35583

Published online 11 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** We investigated the growth of TiO<sub>2</sub> on poly((tetrahydropyran-2-yl *N*-(2-methacryloxyethyl) carbamate)-*co*-(methyl 4-(3-methacryloxypropoxy) cinnamate) (THP-polymer) using thermal heating, octyl isocyanate (OIC), and glutaraldehyde. It is found that TiO<sub>2</sub> can be grown on surfaces terminated with —NH<sub>2</sub> and —O— groups from aqueous solution. However, TiO<sub>2</sub> did not deposit on —CH<sub>3</sub> terminated surfaces, due to the low surface energy of these surfaces. Fourier transform infrared spectroscopy and thermogravimetric analysis data showed that the —THP functional group can be removed and the surface functional

group converted to —NH<sub>2</sub> by heating the material over 180°C. OIC can then be immobilized on the surface after heating, changing the surface functional group from —NH<sub>2</sub> to —CH<sub>3</sub>. As TiO<sub>2</sub> can be deposited from solution on —NH<sub>2</sub> terminated, but not —CH<sub>3</sub> terminated surfaces, THP-polymer can be used to switch the surface properties by thermal activation and subsequent reaction with OIC. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4920–4925, 2012

**Key words:** TiO<sub>2</sub>; tetrahydropyran; carbamate; thermal heating; growth

## INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) films have widespread applications as materials used for optical coatings and protective layers in very large scale integrated circuits.<sup>1–3</sup> Considering modern environmental problems, many scientists have directed attention to TiO<sub>2</sub> as a working electrode in water photoelectrolysis systems because of its high photo-oxidation reaction activity, high resistivity against photocorrosion, and excellent charge transport properties.<sup>4</sup> With the aim of increasing the efficiency of water photolysis, TiO<sub>2</sub> nanotube arrays appear ideal for allowing efficient charge transfer in combination with a high surface area readily accessible to electrolyte percolation. TiO<sub>2</sub> nanotubes and arrays thereof have been produced by a variety of methods such as depositing into free standing nanoporous alumina used as a template, sol-gel transcription processes using organo-gelators as templates, a seeded growth mechanism, and hydrothermal processes.<sup>5–8</sup> Selective

growth of TiO<sub>2</sub> in a nano-patterned region is also expected to increase the efficiency of production.

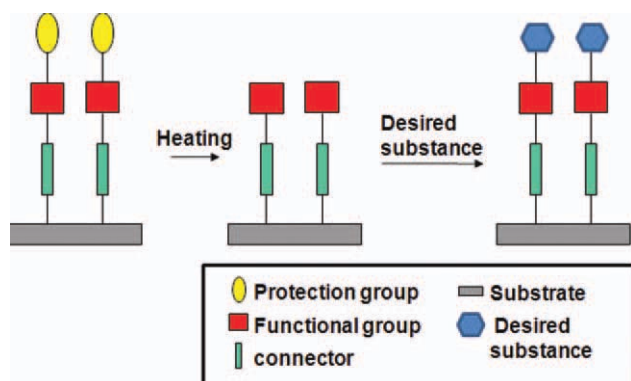
Growth can be happened easily on the materials with high surface energies. The surface energies of materials with —NH<sub>2</sub> functional groups, such as 3-aminopropyltriethoxysilane (APTES), are higher than those of materials with —CH<sub>3</sub> functional groups, such as alkyl isocyanates.<sup>9</sup> If materials with low surface energies are used as protection groups and materials with high surface energies are used for functionality, as shown in Figure 1, then detaching the protection group by external factor manipulation will allow the desired substance to grow on the functional group. Therefore, it is expected that changing the surface functional group from —NH<sub>2</sub> to —CH<sub>3</sub> will make it possible to control the growth conditions of TiO<sub>2</sub>.

In this article, we introduce the growth of TiO<sub>2</sub> by the change of tetrahydropyran (THP) protected groups on a polymer. In particular, poly((tetrahydropyran-2-yl *N*-(2-methacryloxyethyl) carbamate)-*co*-(methyl 4-(3-methacryloxypropoxy) cinnamate) (THP-polymer) is introduced for the growth of TiO<sub>2</sub> in this experiment. THP is introduced to undergo deprotection at a lower temperature and photocross-linkable copolymer analogue is adopted to exhibit no glass transition temperature at or below the deprotection temperature of THP. Contrasts in selectivity for TiO<sub>2</sub> growth have been obtained by converting the —NH<sub>2</sub> functional groups (after thermal deprotection of THP-polymer) into —CH<sub>3</sub> functional

Correspondence to: S. Y. Kim (sooyoungkim@cau.ac.kr).

Contract grant sponsor: The convergence research between Medicine and Engineering, Chung-Ang University in 2010.

Contract grant sponsor: Basic Science and Mid-career research Program [National Research Foundation of Korea (NRF), Ministry of Education, Science and Technology]; contract grant numbers: 2011-0008994, 2011-0028752.



**Figure 1** Basic scheme for the growth of desired substances using polymers composed of protection groups, functionalities, and connectors. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

groups, for example by reacting the surfaces with octyl isocyanate (OIC), as isocyanates are known to react with amines, forming urea. Glutaraldehyde is also introduced to maintain the patterned region during thermal heating. A liquid phase deposition method based on  $(\text{NH}_4)_2\text{TiF}_6$  and  $\text{H}_3\text{BO}_3$  was adopted to deposit  $\text{TiO}_2$  on desired regions.<sup>10</sup> Therefore, heated THP-polymer, OIC, and glutaraldehyde were used to change surface properties, thereby controlling the growth conditions of  $\text{TiO}_2$ .

## EXPERIMENTAL

### Synthesis of tetrahydropyran-2-yl *N*-(2-ethylmethacrylate)

Figure 2(a) shows a synthesis scheme of tetrahydropyran-2-yl *N*-(2-ethylmethacrylate). Tetrahydropyran-2-yl THP and 3-isocyanatopropyl triethoxysilane were charged into a three-necked flask under an inert atmosphere (2.80 mL; 28 mM) and then mixed with 2-isocyanatoethyl methacrylate (3.1 g; 20 mM) and one drop of pyridine until the reaction was complete as verified by <sup>1</sup>H nuclear magnetic resonance (NMR). The resulting viscous mixture was purified by column chromatography on silica to yield a white powder (2.93 g; 57%). <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) 6.09 (s, 1H), 5.81 (and a satellite at 5.90; broad, 1H), 5.57 (*P*, *J* = 1.5 Hz, 1H), 5.05 (and a satellite at 4.83; broad, 1H), 4.21 (t, *J* = 6 Hz, 2H), 3.86 (td, *J* = 8.5, 3 Hz, 1H), 3.63 (dt, *J* = 12, 5 Hz, 1H), 3.5 (q, *J* = 5.4 Hz, 2H), 1.91 (s, 3H), 1.76 (dd, *J* = 9.7, 2.7 Hz, 2H), 1.48–1.68 (m, 4H). <sup>13</sup>C-NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) 167, 155, 136, 126, 93.3, 63.6, 63.3, 40.0, 29.3, 24.8, 19.0, and 18.2. Elemental analysis calculated for  $\text{C}_{12}\text{H}_{19}\text{NO}_5$ : C 56.02; H 7.44; N 5.44; Found: C 56.22; H 7.36; N 5.48.

### Synthesis of THP-polymer

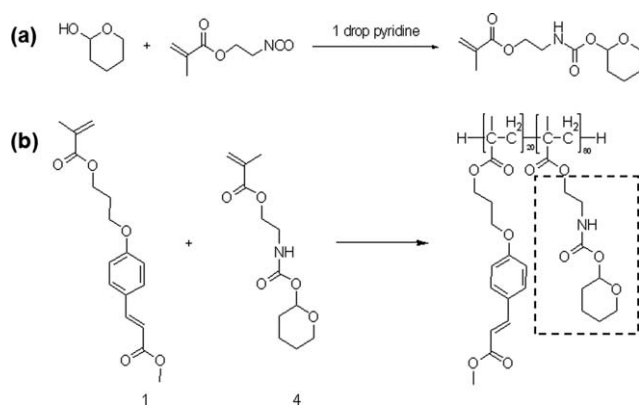
The synthesis of THP-polymer is shown in Figure 2(b). A mixture of tetrahydropyran-2-yl *N*-(2-methacryloxyethyl) (0.50 g; 1.9 mM), methyl 4-(3-methacryloxypropoxy) cinnamate (0.15 g; 0.48 mM), and azobisisobutyronitrile (2.0 mg; 0.012 mM) in tetrahydrofuran (6 mL) was added to a Schlenk ampoule using a Pasteur pipette. The flask was then freeze-pump-thawed a minimum of four times, and the reaction mixture was heated to 60°C for 20 h. Once the reaction mixture had returned to room temperature, it was diluted with dichloromethane (DCM, 30 mL) and added dropwise to hexane (300 mL). The resulting precipitate was removed by vacuum filtration and dried under vacuum to yield a white powder (360 mg, 55%). <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) 7.6 (d broad, 1H), 7.5 (s broad, 2H), 6.9 (s broad, 2H), 6.3 (d, broad, 2H), 5.7–6.0 (m broad, 4 H), 3.3–4.2 (four singlets broad, 23 H), 0.7–2.1 (several m broad, 51H); <sup>13</sup>C-NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  (ppm) 176, 168, 161, 155, 144, 130, 128, 115, 93, 64, 54, 52, 45, 40, 30, 28, 25, 19, and 17.

### Immobilization of THP-polymer on Si

For the immobilization of THP-polymer on Si, the Si substrate was cleaned with piranha solution ( $\text{H}_2\text{SO}_4$  :  $\text{H}_2\text{O}_2$  = 3 : 1). The sample was placed in anhydrous toluene (~ 50 mL) under argon and a solution of 4-(3-(chlorodimethylsilyl)propoxy) benzophenone in toluene (3 mL, ca. 0.28M) was added along with five drops of anhydrous triethylamine for the covalent attachment of polymers to the substrate surface. The sample was left in the solution overnight, washed with chloroform, followed by drying with  $\text{N}_2$ . The solution (20 mg  $\text{mL}^{-1}$ ) of THP-polymer in cyclohexanone was dropped on the sample. The sample was spun at 1000 rpm for 2 min. UV (352 nm) was irradiated on the sample for 1 h to activate the benzophenone moiety and attach the polymer to the surface. UV (300 nm) was also irradiated to crosslink the polymer via dimerization of the cinnamate moieties. The measured thickness of the film was  $75 \pm 5$  nm.

### Immobilization of APTES and hexamethyldisilazane (HMDS) on Si

Two kinds of Si samples were prepared to investigate the role of surface functional group on  $\text{TiO}_2$  growth. One sample was Si coated with APTES. A Schlenk-type beaker was purged with nitrogen and 20 mL dry toluene was added. A Si wafer was placed in the beaker and 0.3 mL of APTES was added. This system was kept for 72 h. After that, the sample was rinsed with toluene, followed by drying with  $\text{N}_2$ . The other sample is Si coated with HMDS.



**Figure 2** Synthesis schemes of (a) tetrahydropyran-2-yl *N*-(2-ethylmethacrylate) and (b) poly((tetrahydropyran-2-yl *N*-(2-methacryloxyethyl) carbamate)-*co*-(methyl 4-(3-methacryloyloxypropoxy) cinnamate).

Si was placed in a clean glass vial filled with a 10.0 mM solution of HMDS in freshly distilled toluene and sealed with a phenolic screw cap. The sealed vial was placed in an oil bath held at 80°C for 3 h. After treatment, the sample was rinsed with toluene, followed by drying with N<sub>2</sub>.

#### Immobilization of OIC and glutaraldehyde on heated THP-polymer

THP-polymer was treated on a preheated hot plate at 200°C for 30 min and left on the plate as it cooled to room temperature to deprotect –THP functional group. The deprotection of –THP group was confirmed by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). To immobilize OIC on heated THP-polymer, the sample was placed in 10 mL of DCM and 1.1 mL of OIC was added. This system was kept for 3 h. After that, the sample was rinsed with DCM, followed by drying with N<sub>2</sub>. Glutaraldehyde was immobilized on heated THP-polymer by using one drop of glutaraldehyde solution. This system was left for 4 h.

#### Growth of TiO<sub>2</sub> using [NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> and H<sub>3</sub>BO<sub>3</sub>

[NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> and H<sub>3</sub>BO<sub>3</sub> were used to grow TiO<sub>2</sub> on Si coated with layers of various functional groups. [NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> and H<sub>3</sub>BO<sub>3</sub> were separately dissolved in DI water at 50°C and kept for 12 h. To keep the molar ratio of [NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> to H<sub>3</sub>BO<sub>3</sub> as 0.05M to 0.15M, 0.2 g of [NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> and 0.18 g of H<sub>3</sub>BO<sub>3</sub> were used with 20 mL of DI water. An appropriate amount of HCl or NH<sub>4</sub>OH was added to the boric acid solution to control the pH to be 2.5–3.5. After that, a [NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub> solution was added. Then, Si wafers with different functional groups were immersed in the solution and kept at 50°C to deposit TiO<sub>2</sub>. The solution was initially transparent.

However, it became hazy after 30 min, indicating that some reactions occurred. After removal from the solution, sonication was used to remove particles that were only loosely bound to the surface.

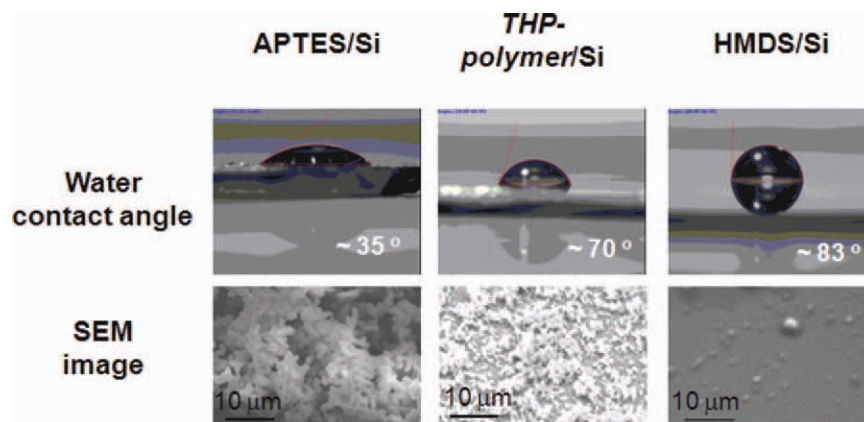
#### Measurement of TiO<sub>2</sub> growth

The contact angle measurement with DI water was performed to determine whether the sample surface was hydrophilic or hydrophobic. The sessile drop method was used to measure the contact angle. A contact angle goniometer using an optical system was employed to capture the profile of water on the substrate. The distance from the syringe to substrate and volume of water were set to be constant. The angle presented in this paper is an advanced angle. A scanning electron microscope (SEM) was used to investigate the TiO<sub>2</sub> image and to estimate the thickness of TiO<sub>2</sub>. X-ray diffraction (XRD) was used to confirm the growth of TiO<sub>2</sub>.

## RESULTS AND DISCUSSION

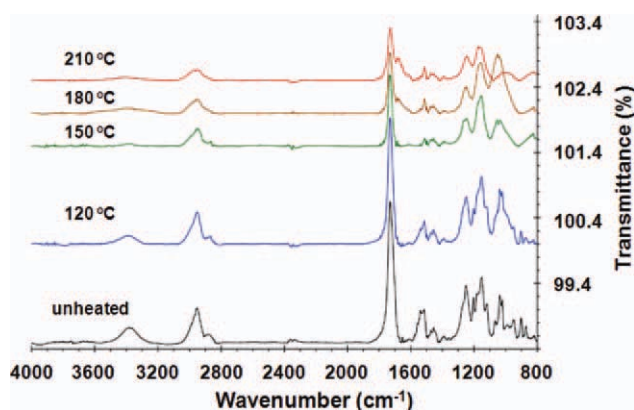
Figure 3 shows the effects of surface functional groups on the formation of TiO<sub>2</sub>. The water contact angles were measured to be 35 ± 5°, 70 ± 5°, and 83 ± 3° for APTES/Si, THP-polymer/Si, and HMDS/Si, respectively. This indicates that the surface changed from hydrophilic to hydrophobic as the surface functional group changed from –NH<sub>2</sub> and –THP to –CH<sub>3</sub>. SEM imaging after the deposition of TiO<sub>2</sub> showed that TiO<sub>2</sub> formed on APTES/Si was not affected by ultrasonication with DI water. The thickness of TiO<sub>2</sub> is proportional to the dipping time, and the estimated thickness of TiO<sub>2</sub> on APTES/Si was 10 μm after 24 h. TiO<sub>2</sub> particles were found on the surface of THP-polymer/Si even after ultrasonication with DI water. In the case of HMDS/Si, it appeared that TiO<sub>2</sub> was deposited on the sample because the Si surface changed from a clean and reflective surface, to a surface with white particle deposits. However, the white particles deposited on the Si surface were stripped after ultra-sonication with DI water. This indicates that the adhesion between the TiO<sub>2</sub> and –CH<sub>3</sub> functional group was weak and that TiO<sub>2</sub> cannot be grown on HMDS/Si substrates.

Transmittance spectra of the THP-polymer upon bulk heating were shown in Figure 4. The spectra were obtained by external reflection FTIR in a N<sub>2</sub> atmosphere. The spectra have been rigidly shifted on the vertical axis for clarity. Each sample was treated on a preheated hot plate at the desired temperature for 30 min and left on the plate as it cooled to room temperature. The decrease in the peak at 1725 cm<sup>-1</sup> starting at 150°C is consistent with the loss of the carbamate carbonyl group. The peak in



**Figure 3** Water contact angles and SEM images for APTES/Si, THP-polymer/Si, and HMDS/Si samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

this spectral region is not expected to disappear entirely, as other carbonyl containing functionalities are present in the polymer and should not be affected by the thermal treatment. The reduction in intensity for the bands in the region from 2800–3000  $\text{cm}^{-1}$ , due to C–H stretching modes, when the temperature increases is also consistent with the loss of the THP group. The weakening of the broad band around 3400  $\text{cm}^{-1}$ , due to N–H stretching modes, would not be expected for a transformation that creates a primary amine. However, this change could be explained by a further broadening of the peak because of hydrogen bonding. Additional experiments would be needed to confirm the assignment of this band. More direct evidence for the formation of a primary amine is the appearance of a new band at 1670  $\text{cm}^{-1}$ , which is likely due to N–H bending, in the spectra of samples treated at 180°C and above. Therefore, it is considered that thermal heating above 180°C could induce deprotection of the –THP group, resulting in surface functional group modification from –THP to –NH<sub>2</sub>.

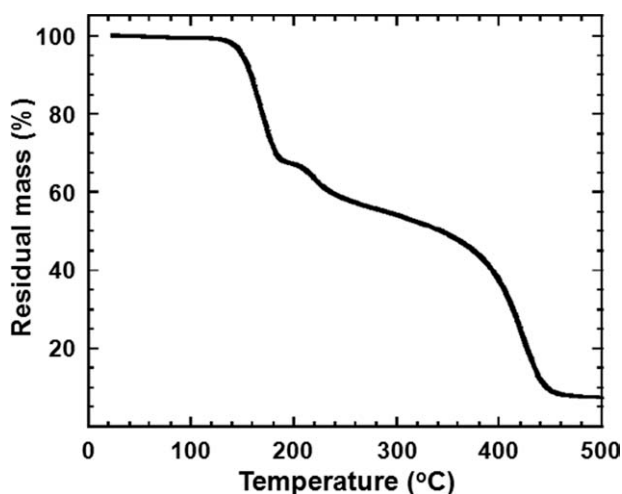


**Figure 4** Transmittance spectra of the THP-polymer upon bulk heating using FTIR. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

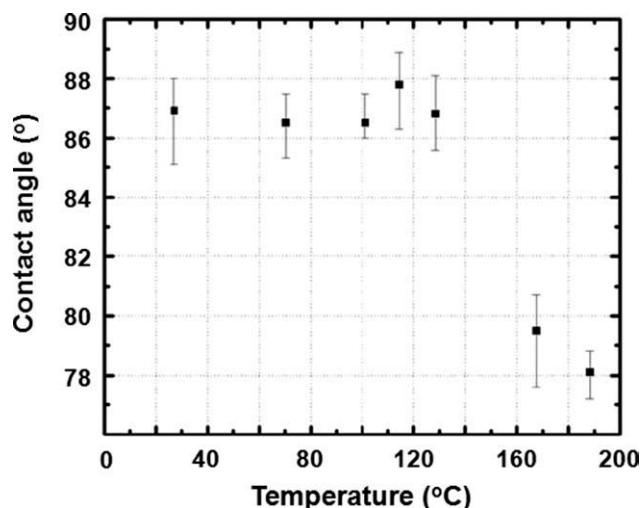
Figure 5 shows the TGA data of the THP-polymer. Upon heating (rate: 5°C min<sup>-1</sup>), the THP-polymer sample exhibits an initial mass loss around 150°C and a subsequent one starting at about 200°C. The overall mass loss through these two steps is consistent with deprotection of carbamate group and unmasking of the amine groups.

Water contact angle data of the THP-polymer upon bulk heating were shown in Figure 6. THP-Polymer samples were bulk heated at selected temperatures using a hot plate for 3 min and then static water contact angles were measured at room temperature after cooling the samples down. The water contact angle was maintained in the range of 86°–88°. However, the water contact angle drops to 78° significantly at temperature above 140–160°C. This result suggested the surface functional group modification from –THP to –NH<sub>2</sub>.

Figure 7 displays the SEM images of TiO<sub>2</sub> grown on THP-polymer after each treatment. The image of TiO<sub>2</sub> on THP-polymer heated at 200°C is shown in Figure 7(a). SEM image suggests that TiO<sub>2</sub> is grown



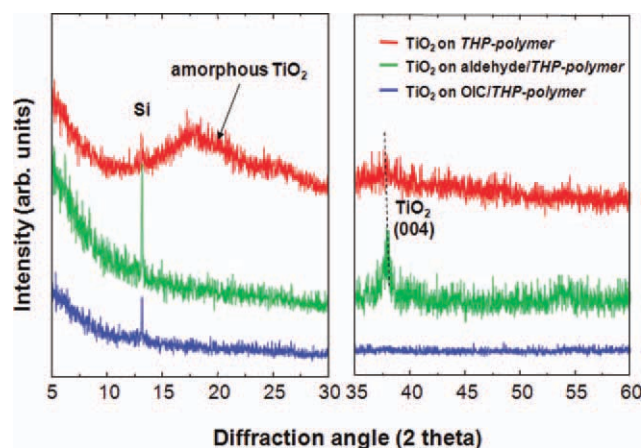
**Figure 5** TGA data of the THP-polymer.



**Figure 6** Water contact angle data of the THP-polymer upon bulk heating.

on heated THP-polymer. The thickness of  $\text{TiO}_2$  is proportional to the dipping time, and the estimated thickness of  $\text{TiO}_2$  on THP-polymer was  $10\ \mu\text{m}$  after 24 h. Figure 7(b) shows the case after immobilization of OIC on heated THP-polymer. Contact angle increased after immobilization of OIC on the heated THP-polymer, which is similar to the contact angle of HMDS. The  $\text{TiO}_2$  layer was not observed in the SEM image, suggesting that OIC is immobilized well on  $-\text{NH}_2$  surface groups, while changing the surface functional group from  $-\text{NH}_2$  to  $-\text{CH}_3$ . The SEM image of  $\text{TiO}_2$  after immobilization of glutaraldehyde on heated THP-polymer is shown in Figure 7(c). According to SEM image analysis, the  $\text{TiO}_2$  layer was found on the glutaraldehyde surface. It should be noted that the  $\text{TiO}_2$  layer was also found on the glutaraldehyde sample after heating to  $200^\circ\text{C}$ .

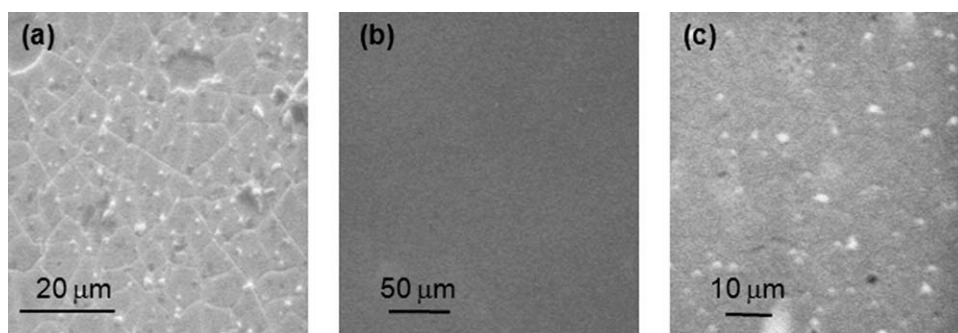
XRD spectra of  $\text{TiO}_2$  on THP-polymer, aldehyde/THP-polymer, and OIC/THP-polymer are shown in Figure 8. The peak located at  $\sim 13^\circ$  is related to Si substrate. The broad peak, in the range between  $15$  and  $25^\circ$  was observed in THP-polymer sample, indicating the existence of amorphous  $\text{TiO}_2$ . The



**Figure 8** XRD spectra of  $\text{TiO}_2$  on (a) THP-polymer, (b) glutaraldehyde/THP-polymer, and (c) OIC/THP-polymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

peak located at  $37.8^\circ$  appeared in the aldehyde/THP-polymer sample. This peak indicates  $\text{TiO}_2$  (004) with an anatase structure, meaning that  $\text{TiO}_2$  with anatase structure is grown on  $-\text{O}-$  bonds. A weak and broad XRD peak of the samples indicates less crystallization with respect to annealed  $\text{TiO}_2$  and some defects. However, no peak was shown in the OIC/THP-polymer sample. This result confirmed that  $\text{TiO}_2$  was grown on  $-\text{THP}$  and  $-\text{O}-$  surface functional groups, and not on the  $-\text{CH}_3$  surface functional group.

Based on the experimental observations, the control of  $\text{TiO}_2$  growth conditions on THP-polymer is explained below.  $\text{TiO}_2$  can be deposited on substrates via chemical-equilibrium reaction between a Ti-fluoro complex and a  $\text{TiO}_2$  in aqueous solution. The fluoride ligand was reported to offer a slower, more controllable hydrolysis, where the boric acid acts as  $\text{F}^-$  scavengers.<sup>11</sup> Water contact angle measurements showed that the surface changed from having hydrophilic properties to having hydrophobic properties as the surface functional groups changed from  $-\text{NH}_2$ ,  $-\text{THP}$ , and  $-\text{CH}_3$ . This



**Figure 7** SEM images of  $\text{TiO}_2$  on top of (a) heated THP-polymer, (b) OIC on heated THP-polymer, and (c) glutaraldehyde on heated THP-polymer.

induced the growth of TiO<sub>2</sub> only on —NH<sub>2</sub> and —THP functional groups, and not the —CH<sub>3</sub> functional group due to weak adhesion, as shown in SEM and XRD data. FTIR, water contact angle, and TGA data showed that the surface functional group of THP-polymer was changed from —THP to —NH<sub>2</sub> by a heating process to 200°C due to the deprotection properties of carbamates that are caused by thermal decomposition. SEM data showed that TiO<sub>2</sub> was grown on heated THP-polymer with glutaraldehyde due to the existence of —NH<sub>2</sub> and —O functional group, but TiO<sub>2</sub> on OIC/heated THP-polymer was stripped via sonication due to the existence of —CH<sub>3</sub> functional groups. Furthermore, the glutaraldehyde functional group was not affected by thermal heating as shown by TiO<sub>2</sub> growth, despite heating the sample to 200°C. Therefore, the growth condition of TiO<sub>2</sub> could be controlled using THP-polymer, OIC, glutaraldehyde, and thermal heating.

### CONCLUSIONS

We investigated the growth of TiO<sub>2</sub> that was affected by changing the tetrahydropyran protected group on polymer. TiO<sub>2</sub> was grown on APTES-coated Si and THP-polymer, but TiO<sub>2</sub> on OTS-coated Si was stripped by sonication. This indicated that TiO<sub>2</sub> could be grown on —NH<sub>2</sub> and —THP surface functional groups, but not on —CH<sub>3</sub> surface functional groups. Heating the THP-polymer at 200°C deprotected the —THP group to change the surface functional group to —NH<sub>2</sub>, as shown in Figure 4–6. OIC was immobilized on heated THP-polymer.

SEM data showed that TiO<sub>2</sub> was successfully grown on heated THP-polymer and heated glutaraldehyde/heated THP-polymer, but was not grown on OIC/heated THP-polymer. Therefore, the growth conditions of TiO<sub>2</sub> could be controlled using THP-polymer, glutaraldehyde, and OIC.

The authors are grateful to Dr. Jonas E. Jarvholm, William D. Underwood II, Dr. Mariacristina Rumi, and Dr. Seth R. Marder in the school of chemistry and biochemistry at the Georgia Institute of Technology for assistance with this work.

### References

1. Yun, H. J.; Lee, H.; Joo, J. B.; Kim, N. D.; Yi, J. *Electrochem Commun* 2010, 12, 769.
2. Oja, I.; Mere, A.; Krunks, M.; Nisumaa, R.; Solterbeck, C.-H.; Es-Souni, M. *Thin Solid Films* 2006, 515, 674.
3. Li, W.; Auciello, O.; Premnath, R. N.; Kabius, B. *Appl Phys Lett* 2010, 96, 162907.
4. Valdés, Á.; Qu, Z.-W.; Kroes, G.-J.; Rossmeisl, J.; Nørskov, J. K. *J Phys C: Solid State Phys* 2008, 112, 9872.
5. Foong, T. R. B.; Shen, Y.; Hu, X.; Sellinger, A. *Adv Funct Mater* 2010, 20, 1390.
6. Ji, Q.; Shimizu, T. *Chem Commun* 2005, 35, 4411.
7. Wu, F.; Xu, J.; Tian, Y.; Hu, Z.; Wang, L.; Xian, Y.; Jin, L. *Biosens Bioelectron* 2008, 24, 198.
8. Viriya-empikul, N.; Charinpanitkul, T.; Sano, N.; Soottitanta-wat, A.; Kiruchi, T.; Faungnawakij, K.; Tanthapanichakoon, W. *Mater Chem Phys* 2009, 118, 254.
9. Kim, J.; Seidler, P.; Wan, L. S.; Fill, C. *J Colloid Interface Sci* 2009, 329, 114.
10. Malvadkar, N.; Dressick, W. J.; Demirel, M. C. *J Mater Chem* 2009, 19, 4796.
11. Koumoto, K.; Seo, S.; Sugiyama, T.; Seo, W. S.; Dressick, W. J. *Chem Mater* 1999, 11, 2305.