Nonhydrolytic Layer-by-Layer Surface Sol−Gel Modification of Powdered Mesoporous Silica Materials with TiO2

Wenfu Yan, Shannon M. Mahurin,
Steven H. Overbury, and Sheng Dai*

*Chemical Sciences Division, Oak Ridge National Laboratory,
P.O. Box 2008, Oak Ridge, Tennessee 37831-6201*

Since their discovery in 1992, silica-based mesoporous materials have attracted intense interest because of their potential applications in catalysis and separations.[1−4] However, the applications of these mesoporous materials usually require functionalization of relatively inactive silica surfaces through the reaction of surface silanol groups with desired bifunctional siloxane ligands.[5−9] To date, several methods have been successfully developed to modify the surfaces of mesoporous silica materials, including surface monolayer functionalization,[5] direct surface grafting,[6,10−13] and surface imprinting.[14−16]

Kunitake and co-workers[17] have recently developed a hydrolytic surface sol−gel (HSS) process for the layer-by-layer functionalization of planar substrates with a monolayer precision. This novel technology enables a molecular-scale control of film thickness over a large two-dimensional substrate area and can be viewed as a solution-based methodology for atomic layer deposition (ALD) synthesis.[18] Compared with conventional deposition methods, the surface sol−gel technique offers the advantage of producing ultrathin conformal films, with control of the thickness and composition of the films possible at the atomic level. This technique

generally consists of two half reactions as shown in Scheme 1 a: (1) nonaqueous condensation of metal-alkoxide precursor molecules with surface hydroxyl groups and (2) aqueous hydrolysis of the adsorbed metal-alkoxide species to regenerate surface hydroxyls. The iteration of the above sequential condensation and hydrolysis reactions allows the layer-by-layer coating of a selected metal oxide on a hydroxyl-terminated surface. By using this method, Kunitake and co-workers have successfully prepared ultrathin films of metal oxides such as TiO_2, ZrO_2, and Al_2O_3 with molecular precision on a quartz crystal microbalance (QCM).[17] More recently, this layer-by-layer method has been applied to modify the surface of powdered mesoporous silica materials (i.e., SBA-15) with TiO_2 for the assembly of ultrasmall gold nanoparticles [Scheme 1b] and the controlled functionalization of mesopores with monolayer precision.[19,20] However, the main disadvantage of this HSS process is that it alternatively involves both nonaqueous condensation and aqueous hydrolysis (two opposite reaction environments) in the same reaction protocol. The sample resulting from the hydrolysis reaction needs to be completely dried in each cycle before the next nonaqueous condensation reaction begins. Thus, even though the HSS process is very successful for use on flat substrates, this synthesis protocol is very inconvenient for conducting the layer-by-layer HSS process on powdered samples (e.g., powdered mesoporous materials).

Through the work by Corriu and co-workers,[21−25] it is well-known that metal or silicon halides can react with the corresponding metal or silicon alkoxides to generate metal oxides and volatile alkyl halides under anhydrous conditions (eq 1).

$$\equiv M-X + \equiv M-O-R \rightarrow \equiv M-O-M\equiv + R-X \quad (1)$$
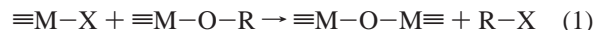
Corriu and co-workers have successfully demonstrated that this nonhydrolytic sol−gel process can be employed to prepare not only powdered metal or silicon oxides but also monolithic metal or silicon oxide gels.[21] In this nonhydrolytic reaction, metal or silicon alkoxides act as both oxygen donors (replacing water) and metal or silicon sources. The metals in metal halides and metal alkoxides may be either the same or different, with the latter combination resulting in the formation of mixed metal oxides.[22−26] Recently, this nonhydrolytic sol−gel process has been employed by Colvin and co-workers to synthesize oxide nanoparticles.[27] Ritala

* To whom correspondence should be addressed. Email: dais@ornl.gov
(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
(2) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
(3) Davis, M. E. *Nature* **2002**, *417*, 813.
(4) Stein, A. *Adv. Mater.* **2003**, *15*, 763.
(5) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923.
(6) Mercier, L.; Pinnavaia, T. J. *Adv. Mater.* **1997**, *9*, 500.
(7) Stein, A.; Melde, B. J.; Schroden, R. C. *Adv. Mater.* **2000**, *12*, 1403.
(8) Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 853.
(9) Brunel, D. *Microporous Mesoporous Mater.* **1999**, *27*, 329.
(10) Hall, S. R.; Fowler, C. E.; Lebeau, B.; Mann, S. *Chem. Commun.* **1999**, 201.
(11) Morey, M. S.; O'Brien, S.; Schwarz, S.; Stucky, G. D. *Chem. Mater.* **2000**, *12*, 898.
(12) Sinha, A. K.; Seelan, S.; Akita, T.; Tsubota, S.; Haruta, M. *Appl. Catal., A* **2003**, *240*, 243.
(13) Zheng, S.; Gao, L. A.; Zhang, Q. H.; Guo, J. K. *J. Mater. Chem.* **2000**, *10*, 723.
(14) Dai, S.; Burleigh, M. C.; Shin, Y.; Morrow, C. C.; Barnes, C. E.; Xue, Z. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1235.
(15) (a) Shin, Y. S.; Liu, J.; Wang, L. Q.; Nie, Z. M.; Samuels, W. D.; Fryxell, G. E.; Exarhos, G. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2702. (b) Kruk, M.; Asefa, T.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2002**, *124*, 6383. (c) Kruk, M.; Antochshuk, V.; Matos, J. R.; Mercuri, L. P.; Jaroniec, M. *J. Am. Chem. Soc.* **2002**, *124*, 768.
(16) Huh, S.; Chen, H. T.; Wiench, J. W.; Pruski, M.; Lin, V. S. Y. *J. Am. Chem. Soc.* **2004**, *126*, 1010.
(17) Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Lett.* **1996**, 831.
(18) Leskela, M.; Ritala, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5548.

(19) Widenmeyer, M.; Grasser, S.; Kohler, K.; Anwander, R. *Microporous Mesoporous Mater.* **2001**, *44*, 327.
(20) Yan, W. F.; Chen, B.; Mahurin, S. M.; Hagaman, E. W.; Dai, S.; Overbury, S. H. *J. Phys. Chem. B* **2004**, *108*, 2793.
(21) Corriu, R. J. P.; Leclercq, D.; Lefevre, P.; Hubert Mutin, P.; Vioux, A. *J. Mater. Chem.* **1992**, *2*, 673.
(22) Corriu, R. J. P.; Leclercq, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1420.
(23) Andrianainarivelo, M.; Corriu, R. J. P.; Leclercq, D.; Hubert Mutin, P.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1665.
(24) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Hubert Mutin, P.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1925.
(25) Arnal, P.; Corriu, R. J. P.; Leclercq, D.; Hubert Mutin, P.; Vioux, A. *Chem. Mater.* **1997**, *9*, 694.
(26) Vioux, A. *Chem. Mater.* **1997**, *9*, 2292.

Scheme 1. Hydrolytic Surface Sol−Gel Process
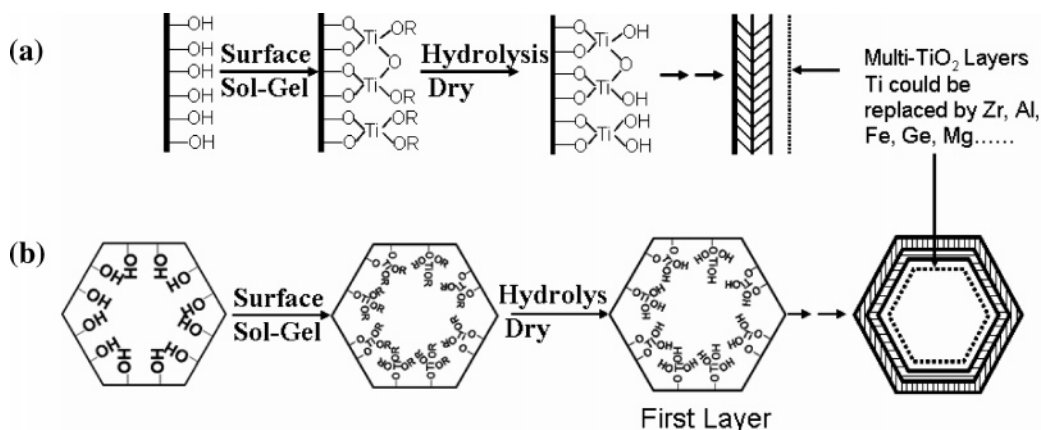
Scheme 2. Nonhydrolytic Surface Sol−Gel Process
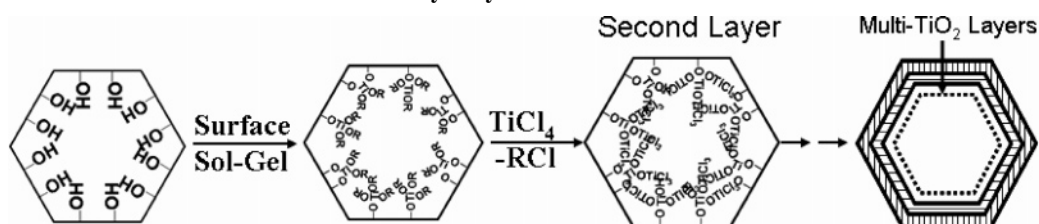
and co-workers have applied this reaction in the preparation of ultrathin oxide films on a silicon wafer at or above 300 °C via gas-phase ALD.[28] Herein, we report a nonhydrolytic surface sol−gel (NSS) process and its application in the layer-by-layer modification of powdered mesoporous silicas (SBA-15) with titania. The synthesis protocol of the NSS process is shown schematically in Scheme 2.

Our overall objective is to coat the surface of mesoporous silica materials with ultrathin films of titanium oxide or other metal oxides via this NSS process through a layer-by-layer growth approach. The SBA-15 materials have hexagonally packed channels with pore sizes of ∼8.5 nm. The large mesopores allow a facile transport of metal-alkoxide and metal-chloride reactants not only for monolayer but also for multilayer functionalization on the internal walls of SBA-15. The SBA-15 silica was prepared using Pluronic P123 (Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) according to the procedure described in the literature.[2] The procedure used for the preparation of multilayered TiO_2 on SBA-15 channels was developed according to the method described by Arnal et al. for the preparation of titania through the direct condensation between titanium tetrachloride ($TiCl_4$) and titanium tetraisopropoxide [$Ti(OPr^i)_4$] in anhydrous chloroform.[25] The initial concentration of the reactant for the double-layer coverage is 2.27 mol/L and the molar ratio of $Ti(OPr^i)_4$: $TiCl_4$ is 1:3 according to the literature.[25] The BET surface area and the pore size of SBA-15 used here is 728 m^2/g and 8.5 nm, respectively, and the surface silanol concentration is $4-8 \times 10^{-6}$ mol/m^2.[29] Typically, a powdered

SBA-15 sample (1.0 g, predried) was loaded into a predried two-neck reflux flask sealed with a rubber septum. Subsequently, 3.4 mmol of $Ti(OPr^i)_4$ (Aldrich) and 6 mL of anhydrous chloroform (Aldrich) were transferred into the bottle through a syringe using a standard Schlenk procedure. The solution was refluxed at 110 °C for 1 h (for the growth of the first layer of titania). For the second-layer deposition, 10.2 mmol of $TiCl_4$ was transferred to the flask through a syringe. The solution was refluxed under stirring for another 1 h. The amount of $Ti(OPr^i)_4$ or $TiCl_4$ required for each layer was determined based on the surface area of the initial SBA-15 sample and surface silanol concentration. Under anhydrous conditions, the majority of titanium species exist in the form of $-Si-O-Ti(OPr^i)_3$ on silica surfaces after the functionalization of the first layer with $Ti(OPr^i)_4$. Based on stoichiometry, the preparation of the second layer requires the mole ratio of the first layer alkoxide precursor [$Ti(OPr^i)_4$] to the second layer halide precursor ($TiCl_4$) to be 1:3 for a complete consumption of the remaining alkoxyl groups in $-Si-O-Ti(OPr^i)_3$ with the assumption of no bridging formation for titanium oxide species. The multilayer (above the third layer) of titanium oxide on SBA-15 can be prepared by the iteration of the above procedure. The final product was washed several times with anhydrous ethanol and DI water and dried at 80 °C overnight.

Figure 1 shows the variation of the pore size distribution as a function of cycles of surface-modification-based N_2-adsorption isotherms. The structural properties for the blank and surface-modified SBA-15 samples were summarized in Table 1. The pore size as well as BET surface area successively decrease with the modification cycle number, resulting in the increase of the pore wall thickness. The reduction of the mesopore size for each cycle should be about twice the single-layer thickness. Accordingly, the effective

(27) Trentler, T. J.; Denler, T. E.; Bertone, J. F.; Agrawal, A.; Colvin, V. L. *J. Am. Chem. Soc.* **1999**, *121*, 1613.
(28) Ritala, M.; Kukli, K.; Rahtu, A.; Raisanen, P. I.; Leskela, M.; Sajavaara, T.; Keinonen, J. *Science* **2000**, *288*, 319.
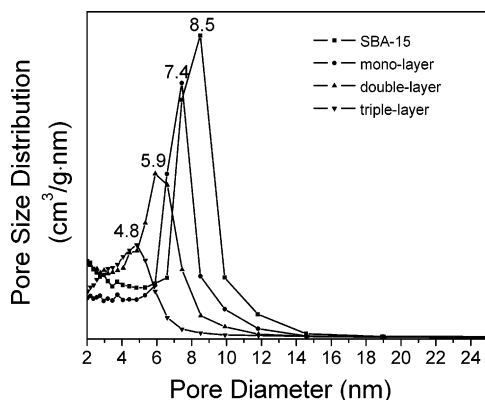(29) Nawrocki, J. *J. Chromatogr. A* **1997**, *779*, 29.

Communications

Chem. Mater., Vol. 17, No. 8, 2005 1925

Figure 1. Pore size distribution as function of the number of TiO₂ layers.

Table 1. Structural Properties for Blank and Surface-Modified SBA-15[a]

samples	unit cell (nm)	BET surface area (m²/g)	pore size (nm)	wall thickness (nm)
SBA-15	11.2	728	8.5	2.7
monolayer	11.2	546	7.4	3.8
double layer	11.2	527	5.9	5.3
triple layer	11.2	499	4.8	6.4

[a] Notation: $d_{100} = \lambda/(2 \sin \theta)$, $\lambda = 1.5418$ (Å) (Cu Kα), unit cell, $a = 2d_{100}/\sqrt{3}$, and wall thickness $= a - $ pore size.

single-layer thickness is about 5–7 Å based on the above BET measurements, which is close to those estimated from the frequency changes of a QCM for ultrathin films prepared by hydrolytic surface sol–gel process on two-dimensional substrates.[30–32] The decreased incremental pore volumes in Figure 1 can be correlated to the reduction of the pore volume and the widened pore size distribution, resulting from NSS.[15] This observation is consistent with the corresponding isotherms (see Supporting Information).

The low-angle X-ray diffraction (XRD) patterns of SBA-15 and monolayer-, double-layer-, and triple-layer-covered SBA-15 shown in Figure 2 indicate that the hexagonal structure of SBA-15 is retained during the NSS layer-by-layer functionalization, which is supported by TEM analyses (see Supporting Information). Although the TEM image of the sample coated with the triple-layer titania is less resolved due to the increased wall thickness, the ordered pore structure can be readily seen. It is not surprising that the position of the (100) peak of the products did not shift even though the pore size distribution decreased gradually from the monolayer to the triple-layer coverage because the d spacings of the SBA-15 matrix did not vary during this NSS process.

The approach described here can be readily expanded to modify the surfaces of other porous or nonporous powdered oxide materials with the proviso that they have surface silanol groups. The first-layer growth of titania was achieved by the reaction of titanium precursor with the surface silanol in chloroform under an atomic-level thickness control. Subsequently, titanium tetrachloride and titanium tetraisopropoxide are alternatively added. Other solvents, such as trioctyl
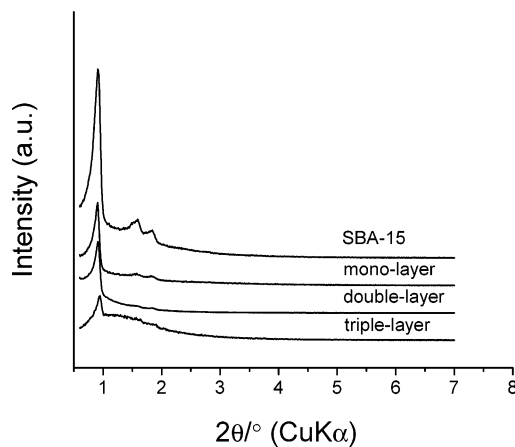

Figure 2. Low-angle XRD patterns of SBA-15, monolayer-, double-layer-, and triple-layer-covered SBA-15.

phosphine and ethylene dichloride, can be used in this NSS process. The maximum reaction temperature is determined by the boiling points of solvents. Because the reaction environment does not change, no separation of reaction products is necessary and the reactants (metal alkoxides and halides) can be added alternatively to the same reaction vessel. This synthesis protocol is very similar to the successive-ionic-layer-adsorption-and-reaction (SILAR) deposition process,[33,34] which has been employed to expitaxily grow sulfide and oxide layers on nanoparticles and planar substrates. Unlike the use of the HSS process in the modification of surfaces of mesoporous silica materials, the NSS process does not involve water. Therefore, the growth process is considerably more efficient than that of the HSS process (Schemes 1 and 2).

In summary, a nonhydrolytic surface sol–gel process has been developed. The application of this method in the layer-by-layer functionalization of mesoporous silica materials has been demonstrated. This approach can be easily expanded to modify other powdered materials (both porous and nanoporous) that contain active hydroxyl groups with unitary or mixed metal oxides.

Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM048118S

(30) Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Mater.* **1997**, *9*, 1296.
(31) Huang, J.; Kunitake, T. *J. Am. Chem. Soc.* **2003**, *125*, 11834.
(32) He, J.; Ichinose, I.; Kunitake, T.; Nakao, A.; Shiraishi, Y.; Toshima, N. *J. Am. Chem. Soc.* **2003**, *125*, 11034.

(33) Li, J. J.; Wang, Y. A.; Guo, W. Z.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. G. *J. Am. Chem. Soc.* **2003**, *125*, 12567.
(34) Park, S.; Clark, B. L.; Keszler, D. A.; Bender, J. P.; Wager, J. F.; Reynolds, T. A.; Herman, G. S. *Science* **2002**, *297*, 65.