

## Surface Sol–Gel Modification of Mesoporous Silica Materials with $\text{TiO}_2$ for the Assembly of Ultrasmall Gold Nanoparticles

Wenfu Yan, Bei Chen, S. M. Mahurin, E. W. Hagaman, Sheng Dai,\* and Steven H. Overbury

Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6201

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The surface sol–gel method has been demonstrated to be an effective method for the modification of silica mesopore surfaces and the tuning of mesopore diameters. This layer-by-layer approach allows the control of mesopore diameters with monolayer precision. Ultrasmall gold nanoparticles were successfully prepared on surface-modified SBA-15 via a deposition–precipitation method. High catalytic activity for CO oxidation was found for such materials.

There has been much interest in the synthesis of gold nanoparticles for diverse applications in catalysis.<sup>1–5</sup> The main difficulty for such applications lies in the controlled assembly of monodispersed gold nanoparticles without aggregation and sintering.<sup>1</sup> The most commonly used synthesis strategies involve the immobilization of gold nanoparticles in organic polymer matrixes<sup>6</sup> or the stabilization of colloidal gold nanoparticles by binding with an organosilane ligand.<sup>7,8</sup> These synthesis approaches have limited applications in catalysis because of the lack of active surface areas. The recent breakthrough in the synthesis of mesoporous materials has led to a new class of materials with a high degree of control of the pore size, shape, and lateral distribution of nanostructures.<sup>9,10</sup> The periodic mesoporous materials are potential candidates for templates to synthesize nanocrystals with controlled size and shape.<sup>11–13</sup> Although the direct deposition–precipitation (DP) method can be used to prepare gold nanoparticles on titanium oxide substrates, it is difficult to synthesize gold nanoparticles ( $<30$  Å) on silica materials with such a methodology. In the DP method, the isoelectric point (IEP) of the support matrixes plays a key role in the successful incorporation and dispersion of nanoparticles on porous oxide supports. To deposit  $\text{Au}(\text{OH})_3$  on the surfaces of oxides via surface reactions, the pH value of  $\text{HAuCl}_4$  solution is normally adjusted to the range of 6–10. The prerequisite for the deposition of  $\text{Au}(\text{III})$  precursors is the interaction of the anionic gold precursor complexes with a positively charged or neutral oxide surface. However, the IEP of silica materials is relatively low ( $\sim 2$ ).<sup>14</sup> This low IEP implies that silica surfaces are highly negatively charged under DP conditions. One strategy to overcome the low IEP of silica surfaces is through surface modification with bifunctional silanes.<sup>15–17</sup> The gold precursors can be chemically complexed within the pores of functionalized mesoporous silica materials,<sup>18</sup> and the growth of gold nanoparticles can be subsequently achieved by mild chemical reductions.<sup>19,20</sup> The drawback of this approach is that the functional groups could interfere with catalytic reactions by capping active sites. Another strategy to overcome the low IEP of silica-based materials is to introduce a high-IEP oxide component into silica materials via either cosynthesis methods or surface modification.<sup>21–23</sup>

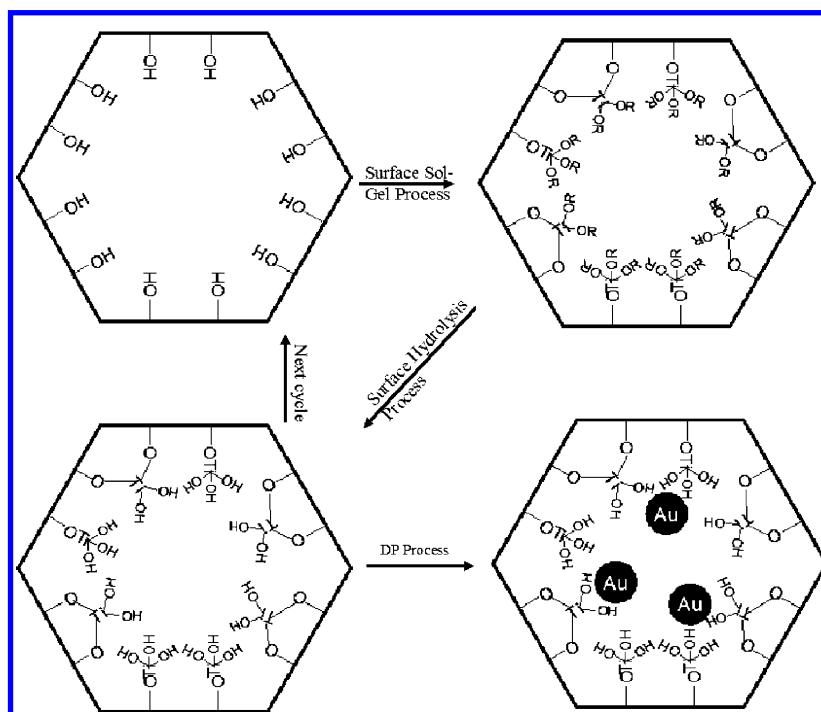
Herein, we report a surface sol–gel process technique to accomplish the formation of gold nanoparticles on ordered mesoporous silica materials via the DP method without the constraint of the low IEP of  $\text{SiO}_2$  surfaces. The essence of this methodology involves the introduction of a high-IEP oxide component on mesoporous silica surfaces to decrease the negative charges of silica surfaces. The high-IEP component used in our synthesis is titania, which has an IEP of  $\sim 6.0$  and has been extensively employed as a support for the DP synthesis of gold nanoparticles for catalysis applications.<sup>1,24</sup> Our objective is to coat the surface of mesoporous silica materials with titanium oxide via a layer-by-layer approach, thereby allowing the uniform deposition of gold precursors on ordered mesoporous silica materials and the precise control of the mesopore sizes. The mesopores of such materials are expected to be more stable against crystallization than those of pure mesoporous titanium oxide.

The surface sol–gel process (SSP) was originally developed by Kunitake and co-workers.<sup>25</sup> This novel technology enables the molecular-scale control of film thickness over a large 2D substrate area and can be viewed as a solution-based methodology for atomic layer deposition (ALD) synthesis.<sup>26–28</sup> The SSP technique generally consists of two half reactions: (i) nonaqueous condensation of metal-alkoxide precursor molecules with surface hydroxyl groups and (ii) 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. Although the original technique was developed to functionalize 2D surfaces, Huang and Kunitake have recently succeeded in using this technique for the fossilization of cellulosic substances.<sup>25b</sup>

The mesoporous material used in this investigation is 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.<sup>29</sup> The procedure used for the preparation of one layer or multilayers of titanium oxide on SBA-15 powders was developed according to the method described by Kunitake and co-workers<sup>30</sup> for the preparation of ultrathin films of metal oxides on hydrolyzed surfaces. Briefly, a homemade apparatus for conducting SSP on the mesopore surfaces of powdered materials consists of two parts: an evacuation system and a fritted reactor. Typically, 1.0 g of

\* To whom all correspondence should be addressed. E-mail: dais@ornl.gov.

## SCHEME 1



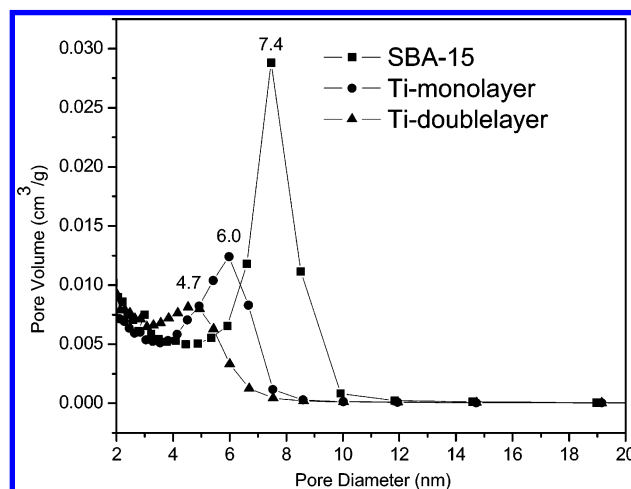
predried SBA-15 powder was loaded into the fritted reactor, which was sealed with a rubber septum at one end and connected to a vacuum system at the other end. The initially loaded sample was evacuated at ambient temperature and purged with nitrogen. This cycle was repeated several times. Subsequently, the stopcock separating the vacuum system and the reactor was closed, and 5 mL of titanium(IV) butoxide (Aldrich, 97%) in a mixture of 10 mL of anhydrous toluene (Aldrich, 99.8%) and 10 mL of anhydrous methanol (Aldrich, 99.8%) was transferred into the reactor through a syringe. After 30 min of reaction, the solution was completely removed via vacuum filtration. Anhydrous methanol (5 mL) was injected into the reactor to wash off the unreacted titanium(IV) butoxide. The resulting sample was dried through vacuum evacuation. An excess amount of deionized water was then injected into the glass tube to hydrolyze the monolayer of titanium oxide. The final product can be washed thoroughly with anhydrous methanol and dried for the coating of the second layer. The multilayer of titanium oxide on SBA-15 can be prepared by the iteration of the above procedure.

The DP procedure used here was based on the method developed by Haruta and co-workers.<sup>31</sup> First, 3.0 g of hydrogen tetrachloroaurate(III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99.9+%, Aldrich) was dissolved in 500 mL of deionized water to form the gold precursor solution. Typically, the pH value of the preweighed gold precursor solution (20 mL) was adjusted to about 10 with vigorous stirring using a solution of 1.0 M KOH at room temperature. The high pH value used here is intended to control the deposition species and concentration.<sup>3a</sup> The solution was then heated in a 60 °C water bath, and surface-modified SBA-15 (0.4 g) was added with stirring. The resulting cloudy solution was continually stirred for 2 h. The precipitates were separated by centrifugation and washed three times with deionized water. The yellow product was dried at 40 °C overnight.

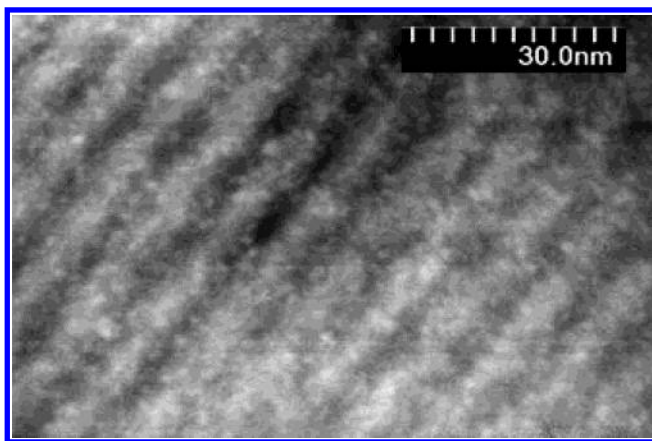
Our overall objective was to coat the surface of mesoporous silica materials with ultrathin films of titanium oxide or other metal oxides via a layer-by-layer approach, thereby allowing the uniform deposition of gold precursors on ordered meso-

porous silica materials without the constraint of the low IEP. Scheme 1 shows the schematic diagram for the basic synthesis protocol for ultrathin  $\text{TiO}_2$  on SBA-15. The SBA-15 materials have hexagonally packed channels with pore sizes of  $\sim 7.4$  nm. The large mesopores allow the facile transport of metal alkoxide reactants inside the mesopores for not only monolayer but also multilayer functionalization on the internal walls of SBA-15. Figure 1 shows the variation of the pore-size distribution as a function of the cycles of surface-modification-based  $\text{N}_2$  adsorption isotherms. The pore size decreases with the modification cycle number. The reduction of the mesopore size for each cycle should be about twice the single-layer thickness. Accordingly, the effective single-layer thickness is about 6–7 Å on the basis of the above BET measurements, which is close to those estimated from the frequency changes of a quartz crystal balance for ultrathin films prepared by SSP on 2D substrates.<sup>25</sup>

Another consequence of this SSP process on SBA-15 is the reduction of the surface silanol groups induced by the condensation reaction with titanium butoxide. The reaction, after hydrolysis, converts surface silanol functionality,  $(\text{SiO})_3\text{SiOH}$ , into



**Figure 1.** Pore-size distribution as function of the number of  $\text{TiO}_2$  layers.



**Figure 2.** Z-contrast TEM image of ultrasmall gold nanoparticles on ordered mesoporous materials. The bright spots (0.8–1.0 nm) correspond to gold nanoparticles.

Ti–OH functionality. Given the similar electronegativity of silicon (1.8) and titanium (1.7), the expected consequence of this modification in the solid-state  $^{29}\text{Si}$  NMR is a decrease in the  $\text{Q}^3$  band and a corresponding increase in the  $\text{Q}^4$  band (i.e., the  $\text{OTi}(\text{OH})_3$  and  $\text{OSi}(\text{OH})_3$  ligands will cause equivalent NMR shift perturbations on the substituted silicon site).

The solid-state  $^{29}\text{Si}$  SPE NMR spectra of SBA-15 and titania surface-coated SBA-15 and Ti–SBA-15 are in accord with this expectation. The spectrum of SBA-15 displays a broad asymmetric peak at 109 ppm ( $\text{Q}^4$  sites) with shoulders at –101 ppm ( $\text{Q}^3$  sites) and 90 ppm ( $\text{Q}^2$  sites) in an area ratio of 79:19:2. The NMR spectrum of Ti–SBA-15 (one layer) shows a reduction of the  $\text{Q}^3$  band intensity relative to the  $\text{Q}^4$  intensity. The normalized  $\text{Q}^4/\text{Q}^3/\text{Q}^2$  site populations become 85:13:2. No asymmetry is observed in the  $\text{Q}^4$  site band. Repetition of the monolayer deposition to form a double layer of titania on silica yields a material whose  $^{29}\text{Si}$  NMR spectrum is indistinguishable from that of Ti–SBA-15 with monolayer coverage. As expected, the titania-insulated silica resonances are unperturbed by the second titania layer.

The gold precursors were readily introduced via the DP method on the surfaces of the modified mesoporous materials. The subsequent reduction of the surface-immobilized gold precursors with CO successfully led to gold nanoparticles assembled inside ordered mesopores. Figure 2 shows the Z-contrast transmission electron microscopy (TEM) image of the resulting materials. The tiny, highly uniform bright spots (0.8–1.0 nm diameter) along the mesopore channels in Figure 2 correspond to the gold nanoparticles. The Z-contrast TEM imaging provides direct proof of the presence of the metallic gold nanoparticles within the channels of SBA-15. The key point with high annular dark-field imaging is that the intensity of the Rutherford scattered beams is directly proportional to  $Z^2$ , where  $Z$  is the atomic number of the scattering element. Thus, heavy atoms (such as gold) stand out very clearly on a light background of silicon and oxygen. The energy-dispersive X-ray (EDX) spectroscopy analysis of the composition of this range in Figure 2 is agreeable with the presence of Au and Ti (Supporting Information). The preparation of gold nanoparticles on SBA-15 with the DP method resulted in only a small population of very large gold nanoparticles aggregated on the external surfaces of SBA-15 (Supporting Information). This observation clearly demonstrated the importance of  $\text{TiO}_2$  surfaces for the immobilization and stabilization of gold nanoparticles.

The activity of the gold catalysts for CO oxidation was characterized using a 0.35-cm<sup>3</sup> plug-flow reactor by 1% CO–

dry air at a space velocity of 40,000 cm<sup>3</sup>/(g cat·h). Comparisons were made between the Au/monolayer  $\text{TiO}_2$ –SBA-15 with Au/commercial nanocrystalline titania support (Degussa P-25).<sup>32</sup> Comparably high activities (i.e., achieving 50% CO conversion above about –40 °C) were found for Au catalysts on the untreated support. High-temperature (300 °C, 30 min) 8%  $\text{O}_2$ –He treatment dramatically decreased the activity of nanocrystalline  $\text{TiO}_2$ -supported catalysts, as shown by the shift of the light-off curve to high temperature. This deactivation can be primarily attributed to the aggregation of gold nanoparticles.<sup>1</sup> In contrast, the activity of the monolayer catalyst did not change significantly, achieving >50% conversion at –25 °C. Work is in progress to provide a complete characterization of the stability and activity of such catalysts at variable Au loadings.

In conclusion, the SSP method has been demonstrated to be an effective method for the modification of silica mesopore surfaces and the tuning of mesopore diameters. This layer-by-layer approach allows the control of mesopore diameters with monolayer precision. Ultrasmall gold nanoparticles were successfully prepared on surface-modified SBA-15 via a DP method without the constraint of surface IEP. These new materials are highly active catalysts for CO oxidation. This general method can be used to modify the surfaces of mesopores with other metal oxides, such as Zr, Mg, Al, Nb, Fe, and Ge oxide monolayers or multilayer species.

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**Supporting Information Available:** EDX spectrum of the TEM area in Figure 2. TEM image of aggregated gold particles on SBA-15. Catalytic light-off curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- (1) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (2) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647.
- (3) (a) Lee, S. J. and Gavrilidis, A. *J. Catal.* **2002**, *206*, 305. (b) Mukherjee, P.; Patra, C. R.; Ghosh, A.; Kumar, R.; Sastry, M. *Chem. Mater.* **2002**, *14*, 1678.
- (4) (a) Pietron, J. J.; Stround, R. M.; Rolison, D. R. *Nano Lett.* **2002**, *2*, 545. (b) Rolison, D. R. *Science* **2003**, *299*, 1698.
- (5) (a) Konya, Z.; Puentes, V. F.; Kiricsi, I.; Zhu, J.; Alivisatos, A. P.; Somorjai, G. A. *Nano Lett.* **2002**, *2*, 907. (b) Zhu, J.; Konya, Z.; Puentes, V. F.; Kiricsi, I.; Miao, C. X.; Ager, J. W.; Alivisatos, A. P.; Somorjai, G. A. *Langmuir* **2003**, *19*, 4396.
- (6) (a) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. *Chem. Commun.* **1995**, 1655. (b) Turkevich, T.; Kim, G. *Science* **1970**, *169*, 873.
- (7) (a) Liz-Marzan, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329. (b) Caruso, F. *Adv. Mater.* **2001**, *13*, 11.
- (8) Cheng, S.; Wei, Y.; Feng, Q.; Qiu, K.-Y.; Pang, J.-B.; Jansen, S. A.; Yin, R.; Ong, K. *Chem. Mater.* **2003**, *15*, 1560.
- (9) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- (10) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152.
- (11) (a) Plyuto, Y.; Berquier, J. M.; Jacquiod, C.; Ricolleau, C. *Chem. Commun.* **1999**, 1653. (b) Besson, S.; Gacoin, T.; Ricolleau, C.; Boilot, J. P. *Chem. Commun.* **2003**, 360.
- (12) (a) Zhang, Z.; Pan, Z.; Mahurin, S. M.; Dai, S. *Chem. Commun.* **2003**, 2584. (b) Zhang, Z.; Dai, S.; Blom, D. A.; Shen, J. *Chem. Mater.* **2002**, *14*, 965.
- (13) Fukuoka, A.; Araki, H.; Sakamoto, Y.; Sugimoto, N.; Tsukada, H.; Kumai, Y.; Akimoto, Y.; Ichikawa, M. *Nano Lett.* **2002**, *2*, 793.

- (14) Okumura, M.; Tsubota, S.; Iwamoto, M.; Haruta, M. *Chem. Lett.* **1998**, 315.
- (15) (a) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, 276, 923. (b) Liu, J.; Shin, Y.; Nie, Z.; Chang, J. H.; Wang, L.-Q.; Fryxell, G. E.; Samuels, W. D.; Exarhos, G. J. *J. Phys. Chem. A* **2000**, 104, 8328.
- (16) Lin, V. S. Y.; Radu, D. R.; Han, M. K.; Deng, W. H.; Kuroki, S.; Shanks, B. H.; Pruski, M. *J. Am. Chem. Soc.* **2002**, 124, 9040.
- (17) Dai, S.; Burleigh, M. C.; Shin, Y.; Morrow, C. C.; Barnes, C. E.; Xue, Z. L. *Angew. Chem., Int. Ed. Engl.* **1999**, 38, 1235.
- (18) Antochshuk, V.; Kruk, M.; Jaroniec, M. *J. Phys. Chem. B* **2003**, 107, 11900.
- (19) Zhu, H.; Lee, B.; Dai, S.; Overbury, S. *Langmuir* **2003**, 19, 3974.
- (20) Guari, Y.; Thieuleux, C.; Mehdi, A.; Reye, C.; Corriu, R. J. P.; Gomez-Gallardo, S.; Philippot, K.; Chaudret, B.; Dutartre, R. *Chem. Commun.* **2001**, 1374.
- (21) Morey, M. S.; O'Brien, S.; Schwarz, S.; Stucky, G. D. *Chem. Mater.* **2000**, 12, 898.
- (22) Sinha, A. K.; Seelan, S.; Akita, T.; Tsubota, S.; Haruta, M. *Appl. Catal., A* **2003**, 240, 243.
- (23) Zheng, S.; Gao, L.; Zhang, Q. H.; Guo, J. K. *J. Mater. Chem.* **2000**, 10, 723.
- (24) Zanella, R.; Giorgio, S.; Henry, C. R.; Louis, C. *J. Phys. Chem. B* **2002**, 106, 7634.
- (25) (a) Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Mater.* **1997**, 9, 1296. (b) Huang, J.; Kunitake, T. *J. Am. Chem. Soc.* **2003**, 125, 11834. (c) He, J.; Ichinose, I.; Kunitake, T.; Nakao, A.; Shiraishi, Y.; Toshima, N. *J. Am. Chem. Soc.* **2003**, 125, 11034.
- (26) Leskela, M.; Ritala, M. *Angew. Chem., Int. Ed.* **2003**, 42, 5548.
- (27) Yasuda, T.; Kuse, R.; Iwamoto, K.; Tominaga, K.; Park, J. W. *Chem. Mater.* **2003**, 15, 4157.
- (28) Elam, J. W.; Routkevitch, D.; Mardilovich, P. P.; George, S. M. *Chem. Mater.* **2003**, 15, 3507.
- (29) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, 120, 6024.
- (30) Ichinose, I.; Senzu, H.; Kunitake, T. *Chem. Lett.* **1996**, 831.
- (31) Tsubota, S.; Haruta, M.; Kobayashi, T.; Ueda, A.; Nakahara, Y. *Stud. Surf. Sci. Catal.* **1991**, 63, 695.
- (32) Yan, W.; Chen, B.; Overbury, S. H.; Dai, S. To be submitted for publication.