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Forced Impregnation Approach to Fabrication of Large-Area, Three-Dimensionally Ordered Macroporous Metal Oxides

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Recently, three-dimensionally ordered macroporous (3DOM) materials, prepared by colloidal crystal templating methods, have captured the interest of scientists and engineers owing to their potential applications in the realms of catalysts, separations, photonic crystals, and nanoelectronics.[1−5] To date, almost all of the 3DOM metal oxides have been synthesized by a general route: first, a colloidal crystal template is prepared by ordering monodisperse spheres; then interstices in the template is infiltrated with desired precursors, for example metal alkoxides; finally, the spheres are removed by calcination or extraction.[6−10] Incomplete filling of the templates by the precursor solution can cause collapsed structures and vacancies,[2,11] which is harmful to obtaining the perfect 3DOM structure.

As well-known, the incomplete filling is always caused by poor infiltration ability of the precursor with high viscosity. To reduce fluid viscosity, the precursor is always diluted with all kinds of alcohol for the purpose of easy penetration.[2,5,7−11] However, the diluent precursor solution still has a high viscosity, which could cause the insufficient infiltration.[2,11] Though the dilution can lower the viscosity of an alkoxide precursor, the amount incorporated in the interstices decreases, resulting in thinner walls and larger windows among adjacent voids, which cannot support the network[11] and leads to a numerous vacancies and even collapsed structures. To increase the loading amount of the precursor, the templates are often soaked repeatedly in the precursor solution with optimum dilution. However, the vacancies caused by uneven infiltration have still been observed.[2,5,11−14] Consequently, this method is not able to eliminate vacancies or produce large-scale 3DOM structure.

In addition, most of the metal alkoxides are sensitive to water or vapor; as a result, it is difficult to control their hydrolytic rate in air. In the method of vacuum filtration developed by Holland et al,[1] the precursors would be prehydrolyzed before the filtration[15−17] in the uncovered Buchner funnel because hydrolysis could be induced by exposure to the atmosphere. And if the alkoxide precursors hydrolyze too rapidly to fill the interstices in the template, the formation of 3DOM framework becomes more difficult.

Here, we presented a forced impregnation approach to fabricate large-scale 3DOM structure of metal oxides with no vacancy using undiluted alkoxide precursor. Our approach was inspired by the plastination technique, which was invented by Gunther in 1978 and used in anatomy to preserve bodies or body parts with polymers.[18−20] It succeeded in impregnating reactive polymers like silicone rubber into the whole body without any ruptures of the original appearance after immerging in an acetone bath. The process of injecting polymers into biological specimens bears some analogies to the preparation of 3DOM materials with colloidal crystal templates and could overcome the two obstacles of complete filling effectively. Hence we introduced this strategy to the synthesis of 3DOM macroporous oxides, such as TiO_2, Ta_2O_5, Nb_2O_5, and ZrO_2, by using metal alkoxides with high viscosity and high reactivity.

Figure 1 illustrates the preparation process of 3DOM materials in our study. Monodisperse polystyrene spheres (Figure 1a) with an average diameter of ca. 450 nm were synthesized by emulsifier-free emulsion polymerization according to the reported techniques.[21] The colloidal crystal templates (Figure 1b) were prepared by centrifugation

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(1) Holland, B. T.; Blanford, C. F.; Stein, A. *Science* **1998**, *281*, 538.
(2) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802.
(3) Yan, H.; Blanford, C. F.; Lytle, J. C.; Carter, C. B.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2001**, *13*, 4314.
(4) Zhang, Y.; Lei, Z.; Li, J.; Lu, S. *New J. Chem.* **2001**, *25*, 1118.
(5) Tang, F.; Uchikoshi, T.; Sakka, Y. *Mater. Res. Bull.* **2006**, *41*, 268.
(6) Blanford, C. F.; Yan, H.; Schroden, R. C.; Al-Daous, M.; Stein, A. *Adv. Mater.* **2001**, *13*, 401.
(7) Sadakane, M.; Asanuma, T.; Kubo, J.; Ueda, W. *Chem. Mater.* **2005**, *17*, 3546.
(8) Sadakane, M.; Takahashi, C.; Kato, N.; Asanuma, T.; Ogihara, H.; Ueda, W. *Chem. Lett.* **2006**, *35*, 480.
(9) Sadakane, M.; Horiuchi, T.; Kato, N.; Takahashi, C.; Ueda, W. *Chem. Mater.* **2007**, *19*, 5779.
(10) Sadakane, M.; Takahashi, C.; Kato, N.; Ogihara, H.; Nodasaka, Y.; Doi, Y.; Hinatsu, Y.; Ueda, W. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 677.
(11) Stein, A. *Microporous Mesoporous Mater.* **2001**, *44−45*, 227.
(12) Li, S.; Zheng, J.; Zhao, Y.; Liu, Y. *J. Appl. Polym. Sci.* **2008**, *107*, 3903.
(13) Li, S.; Zheng, J.; Yang, W.; Zhao, Y. *Mater. Lett.* **2007**, *61*, 4784.
(14) Bechger, L.; Vos, W. L. *Chem. Mater.* **2004**, *16*, 2425.
(15) Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Nature* **1997**, *389*, 447.
(16) Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Chem. Mater.* **1998**, *10*, 3597.
(17) Stein, A.; Schroden, R. C. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 553.
(18) Gunther, V. H. 1978, DE2710147, European Patent Office.
(19) Gunther, V. H. 1978, DE2720607, European Patent Office.
(20) Gunther, V. H. *Anat. Rec.* **1979**, *194*, 247.
(21) Okubo, M.; Ise, E.; Yamashita, T. *J. Polym. Sci., Part A:Polym. Chem.* **1998**, *36*, 2513.

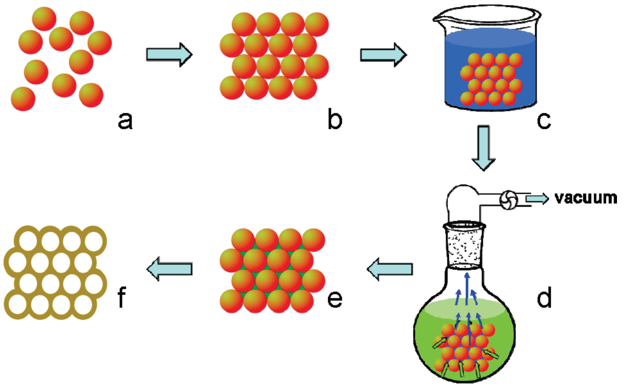

Figure 1. Preparation process of 3DOM materials using a plastination-like approach. (a) Monodisperse polystyrene spheres; (b) polystyrene colloidal crystal template was prepared by centrifugation; (c) colloidal crystal templates soaked in an absolute methanol bath; (d) in a vacuum, methanol is extracted and gradually replaced with metal alkoxide; (e) the alkoxide precursors filled in the interstices of the template hydrolyze slowly; (f) the as-prepared 3DOM samples after the sintering.

of the colloidal suspension, and then placed into an absolute methanol bath as shown in Figure 1c. Unlike acetone used in the plastination, methanol cannot dissolve the polystyrene spheres. After soaking for a while, the interstices in the colloidal crystal template were sufficiently filled with the absolute methanol. These templates were then taken from the methanol bath and immediately immersed into the alkoxide precursor bath (Figure d), i.e., butyl titanate, niobium ethoxide, tantalum ethoxide or zirconium n-propoxide bath. To replace the methanol which occupied the interstices in the templates with active alkoxide precursor, a vacuum was applied at room temperature (Figure 1d). Absolute methanol has lower boiling point and higher vapor pressure compared with the alkoxide precursors. The methanol was removed from the templates by vacuum, thus providing the sites of negative pressure exactly and introducing the liquid alkoxide to the interstices to replace the methanol during the vacuum impregnation. As a result, it was easy for the viscous alkoxides to penetrate every interstice in the colloidal crystal templates due to forced impregnation. If without vacuum, the yield formation and order of 3DOM samples will decrease (see the Supporting Information). The coated templates were removed from the alkoxide bath and were allowed to dry in air at room temperature overnight, and the alkoxide precursors in the interstices of the template hygrolyze slowly. (Figure.1e). Finally, the 3DOM materials were obtained by sintering. (Figure 1f) In previous work, it was noted that products with large grains tended to lose their 3D periodicity.[3] Therefore, to keep the structure as ordered as possible, these samples were sintered at low temperatures (e.g., 450−575 °C) for a short time (e.g., 5−6 h), and a slow heating rate (e.g., 1 °C/min) was employed to ensure a gentle process. After this calcination process, the ordered honeycomb structures of these four metal oxides were obtained very well. The phases of the final inorganic oxides have been identified by powder X-ray diffraction (see the Supporting Information). The bulk macroporous TiO_2, Nb_2O_5, and ZrO_2 samples were crystalline, whereas the macroporous Ta_2O_5 was amorphous. The samples of macroporous ZrO_2 and Nb_2O_5 could be indexed as the tetragonal phase and the hexagonal phase, respectively. The macroporous TiO_2 obtained by annealing at 575 °C was assigned to a mixture of anatase and rutile.

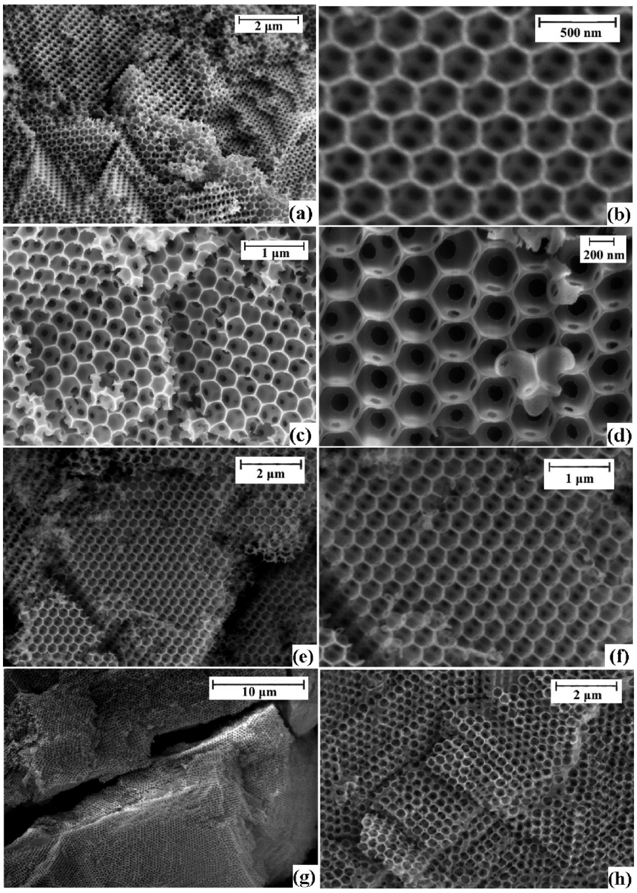

Figure 2. SEM images of macroporous oxides: (a, b),TiO_2; (c, d), Nb_2O_5; (e, f), Ta_2O_5; (g, h), ZrO_2.

Figure 2 shows SEM images of the 3DOM TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2 samples. Well-ordered 3DOM structures of these oxides were obtained in high yield. Large fractions ($>98\%$ of particles by SEM images) of the samples had highly ordered porous structure in three dimensions over a range of tens of micrometers. These four oxides have clearly retained the thress-dimensional crystalline order of the colloidal crystal template covered a large area and exhibited an ordered pattern of pores. Though their precursors (metal alkoxides) are remarkably visious, the incomplete filling can be avoid effectively due to forced impregnation. The spherical pore sizes of TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2 are about 250 ± 10, 300 ± 5, 305 ± 5, and 300 ± 15 nm, respectively. In comparison with the size of the original polystyrene spheres, therefore, the shrinkage of the pore size of 3DOM TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2 is about 44, 33, 32, and 33%, respecitively. This shrinkage was caused by both melting of the polystyrene spheres and sintering of the produced powders.[22]

In the case of TiO_2, the wall thickness (ca. 25 nm) of the 3DOM structure is much thinner compared with the

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(22) Yan, H.; Blanford, C. F.; Holland, B. T.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2000**, *12*, 1134.

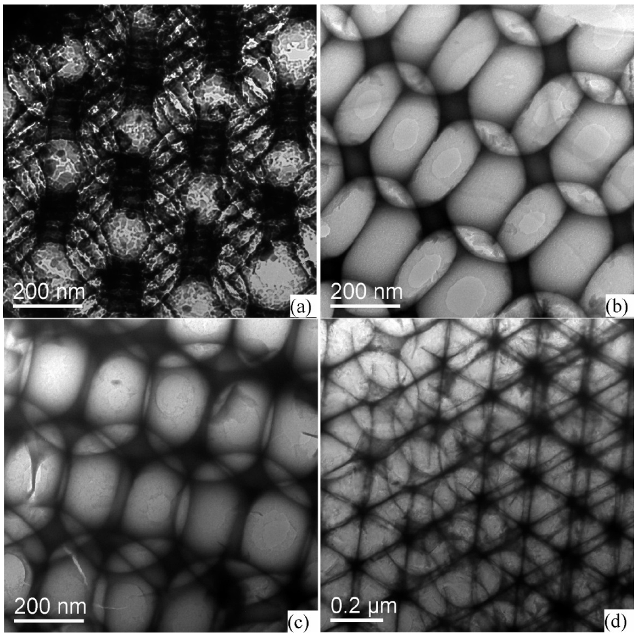

Figure 3. TEM images of 3DOM: (a) TiO_2, (b) Nb_2O_5, (c) Ta_2O_5, and (d) ZrO_2. The dark regions represent the wall structure, and the light regions represent void spaces.

previous researches in which the conventional infiltration method was used.[2,5,12] The thicker wall framework for the TiO_2 porous materials is induced by the rapid condensation and gelation of titanium alkoxide, which is sensitive to the atmospheric humidity, during the process of slow infiltration.[5,23,24] In our study, however, the alkoxide precursor was kept in the vacuum chamber all along, thus preventing the exposure to the moisture and hindering premature hydrolytic particles precipitation during the loading of the precursor into the interstices in the colloidal crystal templates. Especially in the case of Nb_2O_5, there are small triangular openings on the walls, confirming that surface templating has taken place in some regions.[24] These triangular openings are essentially shrinking pores during the condensation of the precursor.

Figure 3 displays TEM images of the above four inorganic 3DOM structures. In each image, the dark regions correspond to the ceramic framework and the light regions represent the void space. These images illustrate the intact spatial periodicity of multiple layers of close packed macropores.

Photocatalytic properties of periodic photonic structures of TiO_2 have attracted interest.[25] Gaseous isopropanol (IPA) can act as a model organic compound for evaluating the activity of a photocatalyst. The photocatalytic oxidation processes of IPA under light irradiation were carried out to investigate the photooxidation property. Samples of 3DOM TiO_2 and nanoparticle TiO_2, which was prepared at the same sintering temperature, were selected as a typical sample and a reference, respectively. As shown in Figure 4, 3DOM TiO_2 showed a much higher activity than the particle TiO_2 during the photooxidation of IPA to CO_2. The enhancement in photocatalytic property may involve the use of the 3DOM structure to increase the path length of light within this catalyst and enhance the absorption of light. Another reason is that the 3DOM TiO_2 has a larger specific surface (37 m^2/g) than the nanoparticle TiO_2 (21 m^2/g), which is useful for improving the gas adsorption on the surface of catalyst.

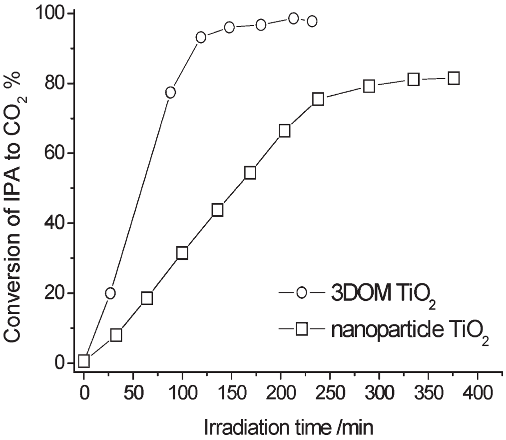

Figure 4. Photooxidation of IPA to CO_2 over the 3DOM TiO_2 and the nanoparticle TiO_2.

In this study, we have presented a facile procedure to produce 3DOM structure, which needs no pretreatment of the high viscous and reactive metal alkoxides. Large-area 3DOM structures of TiO_2, Nb_2O_5, Ta_2O_5, and ZrO_2 with high porosity were prepared through this new route. Owing to simplicity and versatility of this approach, it is potential to commercial scale-up for the application of the 3DOM materials as catalysts, thermal or electrical insulators and porous electrodes or electrolytes.[1,26] And in future, the 3DOM materials can be expected societal benefits in the fields of energy conversion and storage, environmental protection, communications, and medicine.[27]

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Supporting Information Available: Experimental section and XRD patterns of the samples, physical properties of the samples, and side-by-side structural comparison of 3DOM product prepared by forced impregnation method with one prepared conventionally (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Chem. Mater.* **1999**, *11*, 795.

(24) Schroden, R. C.; Al-Daous, M.; Blanford, C. F.; Stein, A. *Chem. Mater.* **2002**, *14*, 3305.

(25) Chen, J. L. L.; Von Freymann, F.; Choi, S. Y.; Kitaev, V.; Ozin, G. A. *Adv. Mater.* **2006**, *18*, 1915.

(26) Stein, A.; Li, F.; Denny, N. R. *Chem. Mater.* **2008**, *20*, 649.

(27) Zhang, G.; Zhao, Z.; Liu, J.; Jiang, G.; Duan, A.; Zheng, J.; Chen, S.; Zhou, R. *Chem. Commun.* **2010**, *46*, 457.