Communication

Highly Crystalline Inverse Opal Transition Metal Oxides via a Combined Assembly of Soft and Hard Chemistries

M. Christopher Orilall, Neal M. Abrams, Jinwoo Lee, Francis J. DiSalvo, and Ulrich Wiesner

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Highly Crystalline Inverse Opal Transition Metal Oxides via a Combined Assembly of Soft and Hard Chemistries

M. Christopher Orilall, Neal M. Abrams,[†] Jinwoo Lee,[‡] Francis J. DiSalvo, and Ulrich Wiesner*

Departments of Chemistry & Chemical Biology and Materials Science & Engineering, Cornell University, Ithaca, New York

Received March 25, 2008; E-mail: ubw1@cornell.edu

Inverse opal (or three-dimensionally ordered macroporous, 3DOM) transition metal oxides, synthesized by colloidal crystal templating (CCT), are particularly interesting because of potential applications in catalysis, photocatalysis, sensors, photonic crystals and electrode materials.[1] For many of these applications, high crystallinity (least amorphous character) is essential for device performance.[2,3] To achieve high crystallinity, one must heat treat the amorphous as-made material to high enough temperatures for full conversion to the crystalline state. 3DOM transition metal oxides are generally synthesized from monodisperse colloids,[4–7] typically silica or polymer, such as polystyrene. High temperature treatments can be achieved when silica spheres are used for the CCT but subsequent removal of this hard template can be tedious. When polymer spheres are used for the CCT, one cannot go to high temperatures and the template is usually calcined off around 400 °C. Subsequent increase in temperature, needed to further crystallize the amorphous metal oxide, results in collapse of the macroporous framework.[8] This is a significant drawback as polymer spheres have been preferred to silica spheres as templates because (i) the connectivity of the macropores can be controlled due to the soft characteristics of polymer materials (T_g of PS ≈ 100 °C),[9] (ii) the ease of removing the template (less steps) and (iii) the multitude of available polymer colloidal sizes and shapes.

Here, we demonstrate that the method of using a combined assembly by soft and hard (CASH) chemistries[10] can be employed to overcome the limitations of the polymer CCT approach for preparing highly crystalline 3DOM metal oxides. In this novel method, the amorphous metal oxide is structure-directed using a polymer that has sp^2-hybridized carbon atoms that when heat treated under an inert environment is converted to a sturdy amorphous carbon material (evidenced by D- and G-bands in Raman spectroscopy as well as thermogravimetric analysis). This carbon acts as a scaffold to the metal oxide structure, enabling high temperature heat treatments without structural collapse. The carbon is subsequently removed by heating in air at moderate temperatures (~450 °C) to leave the stable and highly crystalline, structured metal oxide. By using polymer spheres with sp^2-hybridized carbon atoms, the preparation of highly crystalline inverse opal structures can be achieved. In this paper, Nb_2O_5 and TiO_2 structures were fabricated using a reverse-template infiltration technique based on the aqueous liquid phase deposition (LPD)[11–13] of the metal oxide in the interstitial spaces of a colloidal assembly.[14] For these experiments, carboxy-modified polystyrene spheres (PS) were used for the CCT.[15] The CASH method can then be employed on the metal oxide infiltrated PS colloidal assembly because of the presence of sp^2-hybridized carbon atoms in polystyrene. Styrene has previously been used in a similar manner to make mesoporous carbon.[16] Heat treatment of this hybrid under an inert environment generates a
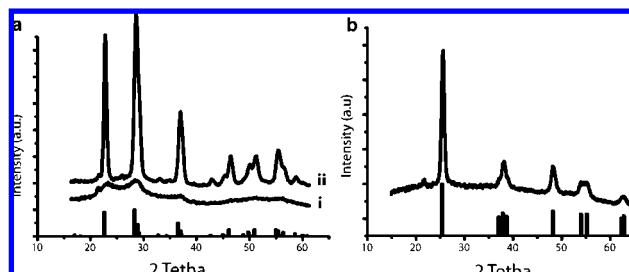

Figure 1. XRD analysis of differently heat treated transition metal oxides: (a) Nb_2O_5/PS hybrid heat treated at (i) 450 °C in air and (ii) 700 °C under argon (bar markers: reflections for crystalline Nb_2O_5, PDF no. 27-1003); (b) TiO_2/PS hybrid heat treated at 700 °C under argon (bar markers: TiO_2, PDF no. 89-4921).
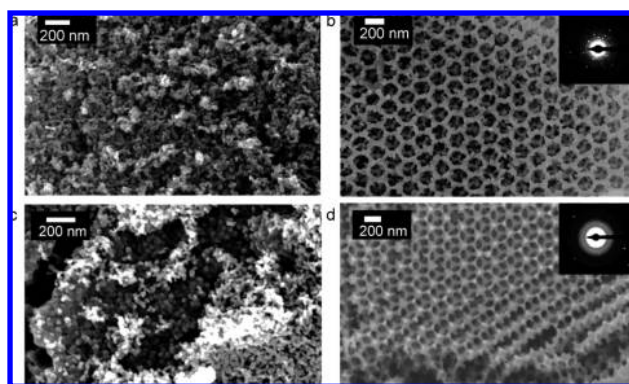

Figure 2. SEM images showing the effectiveness of the CASH method: Nb_2O_5/PS hybrid heat treated at (a) 700 °C in air and (b) 700 °C under argon (inset showing electron diffraction pattern); TiO_2/PS hybrid heat treated at (c) 700 °C in air and (d) 700 °C under argon (inset showing electron diffraction pattern).

sturdy amorphous carbon support which allows for high temperature treatments without collapse of the inverse opal metal oxide structure. The *in situ* formed carbon is subsequently removed by heating in air (see Scheme 1).

For the synthesis, carboxy-modified PS spheres were purchased from Seradyn (10% by weight) with an average diameter of 291 ± 5 nm. The colloidal assembly was grown on a silicon wafer using the vertical LPD method. High colloidal crystallinity was confirmed by the presence of a photonic bandgap centered around 630 nm (orange/red). The spheres were infiltrated using a metal oxide precursor, followed by hydrolysis. For Nb_2O_5 and for TiO_2 ammonium hexafluoroniobate [NH_4NbF_6] and ammonium hexafluorotitanate [$(NH_4)_2TiF_6$] were used as the metal precursors, respectively. An aqueous solution of the metal precursor was reacted with boric acid (pH 3) at 25 °C and the Si wafer with the PS colloidal assembly was quickly immersed in this solution (see Supporting Information for a more detailed procedure). This results

---

† Current address: SUNY-ESF, Syracuse, NY.
‡ Current address: Pohang University of Science and Technology, Korea.

Scheme 1. Schematic Representation of the CASH Method and CCT[a]
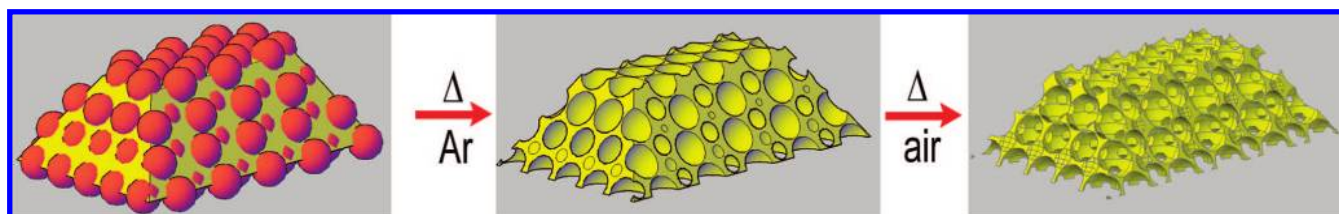
[a] The metal oxide infiltrated colloidal assembly is heat treated at high temperatures under an inert environment to give an in-situ formed carbon, which acts as a rigid support to macrostructure of the highly crystalline metal oxide framework. The carbon is subsequently removed by heating in air to leave the highly crystalline inverse opal metal oxides.

in the infiltration of the metal oxide into the interstitial spaces of the PS colloidal assembly to form a metal oxide/PS 3DOM hybrid. The resulting thin film appears near colorless due to the refractive index matching of the PS spheres ($\eta = 1.6$) with the metal oxide and accompanying hydroxyl groups.

Removal of the PS spheres results in a highly ordered replica consisting of the metal oxide frame (an inverse opal structure). To this end, the 3DOM hybrid structures were first heat treated at 450 °C in air to simulate conventional CCT approaches. The resulting photonic bandgap was centered around 470 nm (blue). Under these conditions, however, the resulting degree of crystallinity strongly depends on the metal oxide. While for TiO_2, heating to 450 °C may already lead to appreciable crystallinity, other oxides like Nb_2O_5 require heat treatment to higher temperatures. This is evident from X-ray analysis of the Nb_2O_5/PS 3DOM hybrid heat treated at 450 °C in air which shows a broad baseline and no sharp reflections, characteristic of poorly crystalline materials (see Figure 1a-i). However, heat treating the Nb_2O_5/PS and TiO_2/PS 3DOM hybrids at 700 °C in air results in the collapse of the macrostructures as evidenced from SEM imaging (see Figure 2a,c), consistent with results from Yan et al.[7]

To overcome this problem, the CASH method was employed. Here, heat treating the metal oxide/PS hybrids under an inert environment converts the sp[2]-hybridized carbon atoms of PS to a sturdy amorphous/graphitic-like carbon material that prevents the collapse of the macrostructure. Heat treatment of the Nb_2O_5/PS 3DOM hybrid at 700 °C under argon results in highly crystalline Nb_2O_5, identified as the orthorhombic phase: PDF no. 27-1003 (Figure 1a-ii). The crystallite size as calculated from the Debye–Scherrer equation is 9.2 nm.[17] For the TiO_2/PS 3DOM hybrid, heat treatment at 700 °C under argon resulted in highly crystalline anatase TiO_2, identified as the tetragonal phase: PDF no. 89-4921 (Figure 1b). The crystallite size as calculated from the Debye–Scherrer equation is 9.8 nm. SEM images of the Nb_2O_5 and TiO_2 3DOM hybrids heated treated at 700 °C under argon show that the inverse opal structure was indeed retained (Figure 2 panels b and d, respectively). Electron diffraction on these materials also confirms the high degree of crystallinity (see Figure 2b,d insets). The carbon is subsequently removed by heat treating at 450 °C in air to leave the highly crystalline inverse opal metal oxide structure. SEM images of these structures look identical to Figure 2b,d (see Supporting Information).

To demonstrate the importance of high annealing temperatures, we also heat treated the TiO_2/PS 3DOM hybrids to 580 °C (previously highest reported heat treatment temperature by Dong et al.[18]) and 900 °C. In both cases the macroporous structure was preserved and the crystal phase was anatase titania (see Supporting Information). From XRD analysis with increasing temperature (see Supporting Information), the estimated crystal domain sizes increased from 8.4 (580) to 9.8 (700) and 12.2 nm (900 °C). This shows that transition metal oxides like anatase titania become more crystalline at higher temperatures, as expected.

In conclusion, we have shown the effectiveness of the CASH method for CCT. Polystyrene (spheres) with sp[2]-hybridized carbon atoms was first employed as a soft template method to form macroporous metal oxides and then subsequently heat treated to high temperatures under an inert environment to become a hard template, which enables the formation of highly crystalline metal oxides while retaining the macroporous structure. Although this work only demonstrates this process for fabricating highly crystalline Nb_2O_5 and TiO_2 inverse opals, we expect that this approach can be applied to any three-dimensionally ordered macroporous metal oxide using CCT which employs polymer spheres that have sp[2]-hybridized carbon atoms. Furthermore, the versatility of the CASH method should, in principle, be applicable to prepare other highly crystalline three-dimensionally ordered macroporous materials, where heat treatment to high temperatures is necessary.

Supporting Information Available: Experimental details for sample preparation, GADDS, SEM, and electron diffraction via TEM. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Blanco, A. L. C. Photonic Crystals: Fundamentals and Applications. In *Annual Reviews of Nanoresearch*; Cao, G., Brinker, C. J., Eds.: World Scientific: Singapore, 2006; *1*, 81−152..
(2) Nishimura, S.; Abrams, N.; Lewis, B. A.; Halaoui, L. I.; Mallouk, T. E.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 6306–6310.
(3) Chen, J. I. L.; von Freymann, G.; Kitaev, V.; Ozin, G. A. *J. Am. Chem. Soc.* **2007**, *129*, 1196–1202.
(4) Holland, B. T.; Blanford, C. F.; Stein, A. *Science.* **1998**, *281*, 538.
(5) Wijnhoven, J. E. G. J.; Vos, W. L. *Science.* **1998**, *281*, 802.
(6) Subramania, G.; Constant, K.; Biswas, R.; Sigalas, M. M.; Ho, K. M. *Appl. Phys. Lett.* **1999**, *74*, 3933–3935.
(7) Yan, H.; Blanford, C. F.; Holland, B. T.; Smyrl, W. H.; Stein, A. *Chem. Mater.* **2000**, *12*, 1134–1141.
(8) Blanford, C. F.; Yan, H. W.; Schroden, R. C.; Al-Daous, M.; Stein, A. *Adv. Mater.* **2001**, *13*, 401–407.
(9) Sasaki, T.; Shimizu, A.; Mourey, T. H.; Thurau, C. T.; Ediger, M. D. *Chem. Phys.* **2003**, *119*, 8730.
(10) Lee, J.; Orilall, M. C.; Warren, S. C.; Kamperman, M.; DiSalvo, F. J.; Wiesner, U. *Nat. Mater.* **2008**, *7*, 222–228.
(11) Kishimoto, H.; Takahama, K.; Hashimoto, N.; Aoi, Y.; Deki, S. *Mater. Chem* **1998**, *8*, 2019–2024.
(12) Ko, H. Y. Y.; Mizuhata, M.; Kajinami, A.; Deki, S. *Mater. Chem.* **2002**, *12*, 1495–1499.
(13) Nishimura, S.; Shishido, A.; Abrams, N.; Mallouk, T. E. *Appl. Phys. Lett.* **2002**, *81*, 4532–4534.
(14) Jiang, P.; Bertone, J. F.; Hwang, K. S.; Colvin, V. L. *Chem. Mater.* **1999**, *11*, 2132–2140.
(15) Holland, B. T.; Blanford, C. F.; Do, T.; Stein, A. *Chem. Mater.* **1999**, *11*, 795–805.
(16) Xia, Y. D.; Mokaya, R. *Adv. Mater.* **2004**, *16*, 1553–1558.
(17) Krawitz, A. D. *Introduction to Diffraction in Materials Science and Engineering*; Wiley: New York, 2001; *168*.
(18) Dong, W.; Bongard, H. J.; Marlow, F. *Chem. Mater.* **2003**, *15*, 568–574.

JA802093U