Electronic supplementary information for

Controlling material macrostructures and mesostructures through combined hard and soft templating

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This document is meant to help steer inquiring minds to helpful resources, books and review articles, which will hopefully aid further research. Some these documents have been already been cited in the main article. However, a brief description of the topic areas and some of the resources are listed here.

Synthesis of Nanomaterials

The book cited below contains a good overview of different synthesis techniques that can be used to make materials with pores or dimensions under a micrometer.

Ozin, G. A.; Arsenault, A. C.; Cademartiri, L. *Nanochemistry: A Chemical Approach to Nanomaterials*, 2nd ed.; Royal Society of Chemistry: Cambridge, U.K., 2009.

General Information about Hierarchically Structured Materials

As stated throughout the main article, hierarchically structured materials offer distinct advantages in numerous applications when compared to materials with unimodal porosity. Many interesting syntheses for these materials are being pioneered, and novel applications are being explored. In particular, *Hierarchically Structured Porous Materials* provides comprehensive reviews about this rapidly advancing field. Our chapter in the text, chapter 4, goes into further detail on aspects of colloidal crystal templating for generation of hierarchical materials.

Yang, X.-Y.; Li, Y.; Lemaire, A.; Yu, J.-G.; Su, B.-L. Hierarchically Structured Functional Materials: Synthesis Strategies for Multimodal Porous Networks *Pure Appl. Chem.* **2009**, *81*, 2265–2307.

Colombo, P.; Vakifahmetoglu, C.; Costacurta, S. Fabrication of Ceramic Components with Hierarchical Porosity *J. Mater. Sci.* **2010**, *45*, 5425–5455.

Innocenzi, P.; Malfatti, L.; Soler-Illia, G. J. A. A. Hierarchical Mesoporous Films: From Self-Assembly to Porosity with Different Length Scales *Chem. Mater*. **2011**, *23*, 2501–2509

Su, B.-L.; Sanchez, C.; Yang, X.-Y., Eds. *Hierarchically Structured Porous Materials: From Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012.

Characterization

Both of these articles discuss problems commonly encountered in the characterization of porous materials and other materials with nanoscale dimensions. Many books are available about specific characterization techniques (X-ray diffraction, electron microscopy, gas sorption, etc.), and are not listed here.

Weidenthaler, C. Pitfalls in the Characterization of Nanoporous and Nanosized Materials *Nanoscale* **2011**, *3*, 792–810.

Soler-Illia, G. J. A. A.; Angelomé, P. C.; Fuertes, M. C.; Grosso, D.; Boissiere, C. Critical Aspects in the Production of Periodically Ordered Mesoporous Titania Thin Films *Nanoscale* **2012**, *4*, 2549–2566.

Understanding Self-Assembly

Self-assembly is a wide and somewhat ill-defined concept. For equilibrium and kinetically-stabilized structures produced via self-assembly (including colloidal particles), the following are resources for understanding the interactions that drive the process.

Lee, Y. S. *Self-Assembly and Nanotechnology: A Force Balance Approach*; John Wiley & Sons, Inc: Hoboken, NJ, 2008.

Israelachvili, J. N. *Intermolecular and Surface Forces*, 3rd ed.; Academic Press: Waltham, MA, 2011.

Cademartiri, L.; Bishop, K. J. M.; Snyder, P. W.; Ozin, G. A. Using Shape for Self-Assembly *Phil. Trans. R. Soc. A* **2012**, *370*, 2824–2847.

General Aspects of Hard Templating

Further aspects of hard templating are highlighted in these texts, including the use of mesoporous materials as hard templates.

Caruso, R. A. Nanocasting and Nanocoating *Top. Curr. Chem.* **2003**, *226*, 91–118.

Tiemann, M. Repeated Templating *Chem. Mater.* **2008**, *20*, 961–971.

Lu, A.-H.; Zhao, D.; Wan, Y. *Nanocasting: A Versatile Strategy for Creating Nanostructured Porous Materials*; Royal Society of Chemistry: Cambridge, U.K., 2009.

Sol-Gel Chemistry

Sol-gel processes are instrumental for the synthesis of templated porous materials. Despite its age, Brinker and Scherer's work is a great starting place. The other works describe sol-gel techniques that are not emphasized in *Sol-Gel Science*.

Brinker, C. J.; Scherer, G. W. *Sol-Gel Science. The Physics and Chemistry of Sol-Gel Processing*; Academic Press: New York, NY, 1990.

Kakihana, M. Invited Review: "Sol-Gel" Preparation of High Temperature Superconducting Oxides *J. Sol-Gel Sci. Technol.* **1996**, *6*, 7–55.

Mutin, P. H.; Vioux, A. Nonhydrolytic Processing of Oxide-Based Materials: Simple Routes to Control Homogeneity, Morphology, and Nanostructure *Chem. Mater.* **2009**, *21*, 582–596.

Colloid, Interface, and Surfactant Science

As stated in the main text, the foundation for soft templating lies in the science of surfactants and interfaces. These resources will help those interested in this important area of chemistry.

Alexandridis, P.; Hatton, T. A. Poly(ethylene oxide) –poly(propylene oxide) –poly(ethylene oxide) block copolymer surfactants in aqueous solution and at interfaces: thermodynamics, structure, dynamics and modeling *Colloids Surf., A* **1995**, *96*, 1–46.

Hassan, S.; Rowe, W.; Tiddy, G. J. T. Surfactant Liquid Crystals. In *Handbook of Applied Surface and Colloid Chemistry*; Holmberg, K.; Shah, D. O.; Schwuger, M. J., Eds.; John Wiley & Sons Ltd: Chichester, U.K., 2002, vol. 1, pp. 465–508.

Terence Cosgrove, Ed. *Colloid Science: Principles, Methods and Applications*; Blackwell Publishing Ltd: Oxford, U.K., 2005.

Shearman, G. C.; Tyler, A. I. I.; Brooks, N. J.; Templer, R. H.; Ces, O.; Law, R. V.; Seddon, J. M. Ordered Micellar and Inverse Micellar Lyotropic Phases *Liq. Cryst.* **2010**, *37*, 679–694.

Rosen, M.; Kunjappu, J. T. *Surfactants and Interfacial Phenomena*; John Wiley & Sons Inc: Hoboken, NJ, 2012.

General Aspects of Soft Templating

Many syntheses of soft templated mesoporous materials have been developed, along with experiments designed to probe the formation mechanisms responsible for these materials. Furthermore, numerous applications for these mesoporous materials have also been considered. While the following reviews offer a good starting point, there is much more in the literature. Also, this *Chem. Soc. Rev.* issue has more up-to-date reviews.

Wan, Y.; Zhao, D. On the Controllable Soft-Templating Approach to Mesoporous Silicates *Chem. Rev.* **2007**, *107*, 2821–2860.

Sanchez, C.; Boissière, C.; Grosso, D.; Laberty, C.; Nicole, L. Design, Synthesis, and Properties of Inorganic and Hybrid Thin Films Having Periodically Organized Nanoporosity *Chem. Mater.* **2008**, *20*, 682–737.

Fan, J.; Boettcher, S. W.; Tsung, C.-K.; Shi, Q.; Schierhorn, M.; Stucky, G. D. Field-Directed and Confined Molecular Assembly of Mesostructured Materials: Basic Principles and New Opportunities *Chem. Mater.* **2008**, *20*, 909–921.

Orilall, M. C.; Wiesner, U. Block Copolymer Based Composition and Morphology Control in Nanostructured Hybrid Materials for Energy Conversion and Storage: Solar Cells, Batteries, and Fuel Cells *Chem. Soc. Rev.* **2011**, *40*, 520–535.

Soler-Illia, G. J. A. A.; Azzaroni, G. Multifunctional Hybrids by Combining Ordered Mesoporous Materials and Macromolecular Building Blocks *Chem. Soc. Rev.* **2011**, *40*, 1107–1150.

Shi, Y.; Wan, Y.; Zhao, D. Ordered Mesoporous Non-Oxide Materials *Chem. Soc. Rev.* **2011**, *40*, 3854–3878.

Biological Templates

Other organisms and biomolecules have been used for hard templating, including viruses. These reviews primarily focus on hard templating without any added surfactant.

Sotiropoulou, S.; Sierra-Sastre, Y.; Mark, S. S.; Batt, C. A. Biotemplated Nanostructured Materials *Chem. Mater.* **2008**, *20*, 821–834.

Paris, O.; Burgert, I.; Fratzl, P. Biomimetics and Biotemplating of Natural Materials *MRS Bull.* **2010**, *35*, 219–225.

Colloidal Crystals and 3DOM Materials

In addition to the resources listed below, synthesis pathways for hierarchical 3DOM materials and opals are described in the book *Hierarchically Structured Porous Materials*.

Stein, A.; Li, F.; Denny, N. R. Morphological Control in Colloidal Crystal Templating of Inverse Opals, Hierarchical Structures and Shaped Particles *Chem. Mater.* **2008**, *20*, 649–666.

Marlow, F.; Muldarisnur; Sharifi, P.; Brinkmann, R.; Mendive, C. Opal: Status and Prospects *Angew. Chem. Int. Ed.* **2009**, *48*, 6212–6233.

Li, Q.; Retsch, M.; Wang, J.; Knoll, W.; Jonas, U. Porous Networks through Colloidal Templates *Top. Curr. Chem.* **2009**, *287*, 135–180.

Zhang, J. H.; Li, Y. F.; Zhang, X. M.; Yang, B. Colloidal Self-Assembly Meets Nanofabrication: From Two-Dimensional Colloidal Crystals to Nanostructure Arrays *Adv. Mater.* **2010**, *22*, 4249–4269.

Rudisill, S. G.; Wang, Z; Stein, A. Maintaining the Structure of Templated Porous Materials for Reactive and High-Temperature Applications *Langmuir* **2012**, *28*, 7310–7324.

Foams

A general review of cellular materials is presented in the first reference. The other reviews focus more on templates made via emulsions or on the use of emulsions as templates.

Gibson, L. J.; Ashby, M. F. *Cellular Solids: Structure and Properties*, 2nd ed.; Cambridge University Press: Cambridge, U.K., 1999.

Zhang, H.; Cooper, A. I. Synthesis and Application of Emulsion-Templated Porous Materials *Soft Matter* **2005**, *1*, 107–113.

Brun, N.; Ungureanu, S.; Deleuze, H.; Backov, R. Hybrid Foams, Colloids and Beyond: From Design to Applications *Chem. Soc. Rev*. **2011**, *40*, 771–788.

Anodic Al_2O_3 (AAO) Membranes and Polycarbonate (PC) Membranes

With the exception of the review by Platschek, *et al.* these articles do not address multiple templating with porous membranes. However, aspects of hard templating with AAO and PC membranes are covered in the other articles.

Cao, G.; Liu, D. Template-Based Synthesis of Nanorod, Nanowire, and Nanotube Arrays *Adv. Colloid Interface Sci.* **2008**, *136*, 45–64.

Bae, C.; Yoo, H.; Kim, S.; Lee, K.; Kim, J.; Sung, M. M.; Shin, H. Template-Directed Synthesis of Oxide Nanotubes: Fabrication, Characterization, and Applications *Chem. Mater.* **2008**, *20*, 756–767.

Steinhart, M. Supramolecular Organization of Polymeric Materials in Nanoporous Hard Templates– Self-Assembled Nanomaterials II: Nanotubes. In *Advanced Polymer Science*; Shimazu, T., Ed.; Springer: Berlin, 2008; pp 123–187.

Platschek, B; Keilbach, A.; Bein, T. Mesoporous Structures Confined in Anodic Alumina Membranes *Adv. Mater*. **2011**, *23*, 2395–2412.

Other Polymeric Templates

If the reader is interested in polymeric materials that may be effective hard templates, this review provides some examples not are mentioned in the main text.

Wu, D.; Xu, F.; Sun, B.; Fu, R.; He, H.; Matyjaszewski, K. Design and Preparation of Porous Polymers *Chem. Rev*. **2012**, *112*, 3959–4015.

In Situ Templates

While there are not many reviews on in situ templating, there is one about structures made from the unidirectional freezing of water.

Gutiérrez, M. C.; Ferrer, M. L.; del Monte, F. Ice-Templated Materials: Sophisticated Structures Exhibiting Enhanced Functionalities Obtained after Unidirectional Freezing and Ice-Segregation-Induced Self-Assembly *Chem. Mater.* **2008**, *20*, 634–648.

Discrete Particles

These are all resources about hollow spherical particles and core/shell particles. Many different morphologies and syntheses are outlined in these articles, including methods that do not require the use of a template.

Lou, X. W.; Archer, L. A.; Yang, Z. Hollow Micro-/Nanostructures: Synthesis and Applications *Adv. Mater.* **2008**, *20*, 3987–4019.

Wang, W.; Angelatos, A. S.; Caruso, F. Template Synthesis of Nanostructured Materials via Layer-by-Layer Assembly *Chem. Mater*. **2008**, *20*, 848–858.

Liu, J.; Qiao, S. Z.; Chen, J. S.; Lou, X. W.; Xing, X.; Lu, G. Q. Yolk/Shell Nanoparticles: New Platforms for Nanoreactors, Drug Delivery, and Lithium-Ion Batteries *Chem. Commun.***2011**, *47*, 12578–12591.

Hu, J.; Chen, M.; Fang, X.; Wu, L. Fabrication and Application of Inorganic Hollow Spheres *Chem. Soc. Rev.* **2011**, *40*, 5472–5491.

Du, X.; He, J. Spherical Silica Micro/Nanomaterials with Hierarchical Structures: Synthesis and Applications *Nanoscale* **2011**, *3*, 3984–4002.

Chaudhuri, R. G.; Paria, S. Core/Shell Nanoparticles: Classes, Properties Synthesis Mechanisms, Characterization, and Application *Chem. Rev.* **2012**, *112*, 2373–2433.