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Hierarchically Ordered Oxides

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Porous silica, niobia, and titania with three-dimensional structures patterned over multiple length scales were prepared by combining micromolding, polystyrene sphere templating, and cooperative assembly of inorganic sol-gel species with amphiphilic triblock copolymers. The resulting materials show hierarchical ordering over several discrete and tunable length scales ranging from 10 nanometers to several micrometers. The respective ordered structures can be independently modified by choosing different mold patterns, latex spheres, and block copolymers. The examples presented demonstrate the compositional and structural diversities that are possible with this simple approach.

Several approaches are currently available for the preparation of ordered structures at different length scales. For example, organic molecular templates can be used to form crystalline zeolite-type structures with ordering lengths less than 3 nm (*1*); mesoporous materials with ordering lengths of 3 to 30 nm can be obtained using surfactants or amphiphilic block copolymers as structure-directing agents (*2–7*); the use of latex spheres yields macroporous materials with ordering lengths of 100 nm to 1 μm (*8–13*); and soft lithography can be used to make high-quality patterns and structures with lateral dimensions of about 30 nm to 500 μm (*14–16*). Despite all of these efforts in nanostructuring materials, the fabrication of hierarchically ordered structures at multiple length scales, such as seen in nature in diatoms (*17*), has remained an experimental challenge. Such materials are important both for the systematic fundamental study of structure-property relations and for their technological promise in applications such as catalysis, selective separations, sensor arrays, wave guides, miniaturized electronic and magnetic devices, and photonic crystals with tunable band gaps.

Previously, micromolding has been used to form patterned mesoporous materials (*18, 19*). These studies, however, used acidic aqueous conditions to carry out the cooperative self-assembly (*20*), which is disadvantageous because of the limited processibility of the aqueous solutions. Either noncontinuous films were formed (*18*) or an electric field was needed to guide pattern formation, which requires a nonconducting substrate (*19*). Latex spheres have also been used to make disordered macro- and mesoporous silica (*9*). We have developed a simple procedure for preparing hierarchically ordered structures by concurrently or sequentially combining micromolding, latex sphere templating, and cooperative assembly of hydrolyzed inorganic species (metal alkoxides, metal chlorides) and amphiphilic block copolymers. The materials generated from this process exhibit structural ordering at multiple discrete length scales (in this case, 10, 100, and 1000 nm). Patterned macro- and mesoporous materials of various compositions, including silica, niobia, and titania, were synthesized. Such multiple-scale structural organization makes it possible to tune the physical properties of the materials over a wide range of chemical compositions.

The scheme in Fig. 1A illustrates the procedure that was used to fabricate materials with two-scale ordering. Gelation of a self-assembling sol-gel precursor solution was carried out in the confined space of a poly(dimethylsiloxane) (PDMS) mold (*14*). The precursor solution has the same composition as used in the preparation of mesoporous silica films (*3, 21*)—that is, expressed as molar ratios, 0.008 to 0.018 poly(ethyleneoxide)-*b*-poly(propyleneoxide)-*b*-poly(ethyleneoxide) ($EO_nPO_mEO_n$); 1 tetraethoxysilane (TEOS); 20 to 60 ethanol (EtOH); 0.01 to 0.04 HCl; and 5 to 10 H_2O. When Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) was used as the structure-directing block copolymer species, a cubic mesophase resulted, whereas a hexagonal mesophase was obtained when Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) was used (*21*). This sol-gel mesophase chemistry has recently been extended to the preparation of diverse thermally stable mesostructured transition metal oxides, including Nb_2O_5, TiO_2, ZrO_2, WO_3, $AlSiO_{3.5}$, and $SiTiO_4$, by slowing the hydrolysis of inorganic chloride precursor species in alcohol solutions (*4*). These materials were molded by placing a drop of the precursor solution on a freshly cleaned substrate (such as a silicon wafer), after which the mold was placed face down to cover the drop on the surface of the substrate. A pressure of roughly 1×10^5 to 2×10^5 Pa was applied to the PDMS mold. The area of the patterned surface was typically 1 to 5 cm^2, with molded feature sizes in

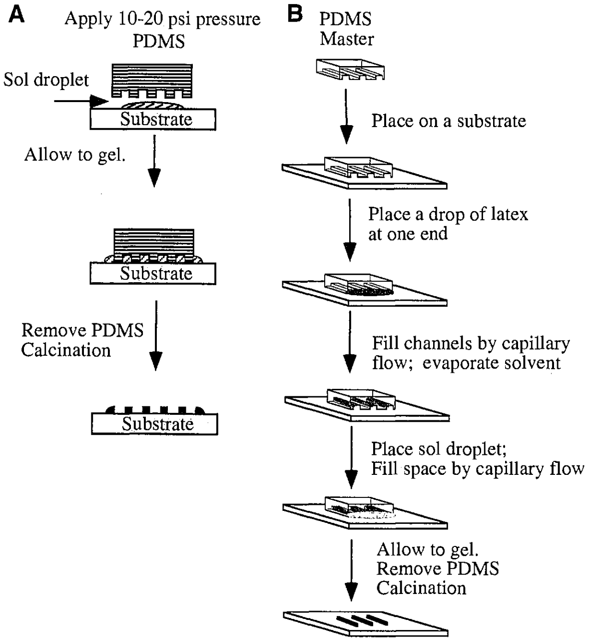

Fig. 1. Schematic diagrams of the molding methods used to fabricate hierarchically ordered structures on a substrate. (**A**) For patterning of mesoporous solids, a droplet of sol-gel–block copolymer precursor solution was compressed between the silicone mold and the substrate by applying a pressure of roughly 1×10^5 to 2×10^5 Pa. The high interfacial free energy of the solution caused the precursor to dewet the substrate where the mold and the substrate were in contact. (**B**) A sequential process for producing hierarchical ordering over three discrete and independent length scales.

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the micrometer size range. The liquid must dewet the surface to permit contact between the PDMS elastomer and the substrate in regions where no mesostructured material is desired. This dewetting is driven by both the applied pressure and the difference between the interfacial tensions of the precursor and the PDMS stamp (*16*). Gelation of the mesophase precursor solutions normally occurred within hours. The mold and the resultant mesostructure were left undisturbed for at least 12 hours to allow increased cross-linking and consolidation of the inorganic oxide network. After removal of the mold, the patterned material was calcined at 400°C in air for 5 hours to remove the amphiphilic block copolymer species and thereby produce patterned mesoscopically ordered porous solids.

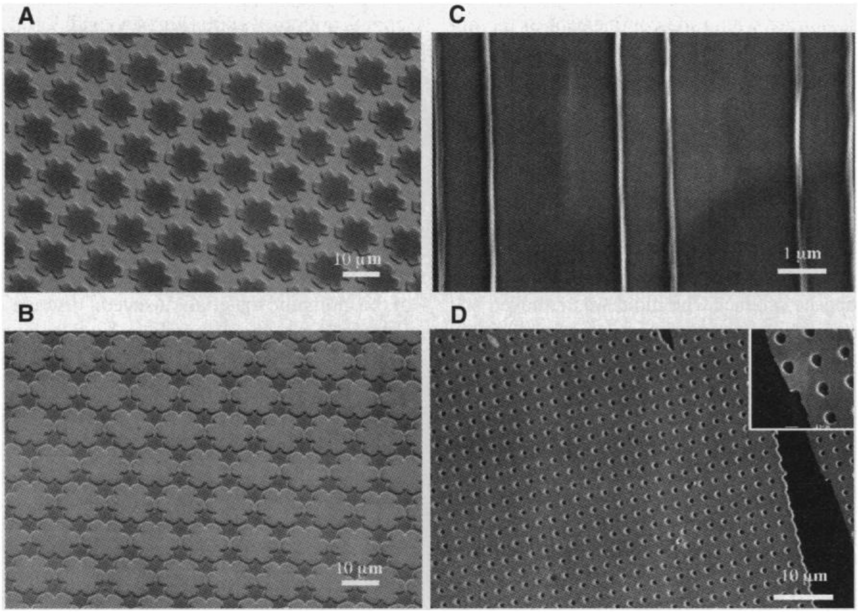

Fig. 2. SEM images of different patterns of mesoporous silica (**A** to **C**) and niobia (**D**) formed using the procedure in Fig. 1A. Materials shown in (A) and (C) are made of hexagonally ordered mesoporous silica prepared using the amphiphilic block copolymer EO$_{20}$PO$_{70}$EO$_{20}$ (Pluronic P123) as the structure-directing agent; the material shown in (B) is made of cubic mesoporous silica prepared using the block copolymer EO$_{106}$PO$_{70}$EO$_{106}$ (Pluronic F127). The material shown in (D) is hexagonally ordered mesoporous niobia prepared using Pluronic P123 block copolymer. Each sample was calcined to remove the block copolymers. Images were taken on a JEOL F6300 SEM operated at 3 keV.

Figure 2 shows several representative scanning electron microscope (SEM) images of the dual scale–ordered materials. The structural ordering observed at the micrometer level is imparted by the micromolding operation using the PDMS stamp, whereas mesoscopic ordering results from the self-assembly of the sol-gel block copolymer solution. Both isolated (Fig. 2A) and continuous (Fig. 2B) features can be produced by this simple overall process. Mesoscopic ordering in these materials was characterized by their low-angle x-ray diffraction (XRD) patterns and transmission electron microscope (TEM) images. The materials shown in Fig. 2, A and C, are hexagonal mesoporous silica (cell parameter $a = \sim 10.5$ nm), and that in Fig. 2B is cubic mesoporous silica. The smallest line feature we have obtained with the micromolding is 100 nm (Fig. 1C). The formation of end caps in self-assembled surfactant cylinders is not favored (*19, 22*) given their high free energy of formation. Thus, within the highly confined geometries of the PDMS micromold, the cylindrical block copolymer ag-

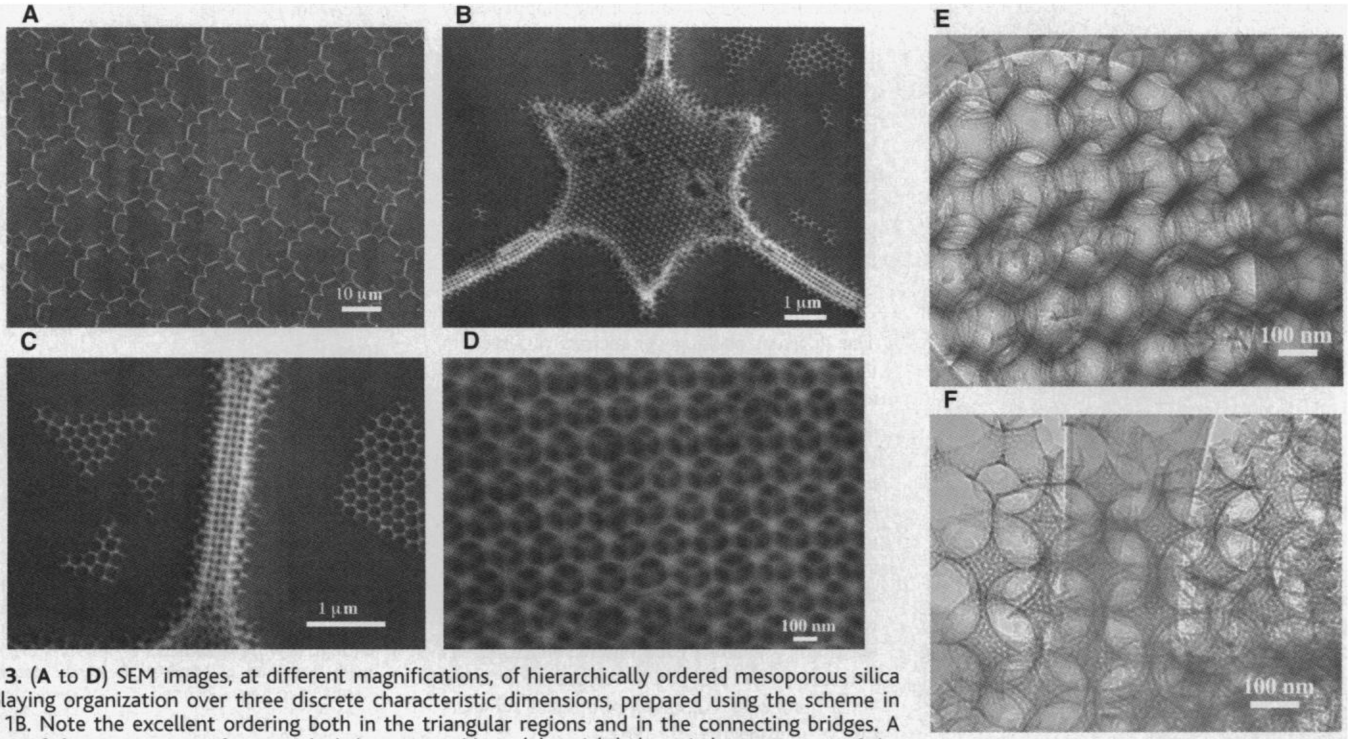

Fig. 3. (**A** to **D**) SEM images, at different magnifications, of hierarchically ordered mesoporous silica displaying organization over three discrete characteristic dimensions, prepared using the scheme in Fig. 1B. Note the excellent ordering both in the triangular regions and in the connecting bridges. A lattice of the macroporous framework skeleton is visible in (B) and (D). (**E** and **F**) TEM images of the same samples, showing that the framework of the macroporous skeleton is made up of ordered cubic mesoporous silica with an ordering length of ~11 nm. This sample was synthesized using Pluronic F127 block copolymer as the structure-directing agent. The sample was calcined at 450°C in air to remove the latex spheres and block copolymers. TEM images were recorded on a JEOL 2010 TEM operated at 200 keV.

gregates are expected to orient preferentially parallel to the micromold walls in order to minimize the number of aggregate end caps (*19*). Such patterned lines of mesoporous silica can be potentially used as wave guides (*16, 23*). In addition, combining these patterning capabilities and the high porosities ($\sim$70%) achievable for such mesoporous silica (*21*) is promising for low-dielectric-constant material applications related to the miniaturization of electronic circuits and devices. Figure 2D shows a similar surface pattern made with mesoporous Nb_2O_5 (*4*), which is a potential ultrasensitive humidity sensor (*24*). The hierarchical ordering process can be further extended to the preparation of other patterned mesoporous metal oxides, such as TiO_2, using sol-gel mesophase self-assembly chemistry (*4*).

Latex-sphere templating was combined sequentially or concurrently with micromolding and cooperative assembly to obtain materials with ordering on three discrete length scales (Fig. 1B). Both ends of the PDMS stamps were cut open to allow the fluid to enter and for air or solvent to escape. The mold was then placed on a freshly cleaned Si substrate. The compliant nature of the PDMS elastomer allowed conformal contact between the mold and the substrate, and a network of channels formed. A drop of a latex colloidal suspension (Bangs Laboratory) containing polystyrene microspheres (diameter 200 nm, 10 weight % in water) was placed at one end, so that the fluid filled the network of the micromold channels by capillary action (*15*). Upon evaporation of the solvent at room temperature, the latex spheres organized into a close-packed array within the confinement of the micromold channel network. A drop of sol-gel block copolymer precursor solution was subsequently placed at the same end of the mold and similarly imbibed into the latex sphere–filled micromold channels by capillary action. The PDMS mold and contents were then left undisturbed for at least 12 hours, during which time cross-linking and polymerization of the inorganic oxide precursor species occurred to yield a robust composite product. The mold was removed and the resulting materials were calcined at 450°C in air for 2 hours to remove the block copolymer species and the polystyrene spheres.

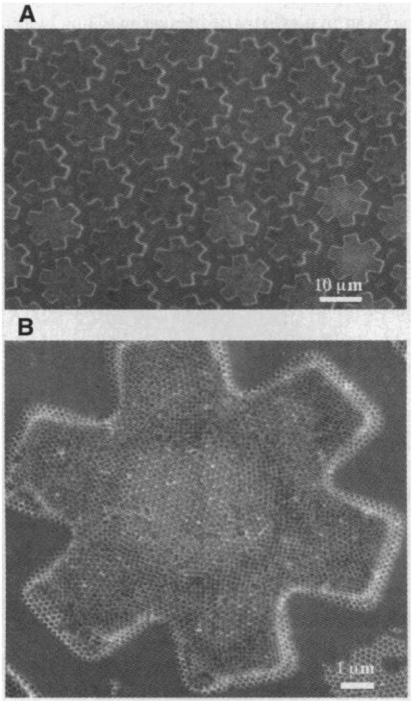

Fig. 4. SEM images, at different magnifications, of hierarchically ordered materials with three distinct order length scales prepared as in Fig. 1B. The overall pattern (**A**) repeats the motif ($\sim$1000 nm) shown in (**B**), which is made up of a macroporous ($\sim$100 nm) framework of cubic mesoporous ($\sim$10nm) silica, as confirmed by TEM and low-angle x-ray diffraction. The sample was calcined at 450°C in air to remove the latex and block copolymer species.

The final materials exhibit hierarchical ordering with discrete characteristic length scales of 10, 100, and 1000 nm in a single body. Structural organization over the three independent length scales is achieved by combining block copolymer–inorganic species assembly (10 nm), latex-sphere templating (100 nm), and micromolding (1000 nm) to produce ordered mesopores (10 nm), macropores (100 nm), and surface patterns (1000 nm). Several typical SEM images for these ordered structures are shown in Fig. 3. Micromolding results in high-quality surface patterns with micrometer-size dimensions (Fig. 3A); the patterned features themselves are made of the inorganic oxide solid organized to form highly ordered macropores that have been templated by close-packed arrays of the latex spheres (Fig. 3, B to D). The high degree of macropore ordering ($\sim$100 nm) can be clearly observed both in the triangular features in Fig. 3B and within the bridges observed in Fig. 3C, although they show different packing sequences. It is believed that the organization of latex spheres in confined geometries involves nucleation (due to capillary attractive forces between the microspheres) and growth (due to evaporation and influx of suspension to compensate for the loss of solvent) (*15*). The different packing symmetries observed in the larger triangular and the smaller bridge areas are presumably the consequence of the different edge effects during the colloidal organization (*25*). In addition, the inorganic oxide (silica, in this case) framework of the macroporous structure is itself made up of mesoscopically ordered cubic arrays of cages with a characteristic dimension of $\sim$11 nm, as established by the Pluronic F127 block copolymer. In typical TEM images recorded for the same hierarchically ordered silica (Fig. 3, E and F) the ordered macroporous structure ($\sim$100 nm) can be seen, along with the silica framework consisting of ordered cubic arrays of mesopores ($\sim$11 nm).

It is similarly possible to use the procedure depicted in Fig. 1A to fabricate materials with three hierarchical ordering length scales into isolated patterned structures. In this case, a drop of sol-gel–block copolymer and latex sphere suspension (volume ratio 1:1) was placed on the substrate before application of the PDMS mold. Figure 4 shows SEM images of such isolated surface pattern features, with ordering lengths of both $\sim$1000 (Fig. 4A) and $\sim$100 nm (Fig. 4B) resulting from micromolding and latex-sphere templating, respectively. TEM images and low-angle XRD patterns (not shown here) of these materials further confirm that the inorganic oxide (silica) frameworks of the macropore structures consist of highly ordered mesopore ($\sim$ 10 nm) arrays. The syntheses of these hierarchically ordered materials demonstrate the ability to control the overall structure of the inorganic materials at several discrete and independent ordering length scales. The assembly of an inorganic sol-gel–block copolymer mesophase around an organized array of latex spheres in a patterned mold leads to singular structures with complex texturing.

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