Supporting Information

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Disassembly and Self-Reassembly in Periodic Nanostructures: a Face-Centered to Simple Cubic Transformation**

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Experimental Section

Colloidal Crystal Templates

To form ordered replica structures, highly ordered colloidal crystals must be used as templates. A variety of methods exists to produce such templates.^[1] Here they were prepared by very slow sedimentation of monodisperse PMMA spheres (synthesized according to literature procedures)^[2] with extreme care taken to minimize perturbation. In detail, the colloidal dispersion was stored in a capped crystallization dish until the PMMA spheres had assembled at the bottom of the dish (ca. 1 month, depending on the thickness of the colloidal crystal). The resulting sediment was opalescent, indicating structural ordering on a bulk scale. Then the cap was removed partially and water was allowed to evaporate at ambient temperature (ca. 1–2 weeks). With water evaporation, PMMA spheres tended to pack more closely due to capillary forces and finally formed self-standing monolithic pieces of the colloidal crystal.

Nanostructure Synthesis

All reagents in the following syntheses were obtained commercially without further purification: titanium isopropoxide (97%, Aldrich), triethyl phosphate (>99.8%, Aldrich), acetylacetonone (*acac*) (>99%, Aldrich), Brij 56 surfactant ($C_{16}EO_n$, $n \sim 10$) (Aldrich), hydrochloric acid (37%, Mallinckrodt), *n*-propanol (Fisher). Metal alkoxides are well known for their relatively high reactivity towards hydrolysis and condensation.^[3] A chelating agent (*acac*) was used to reduce the reactivity of titanium ions through complexation. In an optimized synthesis, 2.93 g (0.010 mol) titanium isopropoxide was first mixed with 0.5 g (0.005 mol) *acac*, followed by the addition of 0.91 g (0.005 mol) triethyl phosphate. This mixture (A) was stirred for 30 min. Another mixture (B) containing 1.37 g (0.002 mol) Brij 56 surfactant, 1.0 g (0.017 mol) *n*-propanol, between 0.20–0.91 g (0.011–0.051 mol) H_2O and 0.2 g (0.002 mol) HCl (37%) was added to mixture A dropwise under vigorous stirring to avoid precipitation. The combined mixture was stirred for another 30 min before it was infiltrated into the PMMA template.

The infiltration was performed in 12 mL glass vials, each containing several millimeter-sized pieces of PMMA templates. The precursor solution was added to the vials until the PMMA templates were about 1/3 immersed in the solution. The precursor mixture filled the voids in the template by capillary forces. After thorough infiltration with precursor (i.e., when the non-immersed parts of the template pieces became completely wet), the template pieces were removed from the vials and extra precursor on the surface was wiped off with tissue paper. Then the template composites were stored in a sealed container at 50 °C overnight and subsequently calcined in flowing air (0.5 L/min) to process the structure and to remove the polymer spheres and other organic components. The temperature was ramped from room temperature to 400 °C over 3 h and held constant for 12 h.

Characterization

The morphologies (sizes and shapes) of the powdery samples obtained after calcination were characterized by electron microscopy. SEM images were taken on a JEOL 6700 field emission microscope (5 kV). Prior to the observation, samples were coated with 5 nm thick Pt to avoid charging effects. Low-magnification TEM images and SAED patterns were recorded on an FEI Tecnai T12 microscope (120 kV). Samples were sonicated for 20 min in ethanol and deposited onto a carbon-film-coated copper grid. High-resolution TEM (HRTEM), Z-contrast imaging and elemental mapping imaging were performed on an FEI Tecnai G2 F30 TEM system (300 kV) equipped with a high angle annular dark field (HAADF) detector and energy-dispersive X-ray spectrometer. Elemental analyses were carried out on a ThermoElemental PQ-ExCell quadrupole ICP-MS. Nitrogen sorption measurements were conducted using a Micromeritics ASAP 2000 porosimeter. XRD patterns were acquired using a Bruker AXS microdiffractometer with a 2.2 kW sealed Cu X-ray source and a Hi-Star 2-D area detector. SAXS measurements were performed on a SAXSess system from Anton Paar Corporation.

References

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Figure S1. The face-centered cubic symmetry is translated from (a) the colloidal crystal template to (b) the initial 3DOM structure. (c) Nanocubes arise from octahedral holes in the fcc template but self-reassemble into simple cubic arrays (d) during the synthesis.

Figure S2. Large overviews of the colloidal crystals. (a) SEM image showing an overview of the mostly simple cubic array of $\text{TiO}_2\text{-P}_2\text{O}_5$ nanocubes prepared via *in-situ* self-reassembly. Figure 1(a) of the main text corresponds to the top left corner of this image. (b) A cross-sectional view.