

271f Fabrication of Ordered Titania Films by the Three-Dimensional Replication of Block Copolymer Templates in Supercritical Carbon Dioxide

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Due to its high refractive index and convenient electronic band gap, titanium dioxide is of interest for numerous optical and photovoltaic applications. In many cases, the preparation of robust, mesoporous TiO₂ films that exhibit large surface area and/or high degrees of order would be enabling for device fabrication. For example, dye sensitized photovoltaic devices require a high surface area TiO₂ to ensure large contact area with the photoactive dye. A mesoporous film would permit sufficient contact as well as minimize exciton recombination. Furthermore, a porous material containing pores oriented perpendicular to a conductive substrate has been proposed to maximize device efficiency. Mesoporous films are traditionally produced using a sol-gel process that involves the cooperative self-assembly of structure directing agents and metal alkoxide precursors in solution. The formation of the structure occurs simultaneously with the condensation of the alkoxide precursor making it difficult to prepare defect-free, thick films as well as control long-range order, pore orientation. This requires long aging periods for pore formation and allows for little flexibility in template selection due to the required mutual solubility of precursor and template.

Recently, we have reported a new approach to form mesoporous silicates involving the infusion and selective condensation of a metal precursor in a hydrophilic domain of a highly-ordered amphiphilic block copolymer diluted with supercritical carbon dioxide. The template can be removed to form mesoporous silica. Using this method, we have successfully replicated spherical and cylindrical morphologies yielding silica films over 1 μm thick while maintaining the structure details of the sacrificial block copolymer template. This approach has been used to fabricate silica films with oriented cylindrical channels. Here we extend the SCF approach to titania. Templates were prepared by spin-coating the proper block copolymer with acid catalyst, a blend of poly(ethylene oxide)₁₃₂-poly(propylene oxide)₁₃₂-poly(ethylene oxide)₁₃₂ and poly(4-vinyl phenol) ($M_w \sim 20,000$) for spherical pores or poly(*a*-methyl styrene-*b*-vinyl phenol) ($M_w \sim 25,000$) for perpendicular cylindrical channels, onto a silicon wafer. The block copolymer microphase separates upon drying and the acid catalyst partitions into the hydrophilic domain. The templates were then exposed to a solution of supercritical carbon dioxide and titanium diisopropoxide bis(acetylacetonate) at 130 bar for 60°C resulting in precursor condensation into the hydrophilic domain. The template can be removed by slow calcination. This heat treatment also crystallizes titania. X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM), grazing incidence small angle x-ray scattering (GISAXS), and transmission electron microscopy (TEM) was used to characterize the films. Well-ordered spheres or perpendicular cylinders were apparent in TEM and AFM micrographs, with *d*-spacings on the order 10-20 nm. XRD showed consistent data for *d*-spacing as well as the formation of highly crystalline structures upon calcination. GISAXS shows that the cylindrical domains are oriented perpendicular to the substrate and have a *d*-spacing of ~ 20 nm, also consistent with AFM. Spectroscopy shows that the polymer is completely removed after calcination.