

Mesoporous Titania for Hybrid Solar Cells through Fusion of Ultrasmall Nanocrystals

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The nanoscale morphology of porous titanium dioxide has significant impact on the charge carrier dynamics in hybrid solar cells. We have recently developed highly flexible new preparation strategies for the formation of various nano-morphologies, based on the self-assembly and fusion of pre-formed ultrasmall titania nanocrystals.

In a "brick and mortar" approach, the nanocrystalline titania "bricks" are fused by a surfactant-templated sol-gel titania ("mortar"), which acts as a structure-directing matrix and as a reactive precursor for the further growth of the crystalline phase. This synergy leads to a significantly lowered temperature needed for crystallization and the preservation of the mesoporous structure. Coatings with a broad variety of periodic mesostructures can be tuned by varying the surfactant and the fraction of the "bricks", and thicknesses ranging from few nanometers to several micrometers are accessible.

Aiming to prepare titania nanoparticles of small size, enhanced crystallinity and good dispersibility without the need of additional stabilizing ligands, we explored *tert*-butanol as a novel reaction medium in solvothermal synthesis. Ultrasmall anatase nanoparticles of high crystallinity were obtained by a special microwave-based heating procedure that allows the crystal formation within several minutes. This synthetic protocol widens the scope of non-aqueous sol-gel methods to ultrasmall TiO₂ nanoparticles of around 3 nm. Additionally, this new approach permits the direct application of the as-synthesized particles in combination with a commercial polymer template for the preparation of mesoporous titanium dioxide films without the need for particle separation or chemical processing. The resulting thin films were investigated using X-ray scattering and HRTEM measurements to monitor and visualize the seeding effect, crystal growth and mesostructure development during calcination, respectively.

The above strategies also allow us to build various hierarchical structures such as titania inverse opals penetrated by titania mesopores, because we can significantly reduce shrinkage effects. The strategy for the generation of these hierarchical structures involves preparation of inverse opal titania layers and subsequent filling of the interstitial macroporous voids with surfactant-containing titania precursors to obtain a mesostructured titania phase (Figure 1). The formation of mesostructure in the confined space of the macroporous scaffold upon thermal treatment was investigated with *in-situ* GISAXS. The macroporous scaffold strongly influences the mesostructure assembly and leads to much larger structural parameters of the formed mesostructure, this effect becoming more pronounced with decreasing pore size of the macroporous host. Furthermore, the inverse opal scaffold acts as a stabilizing matrix and enhances the crystallization of the mesophase, which is attributed to the crystalline walls of the macroporous host.

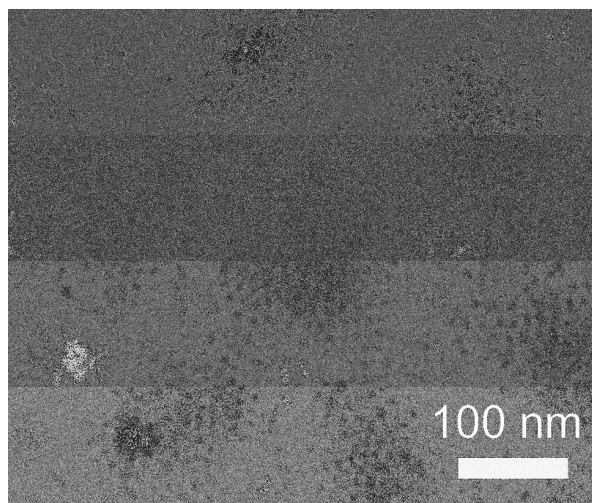


Figure 1. Field-emission scanning electron micrograph of hierarchical titania framework fabricated using 200 nm PMMA beads (top-view) The film was prepared on a silicon substrate and calcined at 450 °C.

The above mesostructured and crystalline films were employed as active layers in thin dye-sensitized solar cells exhibiting high conversion efficiency due to short diffusion paths. We will also show that the ultrathin crystalline walls of the mesoporous “brick & mortar” titania feature extremely fast lithium insertion kinetics. Finally, we discuss the integration of additional sensitizing approaches such as extremely thin absorber layers (ETA) and alternative solid hole conductors.

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