東京大学大学院工学系研究科総合研究機構

結晶界面工学研究室

Crystal Interface Laboratory, The University of Tokyo

Crystal Interface Lab. Seminar Series Institute of Engineering Innovation The University of Tokyo

Nanotubular Structures of TiO₂: Fabrication, Phase Transition, and Their Application

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Nanotubular structures of TiO₂, in particular, with anatase polymorphs and their ordered arrays are promising candidates as high-efficient host materials, charge carrier collectors, and information storage media in dye-sensitized/hybrid solar cells, secondary lithium-ion batteries, and non-volatile memory devices. Their structures, which developed through phase transitions in nanoscale, often control physical properties, for example, electron transport, ion intercalation, and surface adsorption. Phase transitions in the nanostructure of strong-bonded metal oxides are however far from understood by now and quite different from their bulk counterparts. We've synthesized nanostructures of TiO_2 by a template method (using anodic aluminum oxides as templates) with highly conformal coatings of atomic layer deposition (ALD). We present results of the structural, electrical and optical properties of the mesoporous, nanotubular structures of anatase TiO₂ as a function of their physical dimensions, i.e., diameter, length, and wall thickness. We found that under certain thicknesses of their wall (~ 3 nm in thickness) the anatase grain growth was strongly suppressed and were able to control the microstructure of TiO₂ nanotubes. It is noted that the nanotubular structures in the length of few tens of □m (typically 20 □m), outer diameter of around 60 nm, and wall thickness of a few nanometers are expected to accommodate huge mechanical strain for holding the structures with nanocrystallites. We have investigated the physical properties of mesoporous, ordered TiO₂ nanotubes by combining high-resolution transmission electron microscopy (HR-TEM) with temperature-dependant photoluminescence (PL) spectroscopy. Electrical transport properties investigated in an Ohmic-Ohmic device configuration also support our assumptions, demonstrating that the nanotube arrays of the single crystal-like elongated anatase exhibited more than three orders of magnitude enhancement of the electronic conductivity than mesoporous anatase TiO₂ particulate films. Our results suggest that the origin of electron transports in traditional mesoporous TiO₂ materials should be revisited, thus supporting a rational shift of photo-anode materials regime to one-dimensional nanostructures. In addition, we introduce some examples of hierarchical TiO₂ nanostructures such as multiwall, branched, and modulated titania nanotubes which would be extremely beneficial in enhancing their performance in practical applications.

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