Electronic Supporting Information

Highly self-ordered nanochannel TiO₂ structure by anodization in hot glycerol electrolyte

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Experimental

In order to form the highly ordered nanochannelar TiO_2 (NCT) layers, Ti foils (0.125 mm, 99.6 % purity, Advent) were degreased by sonicating in acetone, isopropanol, and methanol, then rinsed with deionized (DI) water and dried in a nitrogen stream.

The electrolyte for anodization was prepared with 10 wt% K₂HPO₄ (Sigma-Aldrich) in anhydrous glycerol (99.8 % purity, < 1 % H₂O, Fluka). Prior to anodization, the electrolyte was held at a 200 °C for 4 h to reduce the water content in the electrolyte. Anodization was carried out in a two-electrode system using a high voltage potential Jaissle IMP 88 PC applying from 1 V to 80 V at 180 °C.

In order to use the channel structure as a photoanode in a DSSC, the channels were formed on Ti by anodization with 15 V for 9 h and then 50 V for 20 min. The additional voltage step to 50 V is needed to remove internal Ti metal species - structure and morphologies were not changed by this short time voltage step.

After anodization, the samples were rinsed with DI water and then dried in a nitrogen stream. For a subsequent etching step, the anodized samples were sonicated in $30 \text{ wt}\% \text{ H}_2\text{O}_2$ in an ultrasonic bath for different times. After etching, the samples were rinsed with DI water and dried in a nitrogen stream.

Some samples were annealed at different temperatures for 3 h with heating and cooling rate of 30 °C/min using a Jetfirst Rapid Thermoannealer (RTA, Jipelec, France).

For morphological characterization of the samples, a field-emission scanning electron microscope Hitachi FE-SEM S4800 was used.

For TEM analysis cross-section samples were prepared by mechanical polishing and dimpling followed by gentle Ar^+ ion beam milling. SAD patterns and TEM images were taken with a Philips CM 30 T/STEM microscope.

X-ray diffraction analysis (XRD) was performed with a X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromized Cu K α radiation (Wavelength 1.54056 Å). In order to compare the crystallinity of the three different morphologies, the incident X-ray beam impinges on the sample at a low angle of 1° and enough large area to avoid detecting the metal signal from edge or substrate. This assures X-ray penetration depth of just a few micrometers (within 10 µm).

For dye-sensitization, Ru-based N719 dye (cis-bis (isothiocyanato) bis (2,2-bipyridyl 4,4-dicarboxylato) ruthenium (II) bis-tetrabutylammonium) was used. Samples were dye-sensitized by immersing for 3 days at 40 °C in a 300 μ M solution of the N719 dye (Solaronix SA, Switzerland) in a mixture of acetonitrile and tert-butyl alcohol (volume ratio: 1:1). After dye-sensitization, the samples were rinsed with acetonitrile to remove non-chemisorbed dye.

To evaluate the photovoltaic performance, the sensitized TMS were sandwiched together with a Pt coated fluorine-doped glass counter electrode (TCO22-15, Solaronix) using a polymer adhesive spacer (Surlyn, Dupont). Electrolyte (Iodolyte R50, Solaronix) was introduced into the space between the sandwiched cells. The current-voltage characteristics of the cells were measured under simulated AM 1.5 illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight) applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2420 digital source meter.

Dye desorption measurements of dye sensitized TiO_2 layers were carried out by immersing the samples in 5 ml of 10mM KOH for 1 h followed by the dye concentration measurements in the solution spectrophotometrically.



Figure S1. Nanochannelar titania formed by anodization at 15 V for 9 h in 10 wt % K_2 HPO₄ in glycerol at 180 °C. (a) high magnified cross-sectional SEM image, (b) TEM image.



Figure S2. Low incident angle (1°) XRD spectra of (a) highly ordered TiO_2 channel structure formed by anodization of Ti at 15 V for 9 h in 10 wt % K₂HPO₄ in glycerol at 180 °C, (b) after etching in 30 wt % H₂O₂ with ultrasonication, and (c) after annealing at 450 °C for 3 h. The peaks are annotated as anatase (A), rutile (R) and Ti metal (T).



Figure S3. SEM images of as formed TiO_2 (a) nanotubes and (b) mesoporous structure. The nanotube layer was formed by anodization with 120 V in 0.2 M HF contained ethylene glycol. The mesoporous structure was formed by anodization with 1 V in 10 wt % K₂HPO₄ in glycerol at 180 °C.



Figure S4. J-V characterization of solar cells using highly ordered TiO_2 channel structure with (a) different etching duration in 30 wt % H₂O₂ in an ultrasonic bath and then annealed at 450 °C for 3 h, (b) different annealing temperature for 3 h, samples are etched by 30 wt % H₂O₂ in ultrasonic bath for 2 h and then annealed, (c) different thickness structure following etching for 2 h in 30 wt % H₂O₂ in ultrasonic bath and then annealed at 450 °C for 3 h.