Electronic supplementary information

Spectroscopic Properties of Electrochemically Populated Electronic States in Nanostructured TiO$_2$ Films: Anatase versus Rutile

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Experimental details

**Chemicals and materials.** TiOSO$_4$ (Aldrich, 99.99%, 15 wt% solution in sulfuric acid), TiF$_4$ (Aldrich), acetylacetone (99+%, Aldrich), Triton X (Aldrich), HClO$_4$ (Sigma-Aldrich, ACS reagent, 70%), DClO$_4$ (Aldrich, 68 wt. % in D$_2$O, 99 atom % D), D$_2$O (Aldrich, 99 atom % D), titanium(III) chloride solution (Aldrich, ~10 wt. % in 20-30 wt. % HCl), NaCl (Sigma-Aldrich, ≥99.8%), ammonium fluoride solution (Fluka, purum, ~40% in H$_2$O) and ethylene glycol (Sigma-Aldrich, anhydrous, 99.8%) were used as received. All H$_2$O solutions were prepared using water with a resistivity of 18 MΩ·cm (Millipore, Milli-Q).

**Thin film preparation.** Rutile (r-NW) and anatase (a-NW) TiO$_2$ nanowire films were grown on F-doped SnO$_2$ (FTO) transparent glass (Pilkington, TEC 8) or,
alternatively, Ti foil (Goodfellow, 99.6+, 25 µm) by chemical bath deposition at 60 °C.\textsuperscript{1,2,3} The precursor solutions ([Ti] = 3 mM, pH 1 for r-NW and [Ti] = 5 mM, pH 1.5 for a-NW) were prepared by adding TiOSO\textsubscript{4} or TiF\textsubscript{4}, respectively, to an aqueous HCl solution. Thin film deposition was performed for 12 h, whereas precursor solutions were renewed every 3 h. The as-deposited NW films were subjected to a post-synthesis treatment consisting of thermal annealing at 200 °C (1 h, a-NW)\textsuperscript{4} or soaking in 0.1 M NaOH (18 h, r-NW).\textsuperscript{5}

Rutile nanowire films with a larger diameter (r-NW(5nm)) were deposited on a Ti foil at 80 °C (4 h) in a teflon-lined autoclave\textsuperscript{6}. The precursor solution was prepared by adding TiCl\textsubscript{3} (0.1 M) to a 3 M NaCl aqueous solution.

Anatase nanotube (a-NT) arrays were obtained by anodization (4 h) of a Ti foil at a voltage of 40 V in ethylene glycol containing 10% H\textsubscript{2}O and 0.5% NH\textsubscript{4}F. A Pt grid was used as the counter electrode. Finally, the films were annealed at 500 °C (1h) to induce crystallization.

Nanoparticulate anatase (a-NP) films were prepared from a commercial TiO\textsubscript{2} paste (Ti-Nanoxide T, Solaronix). The paste was spread with a glass rod onto the FTO or Ti substrates using Scotch tape as spacer. Nanoparticulate rutile (r-NP) electrodes were prepared in the same way by spreading an aqueous slurry (1 g TiO\textsubscript{2}, 3.2 mL H\textsubscript{2}O, 60 µL acetylacetone, 60 µL Triton X) of commercial rutile TiO\textsubscript{2} nanoparticles (Nano-Rutile, Sachtleben Chemie GmbH)\textsuperscript{7} onto the substrates. Afterwards, the dry films were sintered for 1 h at 450 °C in air.

After thin film preparation a copper wire was attached to the conducting substrate with silver epoxy. The contact area and the uncovered parts of the substrate were finally sealed by epoxy resin.
UV/vis/NIR spectroelectrochemical measurements. For UV/vis/NIR measurements a TiO$_2$ film deposited on FTO was used as the electrode. The cuvette was placed in the light beam of a fiber optic system (Ocean Optics, source: DT-MINI-2-GS, spectrometer: Maya2000). The spectra were obtained by averaging 400 scans at an integration time of 25 ms and a boxcar smoothing width of 3. Prior to the spectroscopic measurements polarization at a given potential was performed for 240 s to reach a stable absorbance.

MIR spectroelectrochemical measurements. For MIR measurements a TiO$_2$ film deposited on a Ti foil was used as the electrode. Cathodic polarization at different potentials was performed in the electrolyte bulk prior to moving the electrode to the surface of the ATR prism. Back-polarization to the initial (positive) potential was performed with the electrode being pressed against the prism. The ATR prism was placed in a reflection unit (PIKE Technologies, Veemax II) attached to a Bruker IFS 66/S FTIR spectrometer equipped with a MCT detector. Measurements were performed at an incident angle of 60° using unpolarized light. The spectra were obtained by averaging 500 scans at a resolution of 4 cm$^{-1}$. Prior to the spectroscopic measurements polarization at a given potential was performed for 240 s to reach a stable absorbance.

Electrochemical measurements. Electrochemical measurements were performed with a computer-controlled Autolab PGSTAT101 potentiostat. The current and charge densities are given on the basis of the geometric area.

Structural characterization. Scanning electron micrographs (SEM) were obtained with a SEM-FEG Hitachi S480 microscope. Raman spectra were recorded at 785 nm using a Bruker Senterra Raman microscope.
**Fig. S1.** Raman spectra of rutile (a) and anatase (b) films used in this study.
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