

Supporting Information

Evaluation of Surface State Mediated Charge Recombination in Anatase and Rutile TiO₂

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Experimental

Preparation of dense TiO₂ films

Dense thin films of TiO₂ anatase were grown by atmospheric pressure chemical vapor deposition (APCVD) as reported previously.¹ This preparation involves the reaction of TiCl₄ (titanium source) with ethyl acetate (oxygen source) at 500 °C in a cold-walled reactor. The precursors were stored in steel bubblers and heated to increase their vapor pressures. N₂, which is inert under the imposed conditions, was used as a carrier gas to transfer the vapors of each precursor to the reactor, where the films were grown on quartz substrates heated on a graphite block. The synthetic conditions are listed in Table S1.

Table S1. Reaction conditions used in the APCVD synthesis of nanocrystalline anatase thin-films. The deposition was carried out for 60 s at a reactor temperature of 500 °C under an additional N₂ plain line gas flow of 6 L·min⁻¹. EtAc = ethyl acetate, T = bubbler temperature, F = N₂ carrier gas flow, Vp = vapor pressure and a = mass flow.

Precursor	T (°C)	F (L·min ⁻¹)	Vp (mm·Hg)	a (10 ⁻³ mol·min ⁻¹)	molar ratio (vs. TiCl ₄)
TiCl ₄	70	1.2	91	6.7	1.0
EtAc	40	0.25	185	3.3	0.5

Dense rutile TiO₂ thin films were subsequently obtained by heating the APCVD anatase films from room temperature to 1050 °C, at an oven ramp rate of 20 °C /min, and holding them at this temperature for 2 h. The films were then cooled to room temperature at the same rate.

Preparation of mesoporous TiO₂ films

Mesoporous films in this present study were prepared under the same conditions as reported previously,² with a few exceptions. In our procedure, the paste containing TiO₂ nanoparticles was spin-coated onto quartz substrates rather than doctor bladed onto FTO substrates. These adjustments were made in order to obtain thicknesses that are more comparable to the dense films and to eliminate potential influences from the FTO layer.

The mesoporous anatase TiO₂ films were obtained from a paste of 15 nm sized anatase TiO₂ particles, which was prepared by sol-gel processing followed by hydrothermal treatment as reported in the literature.³ To this end, 40 mL of titanium isopropoxide was mixed with 9.1 g of glacial acetic acid under a nitrogen atmosphere and stirred for 10 min. The mixture was then poured into a conical flask containing 240 mL of 0.1 M nitric acid solution at room temperature and subsequently stirred at 80 °C for 8 h. The TiO₂ colloid was first filtered using a 0.45 mm syringe filter and then autoclaved at 220 °C for 12 h. The colloid was re-dispersed with a 2 min cycle burst from a LDU Soniprobe horn. The solution was then concentrated to 12.5% (in TiO₂ weight) on a rotary evaporator at 45–50 °C and Carbowax 20,000 (50% of TiO₂ by weight) was added. The obtained paste was diluted 3:1 by volume with deionized water and spin coated (Model WS-400A-6NPP/LITE, 1 min, 21165 rpm·s⁻¹, 3000 min⁻¹) onto quartz substrates. The deposited film was dried in air, heated to 100 °C with a ramp rate of 2.2 °C/min, annealed for 20 min, heated to 450 °C at a ramp rate of 6.7 °C, annealed for 30 min, and allowed to cool down to room temperature inside the furnace.

For mesoporous rutile TiO₂, an organic paste was prepared as follows. 25 µL acetic acid was added to 0.5 g rutile TiO₂ nanopowder (< 100 nm, Sigma Aldrich) in a mortar. 5 x 125 µL deionized water, 15 x 125 µL, and 6 x 625 µL ethanol abs. were then added subsequently, while grinding the suspension after each addition. The obtained paste was suspended in 10 mL ethanol abs. and re-dispersed with a 2 min cycle burst from a LDU Soniprobe horn.

2.5 g terpineol was added and the suspension was sonicated for another 2 min. A third 2 min sonication step was conducted after the addition of 4.5 g ethylcellulose (10 % in ethanol abs.). The final paste was obtained by allowing ethanol to evaporate overnight under slow stirring. The paste was then diluted 3:1 by volume with deionized water and spin coated onto quartz substrates as described above for the mesoporous anatase film. The deposited film was dried in air, heated to 100 °C with a ramp rate of 2.2 °C/min, annealed for 20 min, heated to 500 °C at a ramp rate of 6.7 °C, annealed for 30 min, and allowed to cool down to room temperature inside the furnace.

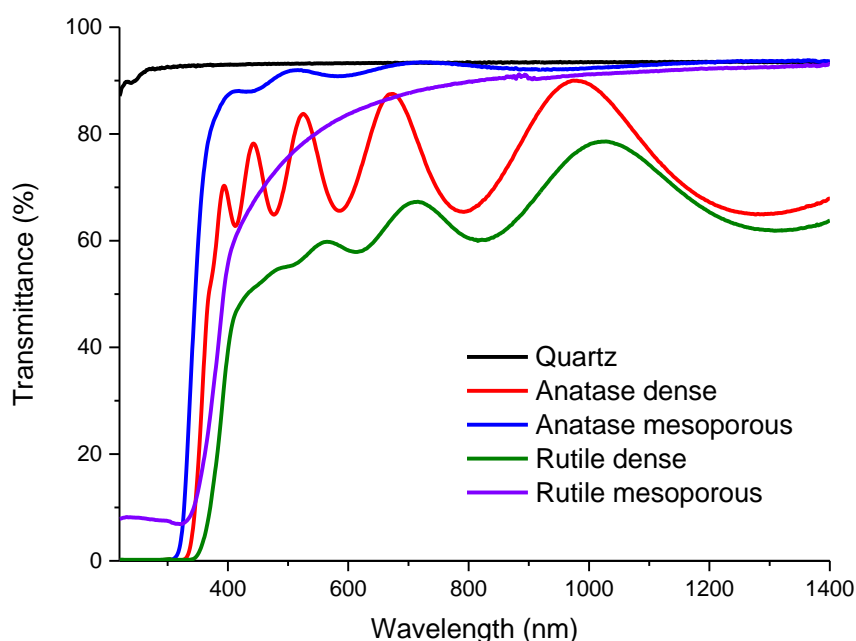


Figure S1. UV-NIR transmittance spectra of the dense and mesoporous TiO₂ anatase and rutile films used in this study.

Transmittance spectra in Figure S1 show that the band gap onset is slightly shifted towards higher energy for mesoporous films relative to dense films. Oscillations observed in the visible and NIR range are due to internal reflections within the film and indicate high film homogeneity.⁴

Ultrafast Transient Absorption Spectroscopy

Transient absorption measurements were conducted on fs-ns timescales using a regeneratively amplified Ti:sapphire laser system (Solstice, Spectra-Physics), which produces 800 nm laser pulses of 92 fs width at 1 kHz repetition rate after the amplifier, in conjunction with Helios spectrometers (Ultrafast Systems). A fraction of the resulting 800 nm beam was directed through a sequence consisting of an optical parametric amplifier (TOPAS Prime, Spectra-Physics) and a frequency mixer (NirUVis, Light Conversion) in order to tune the excitation wavelength (pump). The intensity of this pump beam was subsequently modulated using neutral density filters and pulse energies were measured using an energy meter (VEGA P/N 7Z01560, OPHIR Photonics) equipped with a 500 μm diameter aperture. The pump beam was slightly larger than 500 μm in diameter at the position of the sample. Another fraction of the 800 nm amplifier output was focused onto a Ti:sapphire crystal to generate a NIR wavelength continuum which was used to probe the transient species generated by the pump beam. To probe transients at different times after the excitation, the probe beam was sent through a motorized delay stage before the wavelength continuum generation. This delay stage modifies the path length of the beam and thus delays it up to 6 ns in time with respect to the pump pulse. After the wavelength continuum generation, the probe beam was split into two in order to achieve better signal-to-noise-ratios with only one of the two resulting beams passing through the sample. Both beams are then focused into separate fibre-optic-coupled multichannel spectrometers (InGaAs sensors). During the experiment, every other pump pulse was blocked by a synchronized chopper (500 Hz). In this way, absorption of the excited and unexcited sample is probed alternately and absorption difference spectra are calculated. These absorption difference spectra were averaged over 2 s for each time delay, yielding one time-resolved absorption difference spectrum. The latter were collected for several subsequent runs with all runs being averaged to obtain the final spectra. These spectra were then adjusted so that time zero occurs at the half-amplitude of the initial rise. The decay kinetics shown were averaged over a spectral range of ca. 10 nm.

Results

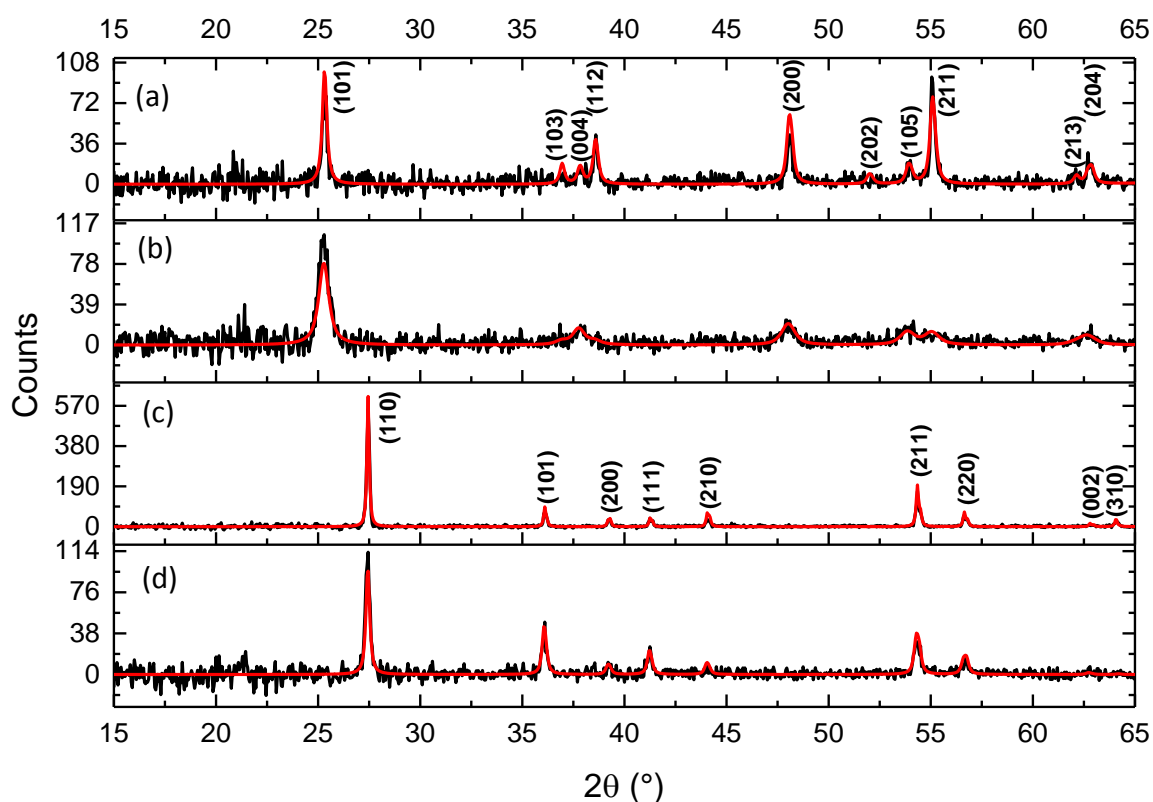


Figure S2. X-ray diffraction patterns of (a) dense TiO₂ anatase, (b) mesoporous TiO₂ anatase, (c) dense TiO₂ rutile, (d) mesoporous TiO₂ rutile.

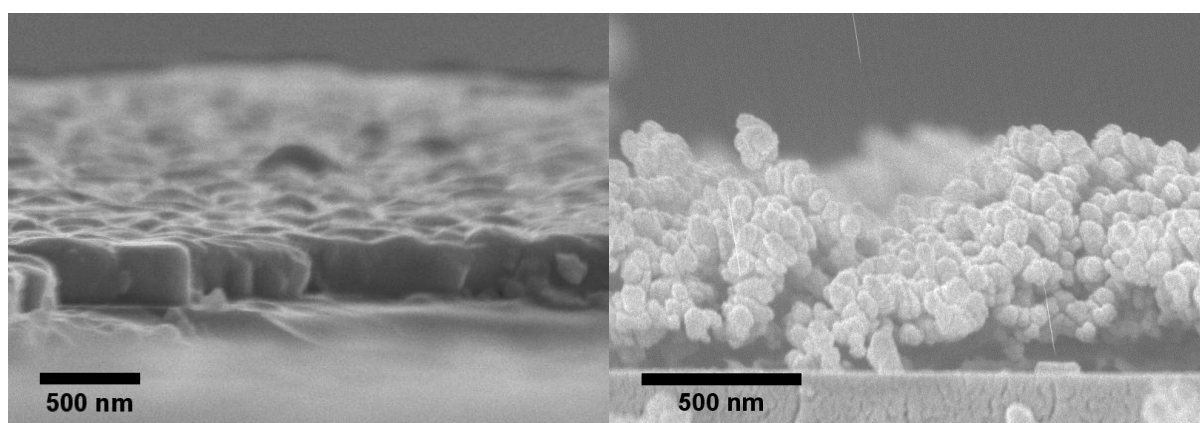


Figure S3. Scanning electron micrographs of dense (left) and mesoporous (right) TiO₂ rutile thin films on quartz glass substrates.

Dense film thicknesses were measured from cross section SEM images with 430 and 250 nm for anatase and rutile, respectively. For mesoporous films, profilometry allows for a more a

more accurate determination of the film thickness, yielding 490 nm for anatase and ca. 600 nm for rutile.

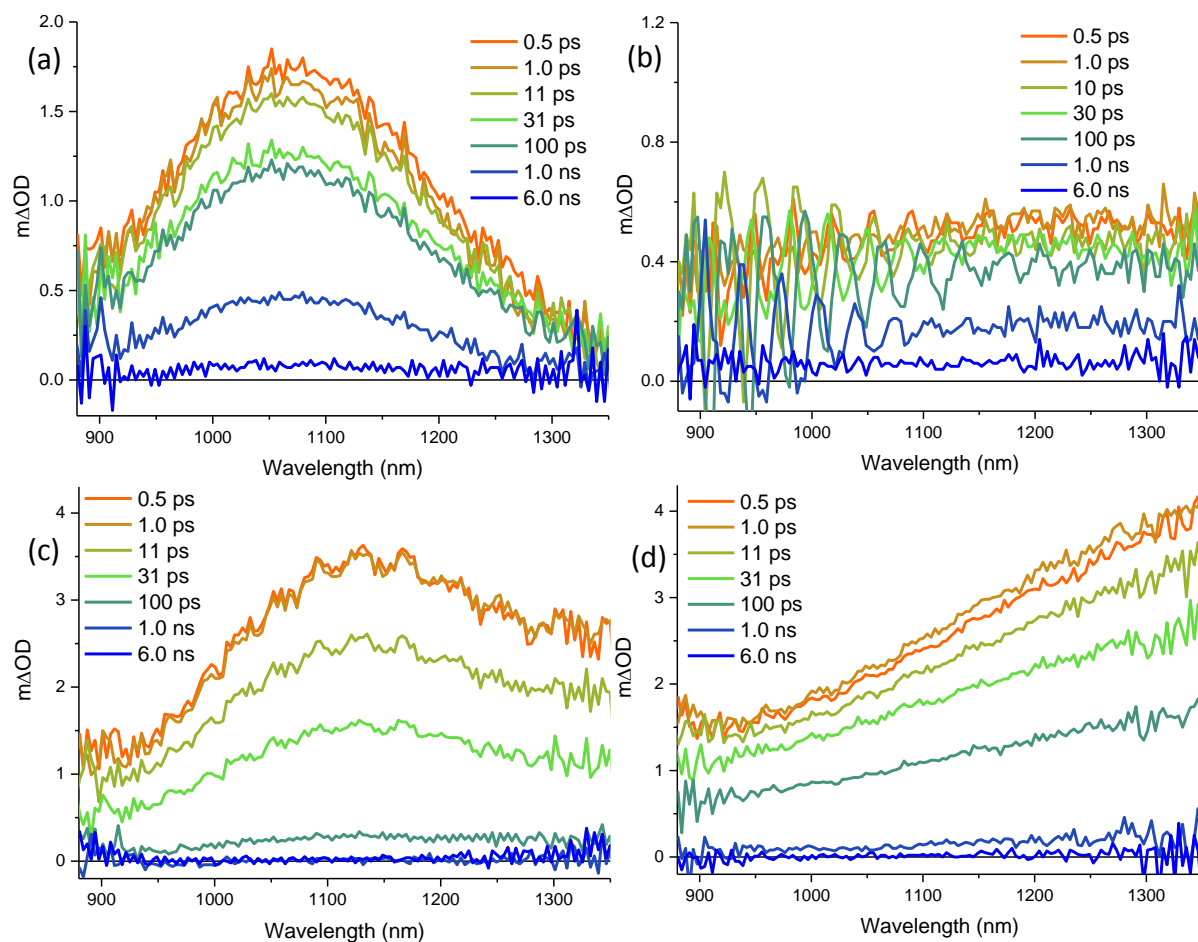


Figure S4. Transient absorption decay spectra in the NIR following 355 nm excitation under argon as a function of time for (a) dense TiO₂ anatase, (b) mesoporous TiO₂ anatase, (c) dense TiO₂ rutile, (d) mesoporous TiO₂ rutile.

The TAS spectra for the mesoporous TiO₂ films are rather featureless throughout the probed wavelength range, whereas the spectra of the dense films exhibit a broad peak centered around 1050 – 1150 nm. We ascribe this broad peak in the TAS spectra of the dense films to optical interference effects, which is consistent with the pronounced oscillations in their transmittance signals (Figure S1).

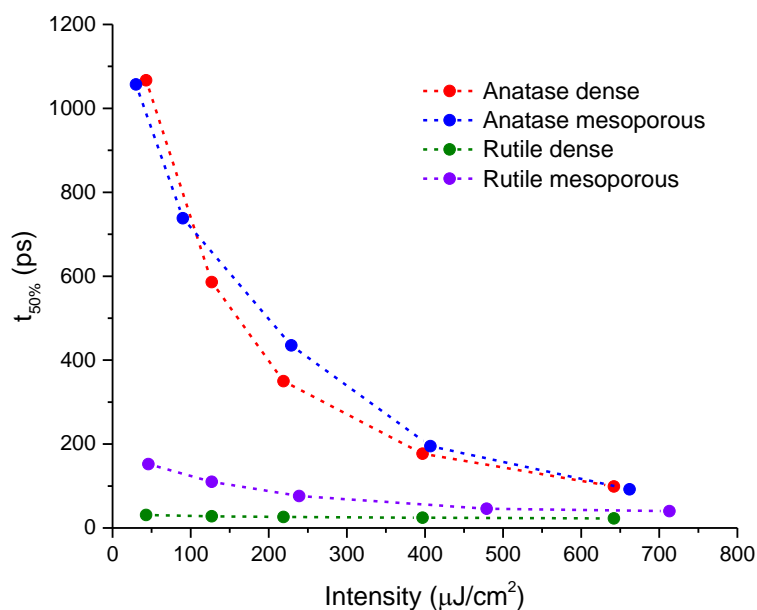


Figure S5. Time of the half-amplitude TAS signal as a function of excitation intensity (disregarding the fast initial decay component observed in the anatase films). The intensity dependence in anatase matches a second order reaction, whereas the rutile films exhibit significantly less intensity dependent, pseudo-first order behavior.

References

- (1) Kafizas, A.; Noor, N.; Carmalt, C. J.; Parkin, I. P. TiO₂-Based Transparent Conducting Oxides; the Search for Optimum Electrical Conductivity Using a Combinatorial Approach. *J. Mater. Chem. C* **2013**, *1*, 6335–6346.
- (2) Wang, X.; Kafizas, A.; Li, X.; Moniz, S. J. A.; Reardon, P. J. T.; Tang, J.; Parkin, I. P.; Durrant, J. R. Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity. *J. Phys. Chem. C* **2015**, *119*, 10439–10447.
- (3) Li, X.; Nazeeruddin, M. K.; Thelakkat, M.; Barnes, P. R. F.; Vilar, R.; Durrant, J. R. Spectroelectrochemical Studies of Hole Percolation on Functionalised Nanocrystalline TiO₂ Films: A Comparison of Two Different Ruthenium Complexes. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1575–1584.
- (4) Swanepoel, R. Determination of the Thickness and Optical Constants of Amorphous Silicon. *J. Phys. E.* **1983**, *16*, 1214–1222.