Charge Carrier Separation in Nanostructured TiO_2 Photoelectrodes for Water Splitting

Alexander J. Cowan,[§]* *Wenhua Leng,*[†] *Piers R. F. Barnes, David R. Klug and James R. Durrant*

Supporting Information:

TiO_2 film preparation: Prior to use the glass was sonicated in acetone and water for 30 minutes each, dried in air and then placed in a furnace at 450 °C in air for 30 minutes. The film thickness was measured using a profilometer (Alpha-Step 200, Tencor Instruments) and found to be approximately 4 μm for each tape spacer layer used. Thicker films were obtained by increasing the number of tape layers; thinner films were made using a k-bar (RK print coat instruments). The TiO_2 films on FTO were cut to approximately 1.0 cm × 2.5 cm pieces with the nc-TiO_2 film covering a surface area of 1.0 cm × 1.5 cm. An electrical contact was made with the FTO substrate using silver conducting paste connected to a copper wire which was then enclosed in a glass tube. The edges of the electrode were covered by one-component silicone adhesive (Dow Corning® 732) leaving an uncoated working geometric surface area of TiO_2 of 1.0 cm × 1.0 cm. The electrodes were cleaned under UV light (75 W Xe) and thoroughly washed with DI water prior to each measurement. No detectable difference in both photocurrent and optical density was observed between electrodes with and without the silicone adhesive.

Optical measurements: The transmittance measurements for a photoelectrochemical cell with the electrolyte were made with a Shimadzu UV-Vis dual beam Spectrophotometer (UV-

1601). Diffuse transmittance and reflectance measurements, both for samples on FTO substrate and for the substrate without coating, were also made with a spectrophotometer (Lambda 950, PerkinElmer) equipped with an integrating sphere. These measurements were carried out for wet films penetrating with the electrolyte. No significant difference in transmittance for the TiO_2 samples between these measurements and those measured in the curette with the electrolyte was found. The fraction of light transmitted by the film with TiO_2 ($T_{TiO2/coverslip}$) and without ($T_{coverslip}$) TiO_2 and of film thickness d was used to estimate the absorption coefficient of the porous TiO_2 film according to Eq. S1.

(Eq. S1) $$\alpha(\lambda) = -\frac{1}{d}\ln\frac{T_{TiO2/coverslip}(\lambda)}{T_{coverslip}(\lambda)}$$

This assumes an exponential variation of light intensity with position. The light harvesting efficiency is calculated in the manner described previously (eq's S13 and S14 in ref [1]), which requires the absolute reflection of the TiO_2 sample to be measured, Fig S1b. Absolute reflection refers to both direct specular and diffuse reflected light.

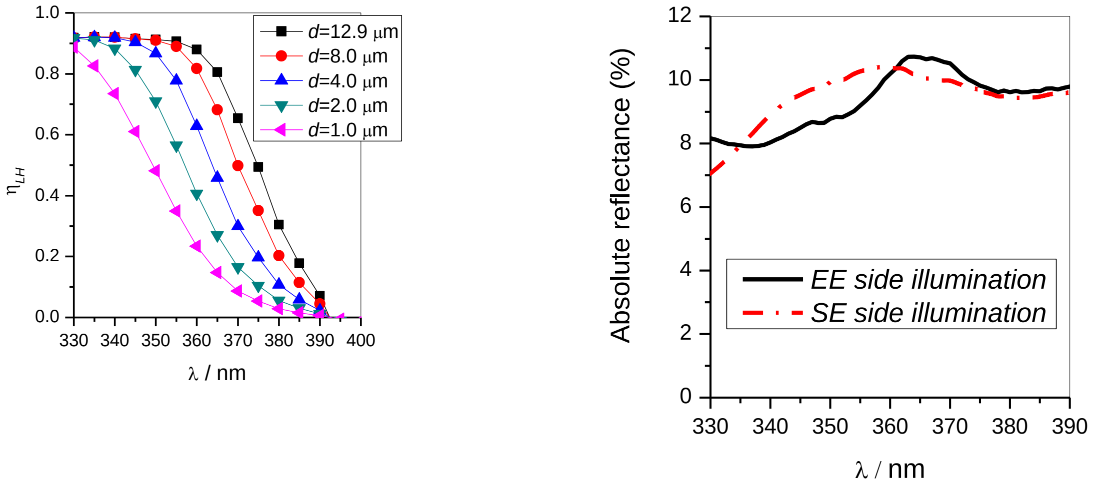

Figure S1. TiO_2 film thickness dependent light harvesting efficiency including reflectance calculated by eqs S13 and S14 in ref [1] and the scattering of the TiO_2 on FTO substrate.

The role of nc-TiO_2 film thickness (d) on IPCE yields. A plot of the dependence of light harvesting efficiency with film thickness is shown in Figure S1. Illumination of the nc-TiO_2 film on the electrolyte side with 355 nm light from a Xe lamp leads to generation of charge carriers at a distance from the FTO substrate. A plot of the APCE (= $\eta_{\mathrm{sep}} \times \eta_{\mathrm{col}}$) versus film thickness is shown in Fig 2. Overall (d = 1.1-8.4 µm) we do not see a clear single trend between the APCE and film thickness. Between 1.1 and 4.2 µm a slight decrease in APCE is observed, as $L_n \sim$ 8.5-12 µm is significantly greater than the film thickness,[1] it is proposed that η_{sep} decreases between 1.1 and 4 µm, from a maximum of $\eta_{sep} \sim 0.13$ at 0.06 V, $d = 1.1$ µm. It has been previously shown that the electrolyte in the porous structure of nc-TiO_2 effectively screens charge carriers from any significant electric fields at distances of greater than 50 nm from the FTO interface[2] which would lead to a variation in η_{sep} in films where a significant concentration of charge carriers are generated very close to the FTO interface decreases ($d < 4.2$ µm). With films of 8.4 µm only a very low concentration of charge carriers are generated close to the FTO interface and no further decrease in APCE is observed, instead we observe a slight increase in APCE compared to the 4.2 µm film. The exact causes of the small increase in APCE at 8.4 µm is currently unknown, however it should be noted that this thicker sample is prepared by deposition of multiple layers of TiO_2 paste, which may lead to subtle morphological changes.

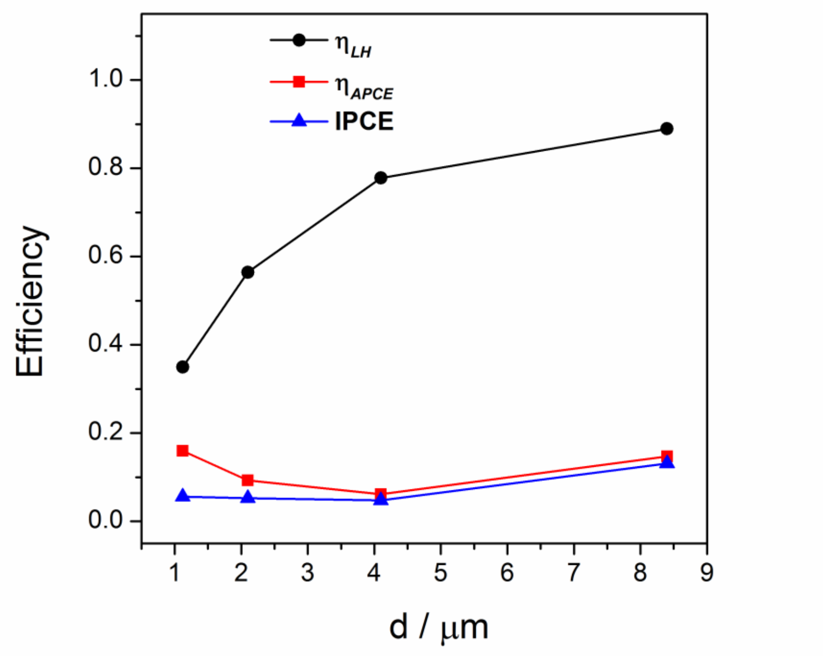

Fig S2. Dependence of IPCE, η_{LH} and APCE ($\equiv (\eta_{col} \times \eta_{sep})$) as a function of nc-$TiO_2$ film thickness (d). The steady state IPCE data is recorded for a nc-TiO_2 electrode illuminated (355 nm) on the electrolyte (EE) side in 0.5 M $NaClO_4$ aqueous solutions (pH=2.0) held at 0.6 V versus Ag/AgCl.

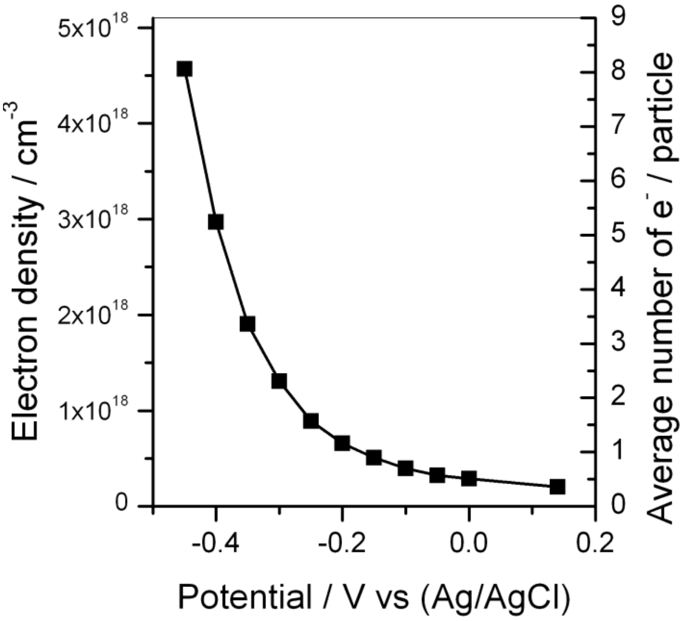

Figure S3. *Change in electron density measured by charge extraction stepping from the value indicated to +0.44V (vs. Ag/AgCl) in the dark, 0.5 M* $NaClO_4$ *(pH 2), nc-*TiO_2 *electrode (4 μm).*

To further confirm that the value of the electron extinction coefficient recorded using steady state spectroelectrochemistry is applicable to our transient measurements we have measured both the decay of the photoelectron at 900 nm using TA and the transient photovoltage (TPV) from a nc-TiO_2 film in nitrogen purged $NaClO_4$ electrolyte following laser UV excitation (SE, 355 nm, 16 μJ cm^{-2}) under open circuit conditions, biased to -310 mV vs Ag/AgCl using a CW bias light, Figure 2(b). The thin nc-TiO_2 film (1 μm) is excited through the substrate and white light biased to -310 mV vs Ag/AgCl to ensure a rapid rise in the TPV signal, which occurs on a submicrosecond timescale which is beyond the detection limit of these experiments. Under open circuit conditions in a nitrogen purged solution rapid electron-hole recombination dominates the kinetics of both the TA and TPV signals on the microsecond to millisecond timescales. By utilization of the measured electron extinction coefficient, and the measured charge density with potential (Figure S1) it is possible to directly scale the TAS data to the TPV signal. It is assumed that on slower timescales in this thin film the photovoltage is an accurate representation of the electron density in the sample. From the electron extinction coefficient it is possible then to convert the tail of the TA signal to an electron density and then using Figure S1, into a voltage reading. There is a good overlap of these two signals confirms the applicability of the measured extinction coefficient at 900 nm to these transient measurements.

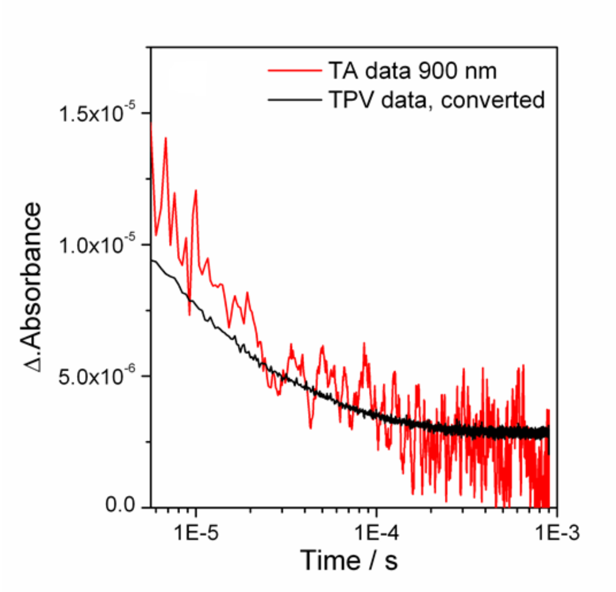

Figure S4. *TA decay trace and TPV decay trace recorded following the UV excitation (355 nm, 16 μJ cm^{-2}) of a nc-TiO$_2$ film under LED illumination (365 nm) at open circuit (-310 mV). TA data is recorded by probing the decay of the transient at 900 nm and is then converted to an equivalent change in photo voltage by use of the extinction coefficient derived in the main text.*

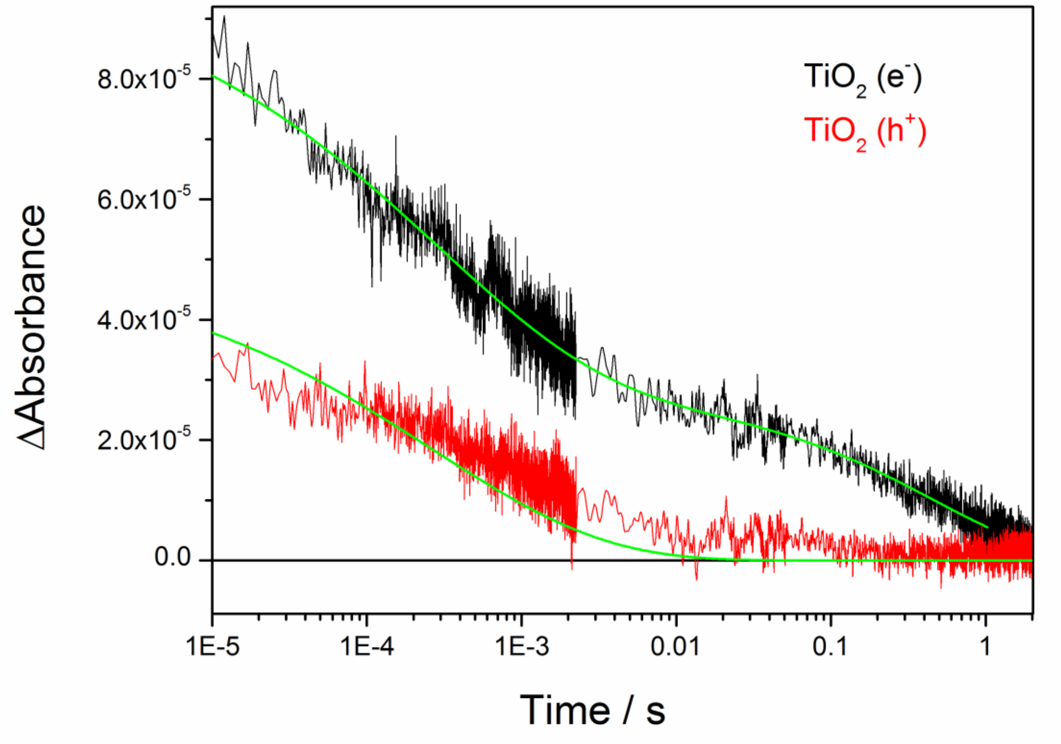

Figure S5: *TA decay traces of nc-TiO_2 holes and photoelectrons recorded 460 nm and 900 nm respectively following the UV excitation (355 nm, 35 μJ cm^{-2}, SE) of nc-TiO_2 (1.1 μm) in 0.5M $NaClO_{4(aq)}$ (pH 2) at 0 V vs Ag/AgCl. The same fast component present in both traces is assigned to electron-hole recombination.*

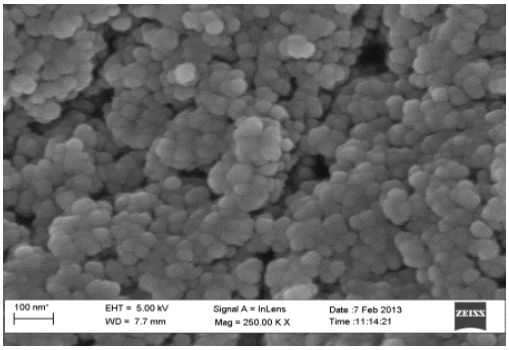

Figure S6: *SEM image of a representative nc-TiO_2 film*

References:

[1] W. H. Leng, P. R. F. Barnes, M. Juozapavicius, B. C. O'Regan, J. R. Durrant *Journal of Physical Chemistry Letters*. **2010**, 1, 967-972.
[2] A. Zaban, A. Meier, B. A. Gregg *Journal of Physical Chemistry B*. **1997**, 101, 7985-7990.