Supporting information

## Calibration of the oxygen electrode in an electrolyte solution

Air saturated 0.05 M NaOH gave a O_2 clark electrode reading of 15.1 nA at 21 ^{o}C.

The solubility of oxygen in this dilute electrolyte solution is only very slightly decreased versus a pure water system. An experimental salting out parameter for the effect of sodium hydroxide on oxygen concentration in aqueous solutions has been reported at 310.2K.[1] This allows a Bunsen coefficient of oxygen solubility to be calculated for an aqueous 0.05M NaOH solution at 310.2K, which is α = 0.0236. This value is very similar to that reported for pure water at the same temperature (α = 0.0241) indicating that there is only a very slight salting out effect, nonetheless in order to minimise experimental error attempts to correct for it have been made. A further experimental study on the solubility of oxygen in KOH solutions has been carried out at room temperature.[2] At 310.2K the Bunsen coefficients of KOH and NaOH for the solubility of oxygen in solution are the same within experimental error, indicating the experimental data on KOH solutions can be used to give a value of oxygen solubility in our system at room temperature. Using the expression derived in reference 2 and correcting for the correct O_2 partial pressure using Henry's law we arrive at an oxygen concentration of 2.76 x 10^{-4} mol l^{-1} in an air saturated solution of aqueous 0.05 M NaOH at room temperature.

Change in electron density with applied potential

The change in number of electrons per TiO_2 particle with applied potential was found by carrying out charge extraction experiments using the same PEC and same conditions in the measurements described in the main text. Following an hour of stabilisation the nc-TiO_2 film was found to be at 0.1 V vs. Ag/AgCl reference electrode in a degassed 0.05 M NaOH solution. The nc-TiO_2 was then held at the potential indicated in Figure S1 for 5 minutes before the potentiostat was rapidly returned to 0.1 V. The charge extracted upon the potential step could then be measured.
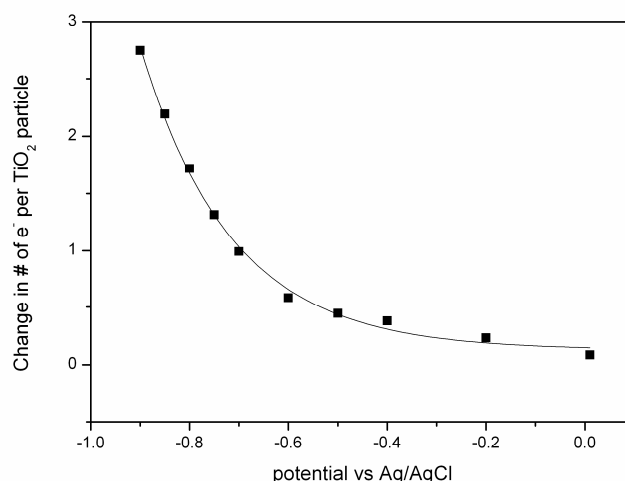
Figure S1: Change in electron density per TiO₂ particle measured by charge extraction following the voltage change voltage shown to 0.1 V (vs. Ag/AgCl) in the dark.

This increase in the electron density with applied bias leads to the observed shape of the I-V plot (Figure 1, main text) between -0.85 and -0.8 V. Before each scan the TiO$_2$ film was held at -0.9V vs the reference electrode for a period of time prior to scanning at 50 mV s^{-1} from negative to positive potentials. At this pH holding the film at -0.9V leads to electron accumulation and trap filling, the tail observed at -0.85 to -0.8 V is due to the discharge of the accumulated electrons. The open circuit potential, under illumination is at ca. -0.85 V, however this is masked by the effects described above in this figure. This has been previously been reported for nc-TiO$_2$ films and a detailed discussion of this can be found in "*G. Boschloo and D. Fitzmaurice, Journal of The Electrochemical Society, 147 (3) 1117-1123 (2000)*".

Calculation of the number of photons absorbed per TiO$_2$ particle per laser pulse

The number of photons absorbed per TiO$_2$ particle is calculated in the manner recently outlined in a paper by Tang et al.[3] Briefly the number of photons absorbed per laser pulse by the 4 μm thick film is calculated by measuring the absorption of the nc-TiO$_2$ film at 355 nm. The incident light intensity on the nc-TiO$_2$ film is found by correcting the laser intensity for absorption and scattering from the reactor vessel, glass/FTO substrate and electrolyte. All reported laser intensities have been corrected for these losses in the text. To calculate the number of TiO$_2$ particles per unit area in a 4 μm thick film the mass of the TiO$_2$ film is measured, then by presuming that the particles are spherical the number present can be calculated by using the mass of the TiO$_2$ film, the density of anatase TiO$_2$ and the known particle radius (7.5 nm). This provides the number of photons absorbed on average per TiO$_2$ particle. As can be seen in Figure S2 in a 4 μm thick film there will be a gradient in the incident light intensity.
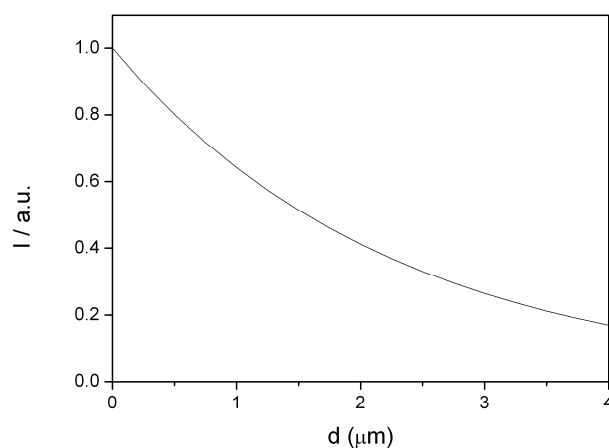
Figure S2: Calculated UV light (355 nm) intensity profile within a 4 micron nc-TiO₂ film. d =
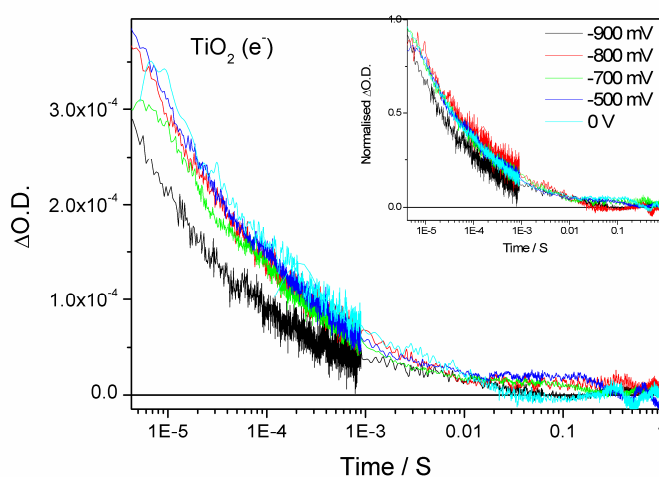*0 corresponds to the substrate (FTO) interface.*

Figure S3: TAS decay traces of the electron on nc-TiO₂ recorded at 800 nm following the UV
excitation (355 nm, 250 μJ cm⁻²) of nc-TiO₂ in 0.05M NaOH at -0.9 V (black), -0.8 V (red), -
0.7 V (green), -0.5 V (blue), 0 V (cyan) versus a Ag/AgCl reference electrode. Inset shows
normalised traces, the lifetimes of all traces is approximately the same.

References

[1] W. Lang and R. Zander, *Ind. Eng. Chem. Fundam.*, **1986**, 25, 775-782.

[2] R. E. Davis, G. L. Horvath and C. W. Tobias, *Electrochimica Acta*, **1967**, 12, 287-297.

[3] J. Tang, J. R. Durrant and D. R. Klug, *J. Am. Chem. Soc.* **2008**, 130, 13885-13891.