

Probing P25 TiO₂ Photocatalysis Using Photoinduced Absorption Spectroscopy (PIAS)

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S1 Preparation of the P25 TiO₂ film

Briefly, the supporting substrate, usually FTO coated glass (20 mm x 15 mm x 4 mm, TEC-15, Pilkington Glass plc) was first coated with a 100 nm dense TiO₂ blocking layer using the spin-coating method reported by Oku et al.¹, in order to prevent direct contact of the background electrolyte (always 1M HClO₄) with the FTO. A small 5 mm x 15 mm track was masked with Scotch® Magic™ tape prior to spin-coating to preserve an area of bare FTO to allow electrical contact to be made with the potentiostat, when used. Each substrate was then spin-coated with a titanium diisopropoxide bis(acetylacetonate) in butanol (0.3 M) solution and the barrier film-coated product annealed at 500 °C for 30 min. This was followed by doctor-blade deposition of a ca. 1.7 μm thick layer of P25 TiO₂ from a paste of TiO₂ (76 mg of P25 TiO₂ in: 20 μL acetic acid, 20 μL water, 3.98 mL ethanol, 0.43 g terpeneol, and 0.74 g of 10% w/w ethyl cellulose in methanol) which was cast as a 60 μm thick wet layer and then annealed at 500°C for 30 min. The UV/Visible absorption spectrum and a photograph of the final, slightly opalescent, 1.7 μm thick, film are illustrated in Fig. S1, along with the emission spectrum of the UV LED used in this work. Scanning electron microscopy revealed the film to be mesoporous, comprising a network of loosely packed interconnected particles ca. 30-40 nm in diameter, and similar in appearance to the P25 TiO₂ photoanodes reported by others.²

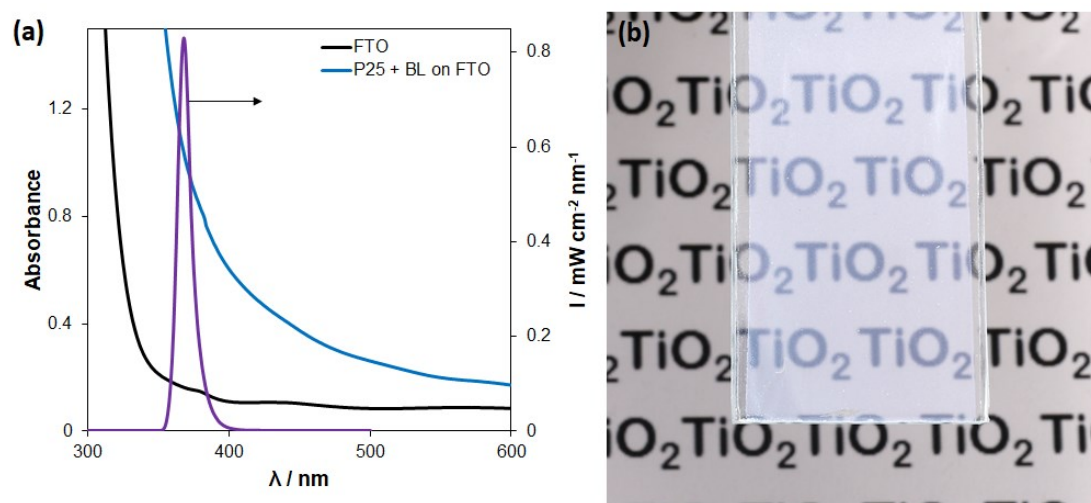


Fig. S1: (a) U/vis absorption spectrum of the FTO coated glass substrate with and without the P25 TiO₂ film and the emission spectrum of the UV LED used in this work and (b) photograph of a typical P25 TiO₂ film on FTO used throughout this work.

S2 Analysis of light off photocurrents

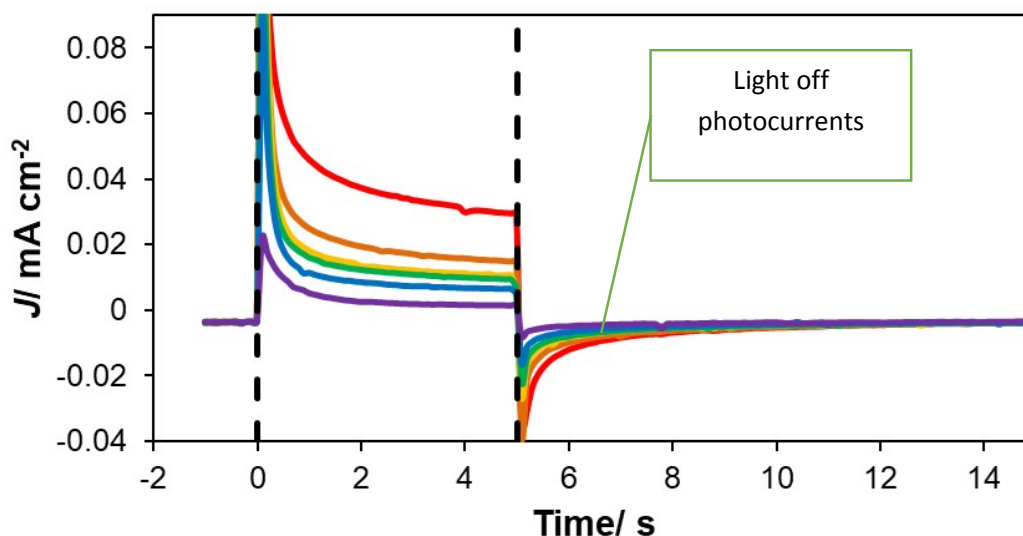


Fig. S2. Plots of the measured photocurrent, J , as a function of time, exhibited by a P25 TiO₂ photoanode poised at -0.19 V vs Ag/AgCl and in 0.1 M 4CP (in O₂-free, 1 M HClO₄), before during and after steady state irradiation, using different 365 nm UV irradiances; namely (from bottom to top): 113, 56, 36, 33, 21 and 6 mW cm⁻², respectively.

The 'light-off' photocurrents illustrated in Fig. S2 are due to back electron-hole recombination.³ It can be shown that for each of these current decays the contribution the concentration of holes involved in the recombination process, $[h^+]_{\text{rec}}$, i.e. the area under the current decay curve, is much less than the associated steady-state value of the accumulated surface holes, $[h^+]_{\text{ss}}$. This is best illustrated using the biggest current decay curve, in red in Fig. S2, which reveals upon integration with time an area = 0.0307 mC cm⁻² \equiv 1.92 holes nm⁻². But, the P25 TiO₂ has a roughness factor of ca. 33, so the real total hole density associated with recombination = 0.058 holes nm⁻². Obviously, this hole density will make a fractional contribution, f , to the measured value of $\Delta\text{Abs}_{\text{ss}}$. The value of $\Delta\text{Abs}_{\text{ss}}$ - for the red line data set under consideration ($\rho = 113$ mW cm⁻²) - was ca. 0.28×10^{-3} , see Fig. 2(b). The value of f can then be calculated by assuming the molar absorptivity of the photogenerated holes on P25 TiO₂ is that reported previously for TiO₂, i.e. ca. 2000 M⁻¹cm⁻¹, which is equivalent to 3.32×10^{-4} nm² holes⁻¹.³ Thus, the total steady-state hole density = $0.28 \times 10^{-3} / 3.32 \times 10^{-4} = 0.84$ nm² holes⁻¹ and so the value of $f = 0.058 / 0.84 = 0.069$, i.e. < 7%. When analysed in the same way all the other current curves illustrated in Fig. S2 yield values for f that are < 7%. Thus, in all this work back electron-hole recombination does not make a significant contribution (i.e. < 7%) to the measured values of $\Delta\text{Abs}_{\text{ss}}$, J_{ss} and the decay kinetics exhibited by $\Delta\text{Abs}_{\text{ss}}$, upon switching off the light. Further evidence for the latter is provided by the excellent fit to all the $\Delta\text{Abs}_{\text{ss}}$ vs time profiles illustrated in fig. 2(a) to first order kinetics with a rate constant of 0.3 s⁻¹. In addition, the light-off photocurrents exhibit bi-exponential decay kinetics, dominated (> 65%) by a fast step ($k = \text{ca. } 7$ s⁻¹) which is over 20 times quicker than the decay of $\Delta\text{Abs}_{\text{ss}}$ on switch off (0.3 s⁻¹); these very different kinetic profiles suggest, once again, that back electron-hole recombination kinetics involves a relatively low value of $[h^+]_{\text{rec}}$ compared to $[h^+]_{\text{ss}}$, and so contributes little to the measured values of $\Delta\text{Abs}_{\text{ss}}$ and J_{ss} . As a result, the values of $\Delta\text{Abs}_{\text{ss}}$, J_{ss} and the decay kinetics exhibited by $\Delta\text{Abs}_{\text{ss}}$, upon switching off the light

are determined by the kinetics of oxidation of 4CP by surface accumulated, photogenerated holes.

References

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