Electronic Supplementary Material (ESI) for ChemComm.

ESI

Kinetics of the Photocatalysed Reduction of Oxygen by CdS Probed using Photoinduced Absorption Spectroscopy (PIAS)

Aaron McNeill, Christopher O'Rourke and Andrew Mills*
Queens University Belfast, School of Chemistry and Chemical Engineering,
David Keir Building, Stranmillis Road, Belfast, UK, BT9 5AG
*: e-mail: andrew.mills@qub.ac.uk

S1 Preparation of CdS on glass film

CdS paste was made from CdS nanopowder (Sigma Aldrich) using a modified Grätzel method.[1] In this method, 38 mg of CdS nanopowder were added to a mortar and pestle, and then ground upon addition of each the following components (in order): 1 x 20 µL of glacial acetic acid, 5 x 20 µL of DI water, 5 x 60 µL of ethanol, followed by 6 portions of 100 µL of ethanol. The final suspension was transferred to a vial and made up to 5 mL by adding 3.98 mL of ethanol, and then sonicated using a tapered microtip Soniprobe for 2 minutes. Next, 0.43 g of terpineol were added to the suspension, which was sonicated again, followed by 0.74 g of a 10% w/w solution of ethyl cellulose in ethanol. The paste was stirred overnight with the lid off to allow evaporation, thickening the solution, after which the yellow paste was stored in the fridge. A layer of CdS paste was applied to a microscope slide using the doctor-blade method using Scotch tape (~60 µm). The tape tracks are removed before drying and once dried the substrate is then heated to 450 °C for 30 minutes to anneal. Note that when using PIAS to probe the CdS film, a much greater concentration of CB electrons over VB holes is required to produce the Burstein shift, and so will not occur in the bulk, but will at the surface where scavenging of the photogenerated holes by the SED occurs.

S2 Steady-State Photocatalysis (SSPC)

The PIAS setup used in this work was similar to that previously reported PIAS systems.[2, 3] Thus, briefly, the CdS films were irradiated with either a 365 nm LED (RS Components, LZ4-44UV00-0000) or a 420 nm LED (RS Components, ILH-XQ01-S410-SC211-WIR200), the irradiances of which were adjusted to the desired value using a variable power supply. The monitoring beam of wavelength, λ_m, was generated using the combination of a tungsten lamp (SLS301, Thorlabs) and a monochromator set at λ_m and passes through the CdS film, immersed in 20 mL of the 0.1 M SED solution in a 3D-printed PLA cell (5.7 x 3.4 x 5.85 cm), then through another monochromator set also to λ_m, and finally detected using a photodiode detector (DET100A2, Thorlabs). Unless stated otherwise, in this work λ_m was set at 505 nm, the maximum in the difference spectrum exhibited by the CdS film. The signal from the photodiode, which was proportional to the transmitted irradiance of the monitoring beam, was recorded using a National Instruments (NI USB-6211) DAQ card. The data were processed using a custom program from LabView, and the traces presented herein are the average of 20-50 irradiation/dark cycles. A schematic illustration of the PIAS system is given below.

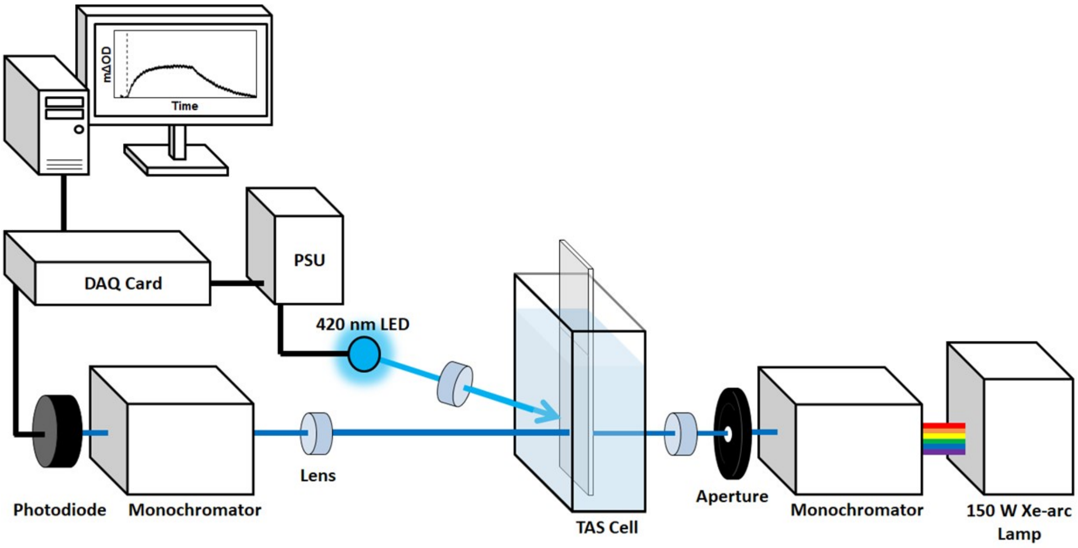

Fig. S1 - Schematic illustration of the photoinduced absorption spectroscopy (PIAS) system.

S3 Analysis of (dark) ΔAbs (measured at 505 nm) vs time decays as function of $\%O_2$

The measured dark decays in ΔAbs as a function of $\%O_2$ are illustrated in Fig. 3(a) and shown in greater detail below in Fig. S2(a). The value of ΔAbs(dark) at any time during the decay process is assumed to be a measure of the dark concentration of the surface-accumulated, photogenerated conductance band electrons, $[e^-]$. All of the ΔAbs(dark), vs time decays exhibited first order kinetics, from each of which a different first order rate constant, k_1, could be extracted. The latter parameter is clearly a function of $\%O_2$ and the plot of k_1 vs $\%O_2$, illustrated in Fig. S2(b), reveals a good straight line, which fits the following expression,

$$k_1 = k_{O_2}\%O_2 + k_0 \qquad (1)$$

where k_{O2} and k_o have values of 0.175 $(\%O_2)^{-1}$ s^{-1} and 1.88 s^{-1}, respectively.

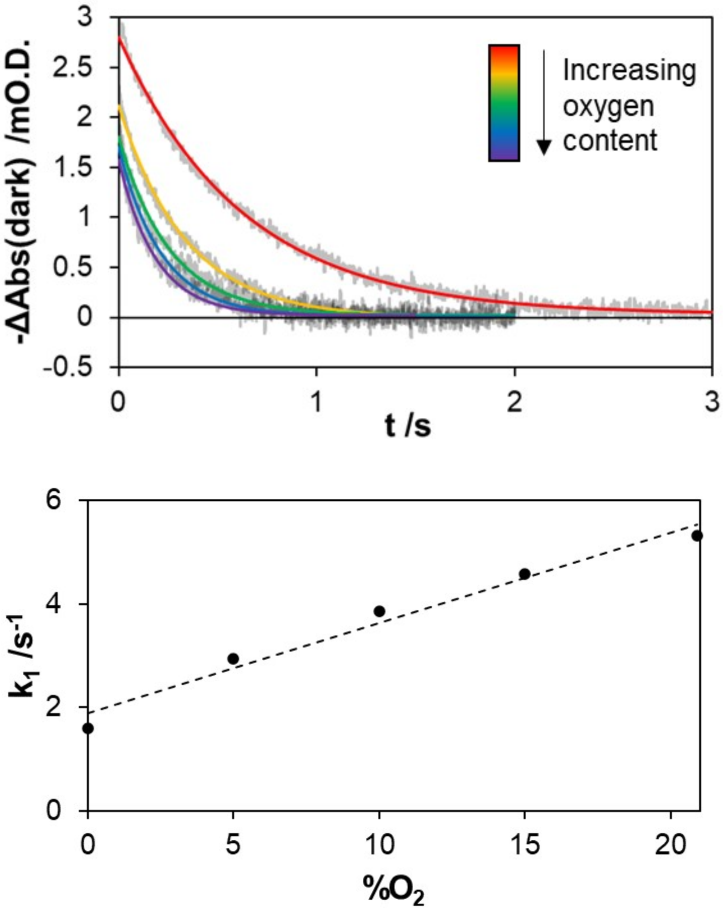

Fig. S2 – (a) Expanded view of dark decays of photogenerated transient, ΔAbs at 505 nm, taken from the traces in Figure 3(a), for the CdS film, in 0.1 M NaA/AA, satrated with different levels of $\%O_2$. The decay curve data is in grey, and 1st order lines of best fit are the solid lines. The $\%O_2$ saturation levels used in this work were, from top to bottom: 0, 5, 10, 15 and 21%, respectively. (b) Plot of first order rate constants, k_1, derived from decay curves in (a) vs $\%O_2$ saturation on the cell. The broken line is the line of best fit, from which, based on eqn (1) above, k_{O2} and k_o equal 0.175 $(\%O_2)^{-1}$ s^{-1} and 1.88 s^{-1}, respectively.

S4 Steady state photoreduction of O_2 measurements

In a typical experiment, either a 1 x 2 cm area of CdS paste film or an 8 mm x 12.5 mm (1 cm^2 area) strip of a CdS-SEN film was cut and stuck to the inside wall of a 1 cm cuvette using double-sided tape. On the adjacent cuvette wall was placed an O_2xyDot® (OxySense[4]), secured with Blu Tack, which was used to measure the level of dissolved O_2, i.e. the %O_2, in the stirred (750 rpm), air-saturated aqueous SED solution. In a typical SSPC experiment, the reaction cuvette, with the photocatalyst film and O_2xyDot® in place, was filled with 4 mL of a sacrificial electron donor solution, i.e. 0.1 M solution of 1:1 molar ratio sodium ascorbate and ascorbic acid (NaA/AA). This solution was then sparged with a predefined Ar/air mixture, allowing the %O_2 level to varied over the range 0 to 21%, for 10 minutes before the cell was sealed with parafilm. The remaining headspace in the cell was approximately 4 mL. The film was then irradiated using a violet LED (420 nm), with an irradiance of 30 mW cm^{-2}. For each Ar/air mixture used, the above set up allowed the rate of the photocatalysed reduction in the concentration of dissolved O_2, i.e. r, units %O_2 min^{-1}, to be monitored as a function of irradiation time, with readings taken every 15 s over a 1 h irradiation period. A schematic illustration of the irradiation set up is illustrated below.

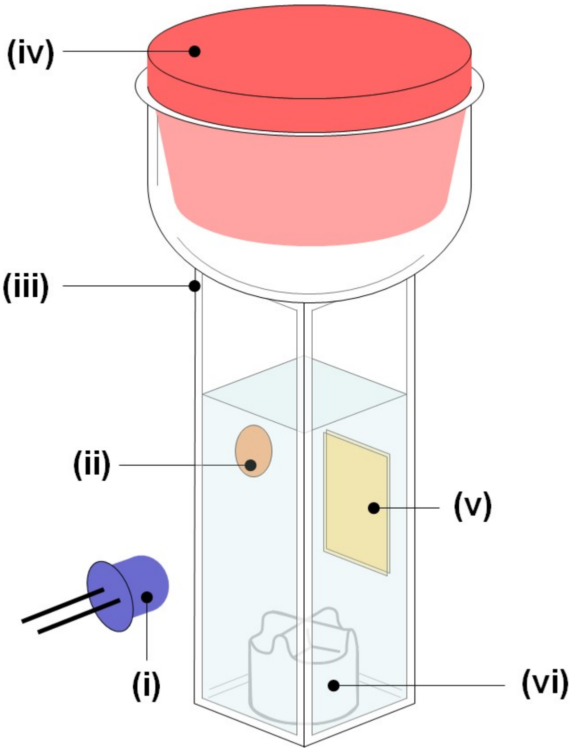

Fig. S3 – Schematic illustration of the gas tight quartz cuvette used for steady-state photocatalysis experiments. (i) 420 nm LED, (ii) O_2xyDot®, (iii) quartz cuvette, (iv) Suba-Seal®, (v) CdS-SEN film, (vi) crown stirrer.

References

1. S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovolt.*, 2007, **15**, 603-612.
2. F. Le Formal, S. R. Pendlebury, M. Cornuz, S. D. Tilley, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2014, **136**, 2564-2574.
3. C. A. Mesa, A. Kafizas, L. Francàs, S. R. Pendlebury, E. Pastor, Y. Ma, F. Le Formal, M. T. Mayer, M. Grätzel and J. R. Durrant, *J. Am. Chem. Soc.*, 2017, **139**, 11537-11543.
4. OxySense, https://oxysense.com, (accessed Accessed December 2020).