Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Over 75% Incident-Photon-to-Current Efficiency without Solid Electrodes

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. Schematic representation of the photoelectrochemical cell

The composition of electrochemical cell in the presence of the coalesced TiO_2 nanoaprticle film at the ITIES is schematically shown in **Cell 1**. The 1,2-dichloroethane (DCE) solution contained 1,1'-dimethylferrocene (DMFc) and (bis(triphenylphosphoranylidene)-ammonium tetrakis(pentafluorophenyl)borate (BTPPA-TPFB) as donor species and supporting electrolyte, respectively. The double bar denotes the ideally polarizable interface. Consequently, introducing a potential bias between the two Ag terminals will lead to changes in the Galvani potential difference at the water/DCE boundary.

Ag	AgCl	7 mg TiO_2 Layer (25nm) 0.10 M LiCl (aq)	x mM DMFc 10 mM BTPPA-TPFB (DCE)	1.0 mM BTPPACl 0.01 M LiCl (aq)	AgCl	Ag

Cell 1. Electrochemical cell composition; the concentration of DMFc (x) was either 1 or 5 mM.

In the case of electrostatically stabilised TiO_2 colloids, the composition of the electrochemical cell is shown as **Cell 2**. The supporting electrolyte in the aqueous solution was limited to 0.01 M LiCl and the pH lowered to 3 in order to avoid compromising the stability of the colloidal suspension. The photoelectrochemical responses of this system has been discussed in previous works.

Ag	AgCl	0.5 mg dm^{-3} TiO_2 Colloid (5 nm) 0.01 M LiCl (aq) pH 3	5 mM DMFc 10 mM BTPPA-TPFB (DCE)	1.0 mM BTPPACl 0.01 M LiCl (aq)	AgCl	Ag

Cell 2. Electrochemical cell including 5 nm TiO_2 colloidal solution in the aqueous phase.

2. Illumination of the Liquid/Liquid Interface

All photoelectrochemical experiments were carried out under UV illumination provided by a light emitting diode (Thorlabs) with the spectral response shown in **Figure ESI-1**. The LED output is characterised by a narrow spectral emission centred at 311 nm. The output emission of the LED was obtained from a calibrated Si photodiode (Oriel) featuring anti-reflective coatings. The LED output power can be tuned between 6.06 μW and 0.93 mW, which can be approximated to photon-fluxes (at 311nm) between 0.1 to 14.6×10^{14} s^{-1}. Approaching the LED to the interfacial region from the *top* of the cell (as depicted in Figure 1a) allows focusing most of the output onto the TiO_2 film. Consequently, IPCE values are based on the total output of the LED, ignoring reflection losses at the water/air and TiO_2/water interfaces. To estimate the photon flux at the interface under *bottom* illumination, we only filled the electrochemical cell with the organic electrolyte. The LED is then placed directly above the organic electrolyte from the top of the cell, while the calibrated photodiode is set against the bottom window. Under this configuration, we are able to probe light attenuation by the organic electrolyte as well as reflection losses from the bottom window.

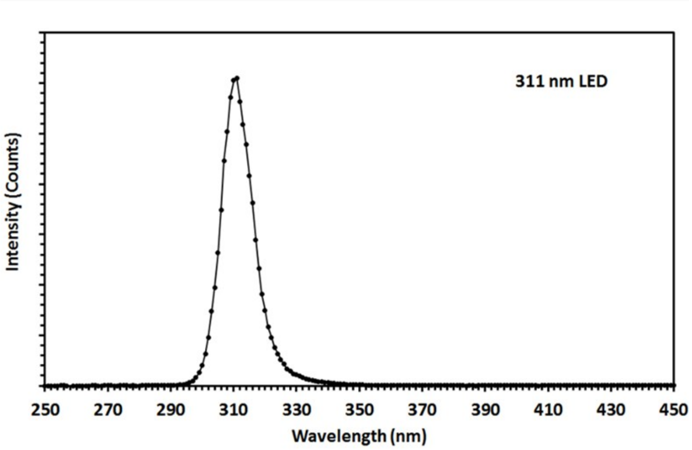

Figure ESI-1. Spectral response of the LED used in the photoelectrochemical experiments.