Electronic Supplementary Material (ESI) for Chemical Communications

Kinetics and Mechanism of Light-Driven Oxygen Evolution at Thin Film α-Fe_2O_3 electrodes

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Supplementary Material

Preparation of α-Fe_2O_3 films

Smooth polycrystalline α-Fe_2O_3 films were deposited by aerosol-assisted chemical vapour deposition (AACVD) on FTO-coated glass substrates (1cm × 2cm pieces of Pilkington TEC 8, 8 Ω/square) using a reactor tube located in a tube furnace. Substrates were cleaned ultrasonically with distilled water, acetone, isopropanol and ethanol before being placed in the reactor tube and heated to 450 ºC for 20 min before starting the deposition. The aerosol was generated from a 0.05 M solution of ferrocene (98%, Lancaster Synthesis) in toluene by positioning a round bottomed flask with the precursor solution in a water bath above the piezoelectric modulator of an ultrasonic humidifier. The aerosol droplets were transported to the heated substrate by the air flow. The flow rate (150 ml/min) was controlled by a thermal mass flow controller (Bronkhorst UK Ltd.)..

IMPS and photoresponse measurements

IMPS measurements on the α-Fe_2O_3 electrodes were carried out using a potentiostat in a three-electrode configuration with a Ag|AgCl,KCl reference electrode and a platinum wire counter electrode. The electrolyte was 1 M NaOH. Some electrodes were treated by placing a drop of 10 mM cobalt nitrate solution on the surface for 1 minute before rinsing thoroughly with de-ionized water. Modulated illumination was provided by a high intensity light-emitting diode (LED: 455 nm) controlled by a home-built LED driver that allowed superimposition of sinusoidal modulation (ca. 10%) on a dc illumination level. The sine wave signal was provided by a Solartron 1250 frequency response analyzer.

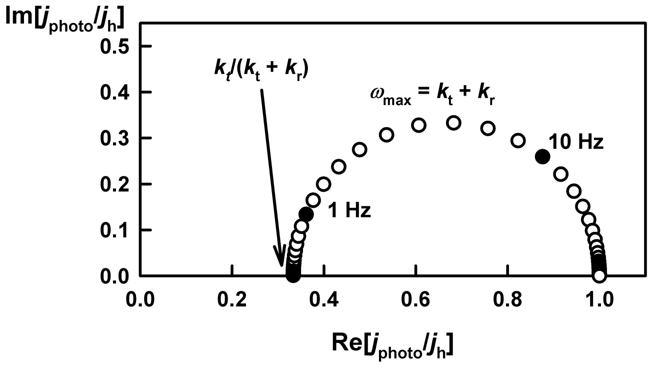

Fig. S1. Extraction of rate constants from IMPS response

LMAS and PMAS measurements

LMAS measurements were performed using a tungsten optical fiber illuminator and a monochromator (Bentham Instruments). The modulated illumination (80% depth) was provided by a 370 nm light emitting diode (LED: Thorlabs) coupled via a LED driver (Thorlabs) to the signal output of the lock-in amplifier. A 2 mm GG400 nm filter (Schott) was used in front of the silicon photodiode detector to minimise light throughput from the UV LED. PMAS measurements were performed using monochromatic light provided by a Xe lamp light source and monochromator (Bentham Instruments). Transmitted light was detected with a silicon photodiode connected to a lock-in amplifier (Stanford Research SR 830) via a low noise current amplifier. The sinusoidal potential modulation (100 mV p-p, 35.4 mV rms) was provided by the lock-in amplifier. Spectra were recorded at a frequency of 2.7 Hz and at 90^o phase shift with respect to the sinusoidal potential modulation in order to eliminate the small background signal arising from electroreflectance effects from the FTO substrate. The frequency response of the LMAS signal at constant wavelength (460 nm) was measured using the Solartron 1250 frequency-response analyser.