Correlation of Hole Population and Photocurrent in Hematite Photoelectrodes for Solar Water Splitting

Stephanie Pendlebury,*[1] Monica Barroso,[1] Alex Cowan,[1] Junwang Tang,[2] James Durrant[1]

[1] Department of Chemistry, Imperial College London; [2] Department of Chemical Engineering, University College London *stephanie.pendlebury08@ic.ac.uk

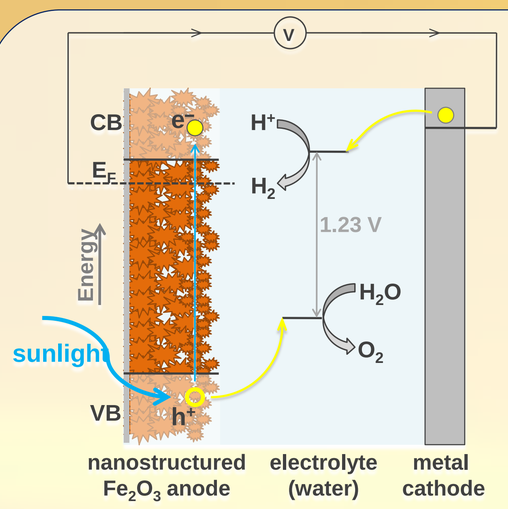

Fig 1: schematic of PEC cell with hematite photoanode

Introduction

Hematite (α-Fe_2O_3) has several advantages as a photoanode material for solar water-splitting photoelectrochemical (PEC) cells: it absorbs strongly in the visible region, with a bandgap of ~2.1 eV (590 nm); the valence band edge is appropriate for water oxidation;[1] it is stable under water photolysis conditions, and is formed from non-toxic, abundant and cheap materials.

However, efficiencies are thought to be limited by poor charge-transport properties,[2] rapid recombination[3, 4] and slow charge transfer kinetics at the semiconductor-liquid junction.[5] Positive applied potential is necessary to reduce the electron-hole recombination rate such that water oxidation can occur,[6] and because the conduction band edge is positive of the H^+/H_2 redox potential.[1]

We use **transient absorption spectroscopy** (TAS, a pump-probe technique) and **transient photocurrent** (TPC) measurements of hematite photoanodes in a complete PEC cell to probe photogenerated holes and electrons respectively.

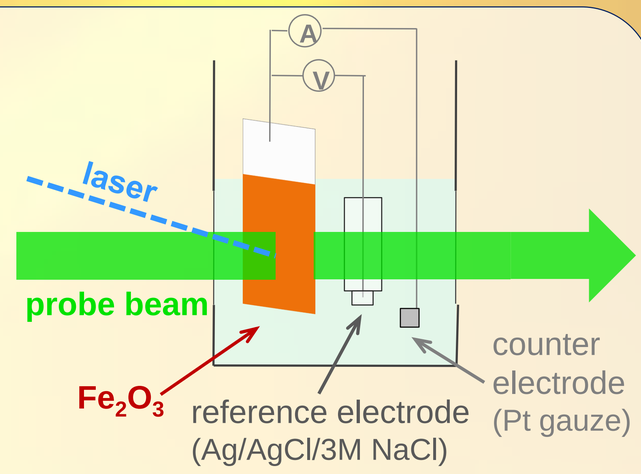

Fig 2: schematic of transient absorption spectroscopy (TAS) of a photoelectrode in a complete PEC cell (0.1 M NaOH, pH 13)

Correlation of photogenerated hole population with photocurrent

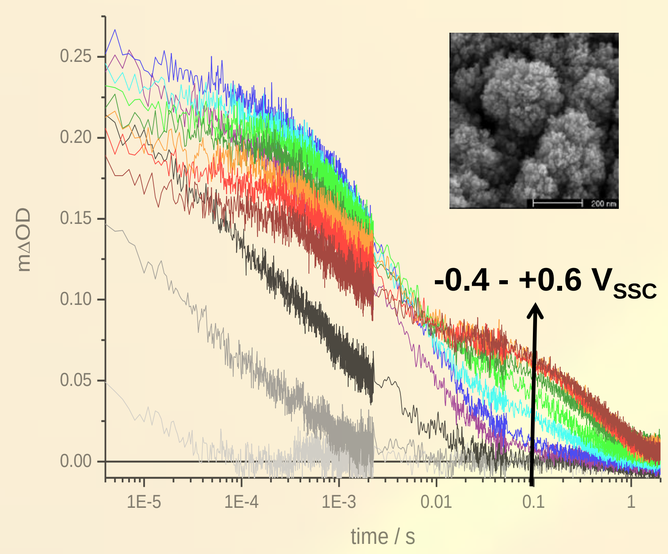

Fig 3: TA decays of the photo-hole (EE 355 nm excitation, probed at 650 nm) as a function of applied bias for Si-doped APCVD hematite photoanodes (SEM[7] inset)

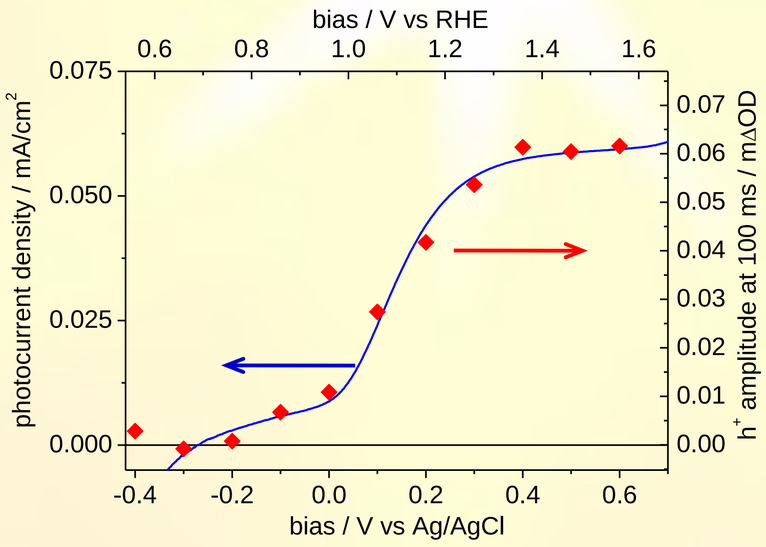

Fig 4: Correlation of long-lived hole signal amplitude (at 100 ms) with photocurrent

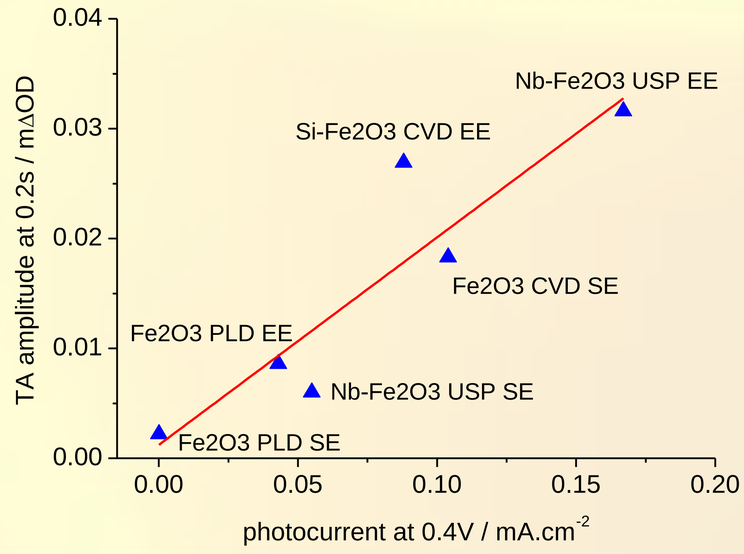

Fig 5: Comparison of long-lived hole population with photocurrent at +0.4 V_{SSC} for various different hematite photoanodes

- The photogenerated holes are monitored by transient absorption spectroscopy (TAS)
- Decay dynamics are strongly dependent on applied electrical bias (Fig 3)
- The fast phase of the TA photo-hole decay (1 µs – 20 ms) is associated with non-geminate electron-hole recombination
- Increasing positive bias reduces the background electron density and increases band-bending, so increasing hole lifetime
- The slow phase (>20 ms) of the TA photo-hole decay is associated with water oxidation
- Water oxidation occurs on a timescale of 100s ms to seconds on hematite
  → very long-lived holes required - positive applied bias necessary
- The timescale of water oxidation is independent of applied bias (Fig 3)
- There is a strong, quantitative correlation between the amplitude of the long-lived photo-hole signal and the photocurrent, as a function of applied bias (Fig 4)
- This correlation is general for different types of hematite (doped, undoped, nanostructured, solid; Fig 5), and also for nanoporous TiO_2 – may be generally true for metal oxide photoanodes

Comparison of transient photocurrent (e^-) and transient absorption (h^+) decays

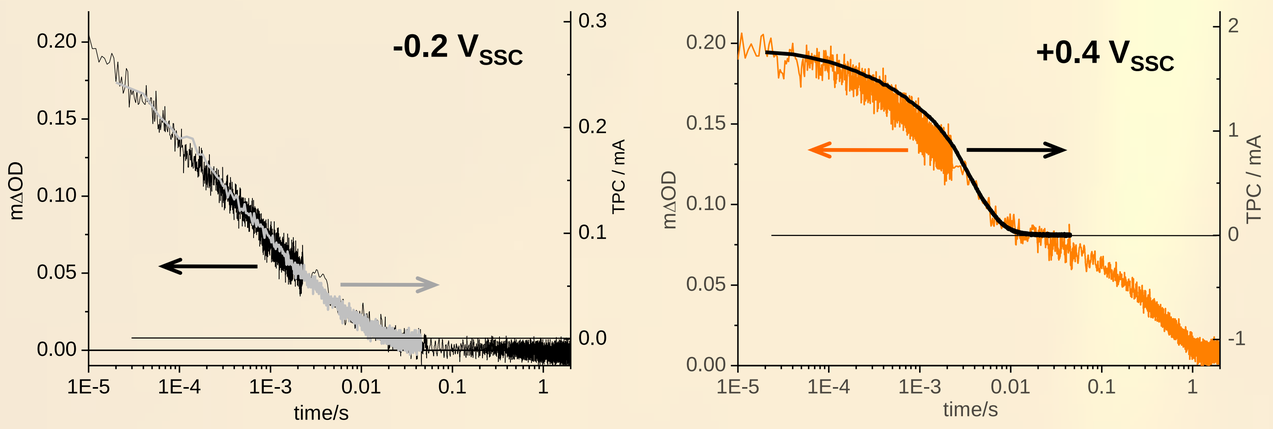

Fig 6: TPC decays (e^-) overlaid on corresponding TA decays (h^+) (355 nm EE excitation, APCVD Si-Fe_2O_3)

- Photogenerated electrons are monitored by transient photocurrent (TPC)
- TPC (e^-) signals very similar to fast phase of transient absorption (h^+) decay (Fig 6)
- Both TPC and fast phase of TA decay dominated by electron-hole recombination
  → transient absorption fast phase and TPC decays have the same shape
- Electron extraction and electron-hole recombination complete by ~20 ms
  → electron extraction >2 orders of magnitude faster than water oxidation
- Long-lived hole population (TA slow phase amplitude) limited by electron-hole recombination[8] at timescales <20 ms
- Significant recombination very likely occurs faster than the timescale of our TA measurements (i.e. <1 µs), particularly at negative bias

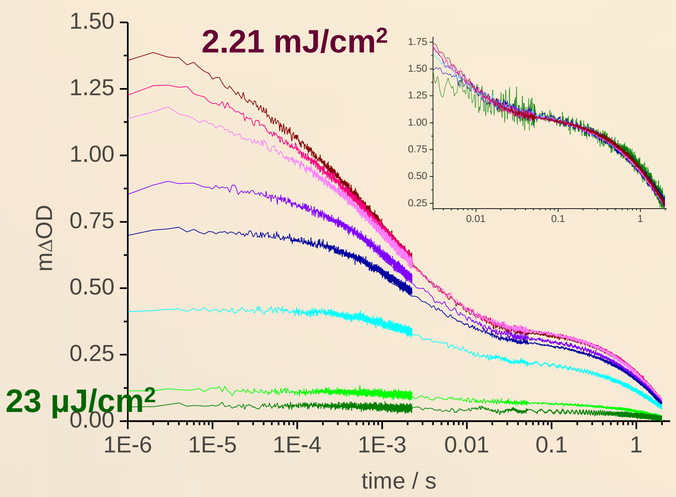

Fig 7: TA h^+ decay as a function of excitation intensity (charge carrier density) at +0.4 V_{SSC} .
Inset: normalised slow phase TA decay.

Excitation intensity dependence

- increasing excitation (charge carrier) density increases the TA fast phase decay rate
  → increases recombination rate
- Decay dynamics at two lowest excitation densities almost identical
  → approaching pseudo-first-order recombination
- water oxidation timescale is independent of hole density (excitation intensity; inset Fig 7)
  → RDS of water oxidation mechanism is a single-hole transfer step, to surface-bound or electrolyte water species,
  i.e. *not* concerted 4-hole oxidation mechanism

Concluding remarks

- Charge carrier dynamics in hematite photoanodes are strongly dependent on electron density (controlled by bias and excitation intensity)
- Electron-hole recombination and electron extraction occur significantly faster than water oxidation; the recombination rate increases with increasing electron density
- There is a strong, quantitative correlation between long-lived hole population and photocurrent – limited by electron-hole recombination
- water oxidation timescale is independent of hole density, indicating RDS is a single-hole transfer, not concerted 4-hole mechanism
- optimisation efforts should concentrate on reducing recombination and/or increasing the rate of electron extraction to the external circuit

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