

## Introduction to Solar Hydrogen

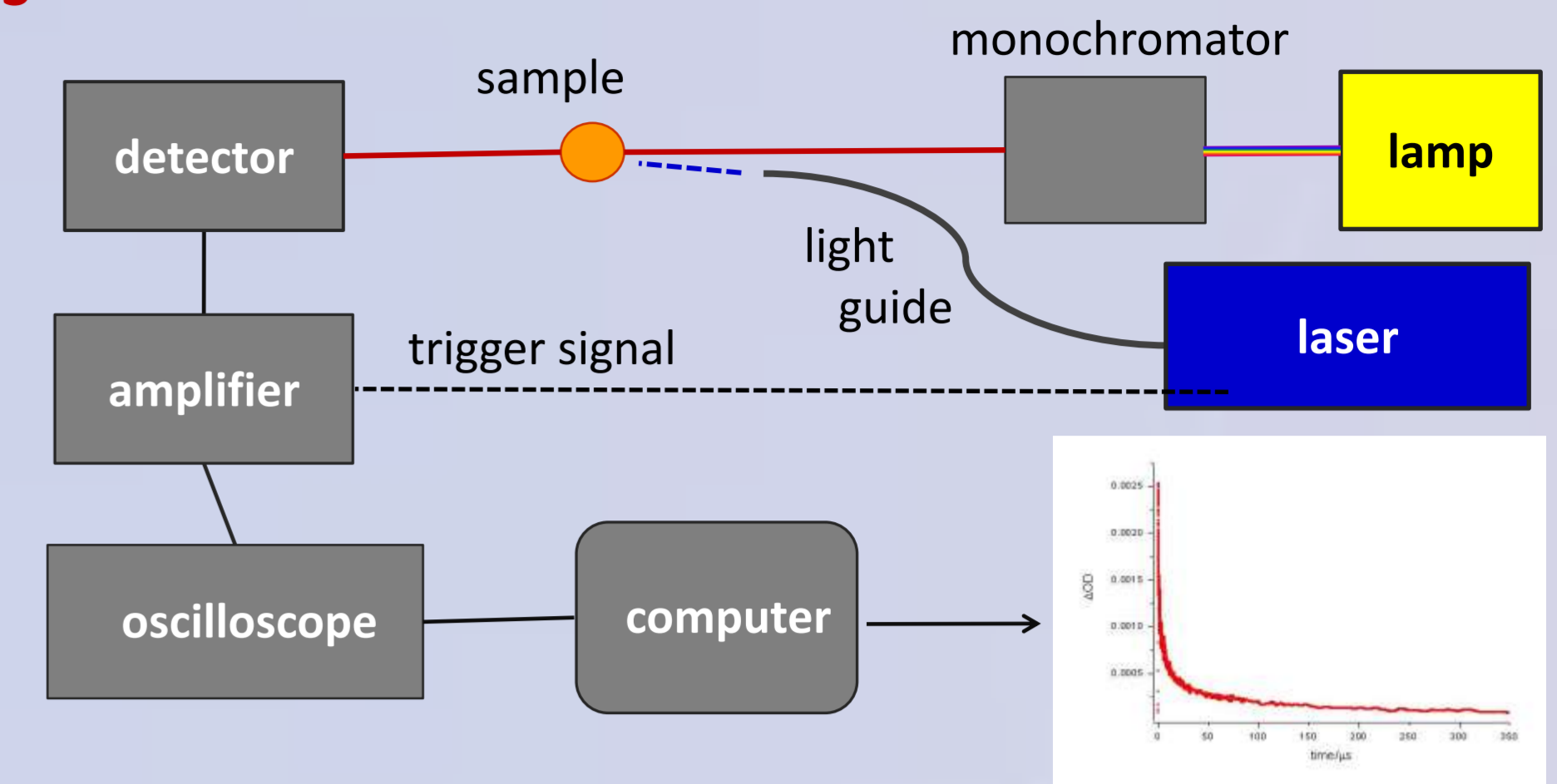
Photoelectrochemical solar hydrogen generation, using a semiconductor photoelectrode such as  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , or  $\text{WO}_3$ , has the potential to directly split water using sunlight, providing a renewable source of hydrogen. Such "solar hydrogen" could be used as a fuel for fuel cells, or as a feedstock. Ideally, the semiconductor should have  $E_g > 1.23$  eV which straddles the  $\text{H}_2\text{O}/\text{O}_2$  and  $\text{H}^+/\text{H}_2$  redox potentials.

## Transient Absorption Spectroscopy - probing photogenerated charge carriers

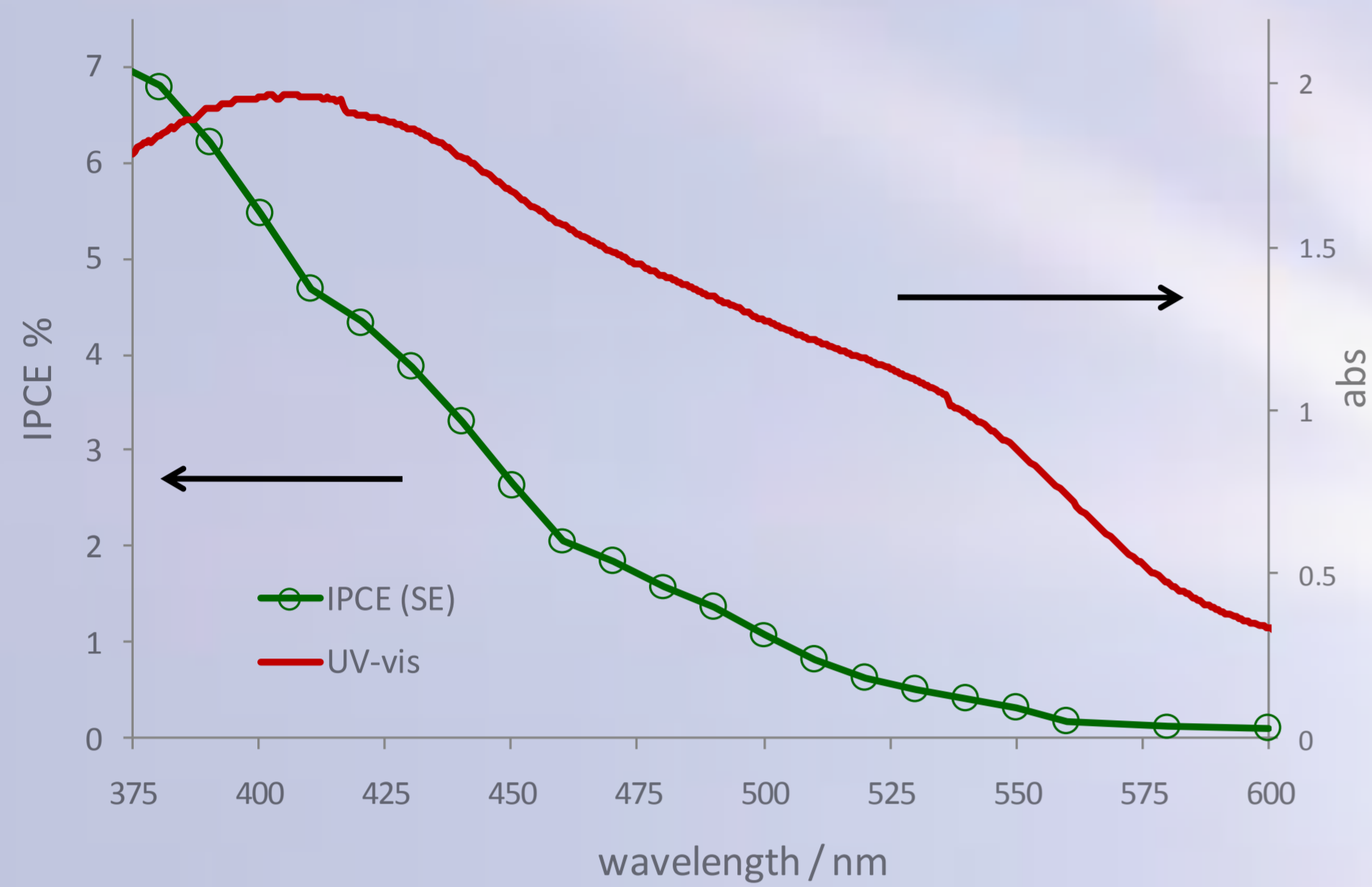
TAS is a pump-probe technique:

1. Sample is irradiated with short, intense pulse of light ("pump"), e.g. a laser pulse, to excite electrons across the semiconductor band gap.
2. Resultant changes in sample's optical density ( $\Delta\text{OD}$ ), caused by light absorption by photogenerated charge carriers, are observed by monitoring the transmission of a second, weaker light ("probe"), e.g. from a tungsten lamp

The resulting  $\Delta\text{OD}$  transient signals allow the trapping, recombination and reaction of photogenerated charge carriers to be probed on timescales of picoseconds to seconds, depending on the TA system employed.



## UV-vis and IPCE



**Fig 1:** Absorption (red) and IPCE (green; SE illumination, at +0.4 V vs Ag/AgCl in 0.1M NaOH, equivalent to +1.4 V vs RHE) spectra for undoped APCVD  $\alpha\text{-Fe}_2\text{O}_3$  films.

## Iron Oxide - an Introduction

Although undoped  $\text{Fe}_2\text{O}_3$  absorbs visible light, it has very low efficiency:

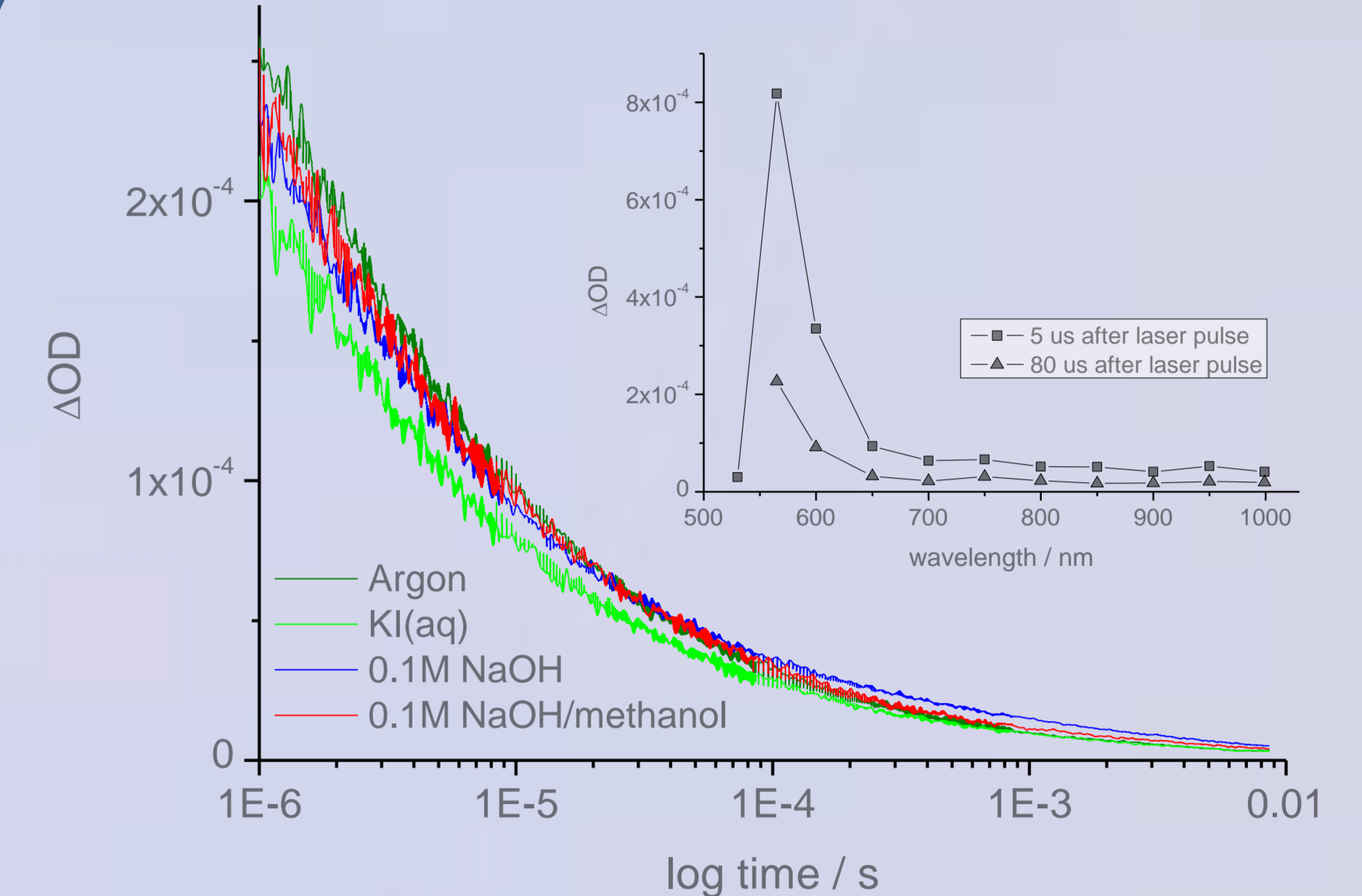
### Advantages:

- absorption spectrum well-matched to solar spectrum: absorption edge  $\sim 600$  nm – can absorb 38% of sunlight, unlike  $\text{TiO}_2$ , which can only absorb 4% of sunlight<sup>1</sup>
- $E_g = 2.0\text{-}2.2$  eV – optimal band gap for solar photolysis<sup>2</sup>
- stable under photolysis conditions
- non-toxic, abundant and cheap

### Disadvantages:

- narrow d-bands result in poor charge carrier mobilities and rapid charge carrier recombination,<sup>3</sup> resulting in low photocurrent and poor efficiency
- slow surface kinetics<sup>4</sup>
- conduction band edge lies below  $\text{H}^+/\text{H}_2$  redox potential - applied bias necessary for  $\text{H}_2$ -evolution

## Hole scavengers - no effect on TA decays

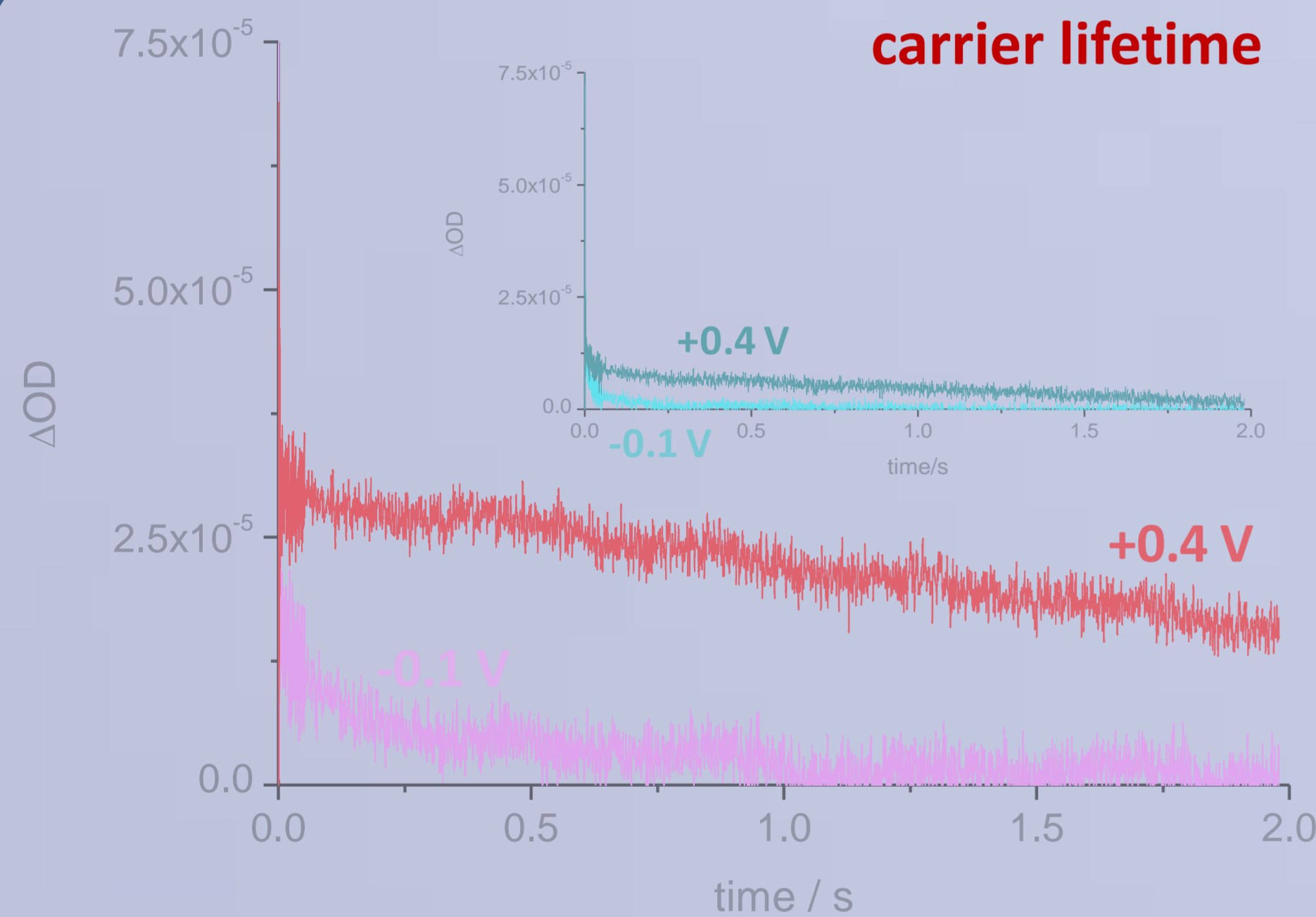


**Fig 2:** TA decays probed at 580 nm (excitation pulse: 337 nm, 0.19  $\text{mJ cm}^{-2}$ , 2 Hz, SE illumination) for  $\text{Fe}_2\text{O}_3$  in argon and with various hole-scavengers; decays probed at 900 nm are similarly unaffected by scavengers. Inset: TA spectrum in argon.

## Discussion: $\text{Fe}_2\text{O}_3$ charge carrier dynamics dominated by bulk recombination

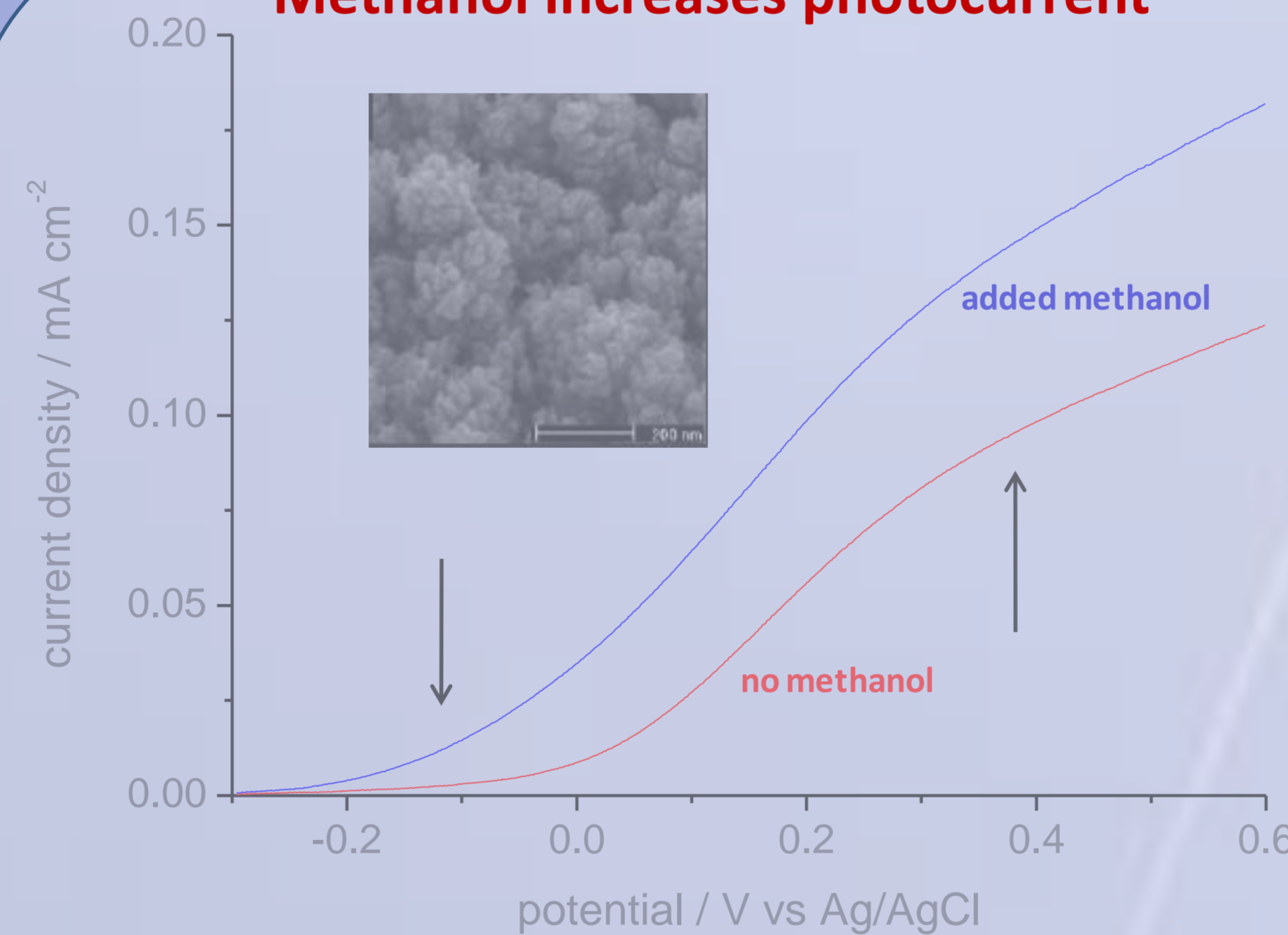
- Hole scavengers - such as methanol and iodide - are expected to be oxidised at the semiconductor surface, causing a reduction in the lifetime of transient decays in the region of the TA spectrum associated with absorption by trapped holes. This results in a change in shape of the TA spectrum.
- However, without applied bias, neither the  $\text{Fe}_2\text{O}_3$  TA decay dynamics nor the TA spectrum change in the presence of hole-scavengers (Fig 2). This indicates that oxidation of scavengers at the  $\text{Fe}_2\text{O}_3$  surface does not compete with charge recombination.
- Iron oxide is an n-type semiconductor with high donor density ( $10^{18}\text{-}10^{21}$   $\text{cm}^{-3}$ , depending on preparation method), and is thought to have a very short hole diffusion length (2-4 nm;  $\sim 20$  nm). It is possible that  $\text{Fe}_2\text{O}_3$  charge carrier dynamics are dominated by bulk electron-hole recombination, due to iron oxide's high electron density.

## TAS + bias: positive bias increases carrier lifetime



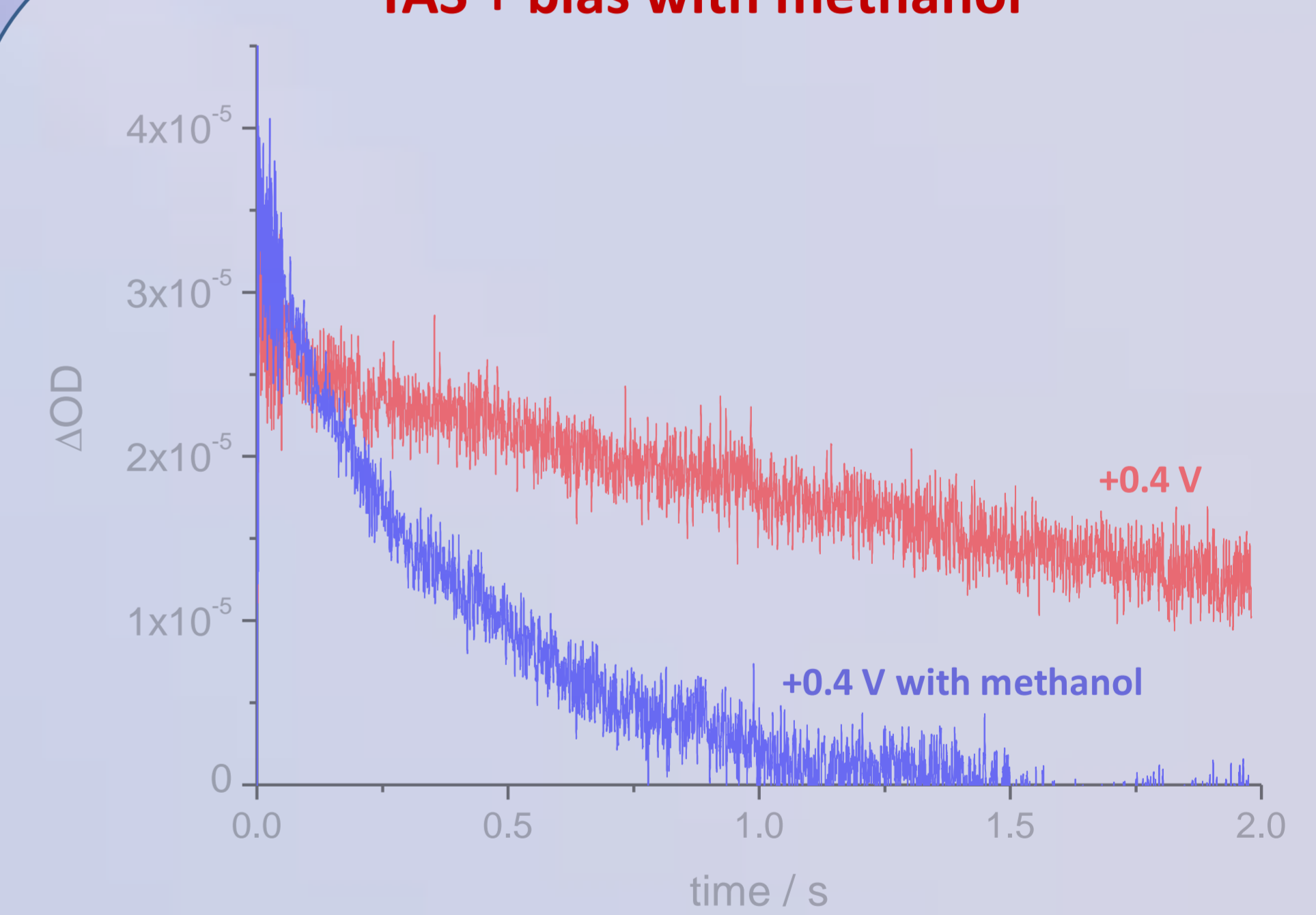
**Fig 3:** TA decays of  $\text{Fe}_2\text{O}_3$  under applied bias, probed at 580 nm and (inset) 900 nm (excitation pulse: 355 nm, 0.19  $\text{mJ cm}^{-2}$  at  $\text{Fe}_2\text{O}_3$ , SE illumination). 580 nm decay lifetime is increased from microsecond timescale at -0.1 V vs Ag/AgCl, to seconds timescale at +0.4 V. A much smaller increase in lifetime is seen at 900 nm.

## Methanol increases photocurrent



**Fig 4:** Photocurrent/voltage curves for APCVD  $\alpha\text{-Fe}_2\text{O}_3$  in 0.1M NaOH (vs Ag/AgCl); dark current is negligible. Addition of methanol results in significant photocurrent increase from  $\sim 0.1$   $\text{mA cm}^{-2}$  to 0.15  $\text{mA cm}^{-2}$ , and cathodic shift of onset potential by  $\sim 100$  mV. Inset: SEM image of APCVD  $\text{Fe}_2\text{O}_3$  film showing nanostructure<sup>5</sup>

## TAS + bias with methanol



**Fig 5:** TA decays of  $\text{Fe}_2\text{O}_3$  at +0.4 V vs Ag/AgCl in 0.1 M NaOH, probed at 580 nm (excitation pulse: 355 nm, 0.19  $\text{mJ cm}^{-2}$  at  $\text{Fe}_2\text{O}_3$ , SE illumination). Without methanol, the TA decay has a lifetime on the seconds timescale; methanol causes attenuation of the lifetime to 100s of milliseconds.

## Discussion: effect of applied bias

- Application of positive bias to  $\text{Fe}_2\text{O}_3$  results in an increase in TA decay lifetime, particularly in the  $\sim 580$  nm region (Fig 3), suggesting that this region of the TA spectrum may be due to absorption by trapped holes. Further evidence for this assignment is provided by the effect of methanol on the TA decay lifetime in this region (Fig 5).
- Under positive applied bias, addition of methanol to the electrolyte causes an attenuation of the lifetime of the TA decay probed at 580 nm (Fig 4), attributed to oxidation of methanol by trapped holes in  $\text{Fe}_2\text{O}_3$ . (There is no change in decay dynamics under negative applied bias.) This indicates that the timescale of methanol oxidation on nanostructured  $\alpha\text{-Fe}_2\text{O}_3$  is on the order of 100s milliseconds.
- Application of a positive bias to the  $\text{Fe}_2\text{O}_3$  film lowers the Fermi level, reducing the occupancy of conduction band/trap states by electrons. This reduction in the electron density of the film decreases the rate of electron-hole recombination (as observed in dye-sensitised solar cells<sup>8</sup>), increasing the hole diffusion length and allowing oxidation of scavengers to become competitive with electron-hole recombination (Fig 6).

## Concluding remarks

- Iron oxide is dominated by bulk recombination, such that oxidation of scavengers at the surface does not compete with electron-hole recombination.
- Positive applied bias is necessary to reduce the electron density and so increase hole diffusion length, increasing the hole lifetime (probed at 580 nm) from a timescale of microseconds to seconds.

## References

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**Fig 6:** schematic representation of occupation of conduction band/trap states of  $\text{Fe}_2\text{O}_3$  and the effect of applying a positive bias. This situation occurs either within the depletion region at the surface of the iron oxide nanoparticles, or - more likely - throughout the nanoparticles if the nanoparticle diameter is smaller than the width of the space-charge layer (i.e. no band bending occurs). Application of a positive bias lowers the Fermi level, reducing the occupation of electron-trap states and hence reducing the rate of electron-hole recombination.

