Kinetic studies of Water and Methanol Oxidation on α-Fe₂O₃ Photoanodes by Photo-Induced Absorption Spectroscopy

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Introduction

Hematite (Figure 1) has emerged as a promising photoanode material for photoelectrochemical (PEC) hydrogen production.[1] However, α-Fe₂O₃ has a limited efficiency due to fast electron-hole recombination and slow water oxidation kinetics.[2] In this poster, a hole scavenger, methanol, is used as alternative oxidation reaction in the photoanode in order to improve the oxidation kinetics on α-Fe₂O₃. Additionally, a recent paper by Hamann and co-workers.[3] showing a competition between methanol and water oxidation reactions on hematite is discussed.

Figure 1. SEM of APCVD α-Fe₂O₃

Methanol and water oxidation kinetics are studied by photoelectrochemical (CV and transient photocurrent) and optical spectroscopic measurements (PIAS, scheme shown in Figure 2). A model describing the kinetics[4] of the methanol oxidation reaction under different applied bias by photogenerated holes is introduced and proposed methanol oxidation mechanisms (Figure 3) are discussed.
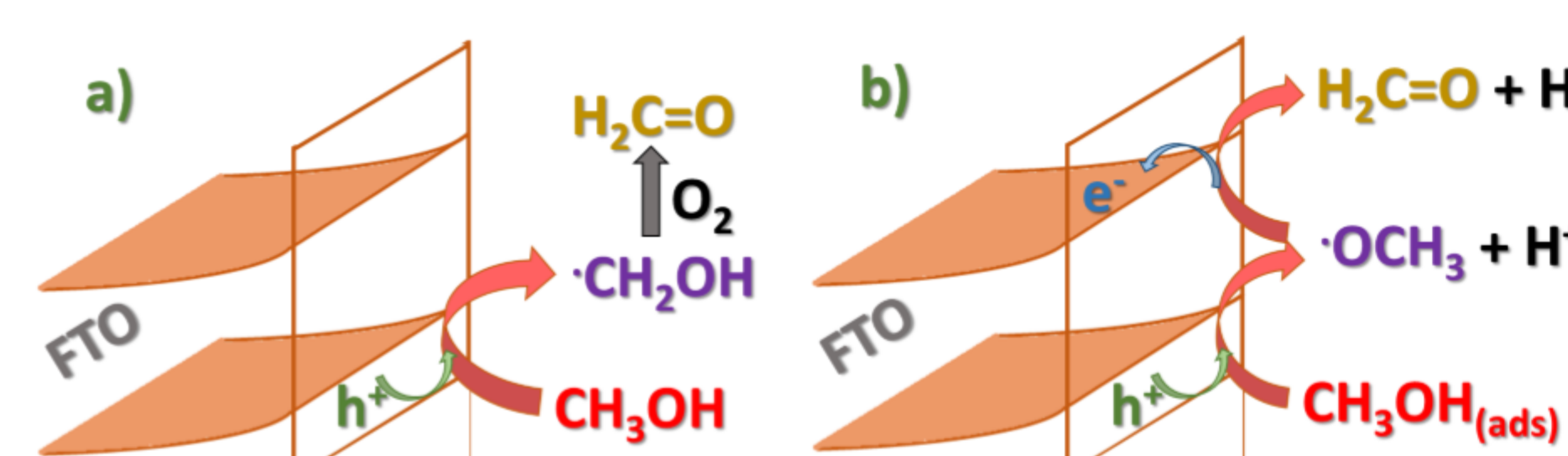
In mechanism a), methanol is adsorbed and oxidised to a hydroxymethyl radical which is further oxidised by oxygen (1 hole transfer process).[5]

In mechanism b), methanol is adsorbed and then oxidised on the surface of the photoanode to formaldehyde, through the methyloxy radical species. (1 hole transfer and photocurrent doubling process).[3,6]

Figure 3. Methanol oxidaiton mechanisms proposed
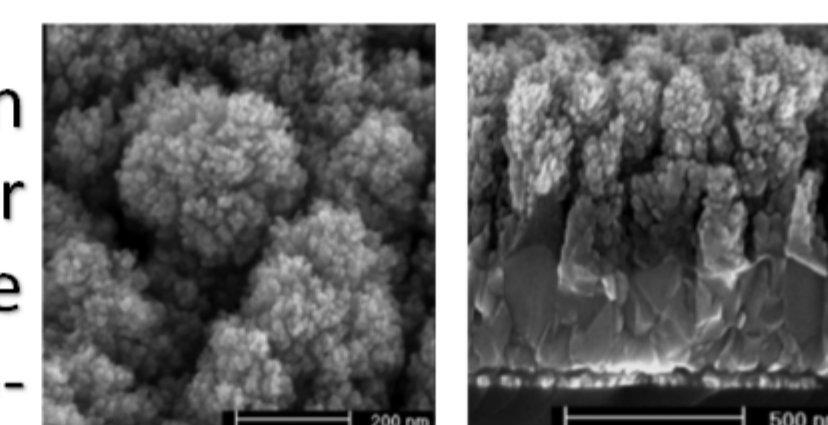
Scheme of photo-induced absorption spectroscopy (PIAS)

- Time-resolved pump-probe technique
- Monitors the formation and decay of photogenerated excited species, with characteristic spectral fingerprints
- PIAS pump pulse (water/methanol oxidation conditions — long-lived holes): 365nm LED light pulses with approximately 5s on/5s off
- Probe: continuous monochromatic light (650nm) passing through the α-Fe₂O₃ photoanode
- Transient photocurrent (TPC): measures the flux of electrons extracted from the photoanode across a resistor set between the counter-electrode and the potentiostat
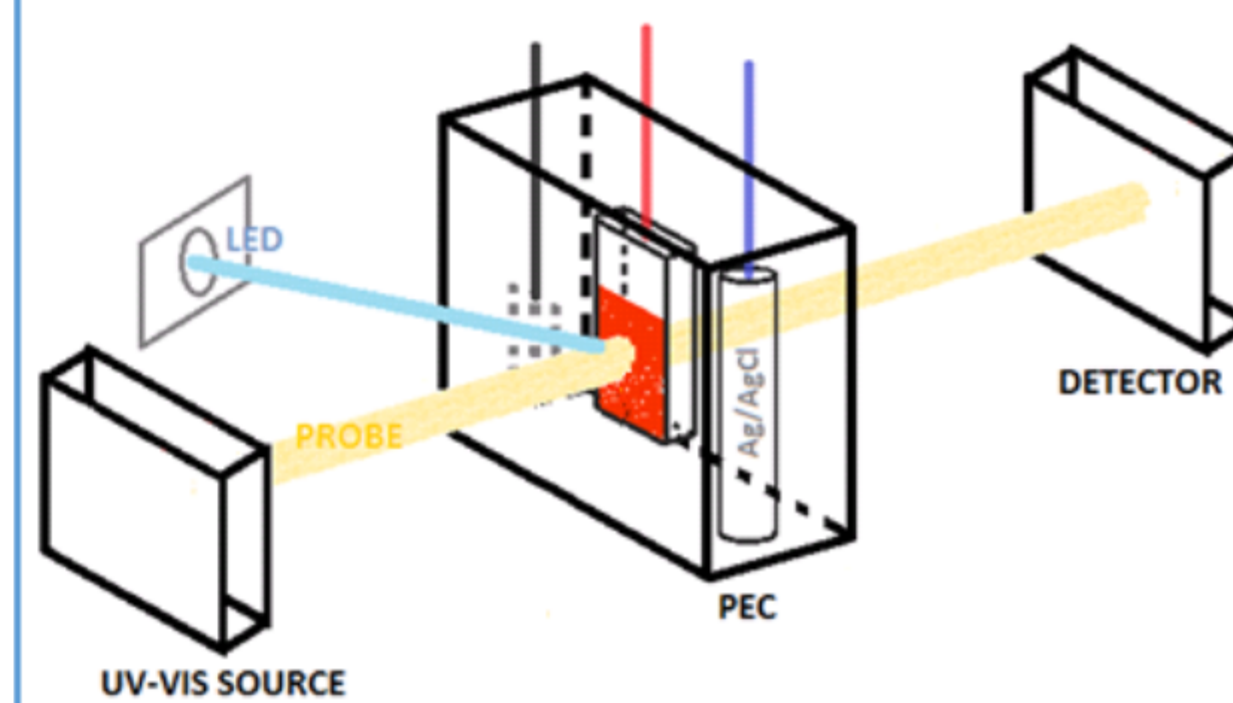

Figure 2. PIAS/TPC Set-up

1. Photo-electrochemistry

- Methanol oxidation requires a smaller driving force compared to water oxidation
- At 0.00 V: no contribution of water oxidation and at 0.55 V competition of water and methanol oxidation is observed (< 90% methanol in electrolyte) in agreement to Hamann and co-workers[3]
- The photocurrent density is independent of methanol concentration > 90% methanol
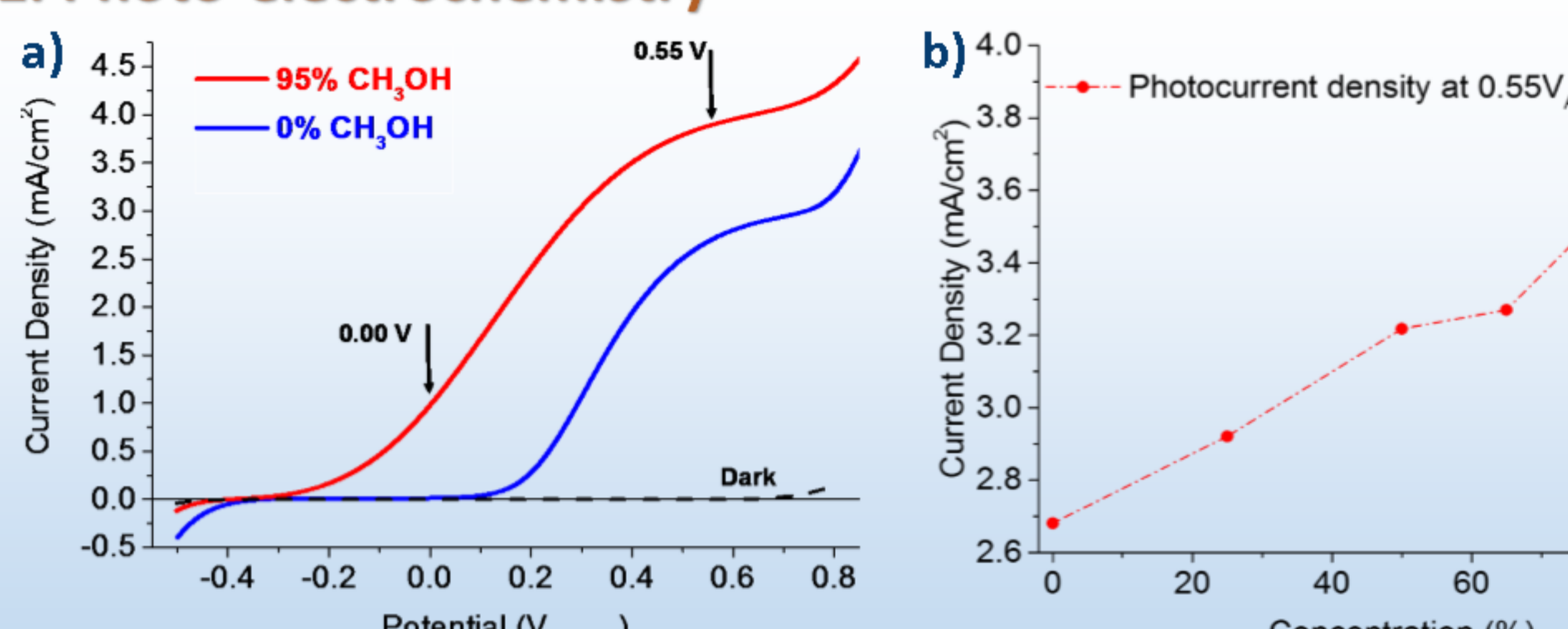- No photocurrent doubling is observed

Figure 4. Photo-electrochemical response of the α-Fe₂O₃ photoanode, a) JV curve under EE illumination conditions, approximately photon flux equivalent to 1 sun, in 0.1M NaOH (blue) and 0.1M NaOH in 95% methanol (red) and dark conditions (black dashed line) at a scan rate of 50mV.s⁻¹, b) Photocurrent density at 0.55 V_Ag/AgCl vs. concentration of methanol in 0.1M NaOH and C) Photocurrent density of 0.1M NaOH in 95% methanol at 0.55 V_Ag/AgCl vs. light intensity

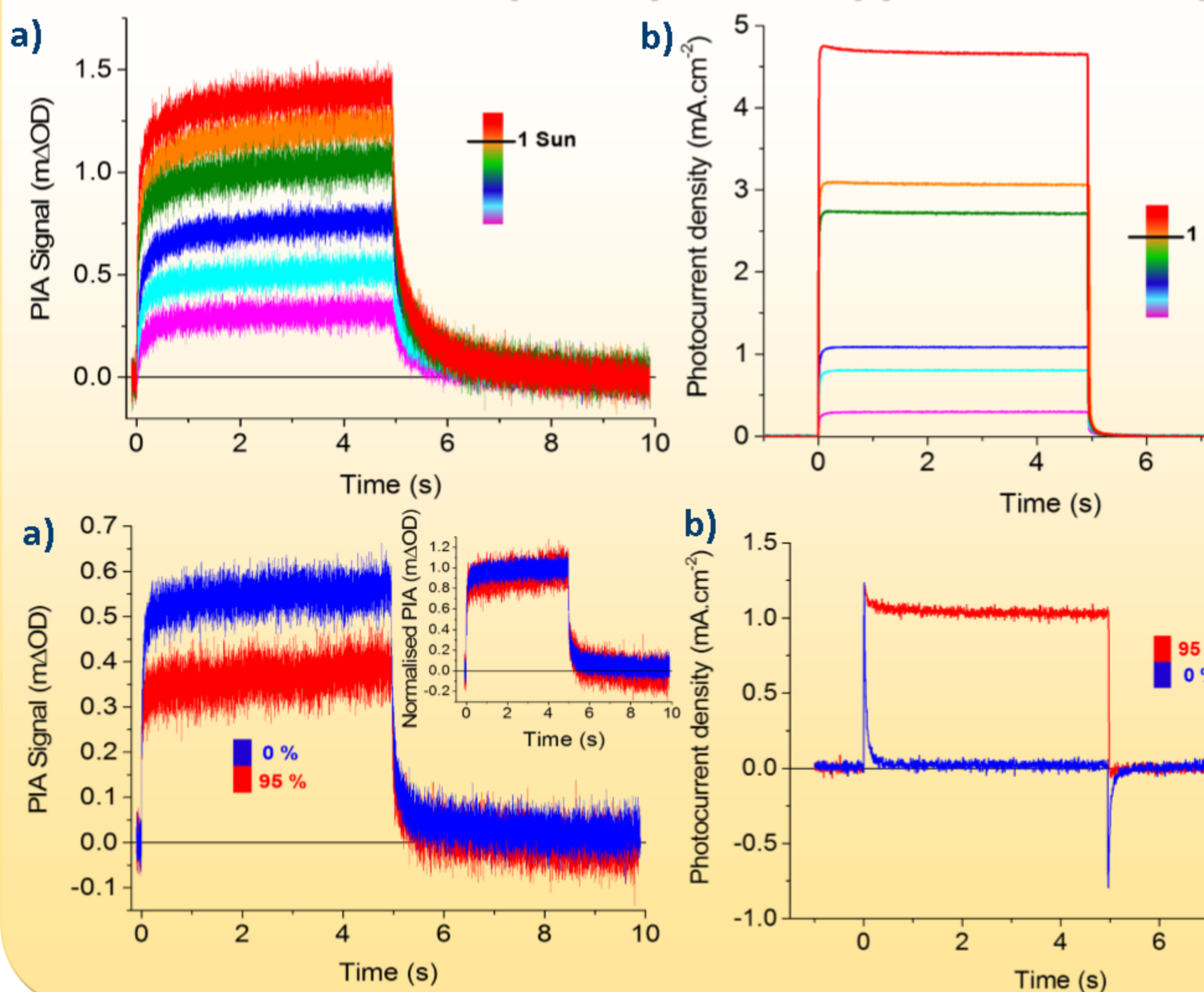## 2. Photo-induced absorption spectroscopy and transient photo-current

Figure 5. Oxidation of methanol under 355nm LED illumination of approximately 0.05–2.8 sun, at an applied potential of 0.55V a) PIA signals for 0.1M NaOH in 95% methanol and b) simultaneous TPC measurement.

- Higher density of holes accumulated when there is no methanol pesent in the electrolyte

Figure 6. Water (0.1 M NaOH—blue trace) and methanol (0.1M NaOH in 95% methanolred) oxidation comparison under approximately photon flux of 1 sun at 0.00 V a) PIA signal and b) TPC measurements
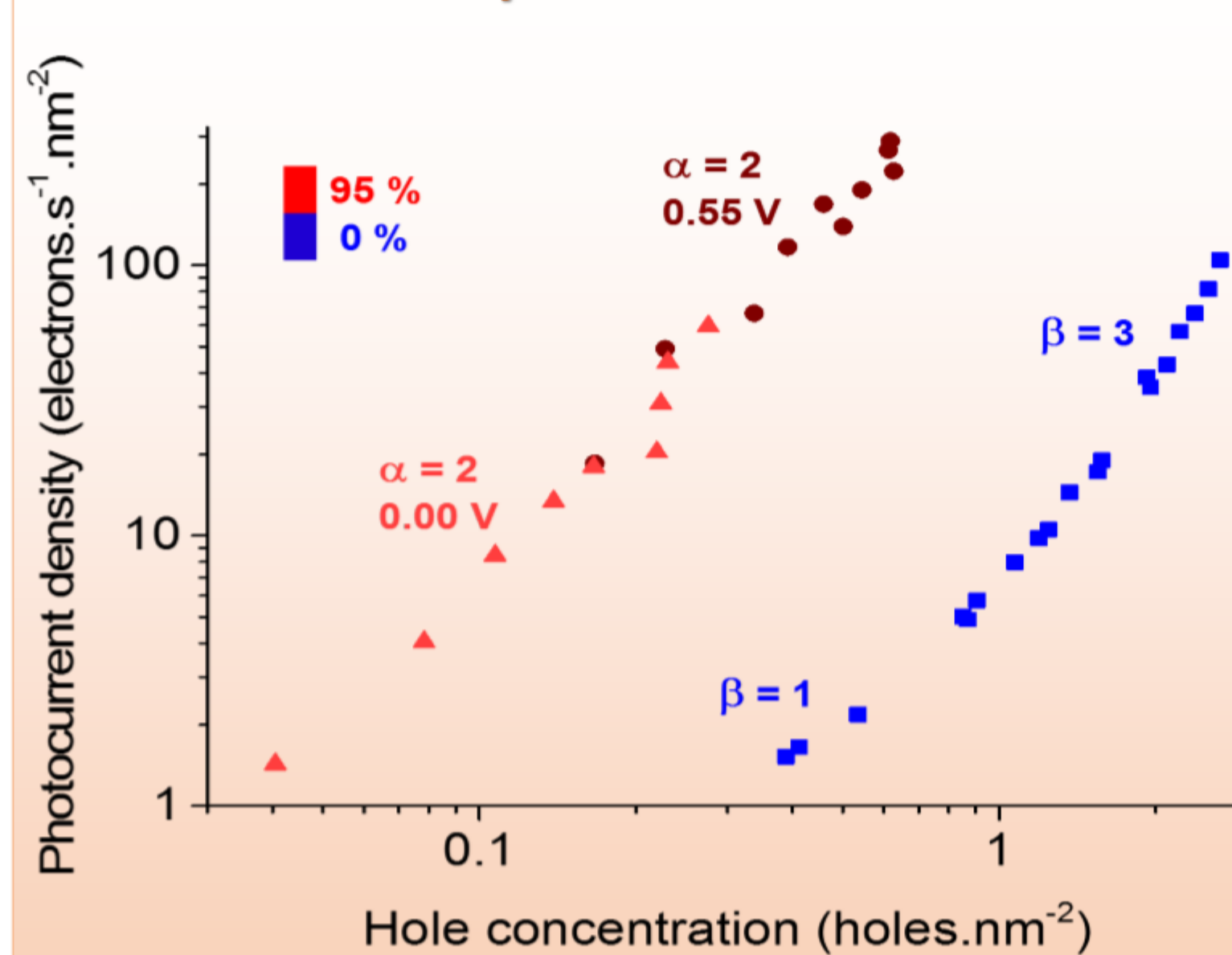
3. Rate Law Analysis

$$\frac{\partial [h]}{\partial t} = J_{holes}{}^{sur} - k_{MeOH}[h]^{\alpha} - k_{WO}[h]^{\beta}$$

$$\frac{\partial [h]}{\partial t} = 0 \, (Steady - State)$$

$$J_{holes}{}^{sur} = k_{MeOH}[h]^{\alpha}$$

Figure 7. Relationship between photocurrent and surface holes density for water oxidation (blue),[4] and for methanol oxidation at an applied potential of 0.00 V (where no water oxidation occurs—light red) and 0.55 V (where a kinetic competition has been investigated[3]—dark red)

- Methanol oxidation requires the accumulation of two holes to overcome its rate limiting step
- Methanol oxidation kinetics are at least one order of magnitude faster than water
- The external applied potential does not change the kinetics of reaction, only supress electron/hole recombination
- **Methanol oxidation rate constant (k_{MeOH}) is independent of the band bending**
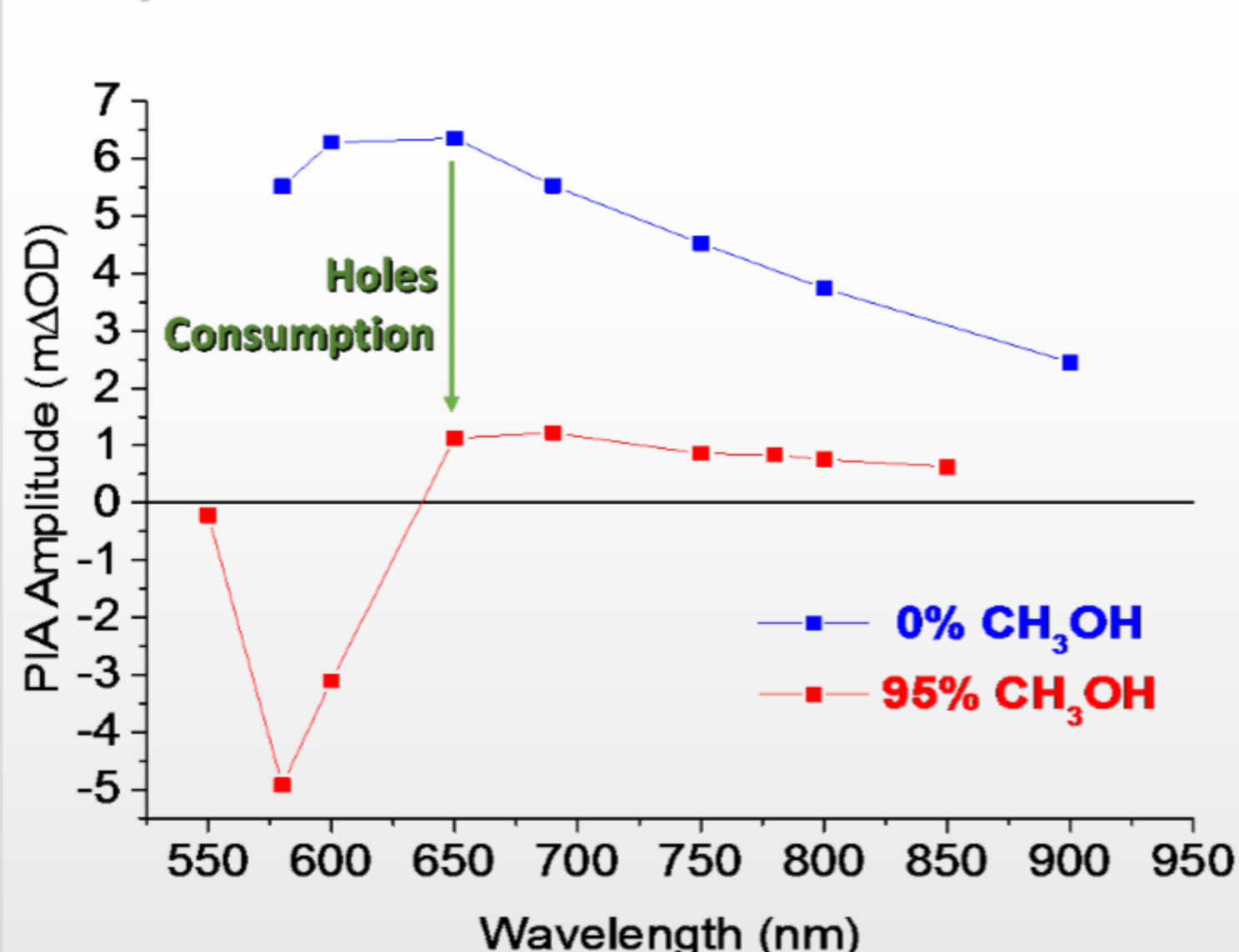
4. Spectral characteristics of holes

Figure 8. Spectral response, under approximately photon flux of 1 sun at 0.00 V and steady-state conditions, of photogenerated holes in α-Fe₂O₃

- Holes accumulated at the surface of hematite have a maximum in absorption around 650nm
- In presence of methanol holes are scavenged at least 10 times faster than in water
- The spectrum (steady-state) in presence of methanol resembles the transient (~100μs) spectrum in water[2]

Concluding remarks

- It has been shown that methanol requires less overpotential to be oxidised producing higher photocurrents compared to water oxidation then methanol can be used as alternative oxidation reaction on hematite for the production of hydrogen
- The competitive oxidation between water and methanol on hematite is controlled by the kinetics of the reactions, in which holes accumulated at the surface react at least 10 times faster with methanol
- The spectral characteristics when methanol is present are similar to the transient spectrum in water at high applied potential, i.e., sames holes, different jobs
- The effect of the applied potential was uniquely to reduce the recombination of electrons and holes resulting in higher photocurrents, i.e., **reaction kinetics are independent of the band bending**
- The order of methanol reaction as a function of density of surface accumulated holes is 2
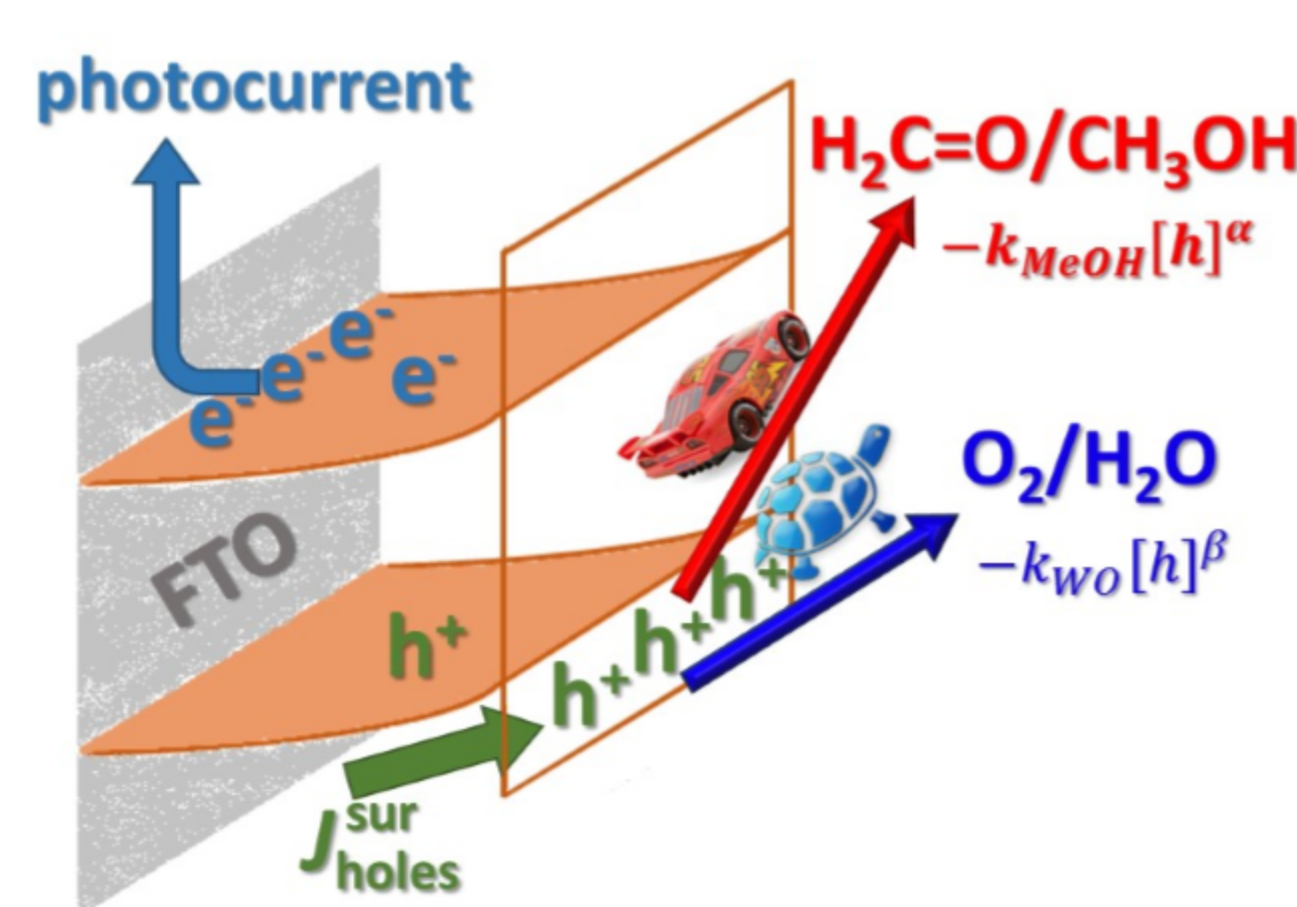
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