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Past, present and future of hematite *(and other metal oxide photoanodes)* ***for solar water splitting***

Dr. Camilo A. Mesa

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Durrant Group

February 25th, 2020

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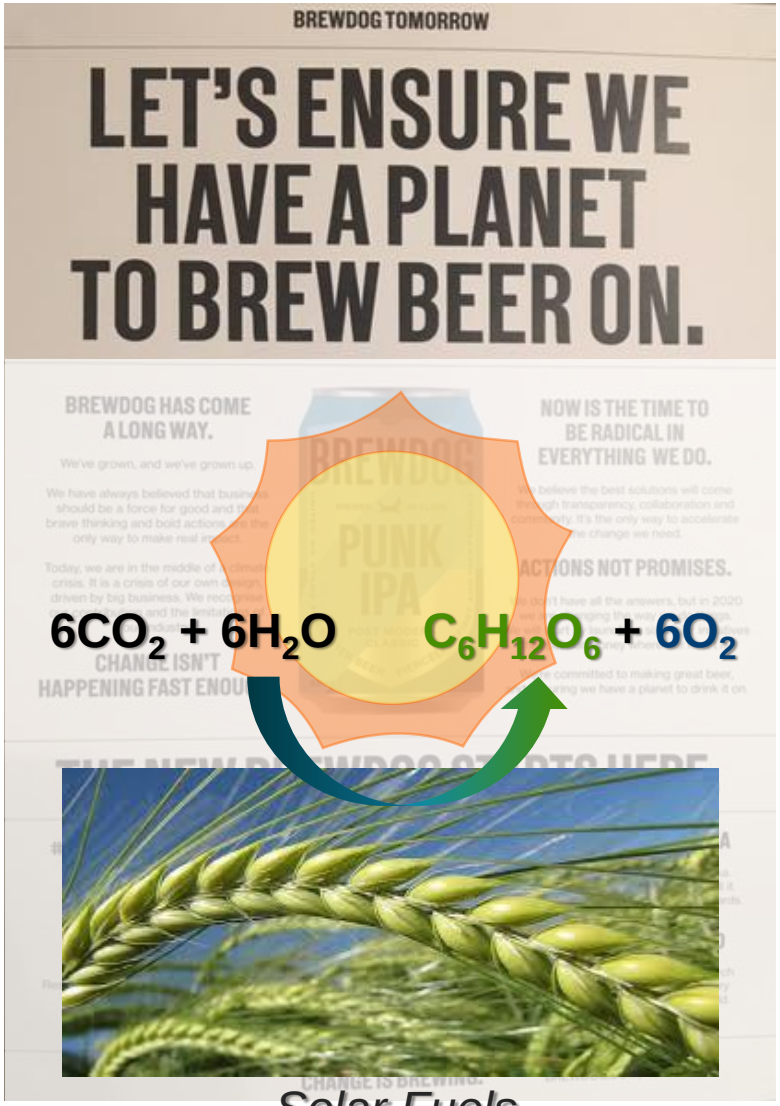
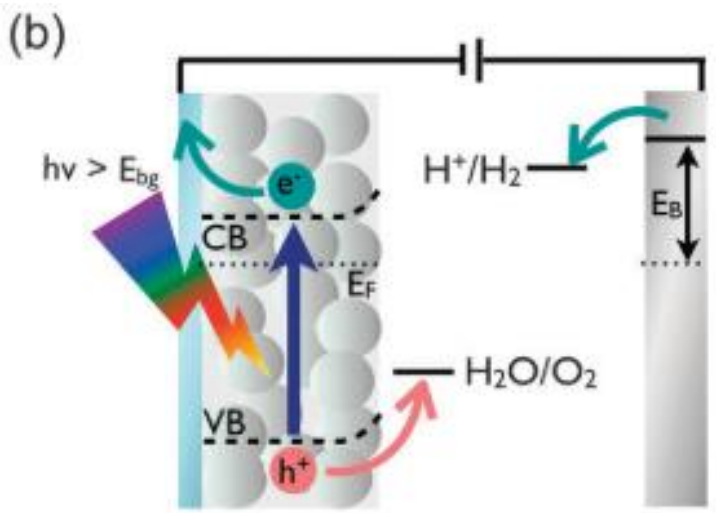
Sustainable Energy (SustE)



Solar Fuels



$2H_2O \rightarrow 2H_2 + O_2$

Photoelectrochemical water splitting

Cowan, A. and Durrant, Chem Soc Rev., 42, 2281, 2013

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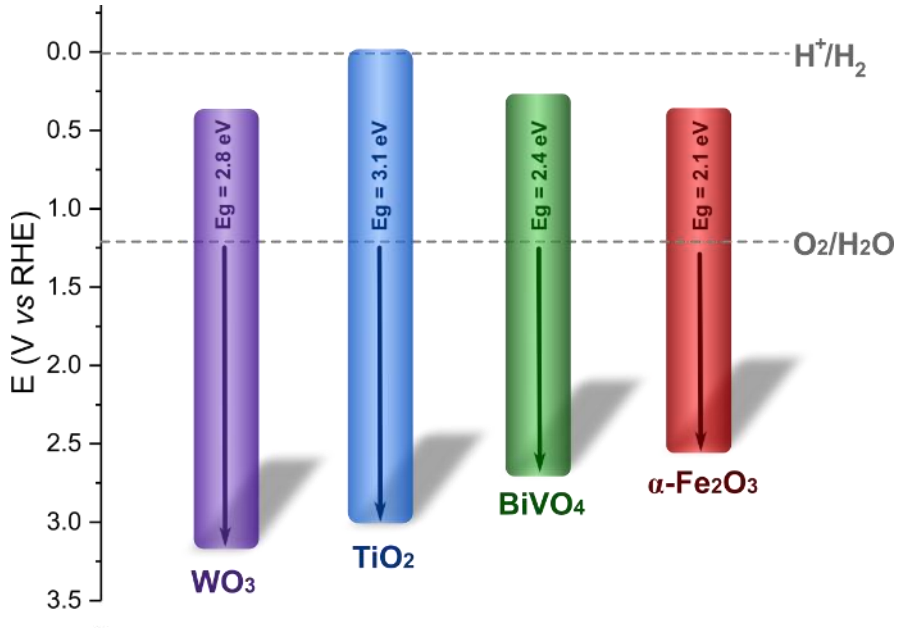
Sustainable Energy Materials (SustEM)



$$2H_2O \rightarrow 2H_2 + O_2$$

Photoelectrochemical water splitting

Corby, S., et. al., JACS, 140, 16168, 2018

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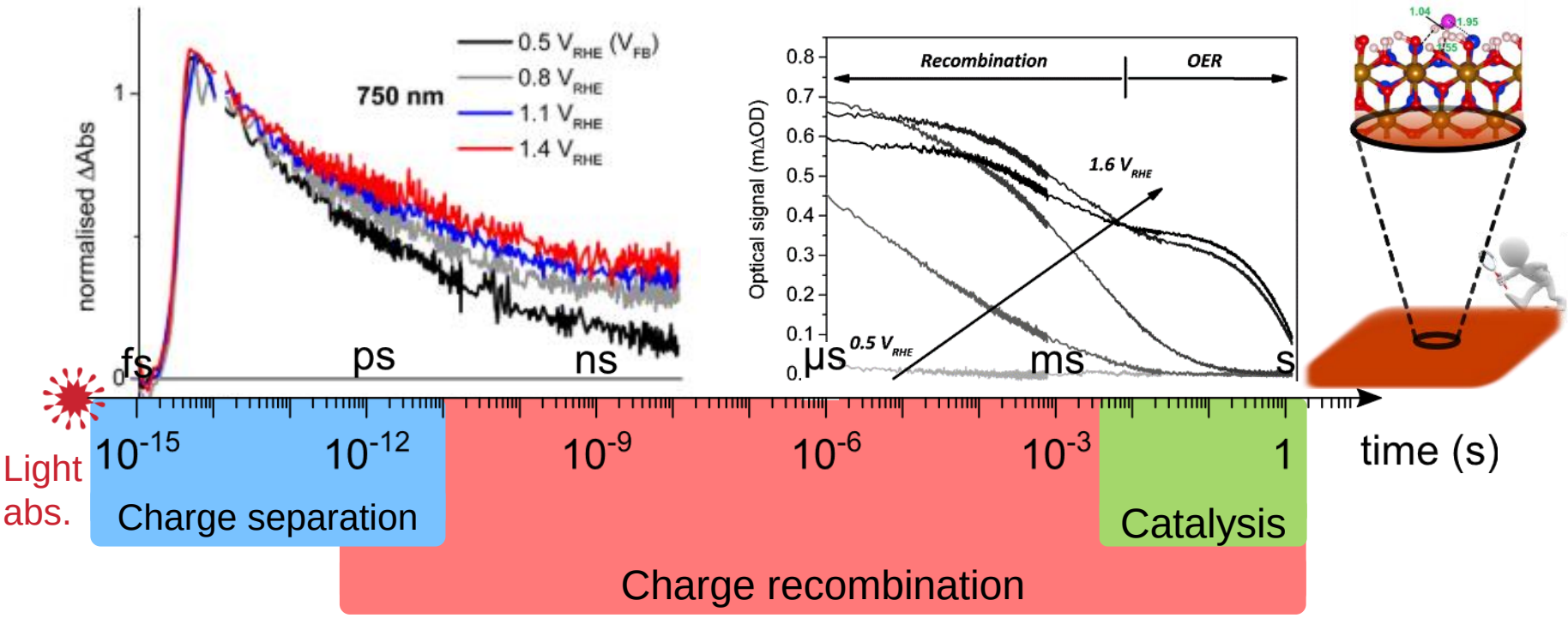
The lifetime challenge
Example of α-Fe_2O_3 photoanodes



Pendlebury, S., et al., JACS.,136, 9854, 2014

Francàs, L., Mesa, C., et. al., Rate law analysis in water splitting photoanodes in: Advances in photoelectrochemical water splitting, RSC, 2018

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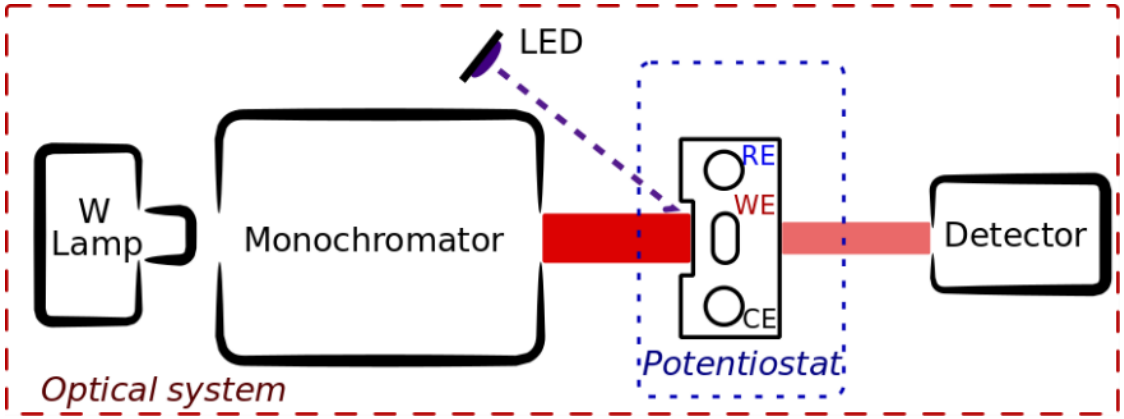
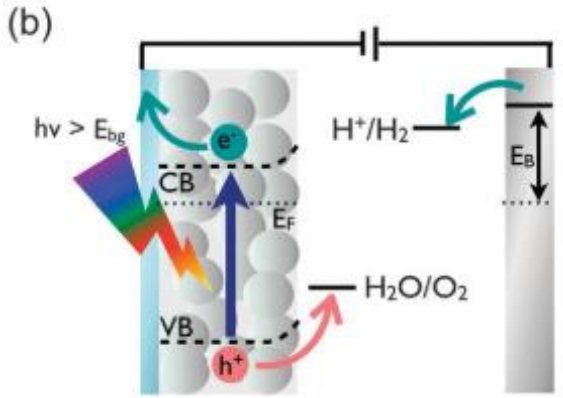
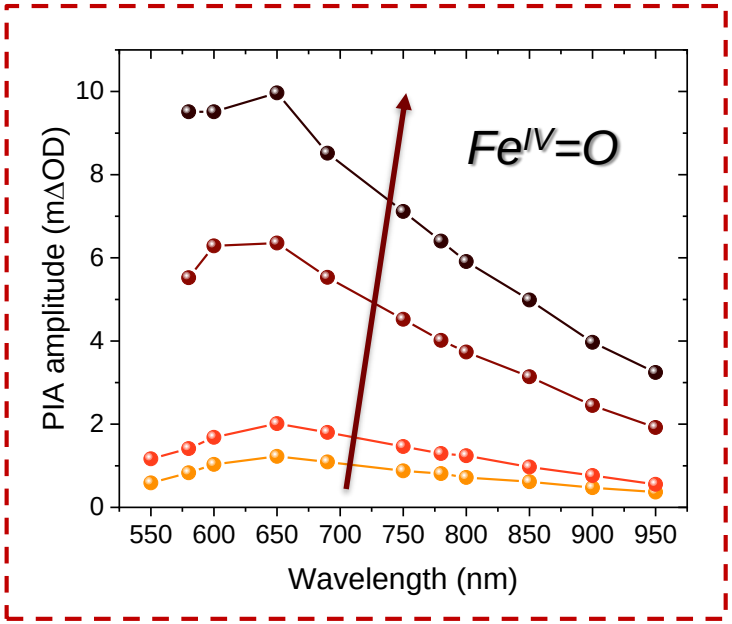
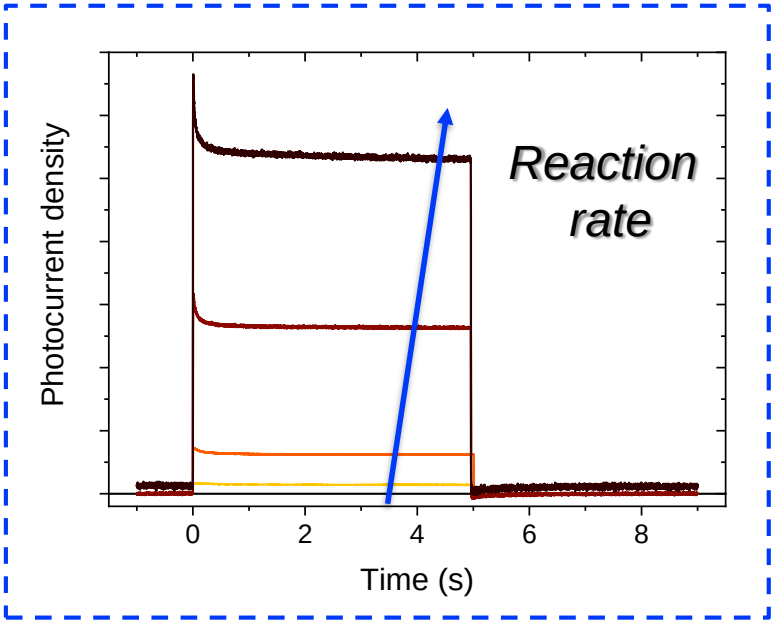
Spectroelectrochemical PIA





Increasing light intensity





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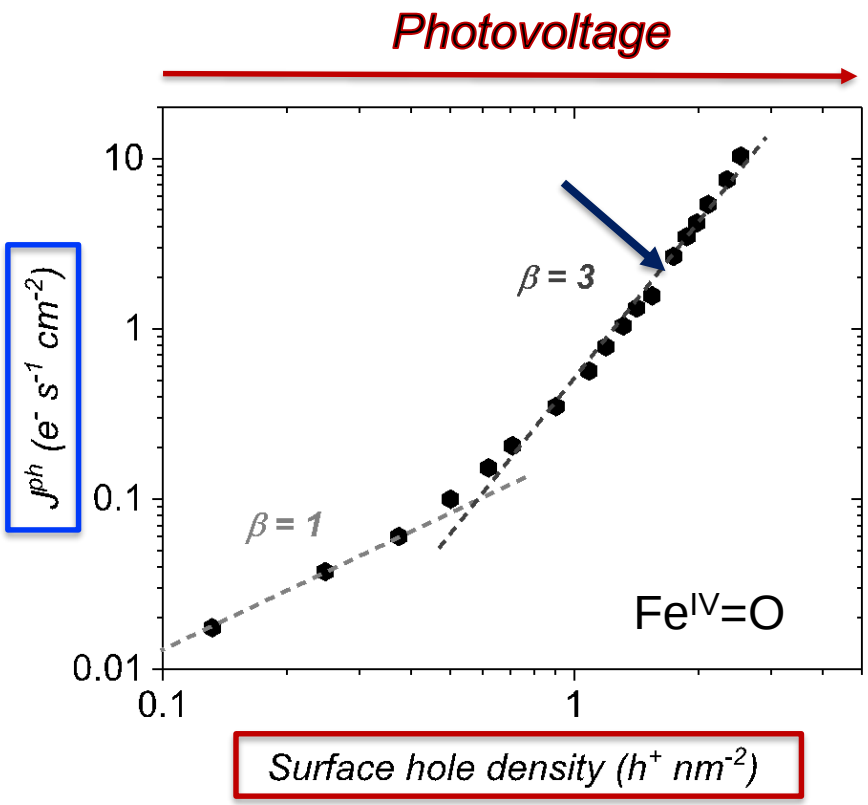
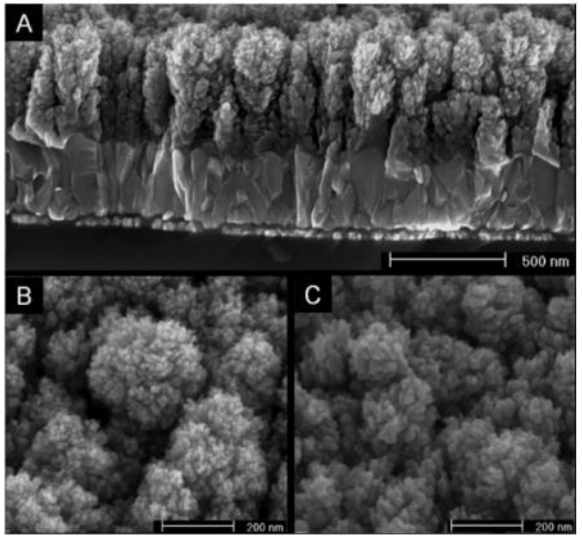
Rate law analysis on APCVD α-Fe_2O_3

$$\log\left(J^{ph}\right) = \beta \cdot log\left(h_s^+\right) + log(k_{WO}) \quad \longleftarrow \quad J^{ph} = k_{WO} \cdot h_s^{+\beta}$$



Le Formal, F. et al., J Am Chem Soc, 2015, 6629



Kay A. et al., JACS, 128, 15714, 2006

Molecular approach

$$3h_s^+ + int^0 \rightleftharpoons int^{+3} + 3H^+$$

$$r = k_{WO} \cdot (h_s^+)^3$$

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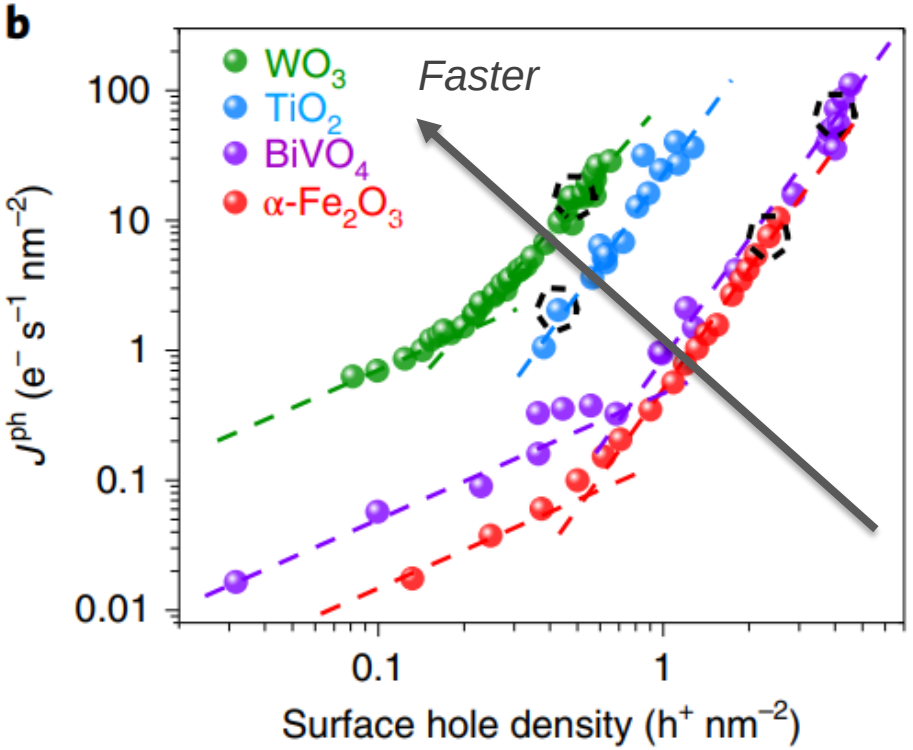
Rate law analysis on other M-O photoanodes



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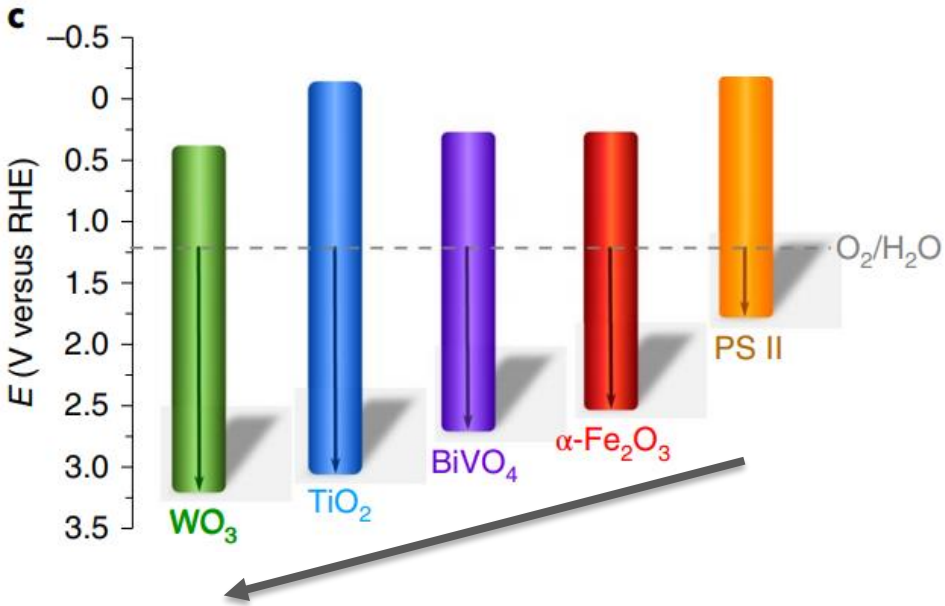

Mesa, C., Francàs, L., et al., Nat. Chem., 12, 82, 2020

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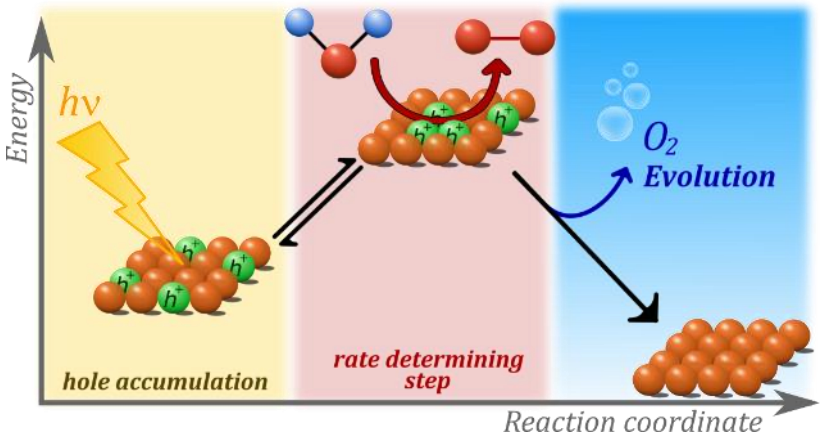
First concluding remark

The studied materials (α-Fe_2O_3, TiO_2, $BiVO_4$ and WO_3) share common oxidative pathways of reaction, based on accumulation of charges, with kinetic differences only associated to the hole redox power



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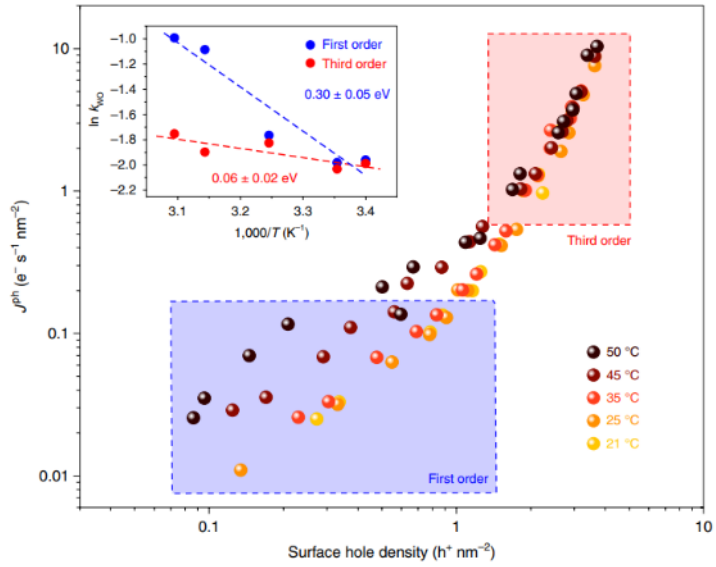
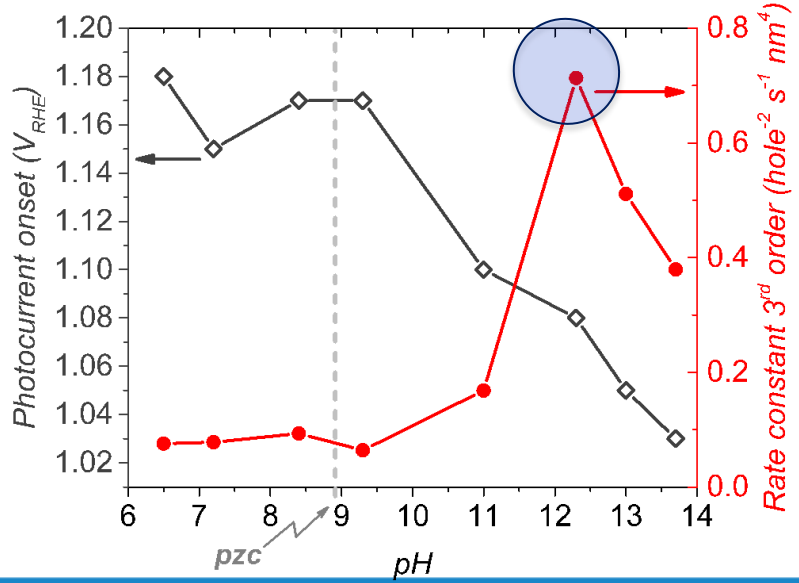
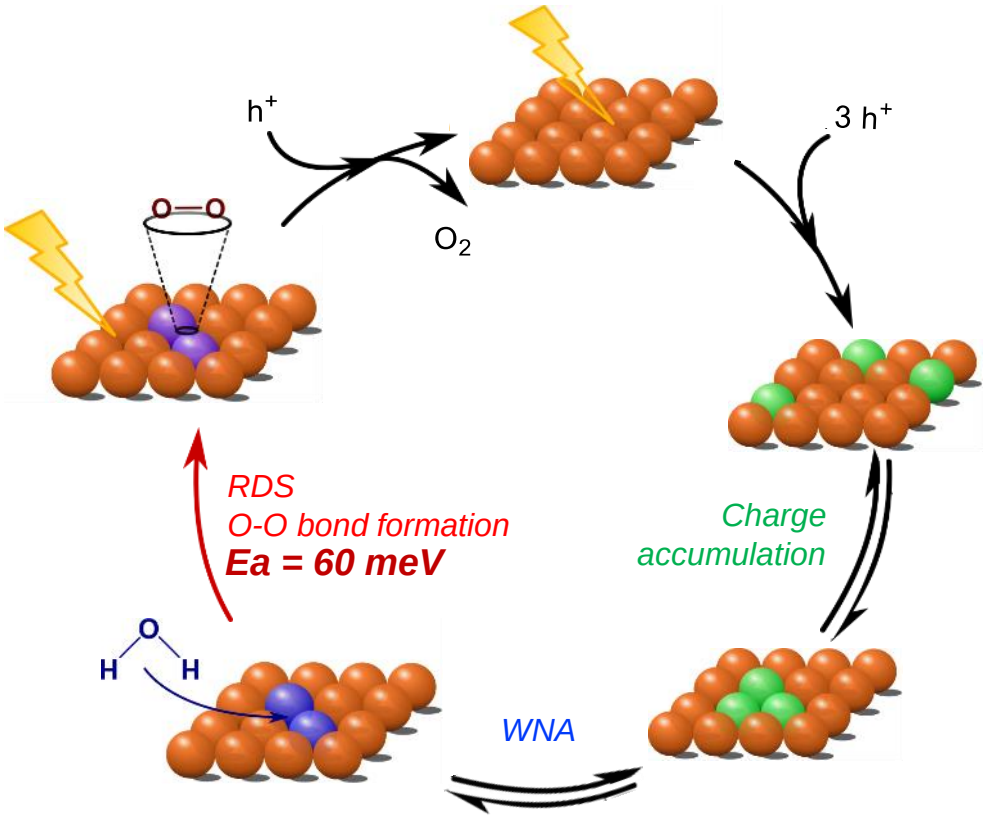
OER mechanism on APCVD α-Fe_2O_3







Mesa, C., Francàs, L., et al., Nat. Chem., 12, 82, 2020

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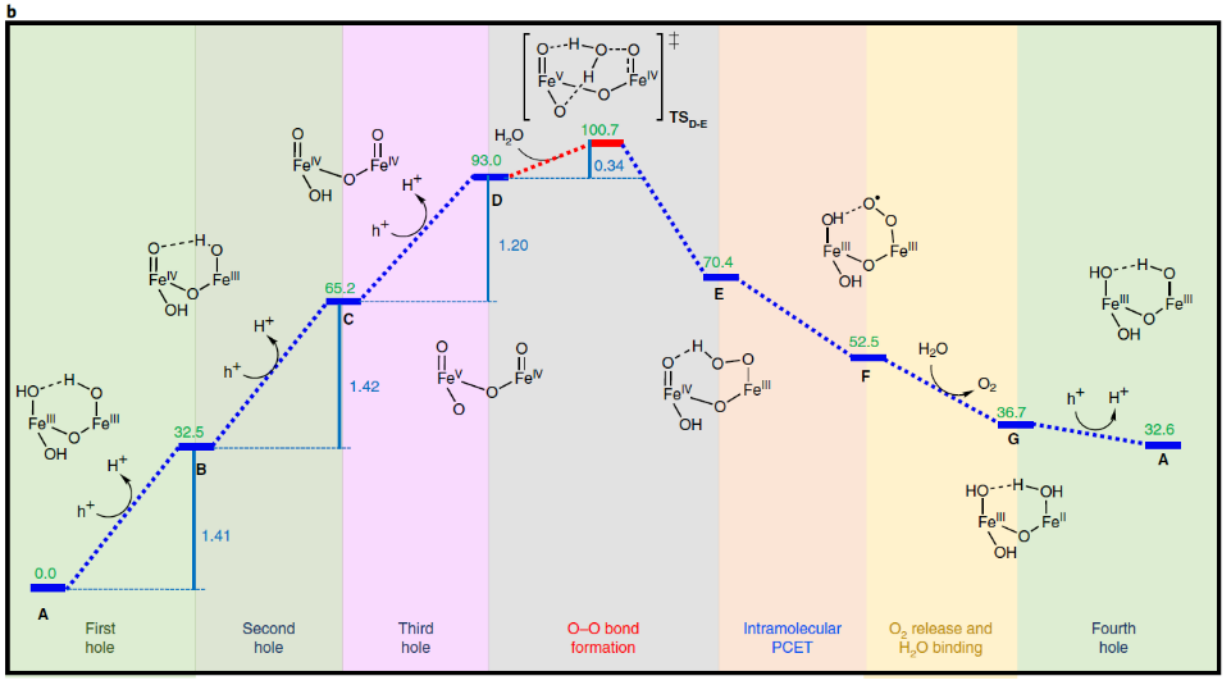
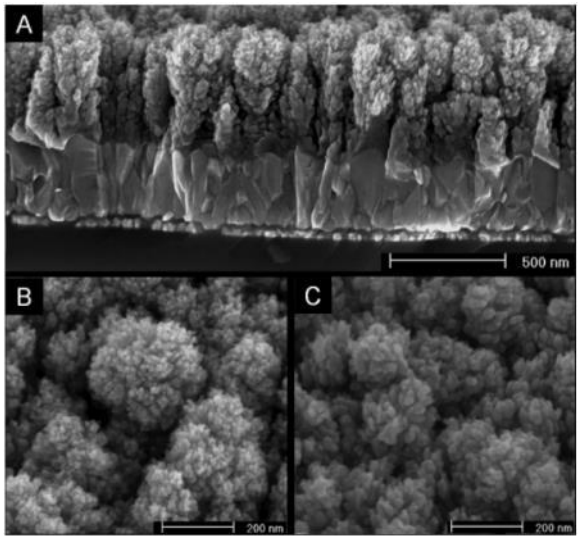
OER mechanism on APCVD α-Fe_2O_3

Morphology effect?





Mesa, C., Francàs, L., et al., Nat. Chem., 12, 82, 2020

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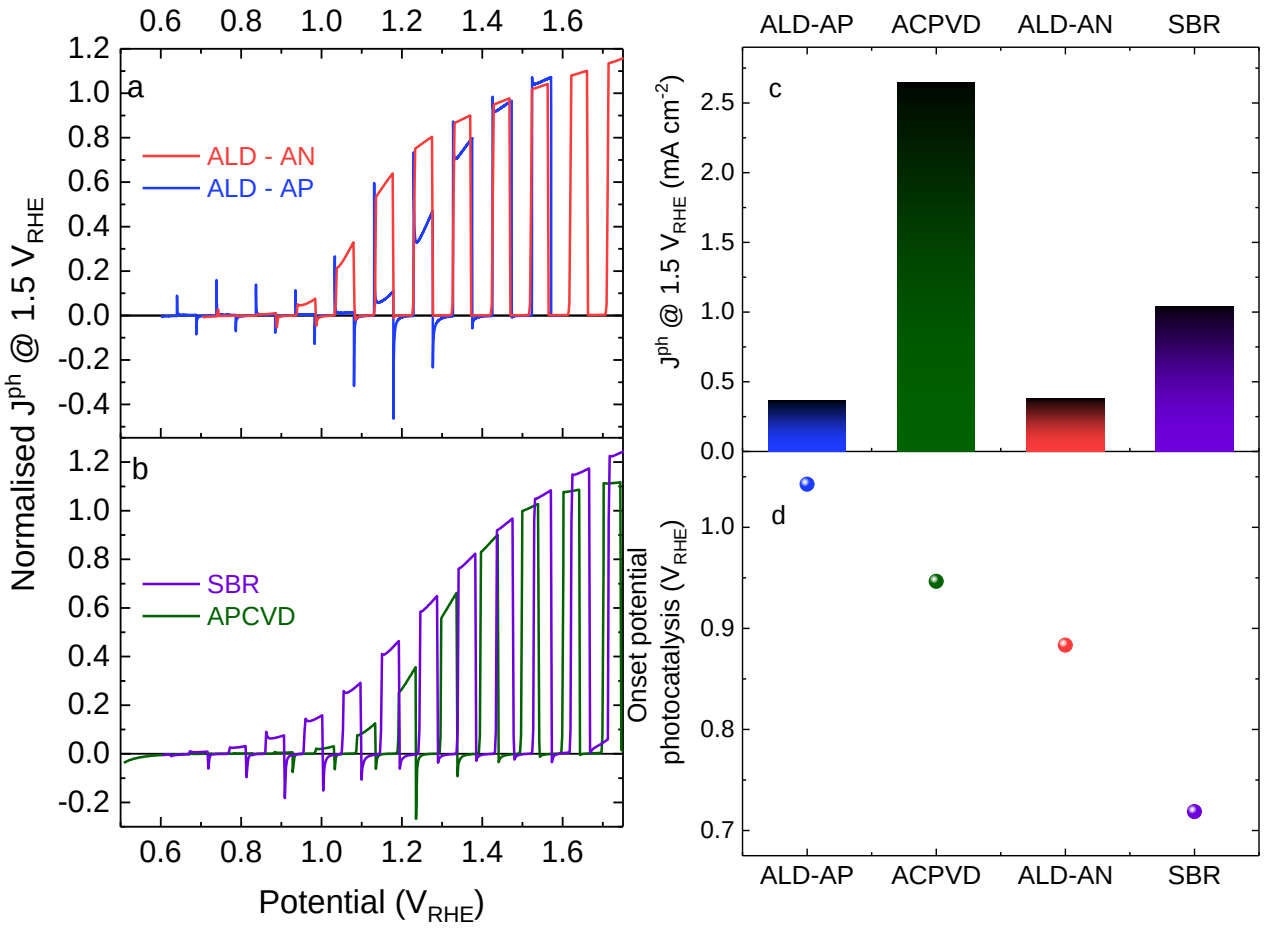
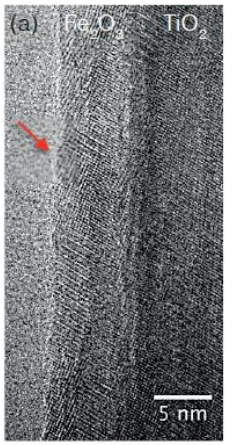
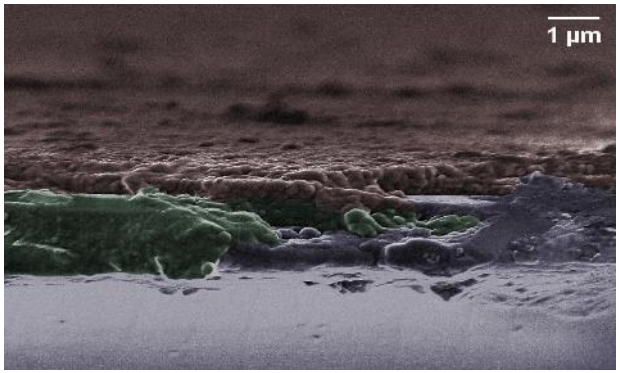
OER mechanism on α-Fe_2O_3 Other morphologies





Steier, L. et al., ACS Nano, 9, 11775, 2015



Mesa, C., et al., Manuscript in preparation

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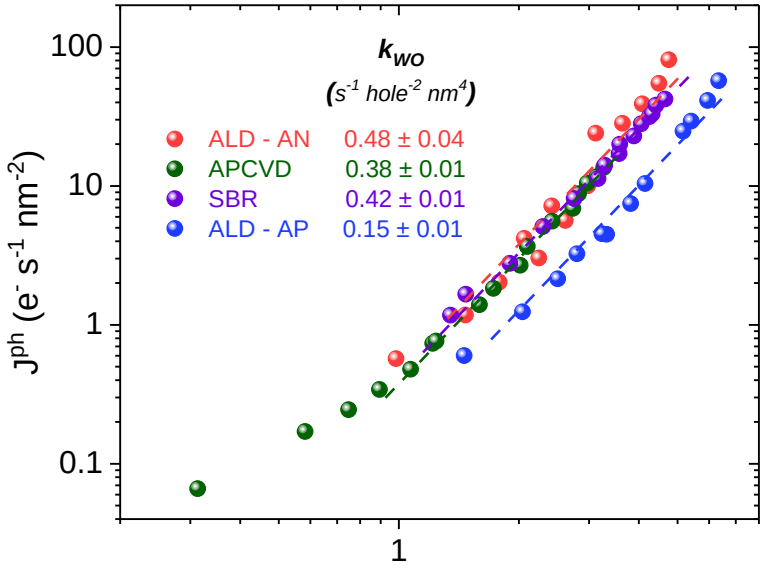
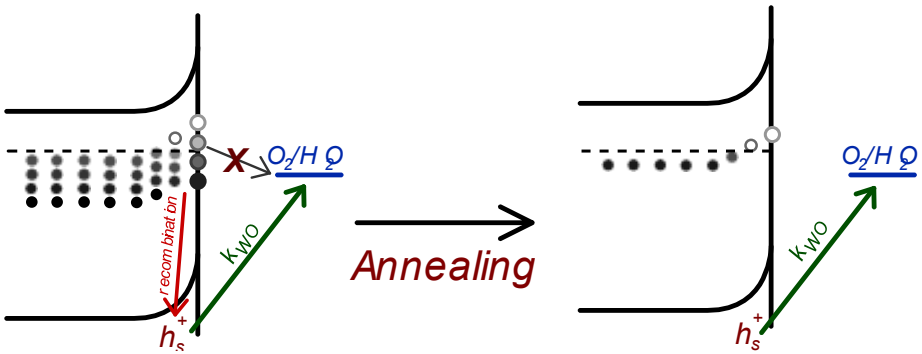
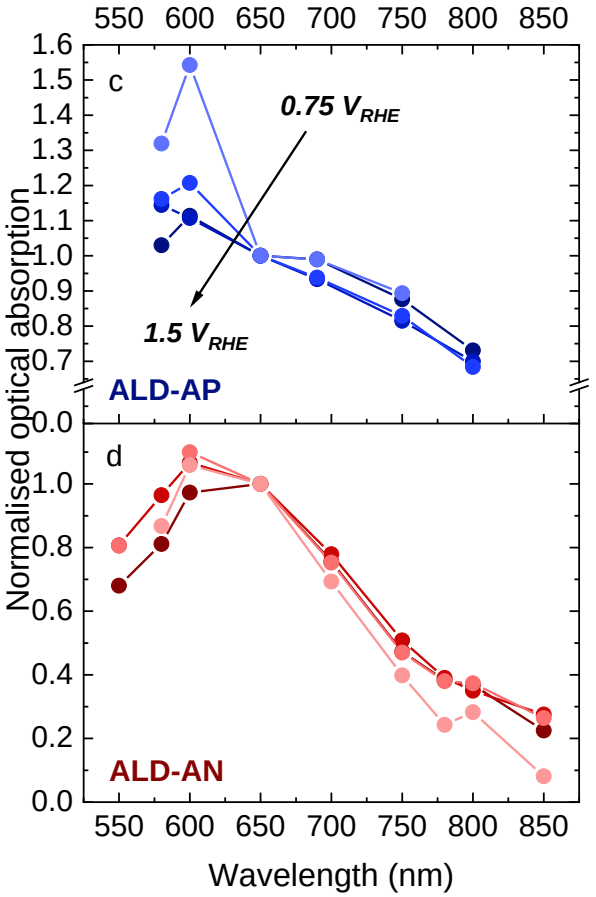
OER mechanism on α-Fe_2O_3
Other morphologies







Mesa, C., et al., Manuscript in preparation

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Second concluding remark

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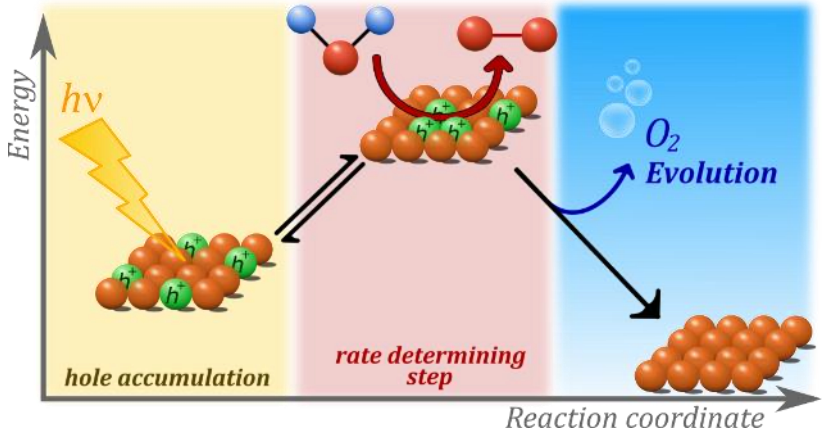
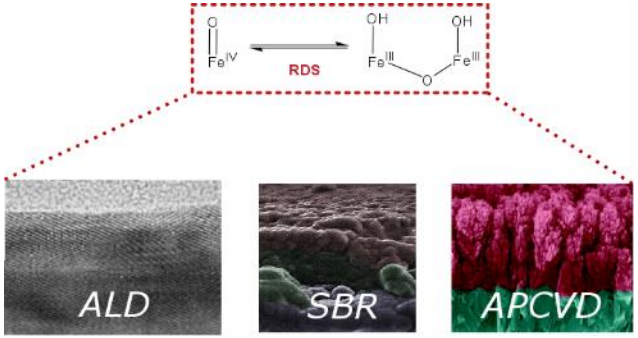


Differently synthesized hematite photoanodes perform water oxidation with the same mechanism



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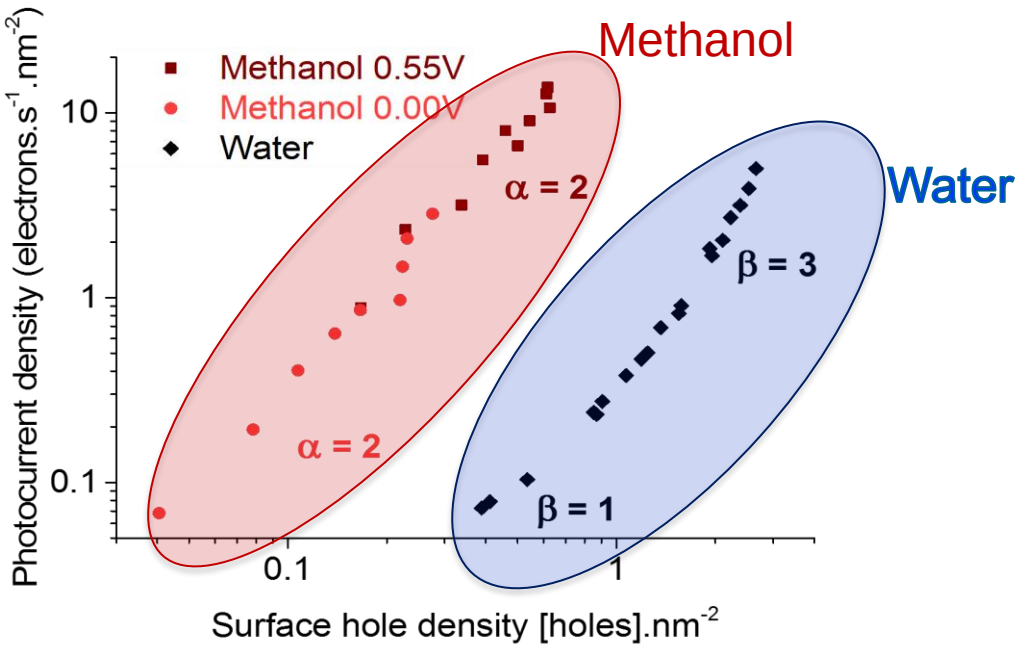
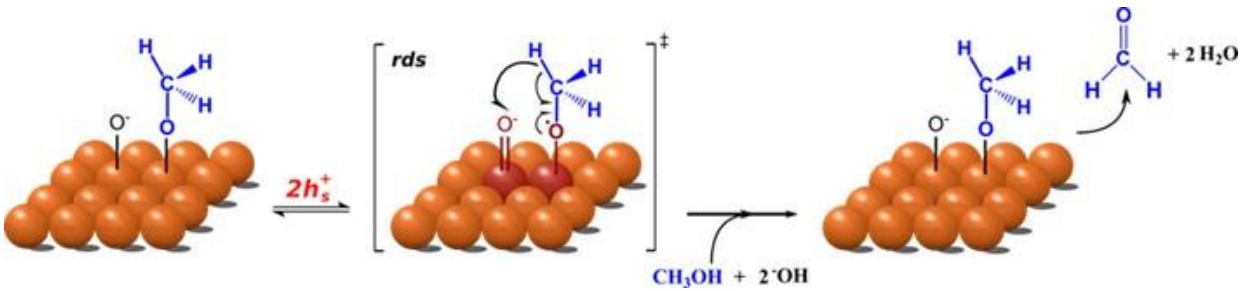
Organic substrates oxidation on α-Fe_2O_3



Proof of concept for oxidation of alcohols with FE ~1



Mesa, C. et. al., JACS, 139, 33, 2017

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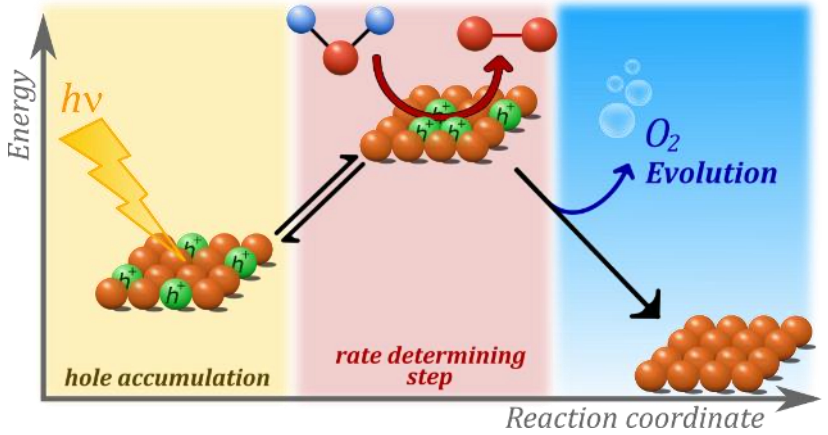

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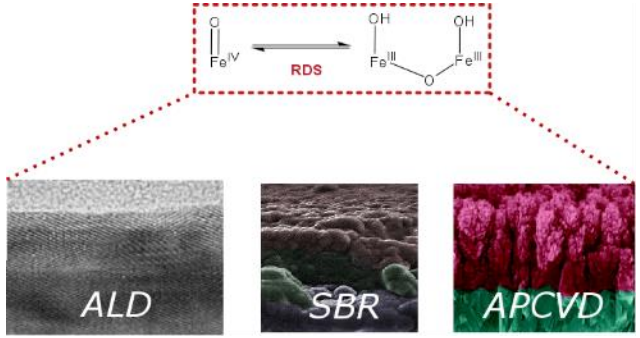

If you can't defeat them, …

Change them for alcohol

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Acknowledgements

Solar Fuels crew - Imperial College
Prof. James Durrant
Dr. Laia Francàs
Dr. Andreas Kafizas
Dr. Yimeng Ma

Grätzel group – EPFL

Reisner group – University of Cambridge

Batista group – Yale University

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