# Understanding the Effect of Pd Co-Catalysts on the Photoelectrochemical Performance of $WO_3$ Photoanodes

**Anna A. Wilson,**[a] Sacha Corby,[a] Laia Francàs,[a] Andreas Kafizas,[a,b] James R. Durrant[a]

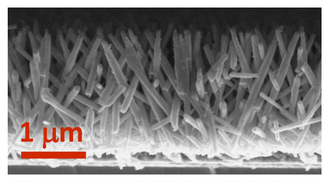
[a]*The Department of Chemistry/*[b]*The Grantham Institute, Imperial College London, South Kensington, London SW7 2AZ, U.K.*

## 1. Background and aims

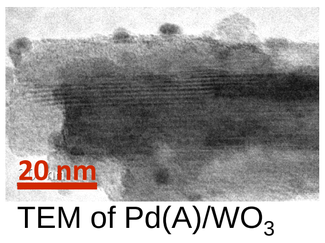
- A renewable source of hydrogen fuel can be obtained directly from sun-light driven photoelectrochemical (PEC) water splitting
- $WO_3$ is a low-cost, abundant and stable photoanode material that can be employed in the process
- The impact of Pd co-catalysts on the PEC water oxidation properties of $WO_3$ photoanodes has not been studied previously – this work aims to synthesise nanostructured $WO_3$, deposit Pd nanoparticles, and investigate the impact of Pd species on performance

## 2. Materials synthesis

- Thin nanoneedle $WO_3$ films were grown via aerosol assisted chemical vapour deposition (AA-CVD) as an up-scalable method, and annealed to modulate the oxygen vacancy concentration
- Pd nanoparticles were deposited in a second AA-CVD step, to obtain $Pd/WO_3$, with those annealed post-Pd deposition labelled $Pd(A)/WO_3$

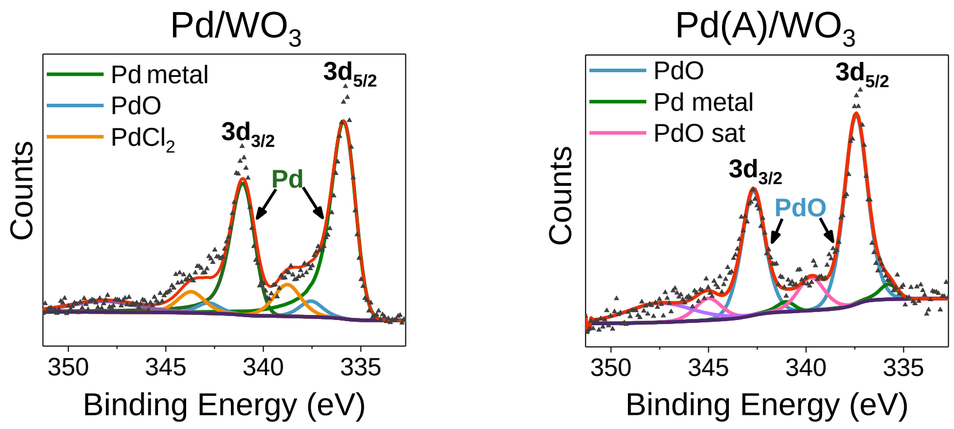



Side-on SEM of $WO_3$



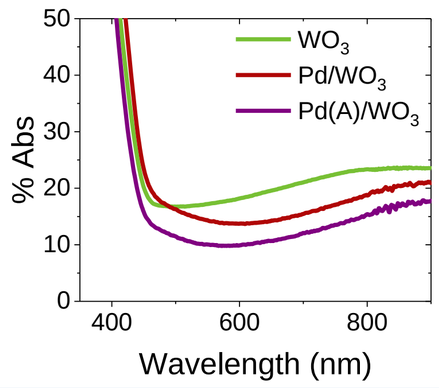

TEM of $Pd(A)/WO_3$

## 3 . XPS reveals a near complete oxidation of Pd following annealing treatment

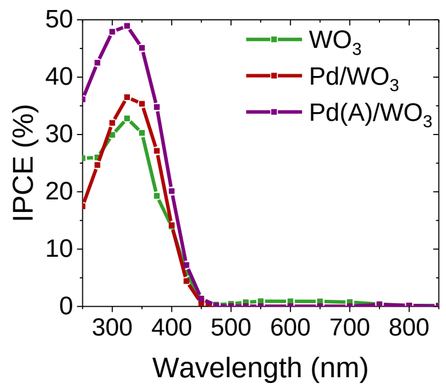


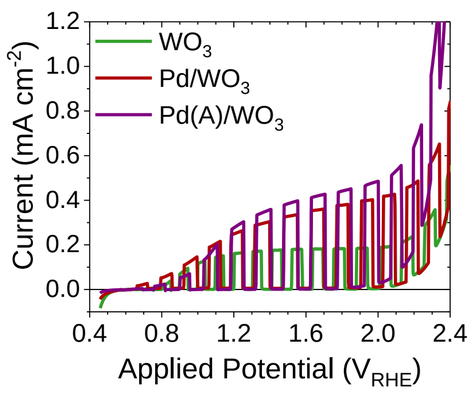

## 4. Optical properties

- The broad absorption feature from red wavelengths of the visible region to the near-IR is assigned to $W^{5+}$ states associated with oxygen vacancies
- This feature is reduced in $Pd(A)/WO_3$, implying a reduction in the oxygen vacancy concentration




## 5. Photoelectrochemical (PEC) performance

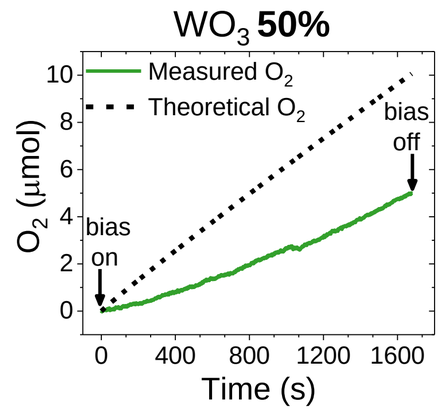


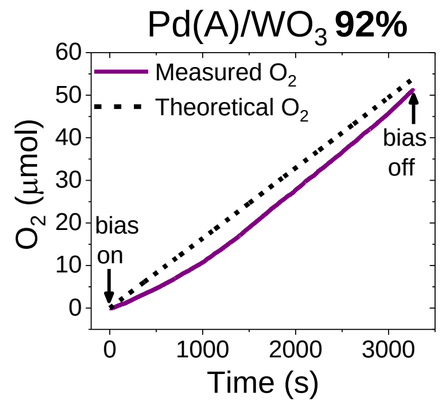




- $Pd(A)/WO_3$ is the superior photoanode material with regards to:

✓ Incident photon to current efficiency (IPCE)
✓ Photocurrent generation
✓ Onset of electrocatalytic water oxidation

## 6. Faradaic efficiency (FE) increase with PdO co-catalyst addition



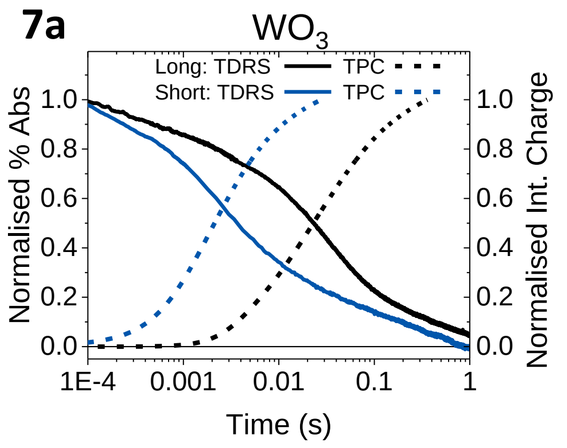

- $WO_3$ suffers from poor FE due to the prevalence of side reactions
- The impressive FE of $Pd(A)/WO_3$ identifies water oxidation as the origin of the increased photocurrents and PdO as an effective oxygen evolution co-catalyst (OEC)

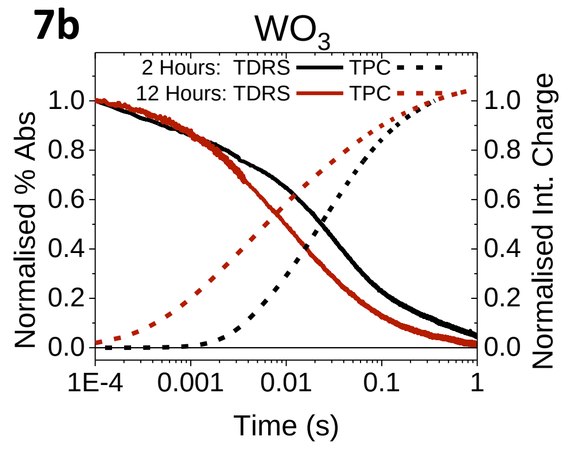
## 7. Electron extraction rates

*Note: faster electron extraction reduces the opportunity for recombination of charges and can enhance efficiency!*

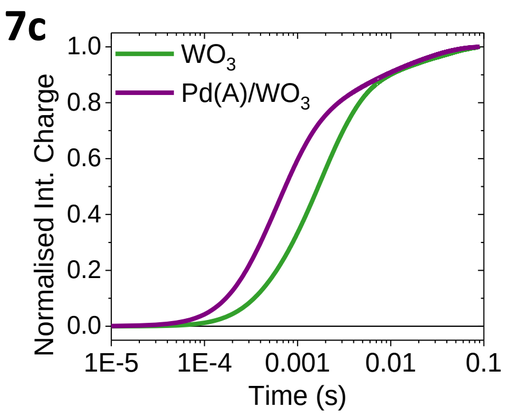
Electron extraction in $WO_3$ is limited by:

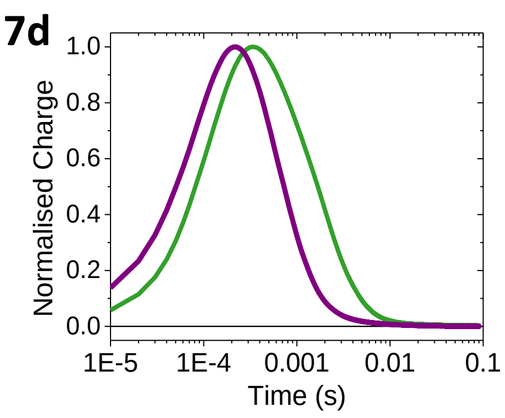
- Electron transport through the nanoneedles, instead of losses at the interfaces (7a)
- Excess oxygen vacancy concentrations (7b)




- $Pd(A)/WO_3$ achieves faster electron extraction rates (7c and 7d), which could be due to the reduced oxygen vacancy concentrations identified from the UV-Vis spectra and the XPS quantification of $W^{5+}$




- Electron extraction rates of $WO_3$ annealed twice were measured to exclude this as the sole cause of these improvements

## 8. Summary

PdO is identified as a promising OEC that dramatically increases photocurrent generation and oxygen evolution capabilities

In addition to improving water oxidation selectivity, PdO enhances the driving forces for charge separation:

- Electron extraction rates to the external circuit are increased
- Holes are extracted to PdO for water oxidation

We suggest that PdO addition improves electron extraction properties by creating a favourable oxygen vacancy concentration in $WO_3$

A. A. Wilson, S. Corby, L. Francàs, J. R. Durrant, A. Kafizas, *Manuscript in preparation*
S. Corby, L. Francàs, S. Selim, M. Sachs, C. Blackman, A. Kafizas and J. R. Durrant, *J. Am. Chem. Soc.*, 2018, **140**, 16168−16177.
M. Sachs, J. S. Park, E. Pastor, A. Kafizas, A. A. Wilson, L. Francàs, S. Gul, M. Ling, C. Blackman, J. Yano, A. Walsh and J. R. Durrant, *Chem. Sci.*, 2019, **10**, 5667–5677.
F. E. Annanouch, S. Roso, Z. Haddi, S. Vallejos, P. Umek, C. Bittencourt, C. Blackman, T. Vilic and E. Llobet, *Thin Solid Films*, 2016, **618**, 238–245.

Engineering and Physical Sciences Research Council