DEVELOPING UPSCALABLE ROUTES TO WATER SPLITTING DEVICES USING CHEMICAL VAPOUR DEPOSITION

Dr. Andreas Kafizas – Imperial College London
EUROCVD 22 Baltic ALD 16 – Luxembourg, 2019

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Outline

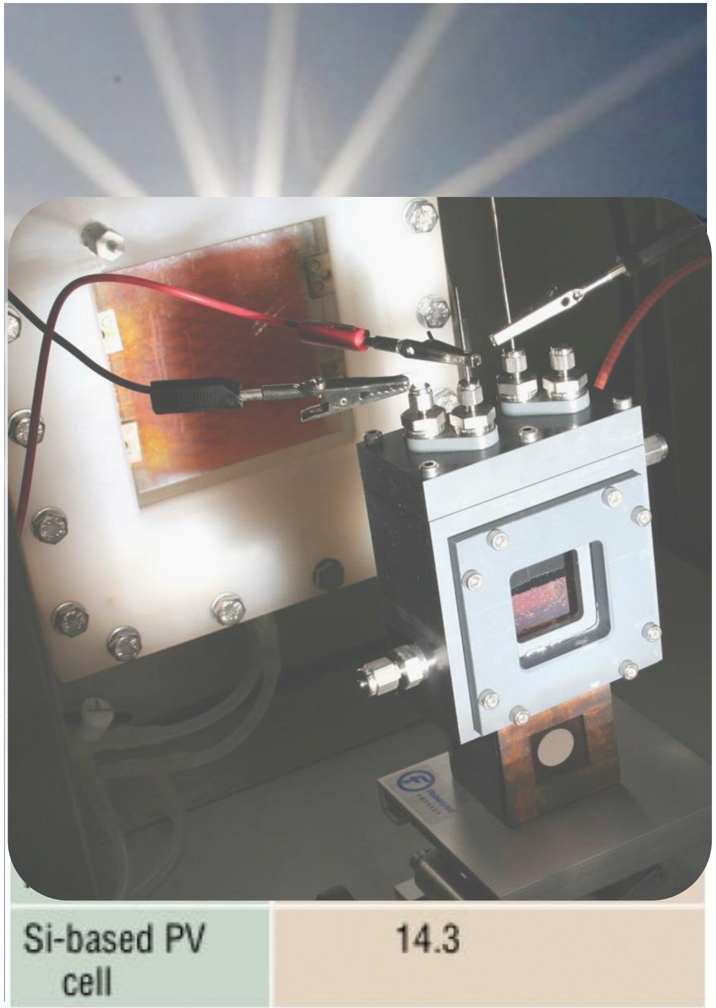
- The need for solar water splitting
- Why metal oxides are a good choice
- Our CVD process
- Metal oxide heterostructures for solar water splitting: WO_3/ $BiVO_4$
  - Synthesis
  - Characterisation
  - Water splitting performance
- Conclusions
- Acknowledgements

The CO_2 problem

- CO_2 emissions from fossil fuels is the primary cause of Global Warming
- Current CO_2 levels in the atmosphere are the highest they have been for more than five million years
- The EU has set the target of cutting its emissions by at least 80% compared to 1990 levels to prevent Global Warming

Solar water splitting

- Sunlight is our largest energy source
- Although solar cells can generate electricity, they have limitations
- Photosynthesis is nature's example of how solar energy can be stored in chemical bonds, and has inspired artificial strategies
- The most promising approach is to split water using semiconductors to produce H_2; which is a versatile fuel



D. Gust, MRS Bulletin, 2008

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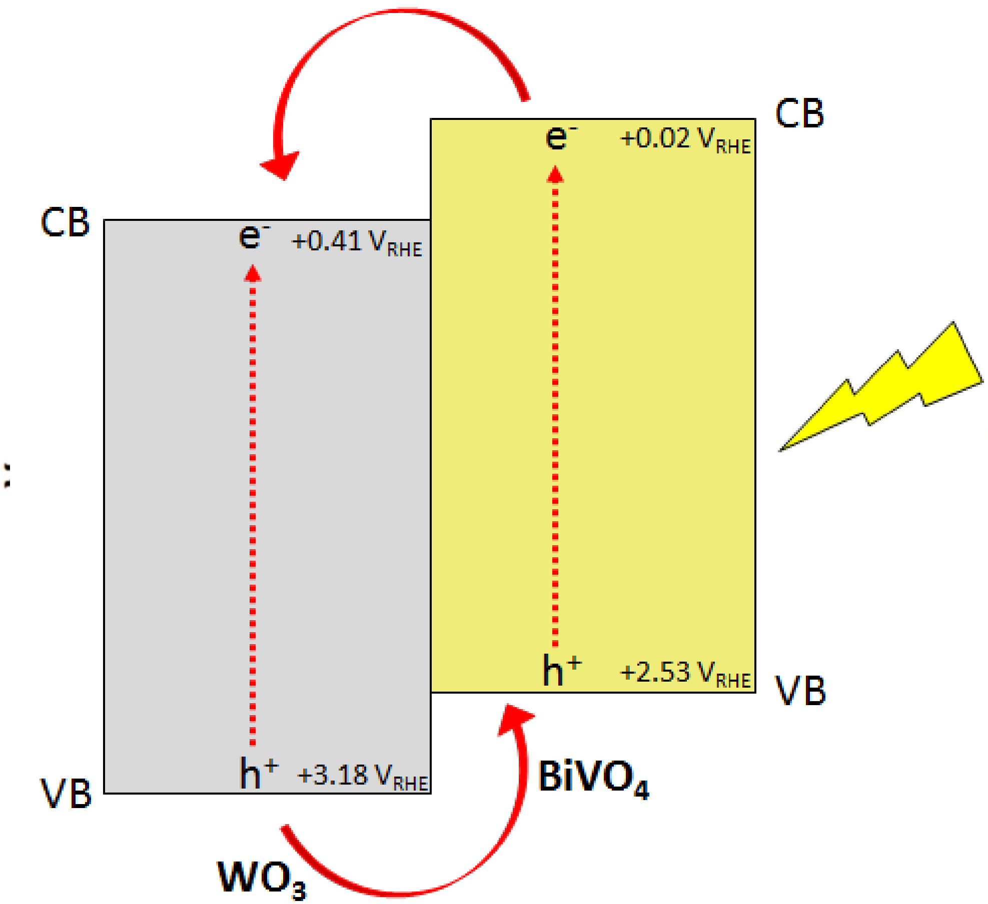
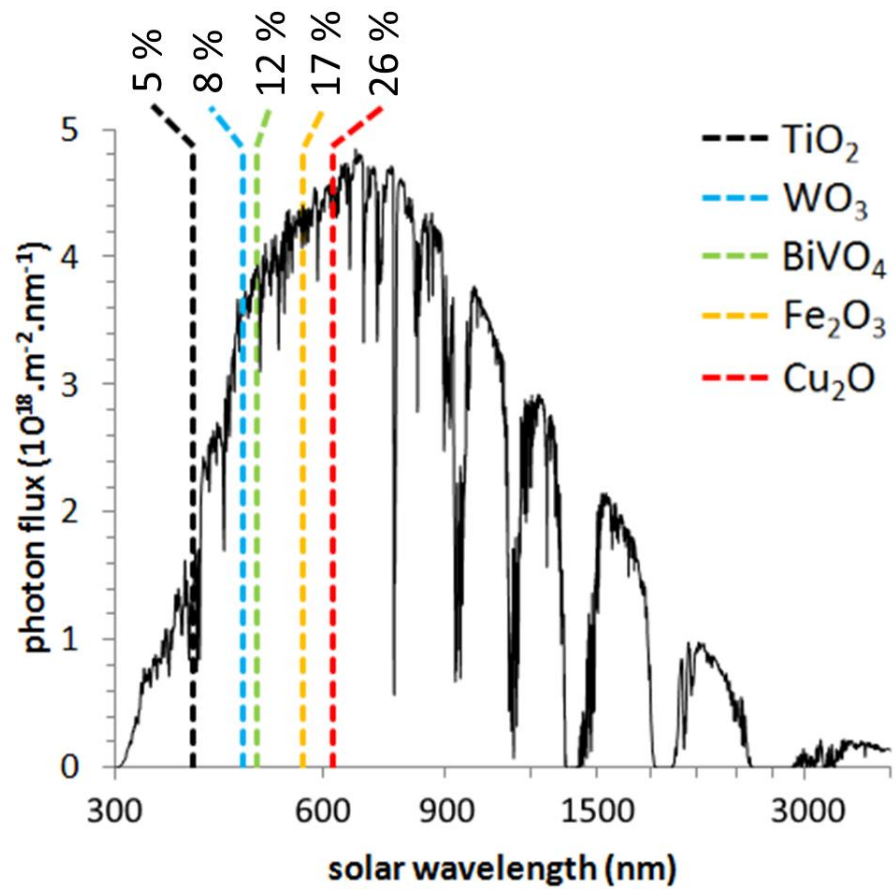
Metal oxide semiconductors

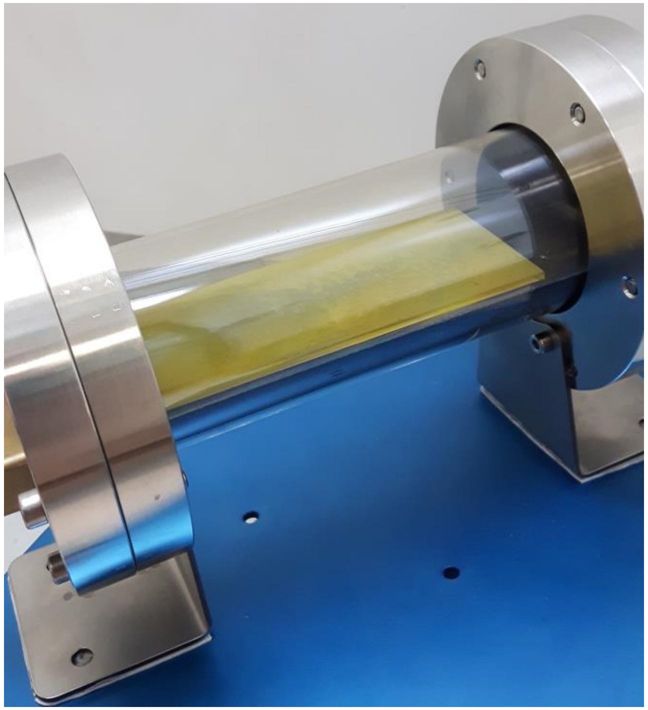
- A semiconductor can split water when photo-excited if:



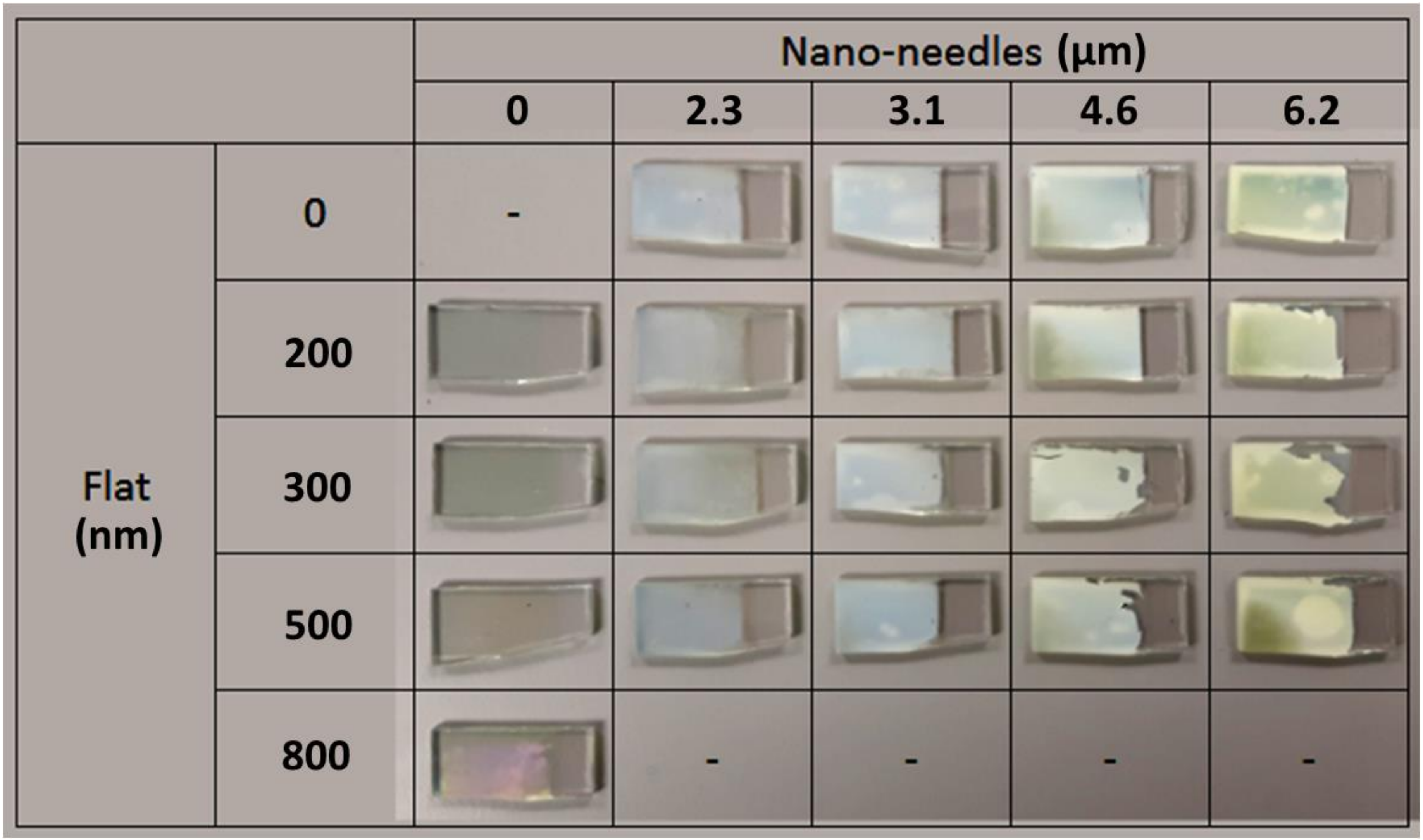


Chemical vapour deposition (CVD)

- All reactions were carried out at atmospheric pressure using a horizontal flow, cold-wall reactor
- The precursors, used to form WO_3 and $BiVO_4$, were dissolved in a volatile solvent and transported into the reactor as an aerosol

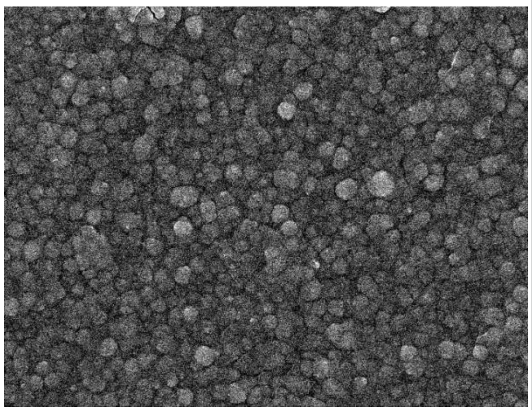
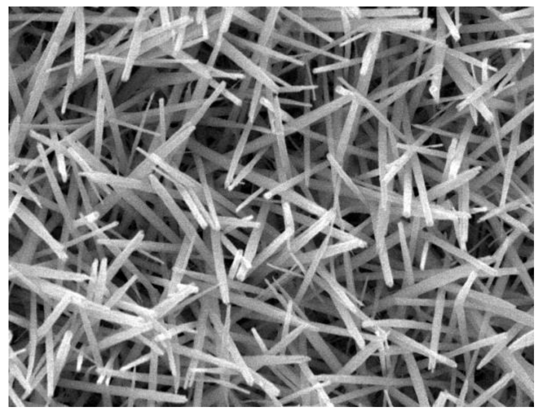
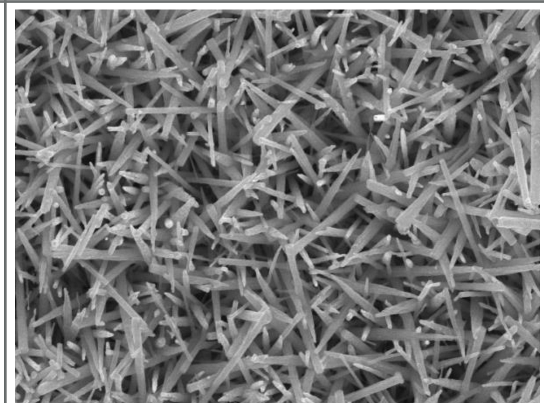
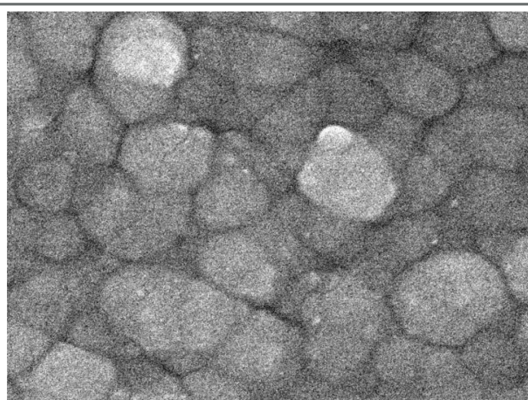
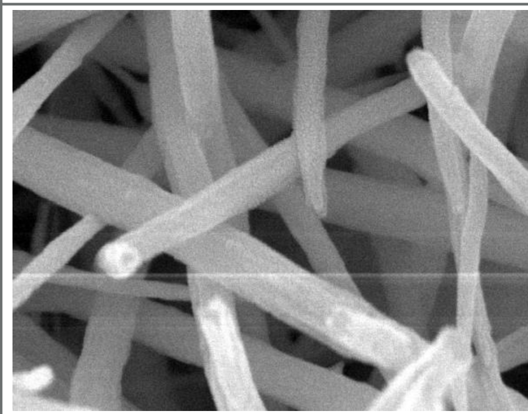
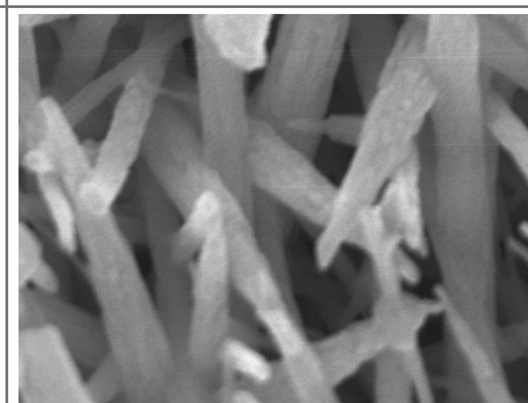


WO_3: synthesis



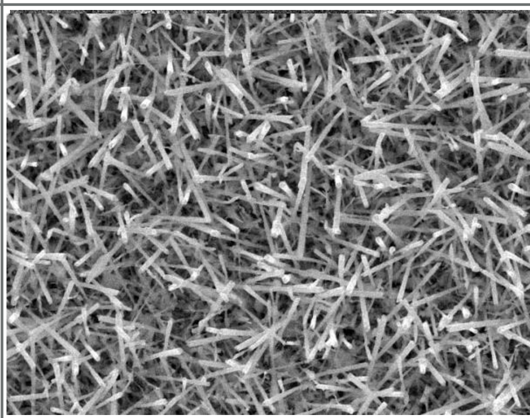
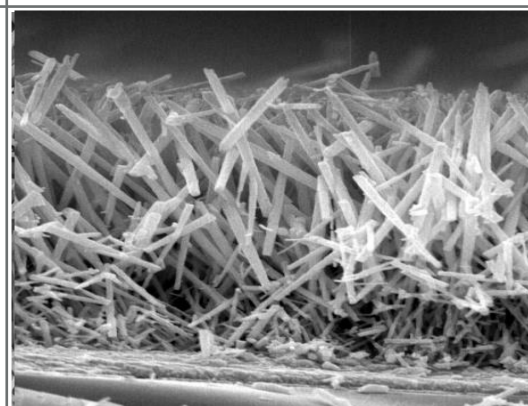
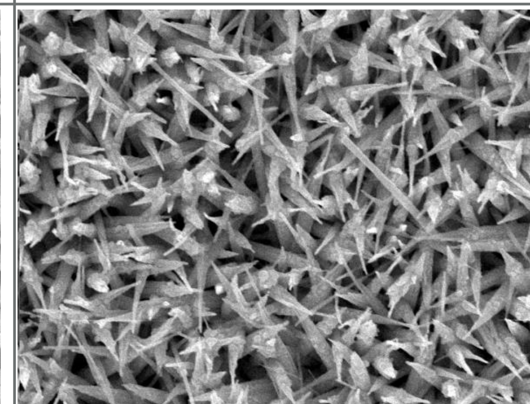
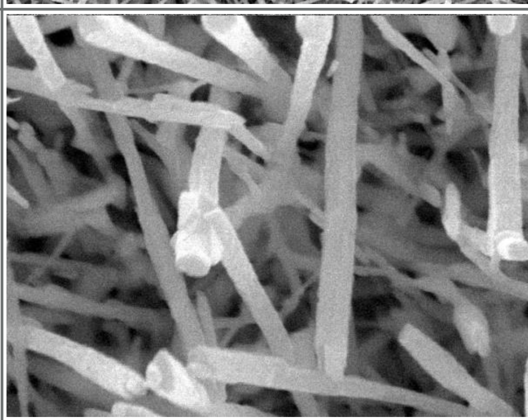
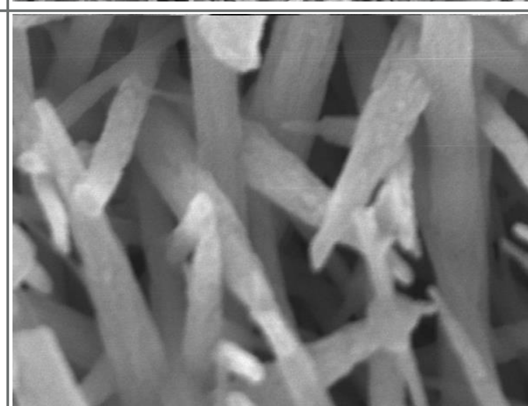
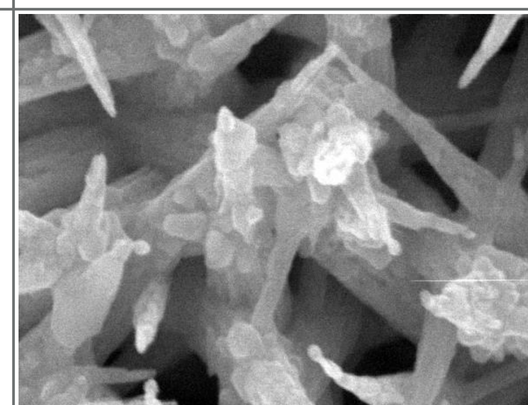
WO_3: physical characterisation

- SEM

	F ~500 nm	NN ~4.2 μm	F ~300 nm, NN ~4.2 μm
7 μm			
1.4 μm			

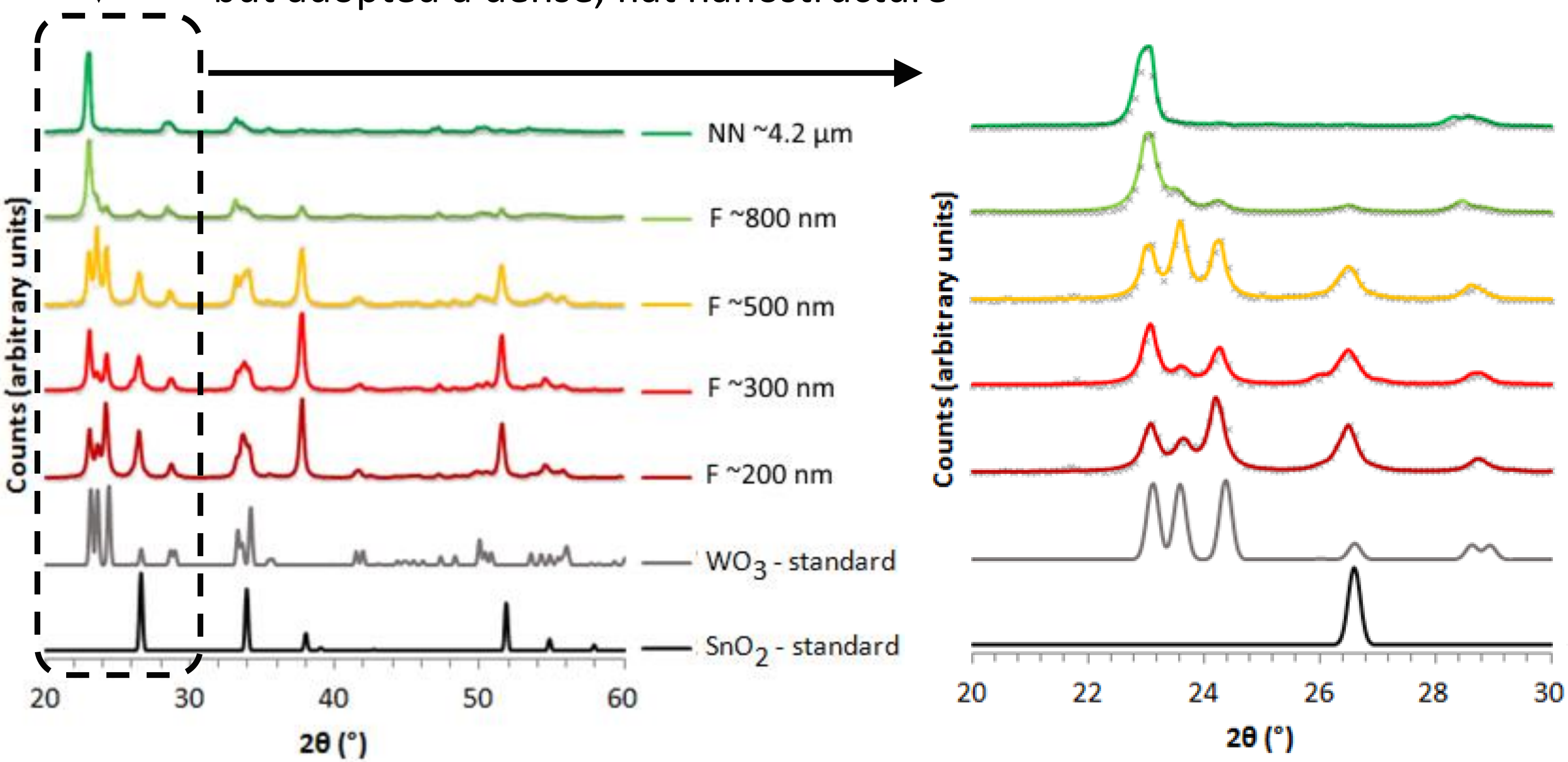
WO_3: physical characterisation

- SEM

	F ~300 nm, NN ~2.3 μm	F ~300 nm, NN ~4.2 μm	F ~300 nm, NN ~6.2 μm
7 μm			
1.4 μm			

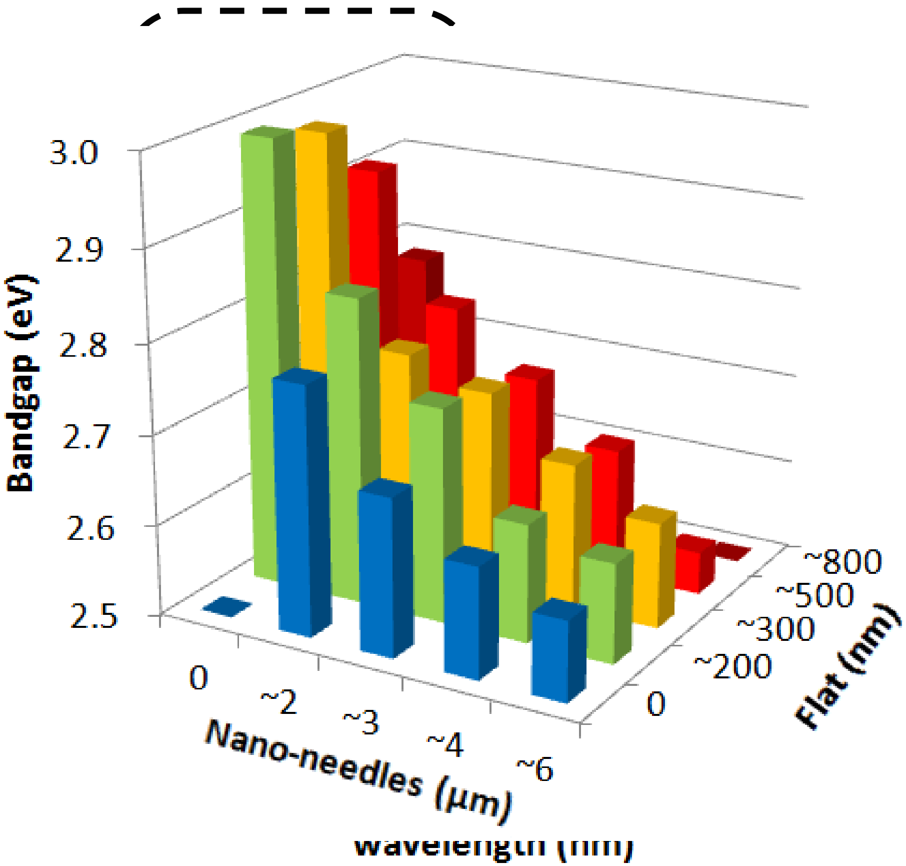
WO_3: physical characterisation

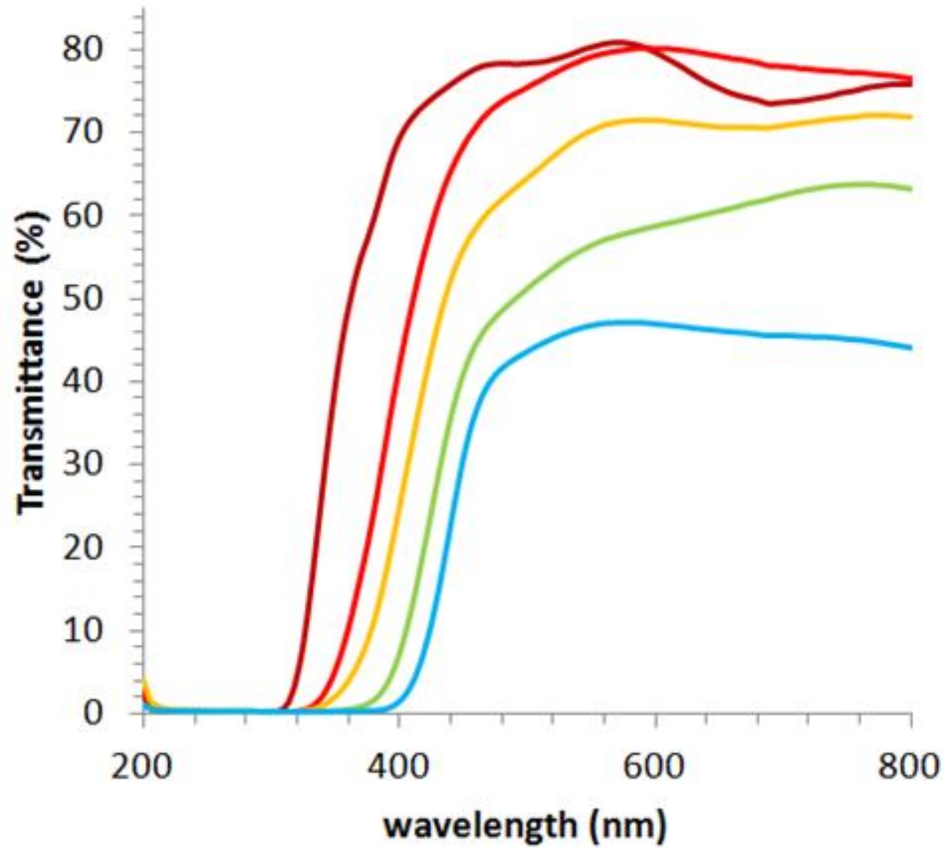
- XRD
  - All samples adopted the WO_3 monoclinic crystal structure
  - Nanoneedles were highly oriented in the (002) crystal plane
  - Thicker flat films showed similar preferred orientation to nanoneedles, but adopted a dense, flat nanostructure



WO_3: physical characterisation

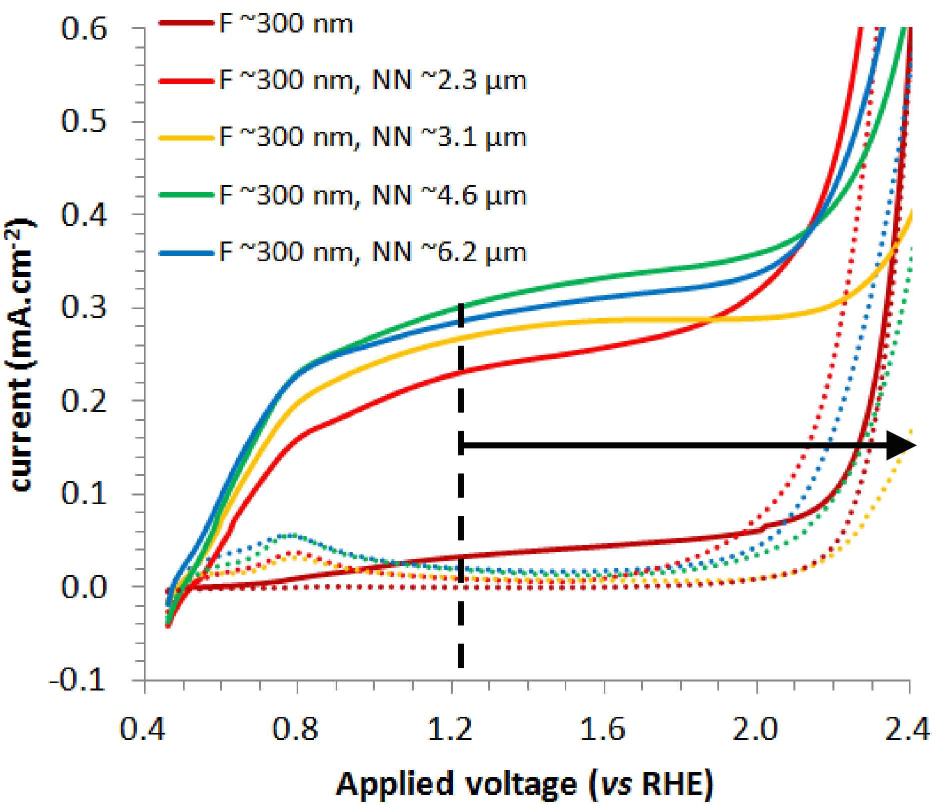
- UV-visible absorption spectroscopy
  - Bandgap decreases with an increase in film thickness or nanoneedle length
  - May be physically related to changes in preferred orientation

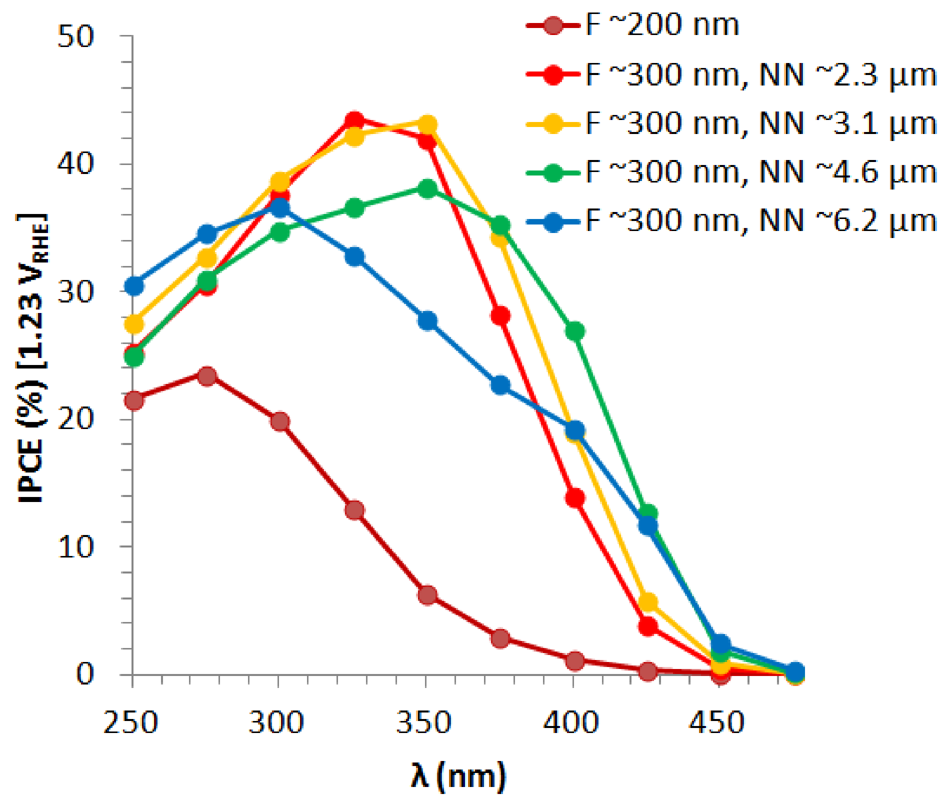




WO_3: water splitting function

- Photoelectrochemistry and incident photon-to-current efficiency (IPCE)
  - Examined in a 3-electrode photoelectrochemical cell (0.5 M H_2SO_4, pH ~1)
  - Longer nanoneedles show stronger visible light activity





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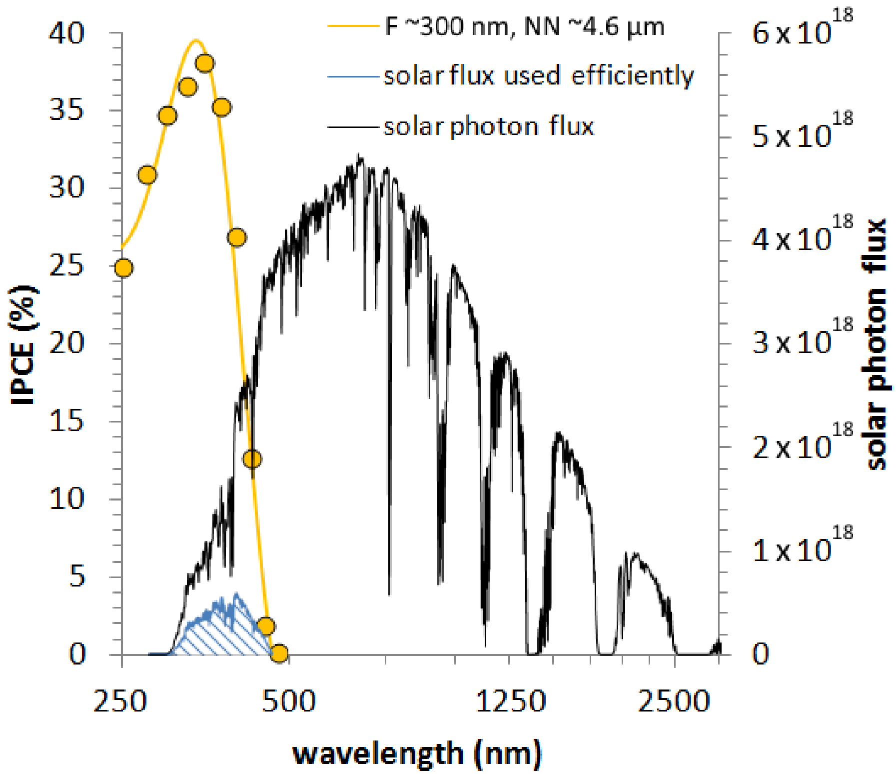
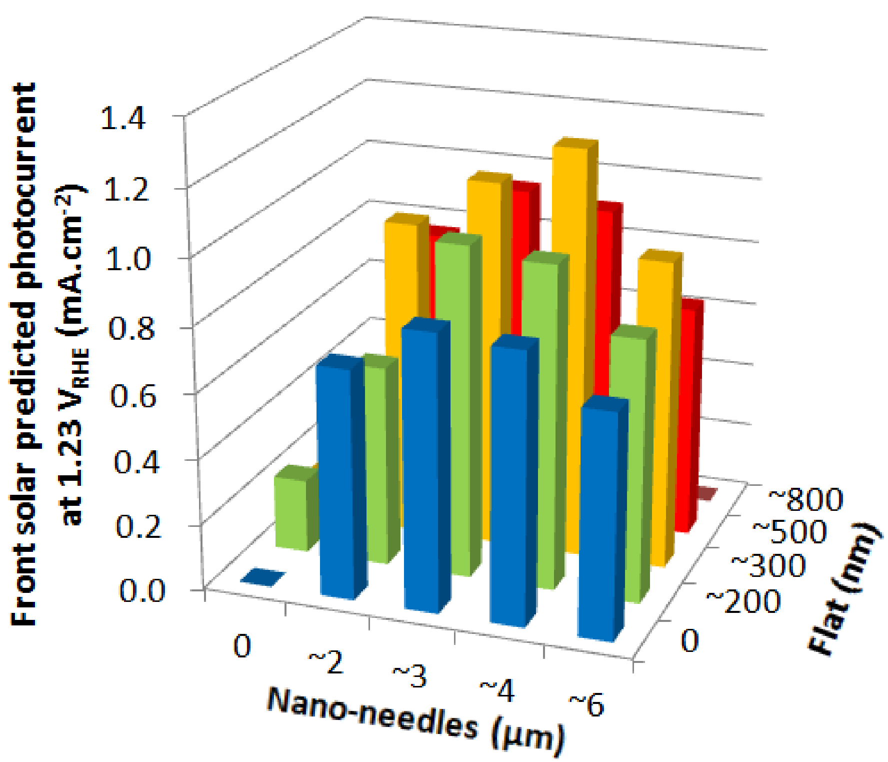
WO_3: water splitting function

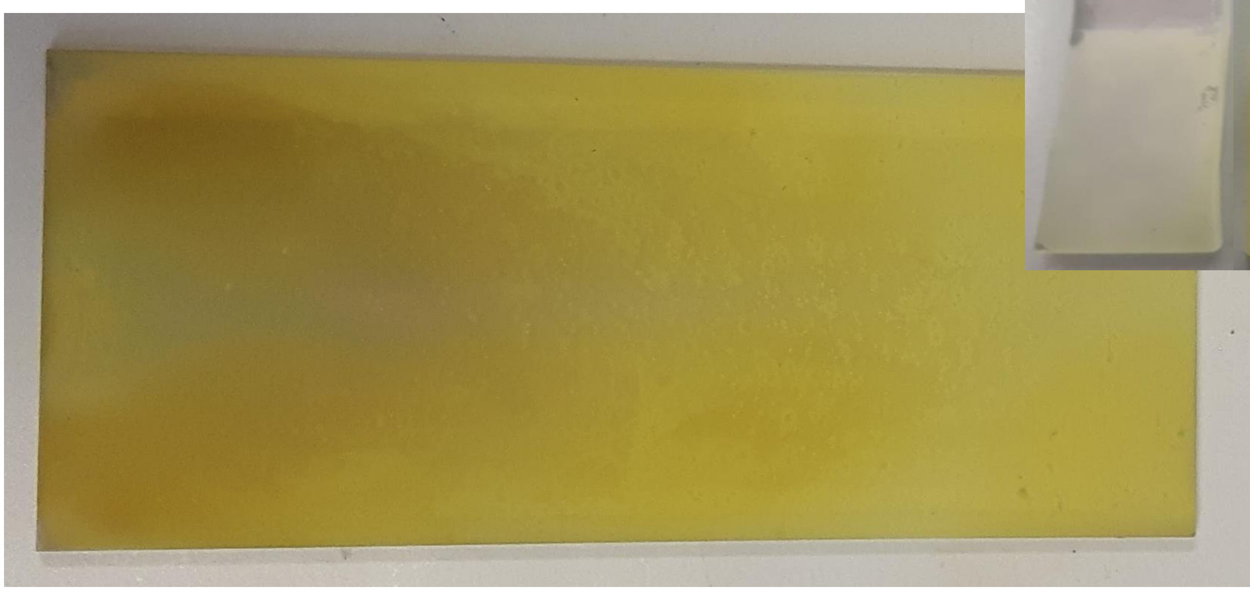
- Predicting solar efficiency using our IPCEs
  - IPCEs multiplied by the solar spectrum to predict photocurrent
  - Optimum activity observed at F ~300 nm, NN ~4.6 µm

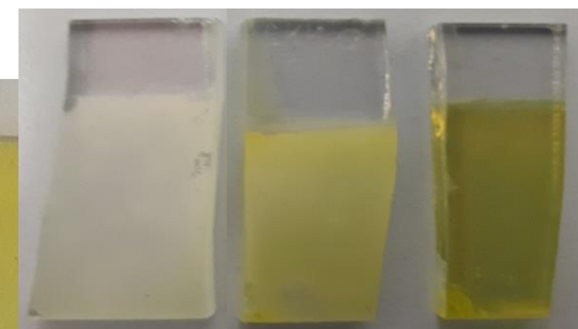




WO_3/ $BiVO_4$: synthesis

- $BiVO_4$ grown using an aerosol-assisted CVD method using a solution of $VO(acac)_2$ (5.3 mM) and $Bi(Ph)_3$ (5.3 mM) in an acetone: methanol (3:1) mixture
- Range of $BiVO_4$ thickness examined individually, and coated onto our best performing WO_3 sample (F ~300 nm, NN ~4.6 μm)





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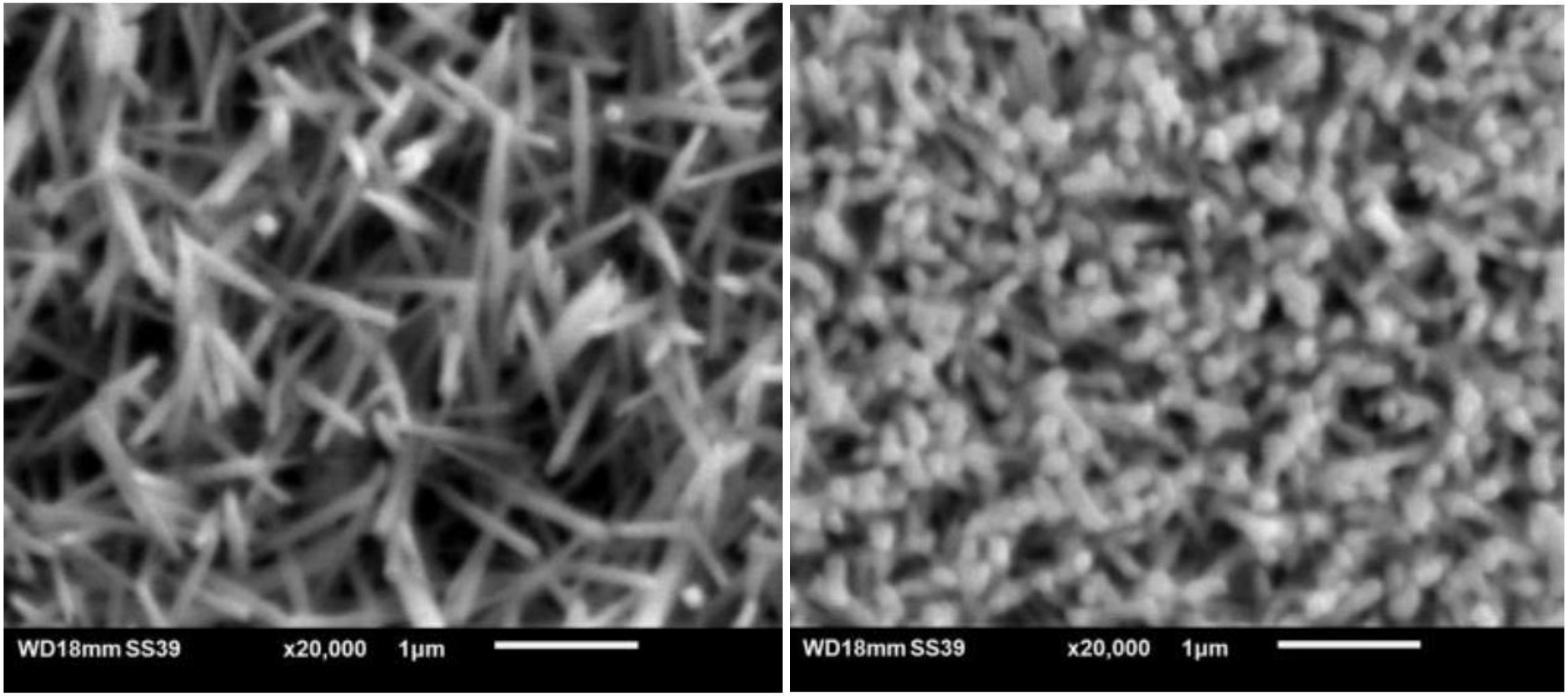
WO_3/ $BiVO_4$: characterisation

- XRD showed the formation of the monoclinic Scheelite $BiVO_4$ structure on monoclinic WO_3
- SEM images reveal the conformal coating of WO_3 nanorods with $BiVO_4$



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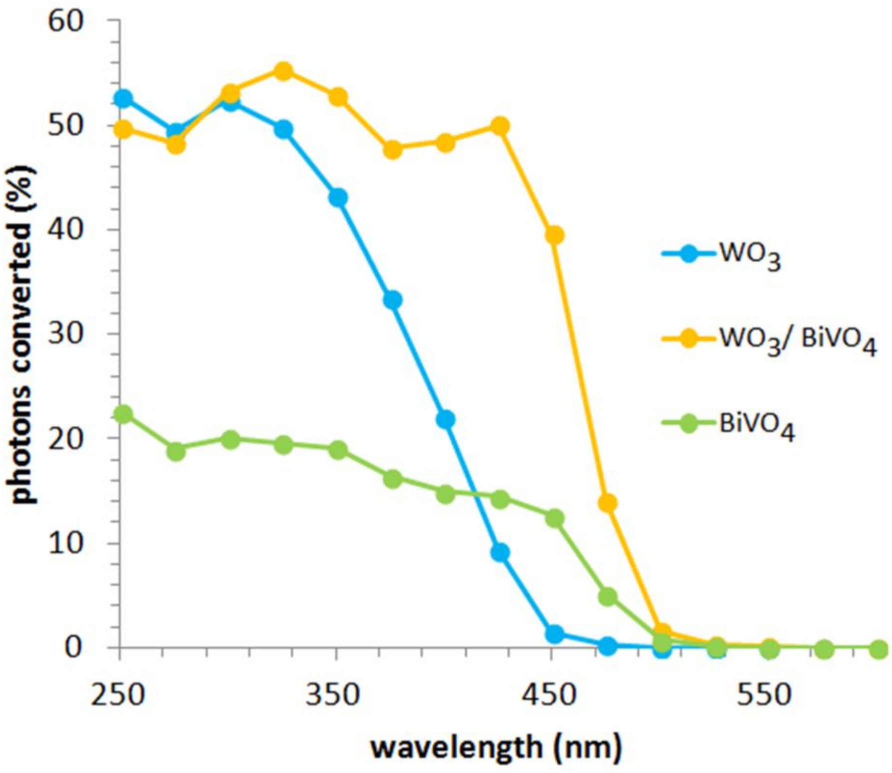
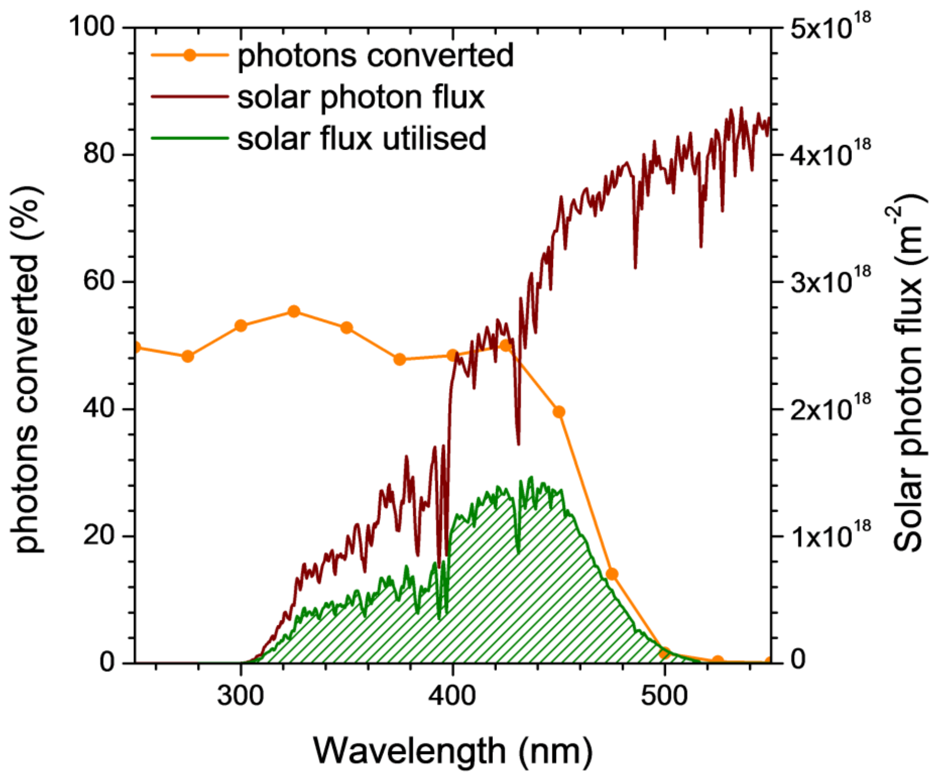
WO_3/ $BiVO_4$: water splitting activity

- Incident photon-to-current efficiency (IPCE)
  - Examined in a 3-electrode photoelectrochemical cell at 1.23 V_{RHE} (0.5 M H_2SO_4, pH ~1) or 0.1 M phosphate buffer, pH ~7)





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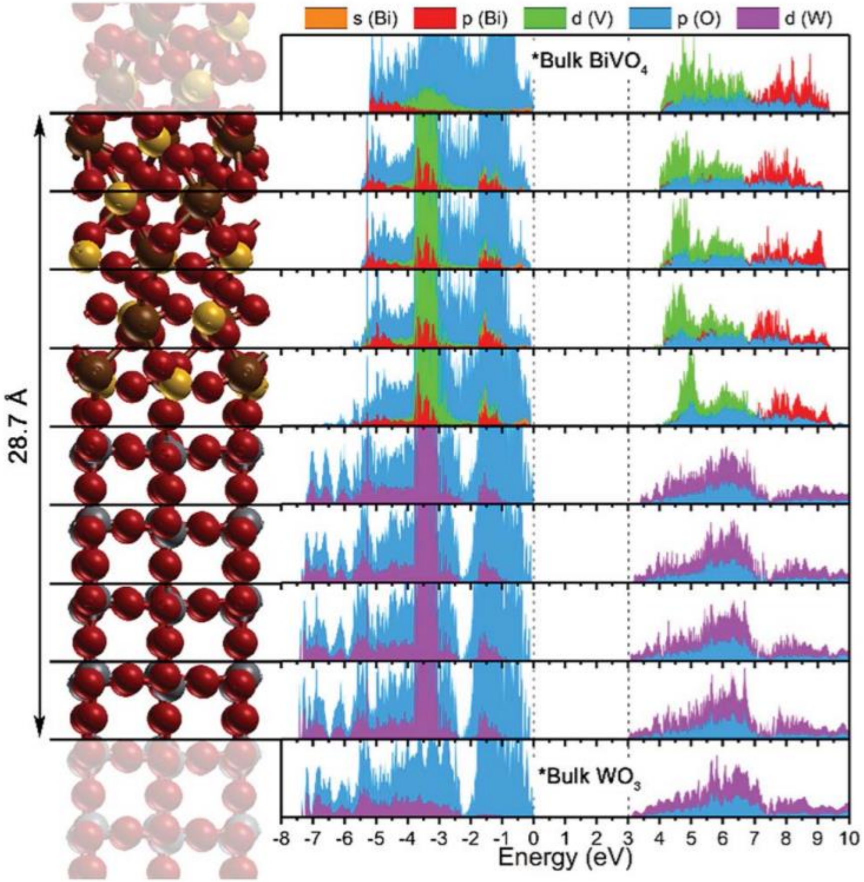
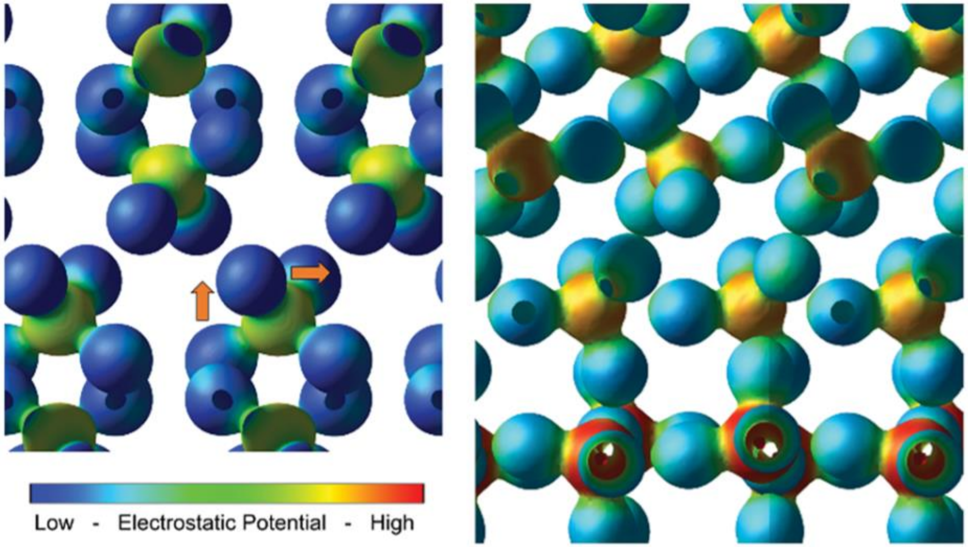
WO_3/ $BiVO_4$: computational modelling

- Band alignment at the interface differs from bulk measurements
- Strong hybridisation of common oxygen anion causes a flat valence band

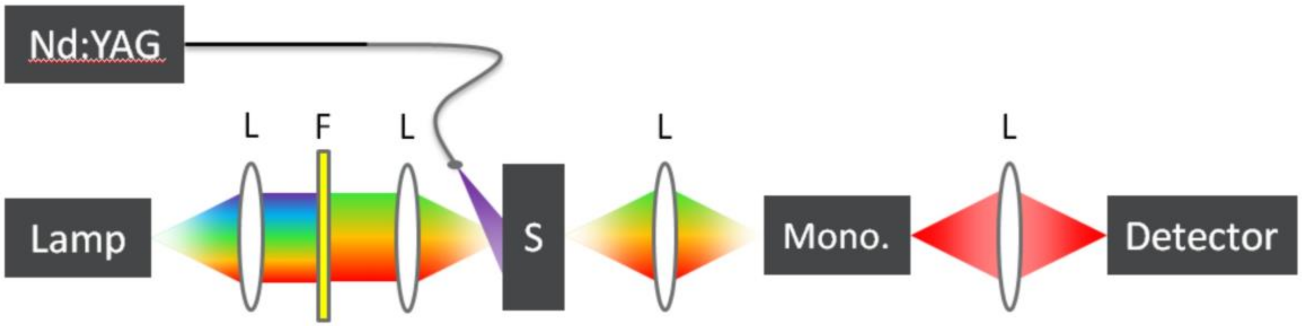


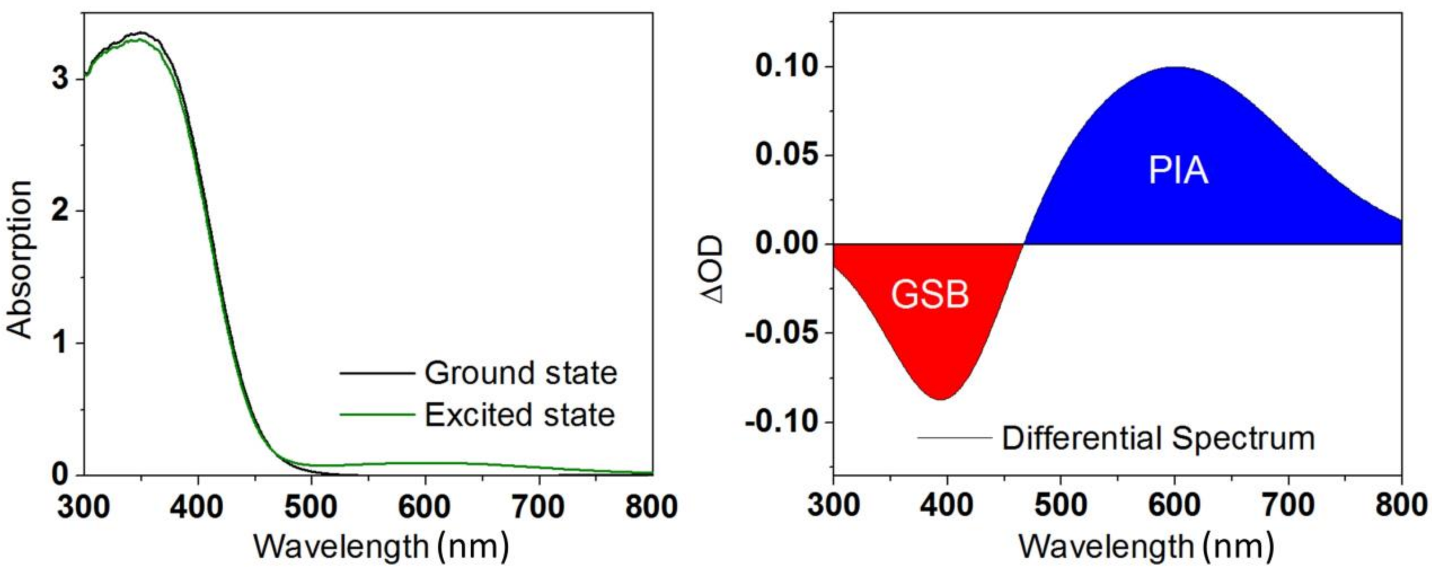


Kafizas *et al.*, *Sustainable Energy Fuels*, 2019,3, 264

WO_3/ $BiVO_4$: charge carrier dynamics

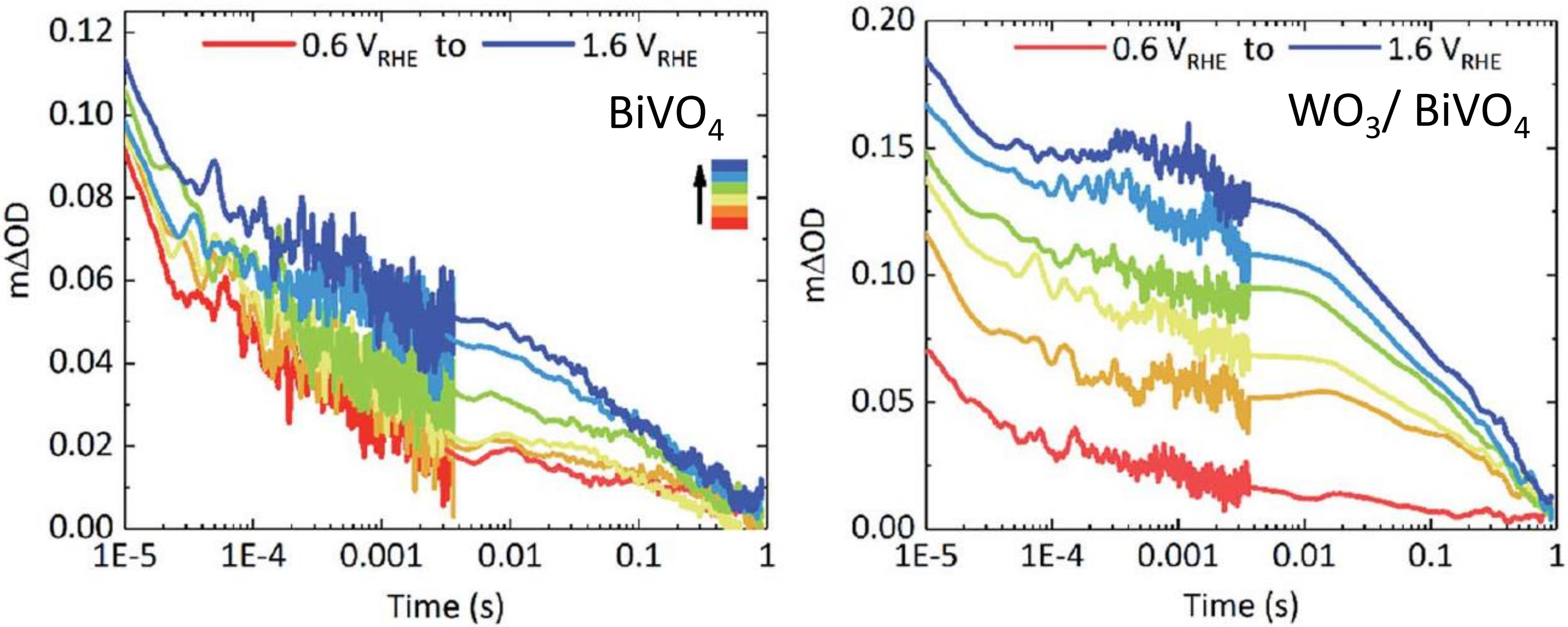
- Transient absorption spectroscopy (TAS)





WO_3/ $BiVO_4$: charge carrier dynamics

- Transient absorption spectroscopy (TAS)
- WO_3/ $BiVO_4$ heterojunction shows a higher hole signal at early timescales, due to enhanced charge carrier separation



Kafizas *et al.*, *Chem. Sci.*, *2019, 10, 2643–2652*

Conclusions

- Renewable H_2 fuel can be produced using sunlight, and used as a medium for storing energy, heating or transport fuel
- Inorganic materials show the highest efficiencies for producing H_2 fuel using sunlight
- WO_3/ $BiVO_4$
  - Nanostructured WO_3 was grown by CVD and optimised
  - Forming a heterojunction with $BiVO_4$ results in a 3 fold improvement in water splitting activity
- My research focuses on improving the economic viability of producing water splitting devices using CVD

Acknowledgements

Research Group

Ms. Shababa Selim
Mr. Benjamin Moss
Mr. Brian Tam
Ms. Louise McGrath
Ms. Yunuo Li
Ms. Francesca Pinto

Collaborators

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Prof. Ivan Parkin (UCL)
Dr. Chris Blackman (UCL)
Prof. Andrew Mills (QUB)

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Imperial College London
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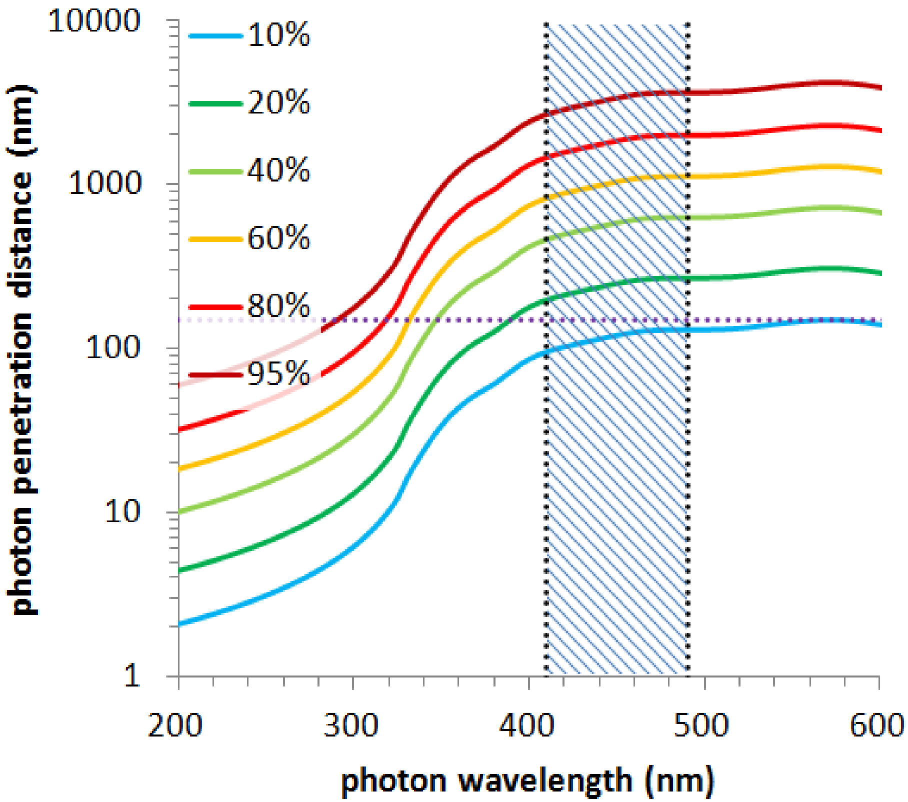
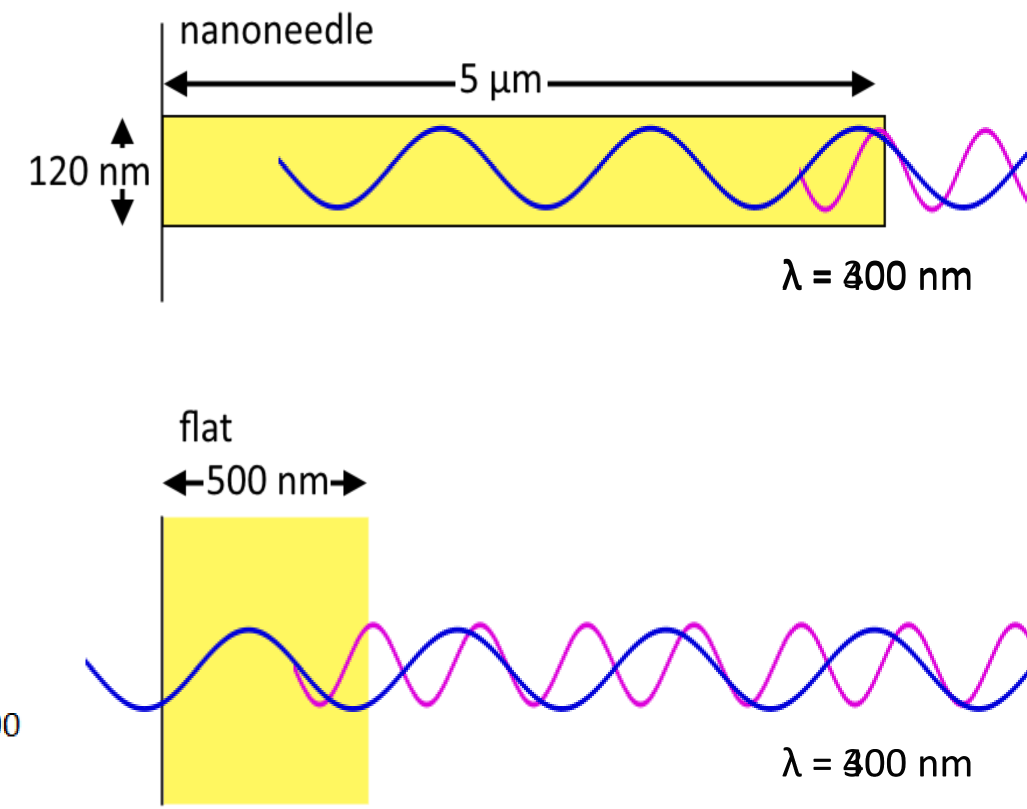
EPSRC

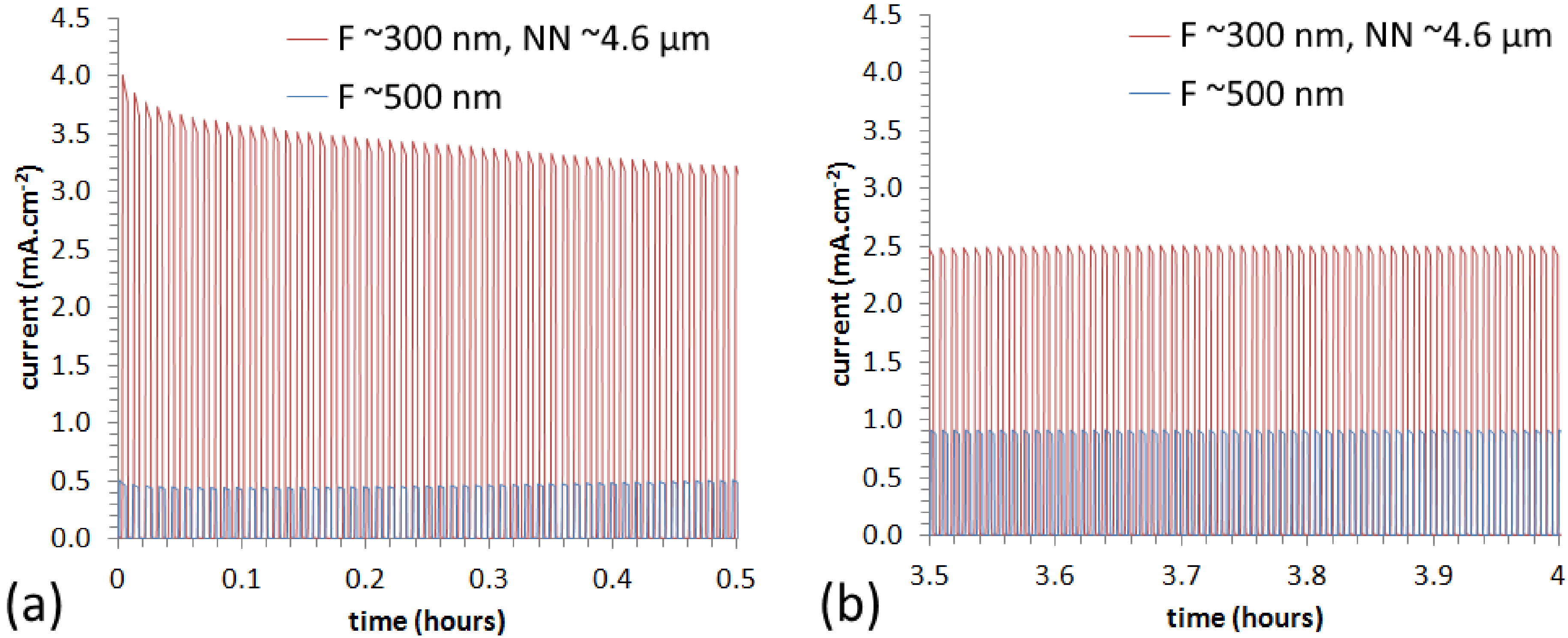
Supplementary Information

- Why are nanoneedle structures better than flat?
  - Flat samples between 200 – 800 nm in thickness and nanoneedles between 1 – 9 μm
  - Penetration depth determined from absorption coefficient
  - Hole diffusion length ~ 150 nm, electron diffusion length > 5 μm



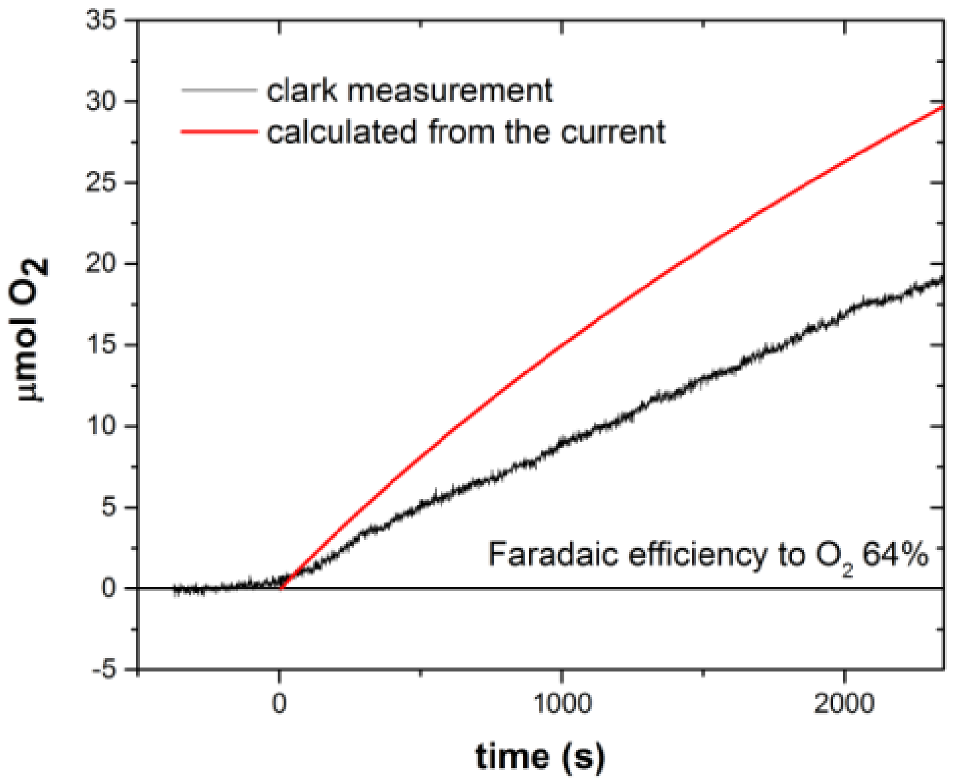


Supplementary Information



Stability test, measuring the change in photocurrent under the action of UV light (chopped 365 nm LED, ~30 mW.cm^{-2}) when held at 1.23 V_{RHE} in 0.5 M H_2SO_4 (pH = 0.56) for a flat sample (F ~500 nm) and a sample with nano-needles (F ~300 nm, NN ~4.6 µm). Samples were irradiated at the semiconductor-electrolyte interface. The stability test was conducted over a 4 hour period, with half hour segments shown from (a) 0 – 0.5 hrs and (b) 3.5 – 4 hrs.

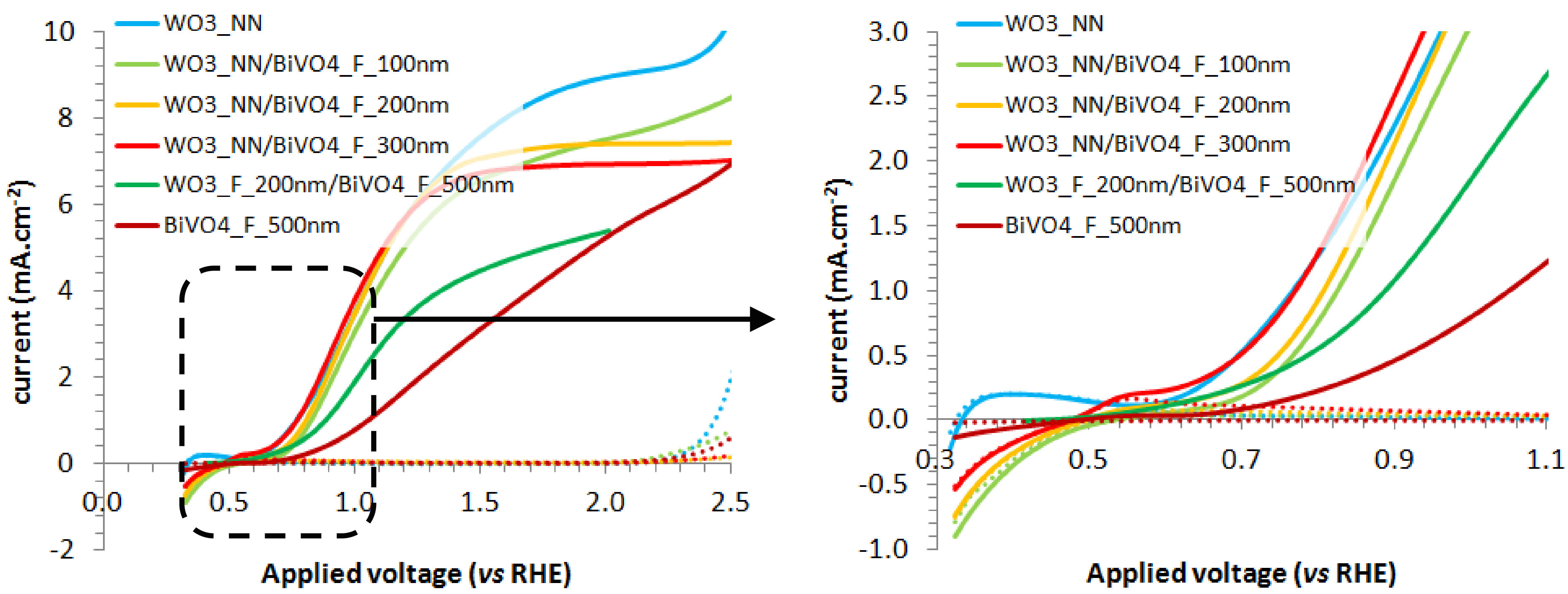
Supplementary Information



Faradaic efficiency measurements of water oxidation to di-oxygen for sample F ~300 nm, NN ~4.6 µm. The sample was held at 1.23 V_{RHE} in 0.5 M H_2SO_4 (pH = 0.56) in the presence of a UV light source (365 nm LED, ~30 $mW.cm^{-2}$). The photocurrent was used to measure the amount of O2 that would be formed if water oxidation was 100 % Faradaic. A Clarke-type oxygen electrode was used to measure the actual amount of O_2 released into the headspace of the cell.

Supplementary Information

- Photoelectrochemistry and incident photon-to-current efficiency (IPCE)
  - Examined in a 3-electrode photoelectrochemical cell
    (0.5 M H_2SO_4, pH ~1) or 0.1 M phosphate buffer, pH ~7)



Supplementary Information