Charge carrier dynamics in WO_3 needles for solar driven water oxidation

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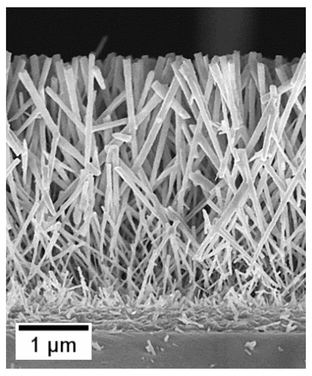
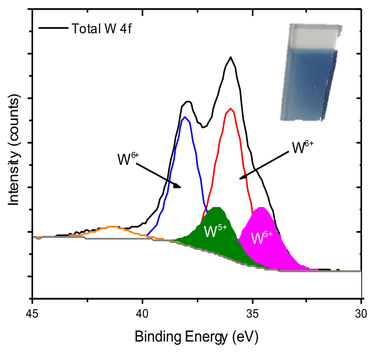
Background

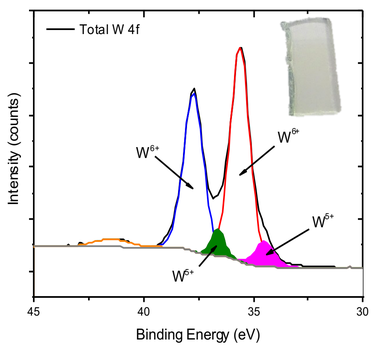
WO_3 is a promising photoanode material for solar water oxidation owing to its inherent aqueous stability in acidic electrolyte and facile synthesis methods.[1,2] With a deep valence band but a narrower band gap than the most frequently studied photoanode, TiO_2, we examine the performance of nanostructured WO_3 and the kinetics under water oxidation conditions, comparing to other transition metal oxides (TMOs). Notorious for harbouring oxygen vacancies (V_o),[3,4] we determine how these defect states affect the kinetics and longevity of the photogenerated charge carriers.

Synthesis and Characterisation

WO_3 films were synthesised by chemical vapour deposition (CVD), generating highly doped (blue) nanoneedles, 4 µm, with early photocurrent onset and high Faradaic efficiency (87%). Annealing is required for active films, which reduces the concentration of intrinsic oxygen vacancies.



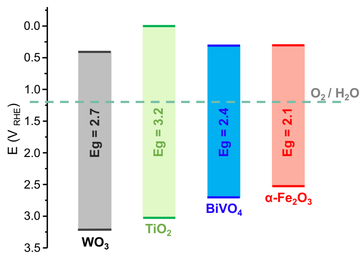


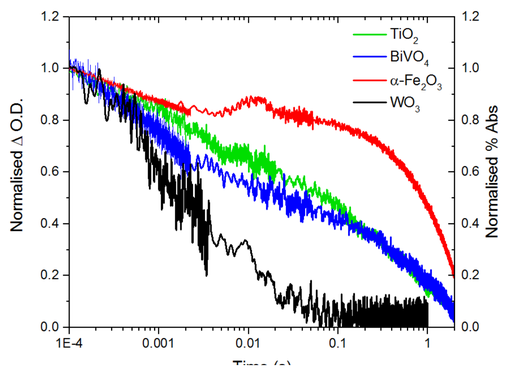


Comparison to other TMOs

Hole kinetics

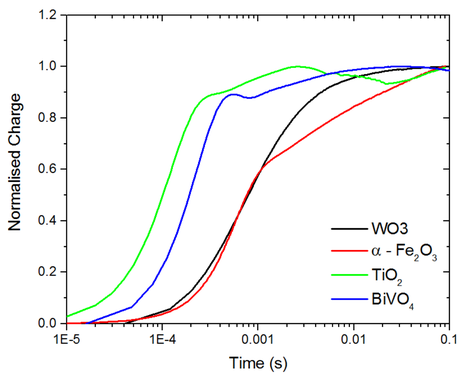
WO_3 has the fastest water oxidation kinetics. This correlates with valence band depth





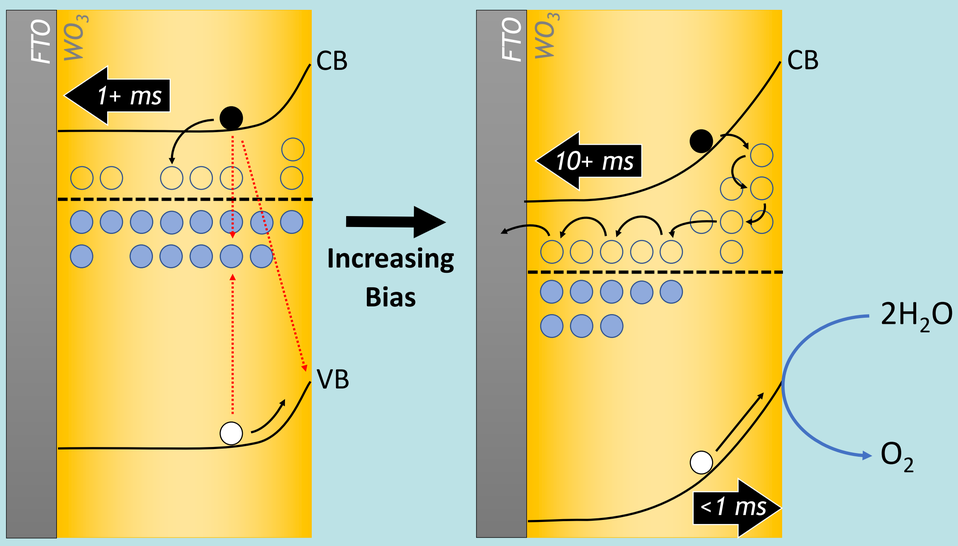
Electron extraction

WO_3 has one of the slowest rates of electron extraction, although the intrinsic doping density is the highest



Conclusions

- WO_3 needles give fast water oxidation due to deeper valence band position
- Slow electron extraction due to trapping in empty V_o states
- Removing V_o reduces the extraction time
- Increasing bias further delays electron extraction, but supresses bulk recombination

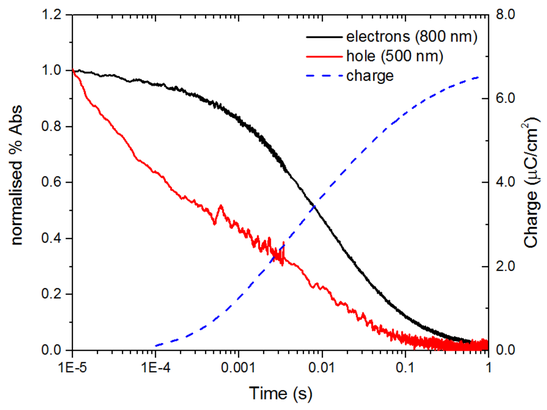


Kinetics

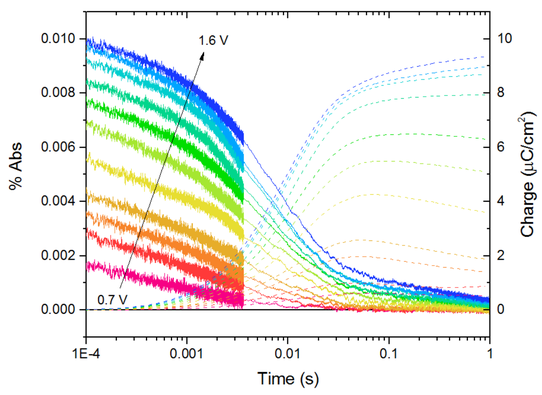
Rapid water oxidation

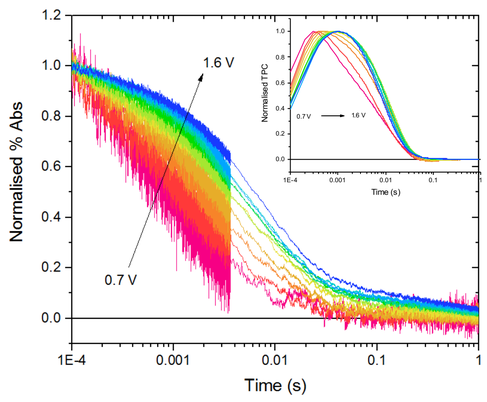
Transient Diffuse Reflectance Spectroscopy (TDRS) shows that water oxidation is much faster than electron extraction in WO_3 needles.

- $T_{1/2}(h^+) < 1$ ms
- $T_{1/2}(e^-) \sim 10$-20 ms



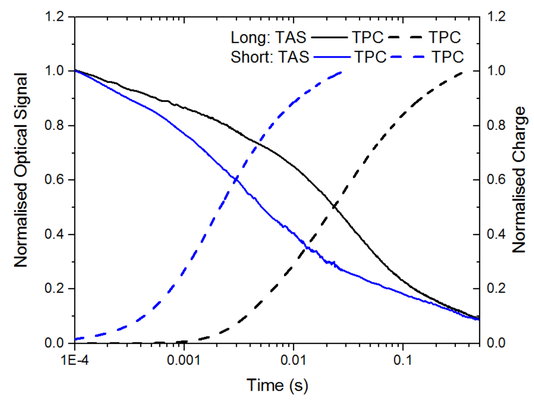
Bias dependent extraction





Bulk recombination is reduced with bias and there is little surface recombination. However there is slower extraction correlating with (e^-) traps below the conduction band

Modifications

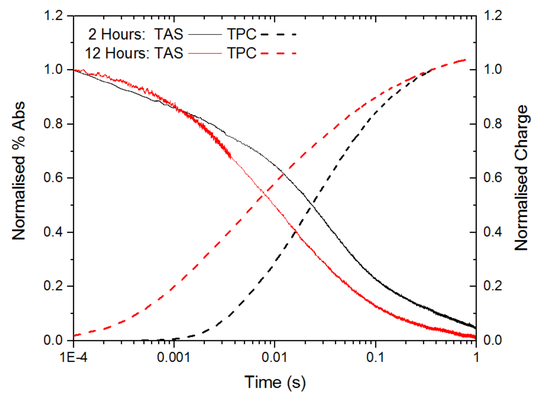


Shorter needles

Shorter needles (2 µm) give faster TDR decay, confirming that slow electron extraction is due to transport limitations.

Fewer oxygen vacancies

Increasing annealing time reduced V_o concentration. A faster decay is observed with fewer V_o. Conversely, a slower decay is observed with more V_o. This confirms that V_o can cause (e^-) trapping.



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1. Wang, G. et al., Energy Environ. Sci. 2012, **5**, 6180-6187.
2. Zhu, T., et al., Chem. Sus. Chem., 2014, **7**, 2974-2997.
3. Wang, F., et al., Phys. Rev. B, 2011, **84**, 73103-73108.
4. Johansson, M.B. et al., J. Phys. Condens. Mat., 2016, **28**, 475802-475812.