

Solution processed tin containing mesoporous hematite for solar water splitting – insights into mechanisms

Halina Dunn, Johann Feckl, Alexander Müller, Dina Fattakhova–Rohlfing, Laurie Peter¹, Christina Scheu and Thomas Bein

Department of Chemistry and Center for NanoScience (CeNS), University of Munich (LMU), Butenandtstr. 5-13 (E), 81377 Munich, Germany

¹Department of Chemistry, University of Bath, BA2 7AY, Bath, UK

The direct splitting of water into hydrogen and oxygen gases, with sunlight as the only input of energy, could provide a vital source of fuel in the context of a future low-carbon economy.¹ Hematite is a promising photo-anode material for the oxidation of water to oxygen – the more complicated half of the overall reaction converting water to hydrogen and oxygen gases. However, despite its suitable valence band position, visible light absorption, and good chemical stability, hematite is hindered by rather weak absorption and poor charge transport. This leads to a trade-off between light absorption and carrier collection in flat devices.

Nanostructures offer a solution to this issue, by decoupling light absorption from minority carrier collection. Mesoporous hematite is particularly interesting, as the small feature sizes favour good hole collection at the semiconductor electrolyte interface. Solution-processing allows the synthesis of hematite on such a scale, but doping is required if high efficiencies are to be reached.^{2,3} By introducing a Sn-precursor into our hematite synthesis, we incorporated 3.2 ± 1.5 atomic % Sn into our hematite nanoparticles. This led to a remarkable increase in photocurrent, reaching 0.4 mA/cm^2 at 1.23 V vs RHE for a 300 nm film under basic conditions under one Sun illumination, Fig. 1.a. Repeated application of hematite layers allowed the film thickness to be tuned from approximately 50 nm to 350 nm , Fig. 2.a-d.

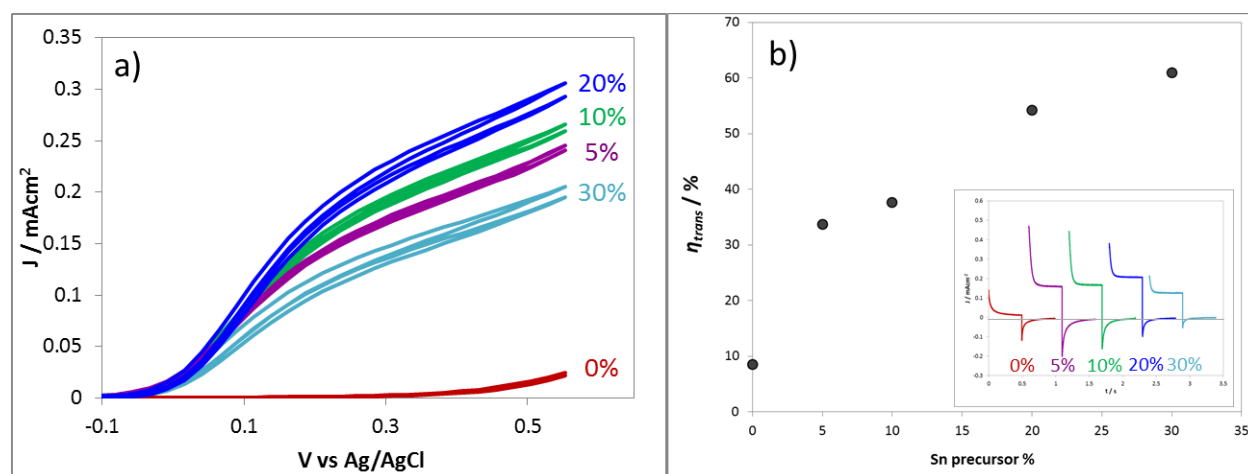


Figure 1: a) Photocurrent versus voltage curves for single layers of mesoporous hematite (red) and hematite doped with 5% Sn (purple), 10% (green), 20% (blue) and 30% (turquoise). Illumination through the substrate from a high power blue LED, intensity: $10^{17} \text{ cm}^{-2}\text{s}^{-1}$. b) Photocurrent transients and transfer efficiencies of hematite and Sn-doped hematite (0%, 5%, 10%, 20% and 30% Sn precursor). Measured at 600 mV vs. Ag/AgCl .

Further photoelectrochemical studies were undertaken to understand the role of Sn in improving the overall photocurrent. The analysis of photocurrent transients under chopped illumination identified a significant improvement in transfer efficiency upon Sn-inclusion into the hematite lattice, see Fig. 1.⁴ This can be explained by a reduced recombination rate or faster hole transfer kinetics to the electrolyte, and is the subject of ongoing research. The more pronounced effect of Sn-inclusion on thin films indicates that Sn atoms may also be responsible for healing the so-called “dead layer effect”.⁵ This manifests itself by a particularly poor performance of thin films, and is thought to be related to significant recombination at the FTO-hematite interface, Fig. 2.e. Despite the dramatic improvements brought about by Sn-inclusion into the hematite structure, the dependence of the photocurrent response to the illumination direction reveals that these films suffer from recombination, Fig 2.f. Further synthetic work in our laboratory thus hopes to overcome this issue by further changes in the absorber layer composition of matter, surface treatments, and host-guest architectures.

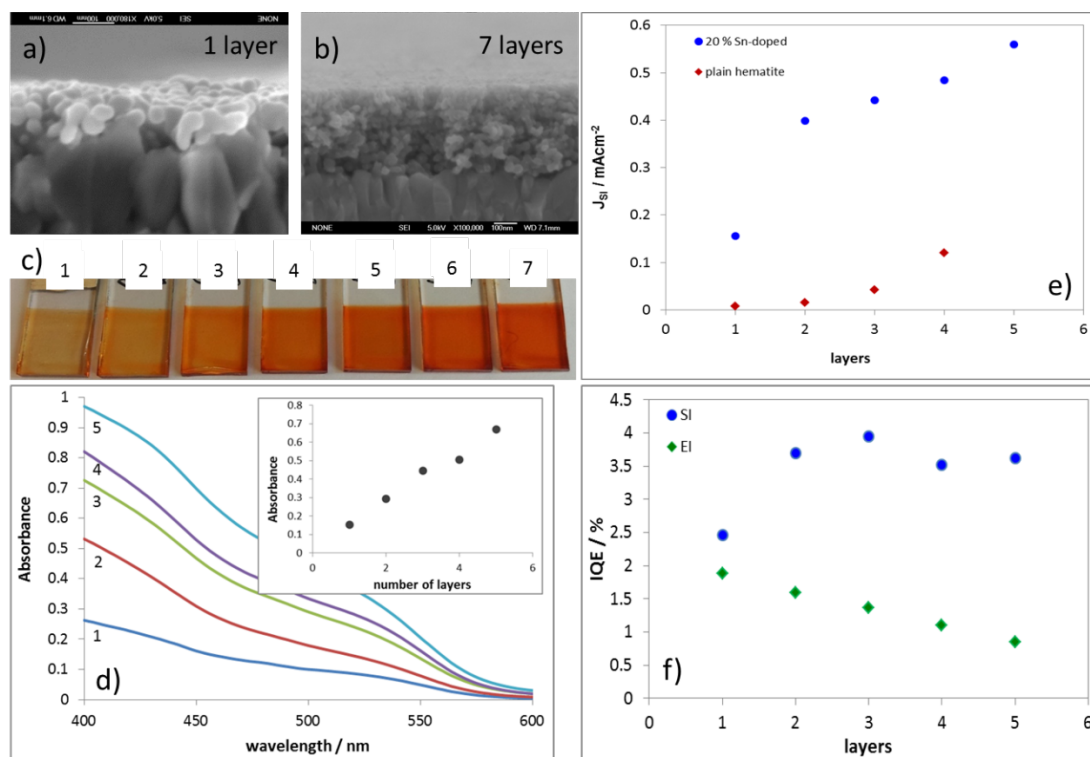


Figure 2: a) and b) SEM cross sections of 1 and 7 layer films, c) photographs of multi-layer films, d) optical absorbance of multi-layer films. e) Thickness dependence of the photocurrent density obtained at 500 mV vs Ag/AgCl under 455 nm illumination of $10^{17} \text{ cm}^{-2}\text{s}^{-1}$ through the substrate. f) IQE measured at 455 nm under 1 Sun bias light, illumination from the substrate (blue circles) and the electrolyte (green diamonds) recorded at 230 mV vs Ag/AgCl.

- (1) van de Krol, R.; Liang, Y.; Schoonman, J. *Journal of Materials Chemistry* 2008, 18, 2311.
- (2) Sivula, K.; Zboril, R.; Le Formal, F.; Robert, R.; Weidenkaff, A.; Tucek, J.; Frydrych, J.; Graetzel, M. *Journal of the American Chemical Society* 2010, 132, 7436.
- (3) Ling, Y.; Wang, G.; Wheeler, D. A.; Zhang, J. Z.; Li, Y. *Nano Lett.* 2011, 11, 2119.
- (4) Peter, L. M.; Wijayantha, K. G. U.; Tahir, A. *Faraday Discussions* 2011.
- (5) Zandi, O., Klahr, B.M., Hamann, T.W. *Energy & Environmental Science* 2013, 6.

