

## Solar Hydrogen Production by Photo-oxidation of Water from Doped Iron Oxide Photoanodes

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### Introduction

High efficiency photoelectrochemical material systems, for the production of hydrogen from water and sunlight, have been proposed and demonstrated;<sup>1</sup> unfortunately, the costs of these systems far exceeds any commercially acceptable value for large volume, low value, fuel production. Unfortunately, the abundant and inexpensive metal oxides such as TiO<sub>2</sub>,<sup>2</sup> ZnO,<sup>3</sup> and WO<sub>3</sub>,<sup>4,5</sup> have wide bandgaps and are therefore limited in overall terrestrial solar energy efficiency to less than ~4%. Metal oxides based on iron including,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite), have several advantages for photoelectrocatalytic chemical conversions using sunlight compared to alternatives. Hematite is an n-type semiconductor with a bandgap of 2-2.2 eV which can capture approximately 40% of the energy in incident sunlight, it is stable in most electrolytes at pH > 3, and it is abundant, inexpensive, non-toxic and environmentally benign. However, as a Mott-insulator it has several inherent disadvantages which give rise to poor charge transfer and high recombination rates for the photogenerated electrons and holes which limit the efficiency of the pure-phase material. In addition, for water photoelectrolysis, the rate of the oxygen evolution reaction (OER) on hematite is relatively slow. Finally, the energy of the conduction band relative to the redox level of the H<sub>2</sub>/H<sup>+</sup> is too low (~0.2 V vs. NHE) to efficiently drive the hydrogen evolution reaction. In order to use hematite as a photocatalyst in large scale solar applications, the factors that limit its performance must be overcome without adding significantly to the cost.

A multi-step optimization approach has been taken which consist improving the optical and electronic properties and improving the catalytic activity. For the improvement of the electronic properties of iron oxide, a synthesis approach has been taken in which iron hydroxide can be co-deposited with other transition metals allowing doped hematite thin films to be created with significantly improved conductivity. By modifying the hematite surface with electronegative species such as Fluoride atoms the flatband potential may be shifted as an alternative to the use of an external applied bias to improve the performance of the photoelectrodes. To increase the rate of the oxygen evolution reaction on hematite photoelectrocatalysts, a diverse set of Ni based electrocatalysts were explored.

### Materials and Methods

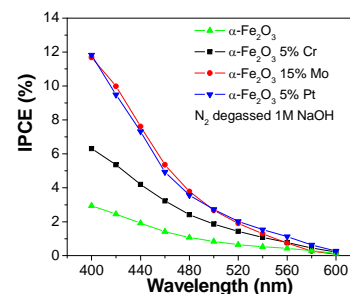
Several transition metals including Cr, Mo<sup>6</sup>, Pt<sup>7</sup>, have been electrochemically co-deposited with iron hydroxide on Quartz/Ti/Pt electrodes to provide dopants to the hematite. The resulting films were calcined to 700 °C in air and their photoelectrochemical performance measured in N<sub>2</sub> degassed 1M NaOH.<sup>6,7</sup> Further modification of the electrodes by grafting of fluoride atoms to the surface or deposition of electrocatalyst was also performed and the films characterized.

### Results and Discussion

Upon doping, the microstructures of the films varied; however, no preferred crystallographic orientation or dopant phase segregation was observed. The PEC performance was significantly improved upon doping with 15% Mo, 5% Cr and 5% Pt doped hematite showing the largest improvements compared to undoped hematite. The incident photon-to-electron conversion efficiencies (IPCE) at 400nm and 0.4V vs Ag/AgCl are 12%, 6% and 12% respectively (Figure 1). Other results related to the structure and performance of the samples, as well as further research in surface modification and electrocatalyst for oxygen reduction reaction with the aim of further improving the samples will be presented. In samples modified with fluoride, no bias was required and the IPCE at 400nm was 1.5 % as compared to 0.2v for the unmodified sample.

### Significance

This work presents a novel electrosynthetic method for the creation of doped hematite thin films. Strategies are shown to improve upon the performance of iron based thin films such that they may be cost effective candidates for solar-to-chemical energy conversion.



**Figure 1** IPCE of the electrodeposited films with and without doping at 0.2V vs Ag/AgCl applied potentials in N<sub>2</sub> degassed 1 M NaOH. All concentrations are of dopant in the electrolyte.

### References

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