Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: The Electrical Conductivity of Thin Film Donor Doped Hematite: From Insulator to Semiconductor by Defect Modulation

By *Johanna Engel* and *Harry L. Tuller*

Surface morphology of the undoped and 1% Ti doped hematite thin films

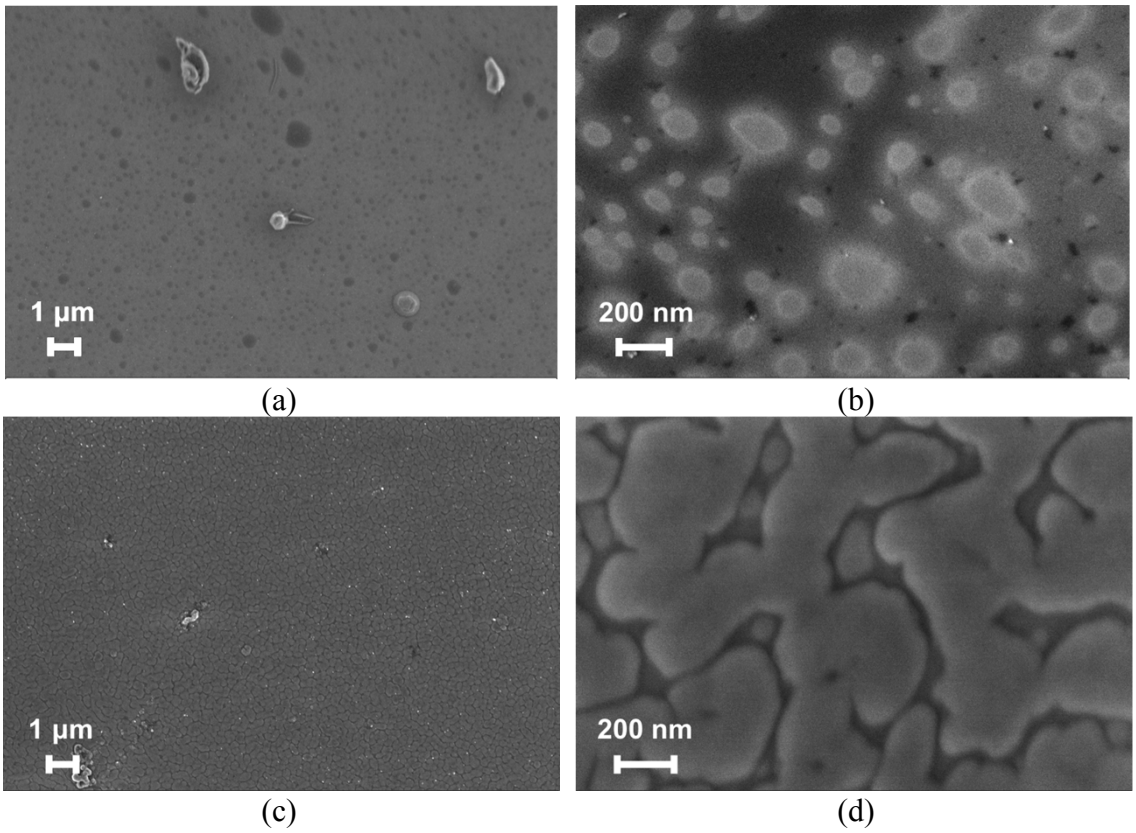

Figure S.1. SEM images of undoped (a and b) and 1% Ti doped (c and d) hematite thin films.

Figure S.1. presents images of the surfaces of the films investigated in this study. High resolution XRD patterns provided evidence that these films grew epitaxially on the sapphire substrates. Scanning electron microscopy (SEM) reveals that the surfaces of these films are not perfectly flat, but exhibit some morphology. The low magnification image of the undoped hematite film (Figure S.1. (a)) shows a smooth surface with pores of typically hundreds of nm in diameter, as also confirmed in the image at higher

magnification shown in Figure S.1. (b), as well as some debris. Atomic force microscopy (AFM) confirmed that these near surface pores lead to height variations of approximately 10 nm (see Figure S.2.). These features can be due to droplets of material that did not fully coalecse on the surface during PLD. Figures S.1. (c) and (d) show SEM images for the 1% Ti doped hematite film at low and high magnification, respectivly. In this case, the surface layer appears to be more coalesced than in the case of the undoped material but otherwise, the observations are similar.

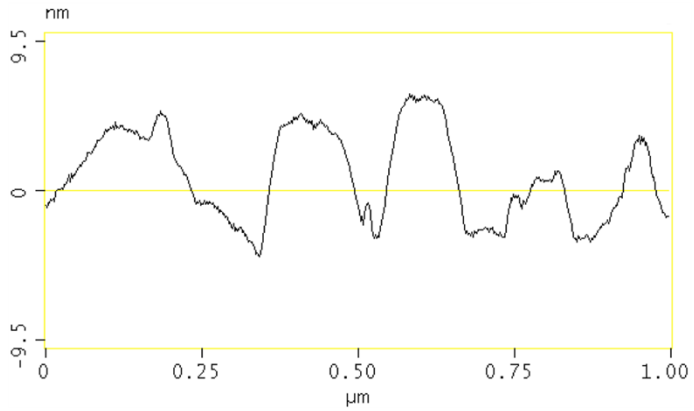

Figure S.2. Height profile analysis of a 1 µm cross section of the undoped hematite thin film surface.

Figure S.3. presents an AFM image of the surface of the undoped hematite thin film based on phase angle data. Noncoalesced droplets in the outermost surface layer of approximately 100 nm are visible. Analysis of the AFM data for roughness resulted in a root mean square value of 2.19 nm. While not perfectly flat, these films clearly do not exhibit a morphology with a surface area anywhere as large as that of purposefully nanostructured photoanodes such as the cauliflower structures grown by Grätzel et al. (S. C. Warren, K. Voitchovsky, H. Dotan, C. M. Leroy, M. Cornuz, F. Stellacci, C. Hébert, A. Rothschild and M. Grätzel, *Nature Materials*, 2013, **12**, 1-8.)

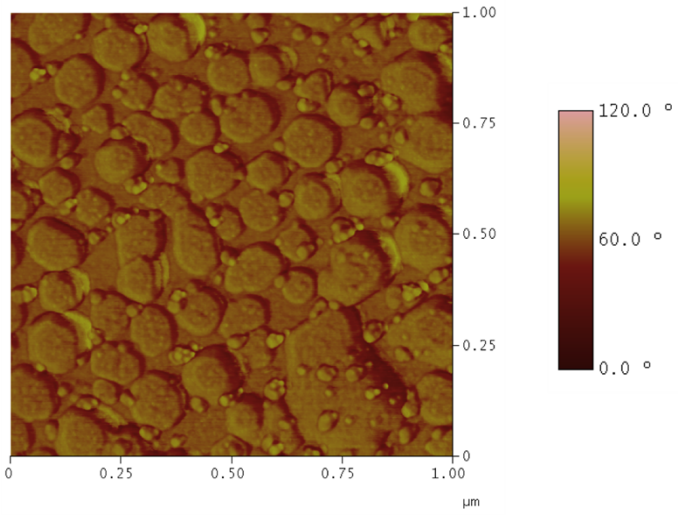

Figure S.3. AFM phase angle image of the surface of the undoped hematite film.