# The influence of Ti- and Si-doping on the structure, morphology and photo-response properties of α-Fe<sub>2</sub>O<sub>3</sub> for efficient water-splitting: insights from experiment and firstprinciples calculations

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Ti- and Si- doping effects on morphology, structure, optical and photo-response of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoscale coatings from atmospheric-pressure chemical vapour deposition (APCVD) have been studied. Si- and Ti-doping led to larger clusters with finer grains and smaller clusters with larger grains, respectively. Photocurrent performance was increased remarkably by doping, especially Si. Excellent agreement was found for band gaps and optical properties compared to hybrid-Density Functional Theory. Substitutional replacement of Fe by Si shrinks the volume more than Ti-doping; it is conjectured that this affects hopping probability of localised charge-carriers more and leads to enhanced photocurrent activity for Si-doping, supported by experiment.

Keywords: Iron oxide, Photocurrent, Density Functional Theory, Optical Properties

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## Introduction

The photocatalytic splitting of water (on photo-anodes) into hydrogen and oxygen using solar energy is a potentially clean and renewable source for hydrogen fuel [1]. Iron oxide ( $\alpha$ hematite Fe<sub>2</sub>O<sub>3</sub>) thin films constitute a very promising material for solar water-splitting applications on consideration of their relative ubiquity, low-cost, non-toxicity and stability, with a seemingly ideal band gap. However, there are many drawbacks, such as poor conductivity and high charge-recombination, which hinder the large-scale application of Fe<sub>2</sub>O<sub>3</sub>. Doping and manipulation of nano-morphology seeks to mollify or, ideally, eliminate these drawbacks [2]. The doping of impurities may affect the properties of synthesised material in many subtle ways, such as, inter alia, structure, nano-morphology, electron conductivity [2]. It has been demonstrated that incorporation of 3d transition metals into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> increases conductivity significantly [2-10]. On the other hand, the nano-structured morphology of hematite thin films with features comparable in size to, or less than, holediffusion lengths have been found to reduce significantly carrier-recombination [10-12]. Success towards the realisation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as a practical photoelectrochemical material has been somewhat mixed [2-9], but achieving greater photo-currents has been a necessary and very promising first step towards making hematite's widespread usage a viable proposition in commercial solar water-splitting applications.

Bearing in mind the potential promise of 're-engineered'  $Fe_2O_3$ , one of the main challenges in photoelectrochemical applications is to find cost-effective, scalable and simple process technologies for the manufacture of solar-device materials, often based on metal oxides. Atmospheric-pressure chemical vapour deposition (APCVD) is a promising technique in this respect due to its ability to yield coatings with controlled nanoscale surface and/or bulk properties; this is achieved at atmosphere pressure, without the need for any operationally- or economically-costly imposition of vacuum conditions. An additional desideratum of APCVD in view of commercial scale-up is that it is more compatible with industrial requirements due to its suitability for high throughput and deposition over large area, high processing speed and straightforward deployment for mass production [13]. In general, in order to achieve robust experimental measurements, it is crucial to use reliable synthesis techniques allowing nano-morphology control, doping and interface engineering to be applied with relative ease; APCVD offers such possibilities.

In this study, we examine how the electronic structure, crystal volume and density of states are affected by the incorporation of transition-metal dopants (Ti and Si) using hybrid density functional theory (DFT) methods in conjunction with high-quality experimental results for physical, structural, absorption coefficients, band gaps and photoelectrochemical properties of pure and doped hematite films deposited using a cost-effective and scalable custom-made APCVD system.

## **Experimental Methods**

Nanoscale-thick hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) thin films (cf. Fig. S1c in Supplementary Information, red-/brown-coloured and translucent) were prepared on FTO glass substrates (TEC 15 from Solaronix, Switzerland) by a custom-made atmospheric-pressure chemical vapour deposition (APCVD) system, as shown in Fig. S1a-b.The APVCD deposition chamber consists of: (i) vapour precursors and an air-delivery system, (ii) a closed-glass deposition chamber, (iii) a substrate heater, and (iv) an exhaust line. Before thin-film deposition, the glass substrates were cleaned ultrasonically in acetone followed by methanol, each for 5 minutes and drying via blowing dry air. The substrate was placed on the hot-plate and heated to 480  $^{\circ}$ C. The three-necked circular glass chamber was then placed on a hot plate. The temperature of the substrate surface was monitored by a thermocouple. For deposition of undoped hematite, iron pentacarbonyl vapour (Fe(CO)<sub>5</sub> Aldrich, 99.999%) was supplied *via* argon (99.9999%) through a bubbler containing liquid precursors at a flow rate of 12.5 µl/min. 2 l/min of dry

air, as an oxygen source, was then mixed with  $Fe(CO)_5$  vapour and directed vertically towards the conductive glass substrate though a 6 mm-diameter glass nozzle. The surface-tonozzle distance was kept constant at 20 mm. For deposition of Si- or Ti- doped hematite films, TEOS and TiCl<sub>4</sub> vapours were also supplied as respective Si and Ti sources, by bubbling argon (99.9999%) through liquid precursors at 25 µl/min. The deposition time for all coatings was 8 min. Gas flow rates were regulated by a mass-flow controller. Before deposition, an SiO<sub>2</sub> layer (of approximately 1 nm in thickness, confirmed by ellipsometry) was deposited onto a glass substrate, to act as a passive layer for improving charge transportation [11], with an argon flow rate of 18 µl/min through a TEOS precursor for 1 min.

The nanoscale surface morphology and roughness were examined using Atomic Force Microscope (AFM), whilst their crystallinity was examined using XRD. X-ray photoelectronspectroscopy (XPS) analysis of the samples was carried out, while light-absorption properties and band-gaps were determined using transmittance and absorption data from UV-Vis spectroscopy measurements. These protocols are described further in Supplementary Information. The photocurrent density, being proportional to the rate of the water-splitting reaction to hydrogen and oxygen on the photo- cathode and anode, respectively, was used as a means of gauging water-splitting in the photo-electrochemical (PEC) cell. The measurements of photocurrent ( $i_{ph}$ ) were carried out using a custom-made (PEC) cell, a GamryG300 potentiostat and a Newport 450 W (xenon arc lamp) solar simulator [14,15]. The PEC cell consists of three electrodes, a working electrode (APCVD-deposited hematite coating), a counter electrode (platinum wire) and a reference saturated calomel electrode (SCE) immersed in an aqueous electrolyte solution of 1 M NaOH, with a pH of 13.6. The hematite electrode was scanned at 50 mVs<sup>-1</sup> between applied biases of -1 to 1 V versus the SCE under light-on/off illumination conditions. The light intensity was measured by a photodiode power-meter. All potentials were reported against the reversible hydrogen electrode (RHE).

## **Theoretical Methods**

The calculations reported herein were performed using three-dimensional periodic spinpolarised density functional theory (DFT) calculations within the generalised gradient approximation (GGA) using the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [16-18]; this was implemented in the Vienna *ab initio* Simulation Package (VASP) code (v5.2.11) [19,20] in conjunction with projector-augmented wave (PAW) pseudo-potentials. The exchange-correlation potential was divided into short-and long-range parts, and Hartree-Fock (HF) exchange-correlation was mixed with Perdew-Burke-Ernzerhof (PBEsol) exchangecorrelation, as adjusted for solids [16], in the short-range part; a proportion of 25% of exact exchange was used. PBEsol has been used due to its superior geometry prediction vis-à-vis PBE exchange-correlation in solids [21,22] leading to more accurate Born-Oppenheimer forces acting on the electronic wave-functions, and providing the best feasible estimation of electronic properties. To avoid the expensive calculation of long-range HF exchange, this term is replaced by long-range PBEsol exchange; further details may be obtained from earlier work applied to photovoltaic properties of titania [23]. In any event, this choice of parameters for HSE06-PBEsol is identical to the recent work of Schimka et al. [24], who have found that this works well for a range of solids, and also of McDonnell et al. [23], both with an exactexchange contribution of 25%. However, it is also possible to change the proportion of exact exchange to tailor the band-gap and optical properties for optimal agreement with experiment; for instance, 10% proportions were used in recent work for bismuth-containing compounds [25, 26]. However, the good general agreement between DFT and experiment in this study (vide infra) justifies the choice of 25% exact exchange in this case.

Bulk calculations were performed on a 2 x 2 x 1 supercell of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> comprising a total of 60 atoms (24 Fe atoms and 36 O atoms). A 4 × 4 × 4 Monohorst-Pack *k*-point mesh [27] was applied over the Brillion zone and plane-waves up to a cut-off energy of 520 eV were found to be sufficient in precision for the calculation of ground-state geometry and optical properties. Both the atomic positions and cell parameters were optimised until residual forces were below 0.01 eV/Å. To simulate substitutional doping, a single iron atom was replaced by either Ti or Si. This corresponds to a dopant concentration of 1.67 mol %.

The frequency-dependent dielectric matrix was determined from the electronic ground state for the optical properties of pure and doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Inter-band contributions to the imaginary part  $\varepsilon_2(\omega)$  of the dielectric tensor  $\varepsilon(\omega)$  were calculated by summation over empty states. The real part of the dielectric tensor  $\varepsilon_1(\omega)$  was obtained by the usual Kramers-Kronig transformation [28,29]; further details are described in Supplementary Information.

#### **Results and Discussion**

The films deposited by thermal CVD processes were found to be semi-transparent and redbrown (cf. Fig. S1c, Supplementary Information). In order to minimise the influence of film thickness on coating properties, the thickness was maintained in the range of 400-450 nm. The variation of surface morphology was found to depend on the type of doping used, as confirmed by FESEM and AFM surface morphological studies. The Ti-doped coating (cf. Figs. 1c & f) exhibited smaller cluster sizes vis-à-vis those of the Si-doped case (cf. Figs. 1b & e) and undoped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> coating (cf. Figs. 1a & 2d). The FESEM cross-sectional image confirmed the presence of irregular open channels between the clusters through the thickness of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> coating. However, the grain size of the Si-doped coating was found to be significantly smaller than the Ti-doped and undoped sample, as confirmed by AFM-surface nanoscale morphological images.

Undoped Fe<sub>2</sub>O<sub>3</sub> coatings are generally electrical insulators in nature. The doping of hematite affects conductivity through the changing of charge-carrier concentrations and/or their mobility. XPS was used to demonstrate the presence and chemical status of dopants in the coatings. Fig. 2 indicates the Si 2p core-level XPS spectra of the Si-doped deposited coating; XPS results confirmed that the coating contained 4.4 at. % of Si. The Si 2p core level spectrum is found to be asymmetric; after curve fitting, the two peaks identified at binding energies ~99 and ~102 eV correspond to the elemental form of Si and Si in SiO<sub>2</sub> structure, respectively. The intense Si 2p peak placed at ~102 eV for the Si-doped sample (cf. Fig. 2) may be indicative of the presence of mainly substitutionally-doped Si in the hematite coating as a  $Si^{4+}$  species [3,30,31]. Conversely, the peak at ~99 eV indicates a certain amount, albeit relatively small, of the elemental form of Si dopant present in the hematite film. However, Ti was not detected in Ti-doped samples. It may be in concentrations below the detection limit of XPS (~ 0.1 at. %) and 'buried' within the signal noise of the peak, or, perhaps more likely, may be below depths possible for probing by highly surface-confined XPS measurements. However, we note from the recent study of Zandi et al [32], which used atomic layer deposition (ALD) methods for the construction of Ti-doped hematite coatings, that the photocurrent-density measurements in this study (vide infra) exceed substantially those both of the pure-hematite case as well as those of the ALD-type Ti-doped coatings of Zandi et al [32]; however, the coatings in the present study are substantially thicker than those of ref. [32], with a different morphology, and thicker coatings would of course be expected to yield a larger photocurrent. In the latter case [32], it is estimated that the Ti concentration level increased by almost 0.5 at. % with each new ALD 'cycle %', and there was certainly a very sharp rise in photocurrent-density between zero and 5 'cycle %' (which is 0 to ~2.4 at. %). Bearing in mind this dramatic rise with Ti-concentration at low dopant-composition (with our ~0.1 at. %, corresponding to the detection limit of XPS, being equivalent to around 0.2 ALD cycles), it is clear *grosso modo* that it would be quite possible for there to be a relatively low Ti concentration (true of the present study), whilst there still being a substantial increase in photocurrent density; this is the case here, as shall be discussed in the latter part of this section.

The XRD patterns of the doped and undoped hematite thin films are given in Fig. S2a (cf. Supplementary Information). The peaks marked by the asterisk symbol (\*) correspond to the fluorine-doped tin oxide (FTO) substrate. The crystalline nature of the deposited film was confirmed by XRD spectra with peaks at  $2\theta \approx 24.14$ , 33.15, 35.61, 40.86, 49.48, 54.05 and 57.5 °. These peaks correspond to the (012), (104), (110), (113), (024), (116) and (018) diffraction plane of hematite respectively according to the JCPDS reference pattern 00-001-1053 (cf. black line in Fig. S2a). The preferential orientation and level of crystallinity were all found to depend on the doping element (*i.e.*, Ti or Si). The intensity ratio of (110) and (104) peaks, *i.e.*, [(110)/(104)], was found to be greater for Si-doped coating with respect to undoped and Ti-doped coatings. This indicates that the hematite coating is more preferentially oriented to the (110) plane in the case of Si-doping. It is important to note that the coating with the intense (110)-diffraction plane peak is more suitable as a photoactive material [10, 11]. This is due to holes (used for water oxidation at the anode) conduction strongly taking place within the (110) plane and electrons (used for hydrogen protons reduction at the cathode) conduction is favoured along the (001) basal plane, which is perpendicular to (110) plane. The formation of crystalline hematite was also confirmed by Raman spectroscopy as shown in Fig. S2b. The peaks at 225, 244, 291, 409, 493 and 609 cm<sup>-</sup> <sup>1</sup> in the Raman spectrum correspond to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) [12]. In addition, a peak at ~658 cm<sup>-1</sup> was also observed in the Raman spectrum of the Si-doped hematite film. Bersani et al correlated the intensity of Raman peak at ~  $660 \text{ cm}^{-1}$  with crystal size of the hematite (finding that the higher the intensity, the smaller the grain size) [33], which suggests that this

peak may be related to surface and grain boundary disorder of hematite. Therefore, in this study, the appearance of a Raman peak at ~ 658 cm<sup>-1</sup> indicates that Si-doped samples have smaller crystal size relative to the Ti-doped and undoped samples [12]. These findings are consistent with the AFM and SEM results (*vide supra*).

In the case of both DFT and experimental measurements, the direct and indirect band gaps were calculated using the conventional Tauc method, taking the value of the extrapolation of the linear portion of the graph with the abscissa (cf. Fig. S3, Supplementary Information). The experimental direct and indirect band gaps thus inferred were 2.15 and 1.98 eV, respectively; this shows excellent, quantitative agreement with the corresponding respective theoretical predictions of 2.2 and 2.0eV (cf. Figs. S3a & b for pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The doping of Ti and Si in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> affects the band gap relatively little vis-à-vis the value for pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, as can be seen in Figs. S3c vs. 5d, and also Figs. S3e vs. f. These obtained values are not only comparable with each other (experimental versus theoretical, doped versus pure) but also for other studies of pure and doped (Ti and Si)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> observed in the literature [2-9]. The good level of agreement between state-of-the-art DFT and experiment tends to arise largely from the use of hybrid functionals in the guise of HSE06-PBEsol. However, often, these properties may be sensitive to dopant concentration, so, in general, care must be taken in comparing theory and experiment directly.

We found from DFT system-volume optimisation to atmospheric pressure that doping via substitution of Fe by Si shrinks the volume of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal with respect to the pure state by more than comparable Ti substitutional doping (by circa 1.5% for Si-doping vis-à-vis ~0.1-0.2% for Ti-doping), owing to the smaller ionic radius of Si relative to both Fe and Ti. It is conjectured that this reduction in volume of the crystal can affect the hopping probability of localised charge-carriers and lead to enhanced photo-current activity, due to more intimate contact between Si and its neighbouring 'host' atoms; it must be emphasised, however, that

there is no direct evidence to support this speculation. Si was observed to form a much more covalent bond to oxygen, and so electrons would occupy anti-bonding orbitals preferentially, verified by the lengthening of Si-O bonds; therefore, added electrons reside on Fe cations in such a less energetically favourable case. In contrast, the Ti dopant traps electrons more preferentially, and contributes fewer electron carriers as a result. Bader charge analysis [34] on the Ti and Si dopant atoms indicated charges of 3.12 and 3.62 |e|, respectively, indicating respective valence characters closer to 3+ and 4+. The, admittedly tentative, finding of a valence configuration closer to an Si 4+ state is in line with experimental XPS results from Fig. 2 and refs. [3, 30, 31]. However, for substitutional replacement of Fe by the dopant, one would expect, ceteris paribus, something closer to a 3+ valence state in the dopants: it is the subtleties of the above-mentioned finding of more electrons residing on nearby Fe cations in the vicinity of the Si dopant that serves to increase the *de facto* charge on Si, 'nudging' the ionisation state somewhat closer to 4+. Rather than the prospect of the system as a whole 'shifting' from being electroneutral to cationic, in any formal sense, with a Si state closer in nature to 4+, we observed that there was enhanced electron (negative) charge on the surrounding ions in the vicinity of Si, *i.e.*, electron 'leakage' or 'dissipation'.

The calculated optical constants are shown in Figs. S4 (a-g) in Supplementary Information, and show the calculated results for the real part of the optical conductivity  $\sigma_I(\omega)$ , index of refraction (*n*), extinction coefficient (*k*), energy-loss spectrum ( $L_s(\omega)$  – surface and  $L(\omega)$  – bulk), reflection coefficient (*R*), and the real part of the inter-band transition strength (Re  $J_{cv}$ ). The broad peaks in the bulk energy-loss spectrum are at about 11 and 21 eV (cf. Fig. S4b), relating to transitions from occupied O 2s and Fe 6s bands lying below the valence band to the conduction band. In addition, the featured peaks at around 7 and 16 eV in the real part of the inter-band transition strength (Re  $J_{cv}$ ) are attributable to electronic transitions from occupied O 2*s* energy levels to lower levels in the empty conduction band (cf. Fig. S4g). The index of refraction and extinction coefficients are directly proportional to the real and imaginary parts of dielectric constant, respectively. The static refractive index (at n = 0) is 2.5, while the maximum occurs at ~3eV. It is interesting to note in particular that Si-doping imparts an 'upward' movement to higher energy by about 1 eV in the Fe 6s band-transition region (cf. Fig. S4b); this is likely due to the more intimate coupling of the Si atom with the neighbouring 'host lattice' atoms, owing to the smaller ionic radius of Si vis-à-vis Fe and Ti (i.e., ~0.55 Å versus ~0.6 and 0.8 Å, respectively [35]), which one would expect to lead to a possible increase in photo-current. The spectra (cf. Fig. S4e) shows low reflectance at lower wavelengths and a sharp increase at around 550 nm, indicating that the band gap is around 2.2eV for both doped and undoped cases, in good agreement with the DFT and experimental findings of Fig. S3.

The calculated band structures along high-symmetry directions of the Brillouin zone are shown in Supplementary Information (cf. Figs. S5 to S7). It can be seen that there is only a shift in the Fermi energy levels after Si and Ti doping and some changes in conduction band minima relative to the undoped case (in Fig. S5). However, there is no conclusive evidence of either a direct or indirect band gap, which tends to echo the DFT findings of Fig. S3 (themselves in good agreement with the corresponding experimental optical results). This subtlety is an important aspect of the hybrid DFT approach here, which is compromised to some extent, for instance, by the use of the PBE approach in the recent study of Xia *et al* [36] on doped hematite.

In order to assess very directly the performance of APCVD-deposited nano-coatings for water-splitting, photo-current densities were obtained [14, 15], as shown in Fig. 3. The measurements were carried out under interrupted solar-simulator light-on/off as a function of applied potential ( $E_{app}$ = -1 V to +1 V SCE) in 1M NaOH aqueous solution. The anodic photo-current was found to be very low for the undoped hematite coating. The doped films

exhibited significantly higher photocurrent (cf. Fig. 3d): > 60 and >13 times for the Si- and Ti-doped samples, respectively. This may be conjectured to arise due to synergistic effects of higher conductivity and smaller grain size (which serves to increase the light-harvesting area) for doped hematite films vis-à-vis pure coatings, which is *ipso facto* an insulator. However, Ti-doped coatings exhibited a lower photo-current relative to Si-doped samples; this may be due to the presence of larger grains, which serve to increase charge recombination, and also arise from the observed less-intense peaks along the (110) plane, as discussed earlier. Also, the more intimate contact between Si and neighbouring atoms serves to promote enhanced energetic transfer in the lattice. Certainly, the significant increase in photocurrent-density upon Ti-doping in comparison to the pure case in Fig. 3 underscores that Ti is present, albeit at levels undetectable within the detection limit of XPS (as mentioned earlier). Again, this is consistent with the findings of Zandi *et al* [32], in terms of very rapid rise in photocurrent-density upon an increase in Ti-concentration at relatively low Ti compositions.

#### Conclusions

Doped (Si and Ti) and pure nano-crystalline hematite photo-electrodes were prepared successfully through custom-made APCVD techniques for solar production of H<sub>2</sub>. Lightabsorption and band-gap properties of the film were gauged by UV-vis techniques. The Siand Ti-doped coatings demonstrated higher photo-current density (> 60 and >13 times respectively) compared to the pure coating. However, it is likely that concentration effects are very important in these results, with the higher observed concentration of Si than Ti being an important factor in leading to higher photo-currents for Si-doping; the marked increase in photocurrent observed by Zandi *et al* [32] upon increasing Ti concentration from low values emphasises this point clearly. Although it is also to be expected that photo-current will be maximised at some dopant concentration (and it is unclear from this study of the relationship of that with respect to Si-concentration), it is rather difficult to conclude *definitively* that Si is *intrinsically* superior to Ti with respect to photo-current (for similar Si and Ti concentrations), despite the suggestive evidence of the DFT results in this vein. Despite these necessary qualifications vis-à-vis dopant concentration, excellent quantitative agreement has been found between experiments and results from hybrid-DFT for band gaps. We find that cationic doping via substitution of Fe by Si shrinks the volume of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> crystal more than comparable Ti substitutional doping. It is speculated that this reduction of volume of crystal can affect the hopping probability of localised charge carriers and may lead to enhanced photocurrent activity; the fact that this higher photocurrent was observed by experimental analysis does not, however, indicate *per se* that this conjecture on hopping probability is necessarily true.

The Si-doped coating displayed larger clusters with finer grains, whereas Ti-doped hematite coating exhibited smaller clusters with larger and smoother grains structure. It is expected that the structure with smaller clusters and finer grain will further enhance performance of the hematite photoanode. Therefore, further study is warranted to achieve the optimally nano-structured doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> electrode (with optimisation of Si-doped, Ti-doped or Ti/Si-codoped coatings) for better PEC performance for solar hydrogen production.

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#### References

- J. Nowotny, C. C.Sorrell, L. R. Sheppard, T. Bak, Int. J. Hydrogen Energy 30, 521 (2005).
- 2. K. M. Rosso, D. M. A. Smith, and M. Dupuis, J. Chem. Phys. 118, 6455 (2003).
- J. A. Glasscock, P. R. F. Barnes, I. C. Plumb, and N. Savvides, J. Phys.Chem. C 111, 16477 (2007).
- Y. S. Hu, A. Kleiman-Shwarsctein, G. D. Stucky, and E. W. McFarland, Chem. Commun. (Cambridge) 2009, 2652.
- Y. S. Hu, A. Kleiman-Shwarsctein, A. J. Forman, D. Hazen, J. N. Park, and E. McFarland, Chem. Mater. 20, 3803 (2008).
- A. Kleiman-Shwarsctein, Y.-S. Hu, A. J. Forman, G. D. Stucky, and E. W. McFarland, J. Phys. Chem. C 112, 15900 (2008).
- 7. A. Kleiman-Shwarsctein, Y.-S. Hu, G. D. Stucky, and E. W. McFarland, Electrochem. Commun.11, 1150 (2009).
- 8. W. B. Ingler, J. P. Baltrus, and S. U. M. Khan, J. Am. Chem. Soc. 126, 10238 (2004).
- S. Kumari, C. Tripathi, A. P. Singh, D. Chauhan, R. Shrivastav, S. Dass, and V. R. Satsangi, Curr. Sci. 91, 1062 (2006).
- 10. R. Morrish, M. Rahman, J.M. D. MacElroy, C. A. Wolden, ChemSusChem, 4,474-479, 2011
- 11. A. Kay, I. Cesar and M. Gratzel, J. Am. Chem. Soc., 2006, 128, 15714
- 12. I. Cesar, K. Sivula, A. Kay, R. Zboril and M. Gratzel , J. Phys. Chem. C 2009, 113, 772–782

- D. Hocine, MS. Belkaid, M. Pasquinelli, L. Escoubas, J.J. Simon, G. Rivière and A. Moussi, Santiago de Compostela (Spain), International Conference on Renewable Energies and Power Quality (ICREPQ'12), Santiago de Compostela (Spain), 2012
- M. Rahman, J.M.D. MacElroy and DP Dowling, J. Nanosci. Nanotechnol., 11 (10), 8642-8651, 2011
- M. Rahman, B.H.Q. Dang, K. McDonnell, J.M.D. MacElroy, D.P.Dowling, J. Nanosci. Nanotechnol., 12, 4729-4735, 2012
- 16. J. Heyd, G.E. Scuseria, M. Ernzerhof, J. Chem. Phys. 118 (2003) 8207.
- 17. J. Heyd, G.E. Scuseria, M. Ernzerhof, J. Chem. Phys. 124 (2006) 219906.
- J. Paier, M. Marsman, K. Hummer, G. Kresse, I.C. Gerber, J.G. Angyan, J. Chem. Phys. 125 (2006) 249901.
- 19. G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
- 20. G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
- 21. J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
- 22. J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, Phys. Rev. Lett. 100 (2008) 136406.
- 23. K.A. McDonnell, N.J. English, M. Rahman, D.P. Dowling, Phys. Rev. B 86 (2012) 115306.
- 24. L. Schimka, J. Harl, G. Kresse, J. Chem. Phys. 134 (2011) 024116.
- 25. N. Wadnerkar and N.J. English, Comput. Mat. Sci, 74, 33-39 (2013).
- 26. K.A. McDonnell, N. Wadnerkar, N.J. English, M. Rahman and D.P. Dowling, Chem. Phys. Lett., 572, 78-84 (2013).
- 27. H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
- 28. M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, Phys. Rev. B 73 (2006) 045112

- 29. S.T. Zhang, M.H. Lu, D. Wu, Y.F. Chen, N.B. Ming, App. Phys. Lett. 87 (2005) 262907.
- 30. S. Saremi-Yarahmadi, K. G. U. Wijayantha, A. A. Tahir, and B. Vaidhyanathan, J. Phys. Chem. C 113, 4768 (2009)
- 31. F. J. Morin, Phys. Rev. 83, 1005 1951
- 32. O. Zandi, B.M. Klahr and T.W. Hamann, Energy & Env. Sci., 6, 634-642 (2013)
- 33. D. Bersani, P.P. Lottici and A. Montenero, J. Raman Spectrosc., 30, 355–360 (1999)
- 34. E. Sanville, S.D. Kenny, R. Smith and G. Henkelman, J. Comp. Chem., 28, 899 (2007).
- 35. R.D. Shannon, Acta Crystallogr., A32, 751 (1976).
- 36. C. Xia, Y. Jia, M. Tao and Q. Zhang, Phys. Lett. A, 377, 1943–1947 (2013)

- Fig. 1: Morphologies of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> coatings: SEM top-surface morphology of (a) undoped (b) Si- and (c) Ti-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film; AFM nano-surface morphology of (d) undoped, (e) Si- and (f) Ti-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> cases.
- Fig. 2: XPS narrow-scan spectra of Si 2p peak for the Si-doped hematite film, with fitted curve and reference SiO<sub>2</sub> data.
- Fig. 3: Photo-current versus applied potential for pure and doped hematite film.







5 100 200 300 nm







(e)



100 200 Г 0 300 nm

(f)



Fig. 2



Applied Potential VS RHE, V

Fig. 3