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# Hydrogen induced interface engineering in Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> heterostructures for efficient charge separation for solar-driven water oxidation in photoelectrochemical cells†

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Semiconductor heterostructure junctions are known to improve the water oxidation performance in photoelectrochemical (PEC) cells. Depending on the semiconductor materials involved, different kinds of junctions can appear, for instance, type II band alignment where the conduction and valence bands of the semiconductor materials are staggered with respect to each other. This band alignment allows for a charge separation of the photogenerated electron–hole pairs, where the holes will go from low-to-high valance band levels and *vice versa* for the electrons. For this reason, interface engineering has attracted intensive attention in recent years. In this work, a simplified model of the Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> heterostructure was investigated *via* first-principles calculations. The results show that Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> produces a type I band alignment in the heterojunction, which is detrimental to the water oxidation reaction. However, the results also show that interstitial hydrogens are energetically allowed in TiO<sub>2</sub> and that they introduce states above the valance band, which can assist in the transfer of holes through the TiO<sub>2</sub> layer. In response, well-defined planar Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> heterostructures were manufactured, and measurements confirm the formation of a type I band alignment in the case of Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>, with very low photocurrent density as a result. However, once TiO<sub>2</sub> was subjected to hydrogen treatment, there was a nine times higher photocurrent density at 1.50 V vs. the reversible hydrogen electrode under 1 sun illumination as compared to the original heterostructured photoanode. *Via* optical absorption, XPS analysis, and (photo)electrochemical measurements, it is clear that hydrogen treated TiO<sub>2</sub> results in a type II band alignment in the Fe<sub>2</sub>O<sub>3</sub>–H:TiO<sub>2</sub> heterostructure. This work is an example of how hydrogen doping in TiO<sub>2</sub> can tailor the band alignment in TiO<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub> heterostructures. As such, it provides valuable insights for the further development of similar material combinations.

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## 1. Introduction

Solar energy-assisted splitting of water into its constituents, hydrogen and oxygen, in a photoelectrochemical (PEC) cell, represents a promising route to convert solar energy into more useful chemical fuels.<sup>1,2</sup> The water reduction process can produce hydrogen, where the required electrons can be generated *via* the water oxidation reaction at the surface of a photoanode through PEC reactions. However, the water oxidation reaction is a demanding electrochemical process, requiring an

oxidatively robust and yet inexpensive semiconducting material as the photoanode.<sup>3</sup> Despite tremendous efforts, developing a highly active photoanode for water oxidation at low cost remains a significant challenge. After the first report on water splitting by Fujishima and Honda,<sup>4</sup> titanium dioxide (TiO<sub>2</sub>) in its anatase phase has been extensively studied in solar-driven photocatalytic processes.<sup>5–7</sup> However, for practical applications, the large bandgap of TiO<sub>2</sub> (~3.2 eV) requires solar radiation with wavelength below 388 nm to create an electron–hole pair; thereby, limiting the overall efficiency of TiO<sub>2</sub> when illuminated under real Sun conditions.<sup>8,9</sup> Another material of high interest for PEC water splitting is hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), due to its suitable band gap (2.1 eV), high stability over a wide range of pH and potentials, and low material cost.<sup>10,11</sup> In spite of these various advantages, the solar-to-hydrogen conversion efficiency of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> falls well below the theoretical maximum value ( $\approx$  12.9%) due to a number of factors such as (i) bulk charge recombination, (ii) interfacial carrier trapping and

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recombination, (iii) surface trapping and recombination, and (iv) improper band positions for unassisted water splitting<sup>12</sup> (see Fig. S1† for further information).

To address the issues with solely  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> based oxide semiconductors and design a photoanode for PEC water oxidation with high solar-to-hydrogen conversion efficiency, the heterostructure of these two semiconductors has been recognized as an attractive candidate to enhance the photocurrents and lower the onset potential.<sup>13,14</sup> The combined properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> allow the heterostructures to absorb a wider range of photons, thanks to the relatively narrow band gap of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>15</sup> Also, the formation of heterostructures between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> can allow band structure engineering to manipulate surface/interface properties for charge transfer/separation, thereby enhancing the water oxidation performance.<sup>16</sup> In particular, the valence and conduction band alignment mechanisms at the interface are crucial for the separation of photogenerated charge carriers.<sup>17</sup> In both oxide semiconductors, the Fermi levels depend on the concentrations of the conduction electrons and hence on the oxygen vacancy concentrations. By appropriate adjustments of the Fermi levels *via* defect concentration, the valence band edge in the bulk of the semiconductor may be brought to a common equilibrium. Using the available data<sup>18</sup> of the electron affinities for Fe<sub>2</sub>O<sub>3</sub> (4.71 eV) and TiO<sub>2</sub> (4.33 eV), together with the generally accepted model of heterojunctions, the discontinuity at the conduction bands (CB) is estimated to be 0.38 eV while that for the valence bands (VB) is estimated to be 0.42 eV. Owing to the mutual positions of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> conduction band edges, photogenerated electrons in TiO<sub>2</sub> can be easily transferred to Fe<sub>2</sub>O<sub>3</sub> and injected into the Indium Tin Oxide (ITO) substrate, and subsequently can migrate through the external electric circuit to reduce water at the cathode, thus suppressing detrimental recombination effects (Fig. 1a). On the other hand, the VB offset at the interface by 0.42 eV act as an energy barrier that blocks the hole transfer from the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to the TiO<sub>2</sub> layer and prevents the water oxidation reaction on the surface of TiO<sub>2</sub> (Fig. 1a). This means the heterostructure between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> forms a type I band alignment at the semiconductors' interface, and the hole transport from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to TiO<sub>2</sub> is energetically impeded, as depicted in Fig. 1a and b.

However, in the case of a thin porous TiO<sub>2</sub> layer (<100 nm) over Fe<sub>2</sub>O<sub>3</sub> and at applied anodic potential, the depletion region and upward band bending in TiO<sub>2</sub> at Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> nano-heterostructure in contact with the electrolyte may extend into the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This high band bending in the thin TiO<sub>2</sub> overlayer, under the influence of anodic potential, can provide a channel to transfer the photogenerated holes from Fe<sub>2</sub>O<sub>3</sub> to TiO<sub>2</sub> where they participate in the water oxidation reaction, thereby improving the water oxidation performance of the Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> photoanode. Barreca *et al.*<sup>15</sup> reported that the use of external potential could transfer of photogenerated holes from porous hematite to TiO<sub>2</sub> layers that can improve the PEC response under simulated light. However, in the case of thick and dense TiO<sub>2</sub> layer over  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the mismatched band alignment can hinder the charge transfer process at Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure, thereby constitute the limiting factor in PEC applications. Therefore, for swift transfer of photogenerated holes from VB of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to the VB of TiO<sub>2</sub>, band edge and band gap tailoring in TiO<sub>2</sub> are required to form a type II band alignment at the Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure interface. In our previous study,<sup>8,9,17</sup> we demonstrated that a high temperature hydrogen treatment in TiO<sub>2</sub> under partial pressure can modify the structural, optical, and electrical properties and significantly improve the photocatalytic and photoelectrochemical performance. An upshift of the valence band of TiO<sub>2</sub> was achieved after the high temperature hydrogen treatment at partial pressure that was useful for band edge engineering at TiO<sub>2</sub>-BiVO<sub>4</sub> heterostructure. However, a downshift of valence band maximum (VBM) was also obtained when TiO<sub>2</sub> thin films were grown *in situ* in hydrogen plasma.<sup>19</sup>

In this study, first-principles calculations on a model Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructure show that the strain at the interface shifts the valence and conduction band positions and affects the bandgap of the TiO<sub>2</sub> layer. Furthermore, the calculations show that neutral and positive charged H interstitials are energetically preferred under hydrogen treatment conditions. These interstitials introduce states in the bandgap of TiO<sub>2</sub>, which can assist in the transfer of holes through the TiO<sub>2</sub> layer. To challenge the theoretical predictions, well-defined planar Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> heterostructures were manufactured. The experimental results show that Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> initially forms a type I band

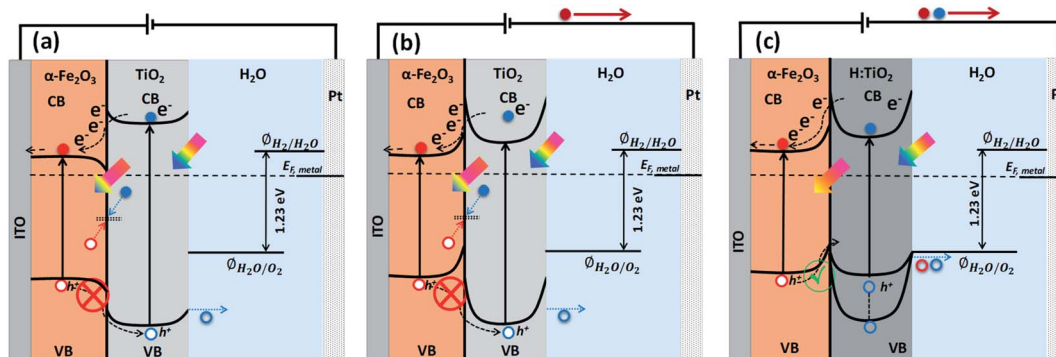


Fig. 1 Approximate energy band diagram and charge transfer mechanism of (a) Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> photoanode without external applied anodic potential, (b) Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> photoanode with external applied anodic potential and (c) Fe<sub>2</sub>O<sub>3</sub>-H:TiO<sub>2</sub> photoanode with external applied anodic potential.



alignment, prohibiting the transfer of holes through  $\text{TiO}_2$ . However, after hydrogen treatment, the  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructure seems to form a type II band alignment; thus, hole transfer becomes possible, leading to an enhanced PEC response.

## 2. Experimental section

### 2.1 Preparation of $\alpha\text{-Fe}_2\text{O}_3$ thin films

The ultra-thin hematite films were prepared onto indium-doped tin oxide ( $\text{SnO}_2\text{:In}$ , ITO, PGO GmbH, sheet resistance  $< 20 \Omega \text{ sq}^{-1}$ ) substrate by using physical vapor deposition technique, followed by annealing of Fe coated ITO substrate in air atmosphere.<sup>20</sup> Briefly, all the substrates were cleaned by using soap solution, acetone, and deionized water followed by ultrasonication in isopropanol for 5 minutes and finally with oxygen plasma for two minutes. Before deposition, 1/3 area ( $5 \text{ mm} \times 10 \text{ mm}$ ) of the substrate was covered with a thermal tape for making the electrical contact later for PEC measurements. To fabricate the ultra-thin hematite film (approximately 25 nm), a 10 nm thick Fe films were deposited on ITO substrate by physical vapor deposition (PVD 225, Kurt J. Lesker, base pressure  $< 5 \times 10^{-7}$  mbar) and annealed in air atmosphere at  $350^\circ\text{C}$  for 8 h with a heating rate of  $4^\circ\text{C min}^{-1}$ . The thickness of the Fe film was measured *in situ* during deposition using a quartz-crystal microbalance monitor integrated in PVD system. After annealing, the samples were allowed to cool down to room temperature naturally.

### 2.2 Preparation of $\text{Fe}_2\text{O}_3\text{-TiO}_2$ and $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$ heterostructures

Thin films of  $\text{TiO}_2$  were deposited onto ITO substrates and also on hematite coated ITO substrate by sol-gel technique.<sup>6</sup> In short, a transparent gel solution of titanium dioxide was prepared by mixing 3 ml titanium tetra-isopropoxide (TTIP, 97% pure) in 20 ml ethanol in the presence of diethanolamine. The solution was stirred for 4 h at room temperature to enhance the reaction rate between diethanolamine and TTIP, and finally, it was converted into a gel. This gel solution was applied on  $\alpha\text{-Fe}_2\text{O}_3/\text{ITO}$  substrate and uniformly coated with the help of a spin coating unit at 3000 rpm for 1 minute. A thin layer of  $\text{TiO}_2$  was achieved by the deposition of prepared gel over the  $\alpha\text{-Fe}_2\text{O}_3/\text{ITO}$  substrates. After deposition, the prepared  $\text{TiO}_2\text{-Fe}_2\text{O}_3$  heterostructure was allowed to dry for 10 min at  $80^\circ\text{C}$  and further annealed at  $350^\circ\text{C}$  for 4 h. The hydrogen treatment was carried out by annealing the  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  heterostructures at  $300^\circ\text{C}$  in 4%  $\text{H}_2$  in Ar at atmospheric pressure for 6 h. We also prepared a hydrogen doped  $\text{TiO}_2$  thin film photoanode under the same annealing conditions to see the effect of hydrogen doping individually on optical, electrical, and PEC properties.

### 2.3 Material characterization

The chemical phase of the prepared samples was determined by using a confocal Raman microscope (alpha300 R; WITec) with a 488 nm laser pulse as an excitation source. The surface morphology of the bare and  $\text{TiO}_2$  coated  $\alpha\text{-Fe}_2\text{O}_3$  samples was

examined by field emission scanning electron microscope (FE-SEM) using a Zeiss Supra 60 VP microscope operated at an acceleration voltage of 10 kV. The optical absorption of all the samples was measured with the help of a Cary 5000 spectrophotometer (Varian). X-ray photoelectron spectroscopy (XPS) spectra were acquired in a PerkinElmer Phi 5500 setup (base pressure  $< 10^{-10}$  mbar) using  $\text{AlK}_\alpha$  radiation of 1.4866 keV. The XPS spectra were shifted using the  $\text{Fe}(2p_{3/2})$  peak corresponding to 710.9 eV as a reference.

### 2.4 Photoelectrochemical measurements

For electrochemical measurements, thin films of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{H:TiO}_2$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  and  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterojunctions were converted into the photoelectrodes with an active surface area of about  $0.50 \text{ cm}^2$ . All the (photo)electrochemical measurements, current-voltage ( $I\text{-}V$ ), capacitance-voltage ( $C\text{-}V$ ), and electrochemical impedance spectroscopy (EIS), were conducted in a three-electrode configuration using a H-type PEC cell made of glass and fitted with a flat optical quartz window containing 0.1 M NaOH as electrolyte ( $\text{pH} = 12.9$ ). The PEC cell was controlled by using the Gamry Ref. 600 potentiostat and a solar simulator (SKU SS150, Sciencetech Inc.) with an output intensity of  $100 \text{ mW cm}^{-2}$  as an illumination source. Here, the prepared photoelectrodes were used as a working electrode, Pt wire as a counter electrode, and  $\text{Ag/AgCl}$  as a reference electrode. For better representation of our results, the  $\text{Ag/AgCl}$  reference potential was converted into the reversible hydrogen electrode (RHE) potential by using the following formula:  $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059\text{pH} + V_{\text{Ag/AgCl}}^\circ$ , where  $V_{\text{Ag/AgCl}}^\circ$  is the standard potential of  $\text{Ag/AgCl}$  at  $25^\circ\text{C}$  (0.1976 V vs. the standard hydrogen electrode, SHE). The cyclic voltammetry sweep scans in the potential range between 0 and  $2.0 V_{\text{RHE}}$  at a scan rate of  $10 \text{ mV s}^{-1}$  were performed to obtain the  $I\text{-}V$  characteristics under dark and illumination. The photocurrent density ( $J_{\text{ph}}$ ) has been calculated by subtracting the dark current from the current measured under illumination and divided by the geometrical area of the photoanode. Electrochemical impedance spectroscopic (EIS) measurements under illumination were carried out in the frequency range  $10^5$  and  $0.1 \text{ Hz}$  at applied potentials between  $1.23 V_{\text{RHE}}$ . Nyquist plots obtained under illumination were fitted using the software EIS spectrum analyzer. Mott-Schottky analysis was performed at an applied frequency of 1 kHz in the dark condition in a potential window between 0 and  $1.5 V_{\text{RHE}}$ . The obtained Mott-Schottky curves ( $1/C^2$  versus  $V_{\text{RHE}}$ ) were used to determine the donor density ( $N_D$ ) and flat band potential ( $V_{\text{fb}}$ ) by using the Mott-Schottky equation:  $C^{-2} = (2/q\epsilon_0\epsilon_s N_D)[V - V_{\text{fb}} - kT/q]$ , where  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon_s$  is the dielectric constant of the hematite,  $q$  is the electronic charge, and  $kT/q$  is the thermal voltage (26 meV at room temperature). The donor density was calculated using the equation,  $N_D = 2/(\epsilon_0\epsilon_s q)[d(1/C^2)/dV]^{-1}$ , from the slope of the linear region, between 0.6 and  $1.0 V_{\text{RHE}}$ , of Mott-Schottky plots.

### 2.5 Computational methods

The first-principles calculations were performed using density functional theory (DFT) as implemented in the VASP



package.<sup>21–23</sup> The interaction between the valence electrons and the core follows the projector augmented wave (PAW) method.<sup>24</sup> PAW potentials with the valence states 1s for H, 2s and 2p for O, 3d and 4s for Fe, and 3d and 4s for Ti have been employed. A plane wave basis with a kinetic energy cut-off 700 eV was used. To improve convergence, a Gaussian smearing broadening of the Fermi surface of 0.1 eV was employed. The exchange–correlation (XC) interaction was treated at the level of the generalized gradient approximation (GGA) using the XC-functional of Perdew, Burke, and Ernzerhof (PBE).<sup>25</sup> In the DFT+U calculations, the rotationally-invariant scheme proposed by Dudarev *et al.*<sup>26</sup> and a  $U - J = 4.3$  eV on Fe atom and  $U - J = 5.2$  eV on Ti atom are employed in all our calculations.<sup>27,28</sup> The HSE06 method, as implemented in VASP, was employed to study H defects in anatase TiO<sub>2</sub>.<sup>29,30</sup> A kinetic cut-off of 600 eV was applied in all calculations. The interface system is composed of a six-layer thick Fe<sub>2</sub>O<sub>3</sub> with a (0001) termination of p(2 × 2), that is joined with a four-layer thick anatase TiO<sub>2</sub> with a (101) termination of p(1 × 2). Owing to the lattice mismatch between Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, the interface will introduce strain to the system. Here the lattice cell ( $a = b = 10.17$  Å,  $\alpha = 120^\circ$ ) of Fe<sub>2</sub>O<sub>3</sub> (0001) surface is kept fixed, which implies a strain to the original lattice cell ( $a = 11.35$  Å,  $b = 10.23$  Å,  $\alpha = 111.69^\circ$ ) of the TiO<sub>2</sub> (101) surface. The strain amounts to 10% compression strain on the  $a$ -axis and 0.6% compression strain to the  $b$ -axis, and an increase of the angle by 7.4%. During the relaxation of the interface system, the anatase TiO<sub>2</sub> reconstructs to amorphous TiO<sub>2</sub> (a-TiO<sub>2</sub>). Here, the term amorphous is used to indicate that the reconstructed TiO<sub>2</sub> in the interface model can not be identified with any known phase (rutile, anatase, brookite, *etc.*) of TiO<sub>2</sub>. However, it should be noted that due to the periodic conditions, this phase should not be considered as genuinely amorphous TiO<sub>2</sub>. Defect calculations were carried out in a  $2\sqrt{2} \times 2\sqrt{2} \times 1$  (96 atoms) supercell of anatase TiO<sub>2</sub>, with a  $\Gamma$ -centered  $1 \times 1 \times 1$   $k$ -point sampling. The effect of higher concentrations of defects is modeled by a  $\sqrt{2} \times \sqrt{2} \times 1$  (24 atoms) supercell and a  $1 \times 1 \times 1$  (12 atoms) unit cell, using a  $3 \times 3 \times 1$  Monkhorst–Pack (MP) sampling.<sup>31</sup> All geometries were relaxed until the maximum force was less than 0.05 eV Å<sup>−1</sup>. The relative stability of the various defects in charged and/or neutral states is determined by the formation energy,

$$\Delta E_f = E_t(D^q) - E_t(\text{TiO}_2) - \Delta n_O \mu_O - \Delta n_H \mu_H + qE_F + E_{\text{corr}}, \quad (1)$$

where  $E_t(D^q)$  is the total energy of the supercell containing a defect D in charge state  $q$  and  $E_t(\text{TiO}_2)$  is the total energy of a perfect crystal in the same supercell.  $\Delta n_O$  and  $\Delta n_H$  are the number of O atom and H atom changed in the defective supercell with respect to the perfect one.  $\mu_O$  and  $\mu_H$  are the chemical potential of O atom and H atom.  $E_F$  and  $E_{\text{corr}}$  refer to the energy of the Fermi level and the Madelung corrections for the electrostatic interaction between the homogeneous background charge and charged defects. The chemical potential of the O atom is selected to satisfy the stability condition of TiO<sub>2</sub>. In the extreme O-rich limit, the  $\mu_O$  is set to  $\frac{1}{2}E(\text{O}_2)$ , where  $E(\text{O}_2)$

is the calculated total energy of isolated O<sub>2</sub> molecule. In the extreme O-poor limit,  $\mu_O$  corresponds to the formation of Ti<sub>2</sub>O<sub>3</sub>, which has a relationship of  $\mu_O(\text{O-poor}) = \mu_O(\text{O-rich}) - 3.97$  eV calculated by HSE06.  $\mu_H$  is selected as one half of the total energy of isolated H<sub>2</sub> molecule,  $\frac{1}{2}E(\text{H}_2)$ .

## 3. Results

### 3.1 Simulation results

The valence band offset (VBO) at the interface of Fe<sub>2</sub>O<sub>3</sub> and a-TiO<sub>2</sub> was calculated through the reference potential method originally introduced by Kleinman<sup>32,33</sup> where the reference potential use the macroscopically averaged electrostatic potential.<sup>34</sup> The calculated results are shown in Fig. 2. The VBO for the individual system, Fe<sub>2</sub>O<sub>3</sub> (0001) and a-TiO<sub>2</sub> thin film, were also calculated and are shown in the ESI (Fig. S2).† The blue curve in Fig. 2 refers to the electrostatic potential calculated using PBE+U method. The valence band edges of Fe<sub>2</sub>O<sub>3</sub> and a-TiO<sub>2</sub> were determined with respect to the macroscopically averaged electrostatic by performing calculations on the separated systems. The values of Fermi energy were calculated to 3.88 eV and 0.87 eV for Fe<sub>2</sub>O<sub>3</sub> (0001) and a-TiO<sub>2</sub> thin film, respectively. The macroscopically averaged electrostatic potential was calculated by,

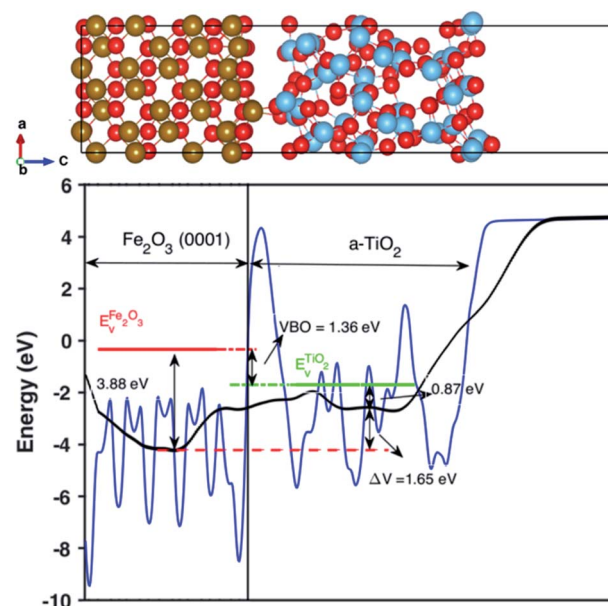


Fig. 2 Up panel is the relaxed structures from the PEB + U calculation for the Fe<sub>2</sub>O<sub>3</sub> and amorphous TiO<sub>2</sub> interface. Bottom panel is the calculated valence band offset (VBO) of the interface with PBE+U methods. The black line is the calculated macroscopically averaged electrostatic potential and the blue line is the electrostatic potential at the interface averaged along the thickness ( $c$ -axis) of the interface. The red line is the position of VBM of Fe<sub>2</sub>O<sub>3</sub> and the green line is the position of VBM of bulk TiO<sub>2</sub> with respect to vacuum level. The electrostatic potential across the interface is  $\Delta V = 1.65$  eV and the calculated VBO at the interface is 1.36 eV. The VBO of the joint interface is slightly larger than that of separated systems by 0.18 eV that indicating the creation of an interface dipole or double layers.<sup>37</sup>





$$V'(z) = \int dz' \int dz'' w_{l_1}(z - z') w_{l_2}(z' - z'') V'(z''), \quad (2)$$

where  $w_l(z - z') = \frac{1}{l} \Theta\left(\frac{l}{2} - z\right)$ ,  $\Theta$  is the unit-step function,  $l_1$  and  $l_2$  are in the order of the (strained) thickness of hematite (0001) and amorphous  $\text{TiO}_2$  thin film along  $z$ , respectively.

$$\Theta = \begin{cases} 0, & z < 0. \\ 1, & z \geq 0. \end{cases} \quad (3)$$

where  $V'(z)$  is the  $xy$ -plane averaged electrostatic potential and  $d_1$  and  $d_2$  are the inter-planar distances along the  $z$  direction (normal to the interface).<sup>35,36</sup>

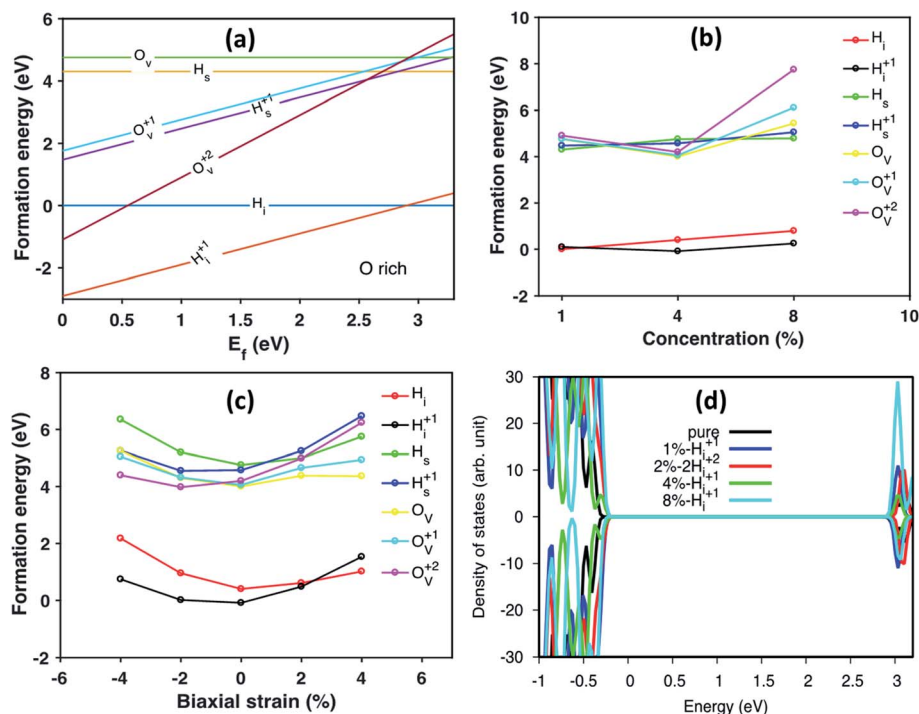
The calculated  $V'(z)$  is the black line in Fig. 2. The VBO was calculated *via*,

$$\text{VBO} = \Delta E_v + \Delta V. \quad (4)$$

The calculated VBO for the individual system is  $-1.18$  eV using DFT+U, which agrees well with the experimental observations ( $\sim 0.5$  eV).<sup>38</sup> However, the calculated VBO at the interface is around  $1.36$  eV, with the valence band edge of  $\text{TiO}_2$  sitting below the  $\text{Fe}_2\text{O}_3$ , which is  $0.18$  eV higher than the separated systems indicating an interface dipole or double layer were created at the interface. The electrostatic potential across the interface is  $\Delta V = 1.65$  eV.

We further studied H defects and O vacancy in anatase  $\text{TiO}_2$ , including their formation energy and electronic structure. The formation energy is calculated using eqn (1), and the results are shown in Fig. 3a, which corresponds to the results from the modeled supercell of 96 atoms. It is clearly shown that the positively charged H interstitial is the most favorable (with negative formation energy) defect when the Fermi energy is located above the valence band edge and below  $2.9$  eV, while the H interstitial becomes stable when  $E_f$  is larger than  $2.9$  eV (see Fig. 3). The formation energy of H interstitial is  $0.04$  eV. In contrast, O vacancies and substitutional H are less energetically favorable.

Next, we have studied the formation energies of different concentrations of defects in anatase  $\text{TiO}_2$  using different supercells, and the results are shown in Fig. 3b. Here, the formation energy plot is shown for O-rich conditions and the Fermi energy is set to  $3.0$  eV. As seen from Fig. 3b, the two most stable defect configurations are neutral and positively charged H interstitials,  $\text{H}_i$ , where the positively charged H interstitial is the most favorable defect at high concentrations. The neutral H interstitial is the second state configuration when H concentration larger than  $4$  at%. The other defects are less stable as their formation energies are very high (larger than  $3$  eV). At high concentration ( $8$  at%), the substitutional  $\text{H}_s$  becomes more stable than O vacancies. Interestingly, under O-poor conditions,



**Fig. 3** (a) The formation energy of different charged defects in anatase  $\text{TiO}_2$  under oxygen rich conditions corresponding to the current experiment condition. The Madelung corrections,  $E_{\text{corr}}$  is taken to be  $0.1$  eV in all our calculations. The x-axis is the Fermi energy level of anatase  $\text{TiO}_2$ .  $\text{O}_v$  denotes the oxygen vacancy and can neutral ( $\text{O}_v$ ),  $+1$  positively charged ( $\text{O}_v^{+1}$ ) or  $+2$  positively charged ( $\text{O}_v^{+2}$ ).  $\text{H}_i$  is the interstitial H defect and  $\text{H}_s$  is the substitutional hydrogen defect. (b) The calculated formation energy of various defects in anatase varying with the defect concentration under O-rich condition. The Fermi energy is set to  $E_f = 3.0$  eV. (c) The calculated formation energy of different charged/neutral defects under biaxial strain from  $-4\%$  to  $+4\%$  under O-rich condition. The Fermi energy is set to  $E_f = 3.0$  eV. (d) The calculated density of states (DOS) of pure anatase and anatase with  $\text{H}_i^{+1}$  in different concentrations. The energy was aligned by the  $1s$  state of O atom far away from the defect.



the  $H_s$  is as stable as the  $H_i$  (the formation energy plot is shown in Fig. S3†).

When constructing the interface, a strain is induced automatically due to the lattice mismatch. Therefore, we also studied the strain effects on defect configurations for defect concentration of 4 at%. The calculated formation energy of different defects under biaxial strain is shown in Fig. 3c. It is interesting to notice that under biaxial tensile strain, the stable defect configuration changes to  $H_i$ . Under compressive strain, positively charged  $H_i^+$  remains as the most stable defect configuration. As shown in Fig. 3c, when changing from compressive to tensile strain, the stable configurations of defects are changed from charged ones to neutral ones, e.g.,  $H_s$  becomes more stable than  $H_s^+$  and  $O_v$  becomes more stable than  $O_v^+$  and  $O_v^{2+}$ . Similarly, the formation energy of defects calculated under O-poor conditions is shown in Fig. S4†. At such conditions, the defect configuration is changing from  $O_v^{2+}$  to  $O_v$  as the strain changes from compression to expansion. However,  $H_i^+$  is still the preferable defect under ambient condition (Fig. S4†). The DOS of anatase with different concentration of  $H_i^+$  compared with pure anatase are shown in Fig. 3d. The energy of doped systems is aligned by shifting 1s state of O atom far away from the defect to that of pure anatase. It can be seen that doping with  $H_i^+$  shifts the valence band edge upwards ( $\sim 0.1$  eV) without changing the position of the conduction band edge. More specifically, the change of the valence band edge can be explained as the hybridization of 2p states of O atom bonded with  $H_i^+$  and Ti 3d nearby (see Fig. S5†).

Under biaxial strain, due to lattice mismatch, the valence band maximum and conduction band minimum (CBM) of pure anatase (32 atoms supercell) under different strain are calculated and plotted in Fig. 4a. It is clear that both VBM and CBM decrease in energy as strain increases from compressive to tensile strain. When strain increases to 2%, the value of VBM decreases around 0.3 eV. Similarly, the CBM decreases around 0.4 eV. Therefore, the band gap is shrinking as strain increases. When doped with  $H_i^+$ , the VBM position is located below the VBM of pure anatase under 2% tensile strain, while the VBM remains unchanged with doped with  $H_i$  (shown in Fig. S4†). Hydrogen doping also introduces distortions to anatase  $TiO_2$ , which results in the formation of the amorphous  $TiO_2$  at the

interface. To shed further light on this, H doped amorphous  $TiO_2$  was studied with the PBE+U method, keeping the same parameters used for the interface. Doping with  $H_i$  is energetically favorable (shown in Fig. S4†) with a formation energy of  $-0.4$  eV for single  $H_i$ . The calculated DOS of H doped systems is shown in Fig. 4b. Compared with pure a- $TiO_2$ , single  $H_i$  introduces one occupied localized state on top of the valence band edge about 0.5 eV high in energy. The doping with H does not seem to change the averaged electrostatic potential, as can be seen from Fig. S5.† Adding two  $H_i$  introduce two localized states in the gap, but with slightly different energies. As more interstitial hydrogens are incorporated, we speculate that these states will eventually form energy levels in the range of up to  $\sim 0.7$  eV above the valence band edge. These energy levels work as the hole acceptance levels and help the transport of photo-excited holes generated from the  $Fe_2O_3$  side to the H: $TiO_2$  electrolyte side, where they can take part in the water oxidation reaction.

### 3.2 Experimental results

To test our hypothesis and to scrutinize the first-principles results experimentally, we have fabricated  $Fe_2O_3$ - $TiO_2$  heterojunction electrodes in two steps. First, we deposited an ultra-thin  $\alpha$ - $Fe_2O_3$  (25 nm) film on ITO substrate by thermal evaporation of Fe followed by air annealing at 350 °C. Further, the as-prepared  $\alpha$ - $Fe_2O_3$  thin films were coated with  $TiO_2$  by sol-gel spin coating method followed by thermal annealing at 400 °C. In as-prepared  $Fe_2O_3$ - $TiO_2$  heterostructure, the band edge engineering was achieved by hydrogen doping ( $Fe_2O_3$ -H: $TiO_2$ ) by further annealing the  $Fe_2O_3$ - $TiO_2$  heterostructure in 4%  $H_2$  in Ar at 300 °C at atmospheric pressure for 6 h.

To determine the crystal structures of  $\alpha$ - $Fe_2O_3$ ,  $TiO_2$ , and  $Fe_2O_3$ - $TiO_2$  heterostructure thin films and possible phase changes after hydrogen doping in  $TiO_2$ , Raman spectroscopy was performed, and its results are shown in Fig. S7a.† In pristine  $\alpha$ - $Fe_2O_3$ , normally seven phonon modes are expected in the Raman spectrum: namely two  $A_{1g}$  modes (225 and 498  $cm^{-1}$ ) and five  $E_g$  modes (247, 293, 299, 412, and 613  $cm^{-1}$ ), but the 293 and 299  $cm^{-1}$  bands can only be resolved at temperatures  $\leq 100$  K. In the present case, six of the observed bands ( $A_{1g}$ , 223 and 498  $cm^{-1}$ ;  $E_g$ , 244, 294, 410, and 607  $cm^{-1}$ ) are detected,

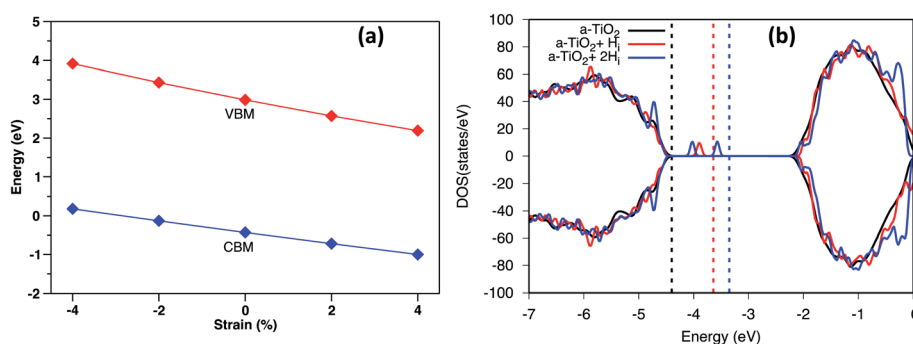


Fig. 4 (a) The calculated VBM and CBM of anatase using HSE06 under different biaxial strain. (b) The DOS of H doped a- $TiO_2$  compared with pure a- $TiO_2$ . The energy was aligned by the 1s state of O atom far away from the defect. The dashed line indicates the Fermi level of each system.



which agrees with the formation of the hematite phase ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ). On the other hand, the Raman spectra of both pristine and hydrogen doped  $\text{TiO}_2$  samples exhibit well-resolved  $\text{TiO}_2$  Raman peaks at  $144\text{ cm}^{-1}$  ( $\text{E}_g$ ),  $398\text{ cm}^{-1}$  ( $\text{B}_{1g}$ ),  $515\text{ cm}^{-1}$  ( $\text{E}_g$ ), and  $640\text{ cm}^{-1}$  ( $\text{E}_g$ ), indicating that anatase is the predominant species, except for  $147\text{ cm}^{-1}$  ( $\text{B}_{1g}$ ), which is suppressed by a much stronger  $\text{E}_g$  peak at  $144\text{ cm}^{-1}$ . No phase change after hydrogen doping in  $\text{TiO}_2$  was observed (ESI Fig. S7b<sup>†</sup>). The Raman spectra of  $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$  heterostructure shows the significant up-shift of  $\text{E}_g$  mode of  $\text{TiO}_2$  from  $141$  to  $155\text{ cm}^{-1}$  and also other bands of  $\text{TiO}_2$ . The shift of Raman bands by  $14\text{ cm}^{-1}$  (inset of ESI Fig. S7b<sup>†</sup>) is probably due to the strain and defect states at the junction with  $\alpha$ - $\text{Fe}_2\text{O}_3$  and lattice mismatch. Morphological characteristics were investigated by scanning

electron microscopy (SEM) (ESI Fig. S8<sup>†</sup>) and transmission electron microscopy (TEM) (ESI Fig. S9<sup>†</sup>). SEM images of pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  electrodes showed uniform deposition of a thin layer of a thickness of about  $25\text{ nm}$  without any inter-particle pores, as shown in Fig. S8<sup>†</sup>. Optimized thickness of  $\text{TiO}_2$  layer (thickness  $< 10\text{ nm}$ ) over the  $\alpha$ - $\text{Fe}_2\text{O}_3$  layer on ITO clearly showed a smooth and dense coverage, as shown in Fig. S8c<sup>†</sup>.

First, we optimized the temperature for optimized hydrogen doping with respect to the reduction in band gap and upshift of band edge position. Fig. 5a displays the optical absorption spectra of the  $\text{TiO}_2$ ,  $\text{H}:\text{TiO}_2$ , samples in the wavelength range  $340$ – $600\text{ nm}$  measured by using the integrating sphere. Optical absorption spectra of all the samples,  $\alpha$ - $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{H}:\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ - $\text{H}:\text{TiO}_2$ , in the wavelength range  $300$ –

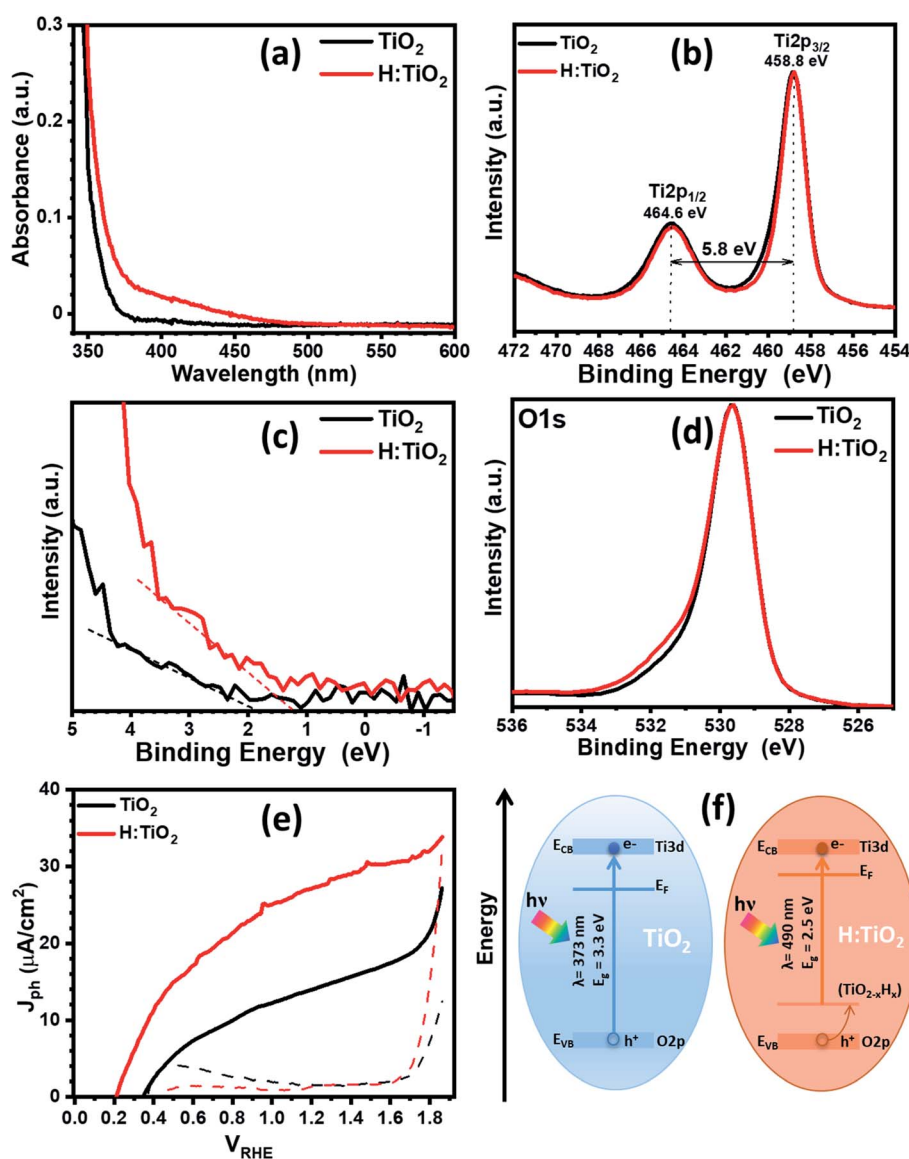


Fig. 5 (a) Optical absorption of pristine and hydrogen treated  $\text{TiO}_2$  thin films. (b) Core-level XPS Ti 2p spectra. (c) Valence band spectra of pristine and hydrogen treated  $\text{TiO}_2$ . (d) Core-level XPS O 1s spectra. (e) Photocurrent density versus applied potential for pristine and hydrogen treated  $\text{TiO}_2$ . (f) Band diagram representation of pristine and hydrogen treated  $\text{TiO}_2$ . Both representations were built using experimental data from UV-vis spectroscopy and valence band XPS analysis. Conduction band offset was estimated using band gap and valence band offsets.

700 nm measured under the same experimental conditions are shown in the ESI (Fig. S10).† In pristine  $\text{TiO}_2$  samples, a steep increase in absorption at wavelengths shorter than  $\sim 373$  nm can be attributed to the intrinsic band gap of crystalline  $\text{TiO}_2$ . The hydrogen doping of the  $\text{TiO}_2$  sample show a significant shift of absorption edge from higher wavelengths down to 490 nm in the visible light absorption. The calculated values of the band gap energy show that the band gap of the pristine  $\text{TiO}_2$  thin films is approximately 3.30 eV, slightly higher than that of bulk anatase  $\text{TiO}_2$ . However, the onset of light absorption in hydrogen doped  $\text{TiO}_2$  thin film is lowered to about 2.5 eV.

To validate the reduction of band gap energy, we have carried out the XPS measurement on both pristine and hydrogen doped  $\text{TiO}_2$  thin films to understand the surface chemical bonds, chemical composition, peak position, and hence the electronic properties. Therefore, the Ti 2p, O 1s, and valance band spectra were measured and analyzed for pristine and hydrogen doped  $\text{TiO}_2$  thin films. The Ti 2p core level XPS spectrum, Fig. 5b, shows that the Ti  $2p_{3/2}$  peak is at  $458.8 \pm 0.1$  eV, which was attributed to  $\text{Ti}^{4+}$  states for both the samples. However, after hydrogen doping, a slight asymmetric narrowing in the Ti  $2p_{3/2}$  peak can be seen. This narrowing in the peak upon hydrogen doping is likely due to a decrease in  $\text{Ti}^{3+}$  states, concurrent with the reduction in oxygen content, and to a disorder due to the thermal annealing of  $\text{TiO}_2$  in hydrogen environment.<sup>39</sup> However, no reduction in the  $\text{Ti}^{4+}$  was observed in  $\text{TiO}_2$  after hydrogen doping. Fig. 5c shows the valance band spectra obtained for the pristine and hydrogen treated  $\text{TiO}_2$  thin films. The VBM were calculated by linearly extrapolating the peaks to

the baselines. The VBM for pristine  $\text{TiO}_2$  thin film was observed at 1.93 eV below the zero potential energy point. However, in the case of hydrogen doped  $\text{TiO}_2$  films, VBM was obtained at 1.27 eV. Therefore, a valance band edge shift by  $\sim 0.66$  eV was observed towards the Fermi level. Moreover, small bands occurred above the VBM, and small bands existed close to the binding energy at zero. In light of the first-principles calculations, the up-shift of the VBM is suggested to be the result of defects states above the valance band induced by interstitial hydrogen in the  $\text{TiO}_2$  thin films. Fig. 5d represents the O 1s spectra of pristine and hydrogen doped  $\text{TiO}_2$  samples. The peak at a binding energy of  $529.6 \pm 0.1$  eV corresponds to O–Ti bonds in  $\text{TiO}_2$  in both the samples. However, in hydrogen doped samples, an additional peak can be seen at  $531.6 \pm 0.1$  eV, which is probably due to oxygen vacancies, formation of hydroxyl groups, and Ti–OH bonds.<sup>39,40</sup> From Fig. S13b and c,† where the XPS spectra of all four samples are shown, it is further visible that  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  displays the same narrowing of the  $\text{Ti}^{4+}$  peak as  $\text{H:TiO}_2$ , and a more accentuate  $\text{OH}^-$  peak in the oxygen 1s spectrum, correlating the formation of the iron oxide heterostructure with the generation of oxygen vacancies and/or hydroxyl groups.

The PEC measurement in the form of photocurrent densities vs. applied potential ( $J_{\text{ph}}$  vs.  $V_{\text{RHE}}$ ) curves are shown in Fig. 5e for pristine and hydrogen doped  $\text{TiO}_2$  samples under 1 sun illumination. The calculated value of  $J_{\text{ph}}$  for pristine  $\text{TiO}_2$  photoanode was obtained  $\sim 14 \mu\text{A cm}^{-2}$  at 1.23  $V_{\text{RHE}}$ . However, hydrogen doping in  $\text{TiO}_2$  enhanced the PEC response significantly and reached a  $J_{\text{ph}}$  to  $\sim 27.4 \mu\text{A cm}^{-2}$  at 1.23  $V_{\text{RHE}}$ . It is

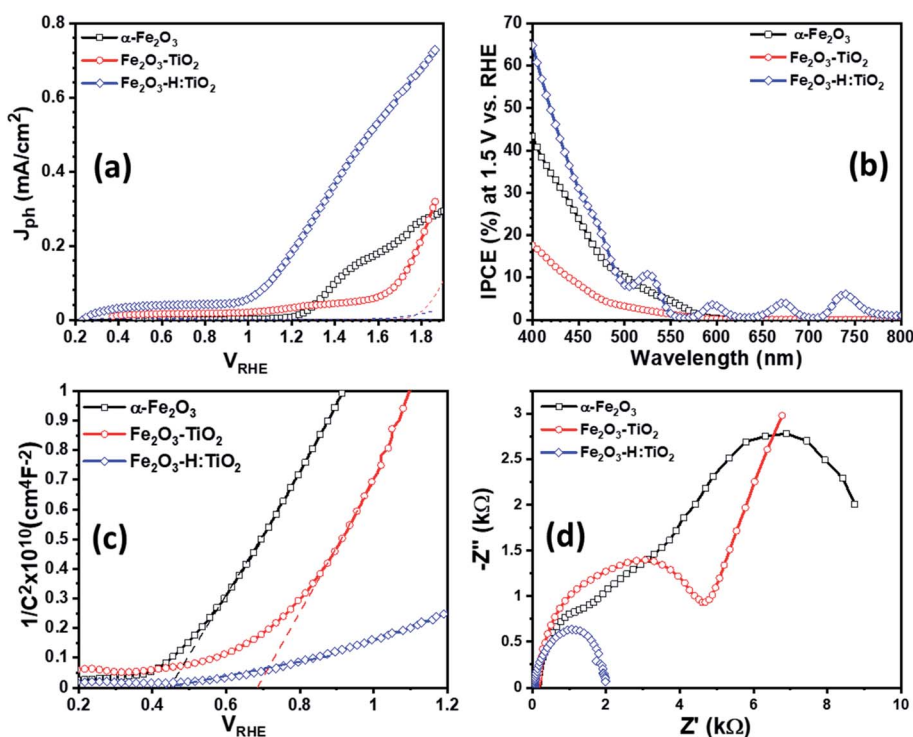


Fig. 6 (a) Photocurrent density versus applied potential (b) IPCE curves measured at 1.5 V vs. RHE for the  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ , and  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructures photoanodes. (c) Mott–Schottky plots for  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ , and  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructures measured in 0.1 M NaOH electrolyte solution under 1 sun illumination. (d) Measured EIS Nyquist plots for  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  and  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructure.



noticed that hydrogen doping in  $\text{TiO}_2$  thin films greatly enhanced the  $J_{\text{ph}}$  and shifted the photocurrent onset potential to  $0.2 V_{\text{RHE}}$ . The relatively low value of photocurrent onset potential indicates that the charge separation and transportation in hydrogen doped  $\text{TiO}_2$  thin films are more efficient than the pristine  $\text{TiO}_2$  thin films. We have also calculated the flat-band potential ( $V_{\text{fb}}$ ) and carrier concentration ( $N_{\text{d}}$ ) for pristine and hydrogen doped  $\text{TiO}_2$  samples using Mott-Schottky plots. The value of  $V_{\text{fb}}$  was calculated from the intercept of the straight line to the x-axis in the linear region of the plot, as shown in Fig. S11.† The pristine  $\text{TiO}_2$  sample exhibit a  $V_{\text{fb}}$  value of  $0.29 V_{\text{RHE}}$ . However, a shift in  $V_{\text{fb}}$  to  $0.15 V_{\text{RHE}}$  was calculated for the H: $\text{TiO}_2$  photoanode. This significant shift of  $V_{\text{fb}}$  by  $0.14 V$  towards the cathodic side in H: $\text{TiO}_2$  is likely because the hydrogen doping can enhance the carrier concentration due to increased oxygen vacancies, which could serve as shallow electron donor and upshift the Fermi level towards the conduction band of  $\text{TiO}_2$ . Schematic positions of band edges of  $\text{TiO}_2$  and H: $\text{TiO}_2$  are shown in Fig. 5f. The band alignment of H: $\text{TiO}_2$  facilitates more efficient charge separation at the semiconductor/electrolyte interface as compared to pristine  $\text{TiO}_2$  by increasing the degree of band bending at the H: $\text{TiO}_2$  surface. The experimental value of  $V_{\text{fb}}$  for H: $\text{TiO}_2$  is more cathodic in comparison to the pristine  $\text{TiO}_2$ , which favors the water splitting reaction. In summary, the enhancement in photocurrent density in the H: $\text{TiO}_2$  sample is thanks to the combined effect of decreased bandgap energy, which allows absorption of a wide range of solar radiation, high donor density which is responsible for the shift in Fermi level towards the conduction band, and more negative flat band potential.

To examine the PEC performance of the targeted heterostructures photoanodes,  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$ , the  $J_{\text{ph}}$  vs.  $V_{\text{RHE}}$  characteristics under dark and illumination was measured in a three-electrode PEC cell. Fig. 6a depicts the PEC performance of the optimized  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  heterostructures compared with pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  photoanode. The dark current densities, for the applied potential range up to  $1.7 V_{\text{RHE}}$ , are negligible for all samples. The  $J_{\text{ph}}$  of the pure  $\alpha$ - $\text{Fe}_2\text{O}_3$  photoanode is  $\sim 10 \mu\text{A cm}^{-2}$  at  $1.23 V$  vs. RHE, which is reasonable as compared to the previously reported values due to the difference in the film thickness and has an onset of photocurrent at  $1.15 V_{\text{RHE}}$ .<sup>20</sup> A much lower onset potential of  $\sim 0.35 V_{\text{RHE}}$  and lower  $J_{\text{ph}}$  of  $\sim 35 \mu\text{A cm}^{-2}$  at  $1.23 V_{\text{RHE}}$  obtained for the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  heterostructure. However, the hydrogen doped  $\text{TiO}_2$  layer in the  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  heterostructure substantially shifted the onset of photocurrent to  $0.21 V_{\text{RHE}}$  and the  $J_{\text{ph}}$  at  $1.23 V_{\text{RHE}}$  increased to  $215 \mu\text{A cm}^{-2}$ . The value of  $J_{\text{ph}}$  for  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  heterostructure photoanode reached  $450 \mu\text{A cm}^{-2}$  at  $1.5 V_{\text{RHE}}$ , which is three and nine times the  $J_{\text{ph}}$  for  $\alpha$ - $\text{Fe}_2\text{O}_3$  ( $153 \mu\text{A cm}^{-2}$ ) and  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  ( $51 \mu\text{A cm}^{-2}$ ) photoanodes, respectively. The obtained value of  $J_{\text{ph}}$  for  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  heterostructured system is significantly high to that of a pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  systems. As the magnitude of  $J_{\text{ph}}$  corresponds to the number of photogenerated holes that reach the electrode surface, the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  sample exhibits a high recombination of photogenerated electrode and holes at the junction due to the discontinuity of the mismatch of band edge

positions, which hinders the water oxidation process at the surface of the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  photoanode. As we reported in our previous work on hydrogen treated  $\text{TiO}_2$  and predicted in our simulation for this work, hydrogen doping in  $\text{TiO}_2$  can upshift the valance band position and create the lattice defects in  $\text{TiO}_2$ . Our simulation results on hydrogen doping in  $\text{TiO}_2$  indicate that heterojunctions of  $\alpha$ - $\text{Fe}_2\text{O}_3$  and hydrogen doped  $\text{TiO}_2$  can lead to considerably enhanced hole transport from  $\alpha$ - $\text{Fe}_2\text{O}_3$  to H: $\text{TiO}_2$  and, thus, to a more efficient separation of photoexcited electron-hole pairs. Consequently, hydrogen treated  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  photoanode exhibits a higher number of photogenerated holes that can participate in the oxidation process before recombining with excited electrons.

Further, to quantitatively investigate the PEC performance of the photoanodes, incident photon-to-current conversion efficiency (IPCE) measurements were performed at  $1.5 V$  vs. RHE in  $1.0 M$  KOH and shown in Fig. 6b. All the samples show photocurrent response to incident light in the wavelength region of  $400$ – $580 \text{ nm}$ , which matches the bandgap of hematite ( $\sim 2.1 \text{ eV}$ ). The pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  photoanode exhibits 42% IPCE at the excitation wavelength of  $400 \text{ nm}$ , which is comparable with the reported IPCE values of  $\alpha$ - $\text{Fe}_2\text{O}_3$  photoanode. A significantly low IPCE, 18%, was recorded in the case of the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  photoanode. This  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  photoanode also exhibits the low photocurrent density in PEC measurements. However,  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  photoanode exhibits substantially high quantum efficiency as compared with pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  photoanodes in the wavelength range of  $400$ – $550 \text{ nm}$ . The IPCE of the  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  photoanode reaches to  $\sim 65\%$  at the excitation wavelength of  $400 \text{ nm}$ , which is 1.5 and 3.6 times that of  $\alpha$ - $\text{Fe}_2\text{O}_3$  (42%) and  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  (18%), respectively.

To gain even more insight into the enhancement of photocurrent density and IPCE values in  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  heterostructure photoanodes, Mott-Schottky measurements were performed with applied potential at  $1 \text{ kHz}$  frequency in the dark. From the Mott-Schottky plots, which represent the changes in capacitance ( $C$ ) against the applied potential, it can be seen that all the samples possess a positive slope (Fig. 6c), which is a characteristic of n-type semiconductors with electrons as majority carriers. The flat band potential ( $V_{\text{fb}}$ ) and carrier density ( $N_{\text{d}}$ ) were calculated from the slopes of Mott-Schottky plots. The value of  $V_{\text{fb}}$  was observed to shift towards the more cathodic side from  $0.44 V_{\text{RHE}}$  for  $\alpha$ - $\text{Fe}_2\text{O}_3$  to  $0.68 V_{\text{RHE}}$  for the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  sample. However, after the hydrogen treatment of the  $\text{TiO}_2$  layer, the flat band potential remains at the same values to  $0.28 V_{\text{RHE}}$  as  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ .

Further, the charge transport properties of the  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  photoanodes were investigated by electrochemical impedance spectroscopic (EIS) measurements at  $1.23 V_{\text{RHE}}$  applied potential under one sun illumination conditions and compared with  $\alpha$ - $\text{Fe}_2\text{O}_3$ . Fig. 6d shows the EIS Nyquist plots for  $\alpha$ - $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ , and  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  photoanodes. The series resistance ( $R_s$ ) at the interface between the ITO substrate and  $\alpha$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  layers display a substantial reduction from *ca.*  $140 \Omega \text{ cm}^{-2}$  for the pristine  $\alpha$ - $\text{Fe}_2\text{O}_3$  sample, to  $120 \Omega \text{ cm}^{-2}$  for  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ , to *ca.*  $40 \Omega \text{ cm}^{-2}$  for the  $\text{Fe}_2\text{O}_3$ -H: $\text{TiO}_2$  photoanode surface. The radii of the semicircle in the



EIS plots from the  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructure is much smaller than that from  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ , which indicates that the hydrogen treatment of the  $\text{TiO}_2$  layer changes the charge distribution in  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$ . The new charge distribution results in a lower magnitude of the equivalent series resistance in  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterojunction photoanodes indicating strongly improved charge transport properties as compared to  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$ .

Finally, in order to assess the durability of the photoanodes, chronoamperometry was performed on the  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  and the  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  electrodes (as presented in Fig. S12 in the ESI†): the resulting photocurrent density, under a bias voltage of 0.5  $V_{\text{RHE}}$  and an illumination of 1 sun, was found to be stable around a value of  $0.4 \text{ mA cm}^{-2}$  for up to 500 minutes for  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$ , with no sign of decreasing, while the non-treated sample displayed a lower photocurrent ( $0.23 \text{ mA cm}^{-2}$ ) at the start, which halved after less than 300 minutes of continuous use. This sustained stability of  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  electrodes confirms the applicability of the device.

## 4. Conclusion

First-principles calculations predict that hydrogen treatment induce states above the valance band, which can transfer holes through the heterostructure junction. The predictions are validated with experimental observation obtained on sol-gel grown  $\text{TiO}_2$  thin films. Optical absorption, XPS analysis, and (photo) electrochemical measurements show that the tailoring in optical band gap, shift in valence band position, and change in electrical properties in hydrogen doped  $\text{TiO}_2$  results in a type II band alignment in the  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructure. The  $\text{Fe}_2\text{O}_3\text{-H:TiO}_2$  heterostructure reduces the electron-hole recombination sharply at the junction and improves the water oxidation performance. This study shows that hydrogen treatment can enhance the photoelectrochemical response of the  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  heterostructure, thanks to the formation of type II band alignment at the interface junction. The theoretical and experimental strategies can be applied to other oxides based heterostructures and might become important tools for engineering efficient and stable photoelectrodes.

## Author contributions

A. P. S., B. W. and A. H. conceived the idea and designed the experimental work. A. H. and R. B. W. supported the work through theoretical simulations. A. P. S. have prepared and characterized the samples for experimental work and R. B. W. performed the thermotical simulation. A. P. S., B. W. and A. H. analyzed the experimental data for the manuscript. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 M. Grätzel, *Nature*, 2001, **414**, 338–344.
- 2 H. Ahmad, S. K. Kamarudin, L. J. Minggu and M. Kassim, *Renewable Sustainable Energy Rev.*, 2015, **43**, 599–610.
- 3 Y. Tachibana, L. Vayssieres and J. R. Durrant, *Nat. Photonics*, 2012, **6**, 511–518.
- 4 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37–38.
- 5 A. Fujishima, T. N. Rao and D. A. Tryk, *J. Photochem. Photobiol., C*, 2000, **1**, 1–21.
- 6 A. P. Singh, S. Kumari, R. Shrivastav, S. Dass and V. R. Satsangi, *Int. J. Hydrogen Energy*, 2008, **33**, 5363–5368.
- 7 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96.
- 8 M. Mehta, N. Kodan, S. Kumar, A. Kaushal, L. Mayrhofer, M. Walter, M. Moseler, A. Dey, S. Krishnamurthy, S. Basu and A. P. Singh, *J. Mater. Chem. A*, 2016, **4**, 2670–2681.
- 9 A. P. Singh, N. Kodan and B. R. Mehta, *Appl. Surf. Sci.*, 2016, **372**, 63–69.
- 10 A. P. Singh, N. Saini and B. R. Mehta, *ChemistrySelect*, 2017, **2**, 1413–1420.
- 11 A. P. Singh, A. Mettenbörger, P. Golus and S. Mathur, *Int. J. Hydrogen Energy*, 2012, **37**, 13983–13988.
- 12 S. Shen, S. A. Lindley, X. Chena and J. Z. Zhang, *Energy Environ. Sci.*, 2016, **9**, 2744–2775.
- 13 L. Pei, H. Wang, X. Wang, Z. Xu, S. Yan and Z. Zou, *Dalton Trans.*, 2018, **47**, 8949–8955.
- 14 S. Choudhary, S. Upadhyay, P. Kumar, N. Singh, V. R. Satsangi, R. Shrivastav and S. Dass, *Int. J. Hydrogen Energy*, 2012, **37**, 18713–18730.
- 15 D. Barreca, G. Carraro, A. Gasparotto, C. Maccato, M. E. A. Warwick, K. Kaunisto, C. Sada, S. Turner, Y. Gönüllü, T. -P. Ruoko, L. Borgese, E. Bontempi, G. V. Tendeloo, H. Lemmetyinen and S. Mathur, *Adv. Mater. Interfaces*, 2015, **2**, 1500313.
- 16 R. d. S. Santos, G. A. Faria, C. Giles, C. A. P. Leite, H. d. S. Barbosa, M. A. Z. Arruda and C. Longo, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5555–5561.
- 17 A. P. Singh, N. Kodan, B. R. Mehta, A. Held, L. Mayrhofer and M. Moseler, *ACS Catal.*, 2016, **6**, 5311–5318.
- 18 M. A. Butler and D. S. Ginley, *J. Electrochem. Soc.*, 1978, **125**, 228–232.
- 19 A. P. Singh, N. Kodan, B. R. Mehta, A. Dey and S. Krishnamurthy, *Mater. Res. Bull.*, 2016, **76**, 284–291.



- 20 A. P. Singh, A. Levinsson, B. Iandolo, J. Oksanen, A. Hellman and B. Wickman, *J. Photochem. Photobiol., A*, 2020, **401**, 112781.
- 21 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 558–561.
- 22 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 23 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 24 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 25 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671–6687.
- 26 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **57**, 1505–1509.
- 27 B. J. Morgan and G. W. Watson, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 144119.
- 28 Z. Hu and H. Metiu, *J. Phys. Chem. C*, 2011, **115**, 5841–5845.
- 29 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.
- 30 J. Heyd and G. E. Scuseria, *J. Chem. Phys.*, 2004, **121**, 1187–1192.
- 31 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188–5192.
- 32 L. Kleinman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **24**, 7412–7414.
- 33 D. M. Bylander and L. Kleinman, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1987, **36**, 3229–3236.
- 34 C. G. Van de Walle, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1989, **39**, 1871–1883.
- 35 M. Peressi, N. Binggeli and A. Baldereschi, *J. Phys. D: Appl. Phys.*, 1998, **31**, 1273–1299.
- 36 A. Baldereschi, S. Baroni and R. Resta, *Phys. Rev. Lett.*, 1988, **61**, 734–737.
- 37 X. Luo, G. Bersuker and A. A. Demkov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 195309.
- 38 B. Iandolo, B. Wickman, E. Svensson, D. Paulsson and A. Hellman, *Nano Lett.*, 2016, **16**, 2381–2386.
- 39 B. Bharti, S. Kumar, H.-N. Lee and R. Kumar, *Sci. Rep.*, 2016, **6**, 32355.
- 40 A. P. Singh, C. Tossi, I. Tittonen, A. Hellman and B. Wickman, *RSC Adv.*, 2020, **10**, 33307–33316.

