PAPER • OPEN ACCESS

Understanding and optimizing the sensitization of anatase titanium dioxide surface with hematite clusters

To cite this article: Kati Asikainen et al 2024 J. Phys.: Condens. Matter 36 295001

View the article online for updates and enhancements.

You may also like

- Morphologically Tunable Fabrication of Hematite Nanostructures for Enhanced Photoelectrochemical Performance Malik Aalim, Arshid Mir, Jaffar Farooq Mir et al.
- <u>Modulation of Magnetism and Optical</u> <u>Properties of Hematite (-Fe₂O₃) Nanorods</u> <u>Fabricated via Thermal Conversion of</u> <u>Hydrothermally Synthesized Akaganeite (-<u>FeOOH)</u></u>
- Malik Aalim and M A Shah
- <u>Visible light driven CZTS QDs/-Fe₂O₃-</u> graphene p—n heterojunction for photoelectrochemical water splitting Ashi Ikram and Mohammad Zulfequar

IOP Publishing

J. Phys.: Condens. Matter 36 (2024) 295001 (14pp)

Understanding and optimizing the sensitization of anatase titanium dioxide surface with hematite clusters

Kati Asikainen^{1,*}, Matti Alatalo¹, Marko Huttula¹, B Barbiellini²

¹ Nano and Molecular Systems Research Unit, University of Oulu, Oulu, FI-90014, Finland

² Lappeenranta-Lahti University of Technology (LUT), FI-53851 Lappeenranta, Finland

³ Sustainable Chemistry and MME, Faculty of Technology, University of Oulu, Oulu, FI-90014, Finland

E-mail: Kati.Asikainen@oulu.fi and Assa.SasikalaDevi@oulu.fi

Received 23 June 2023, revised 9 March 2024 Accepted for publication 4 April 2024 Published 22 April 2024



Abstract

The presence of hematite (Fe₂O₃) clusters at low coverage on titanium dioxide (TiO₂) surface has been observed to enhance photocatalytic activity, while excess loading of hematite is detrimental. We conduct a comprehensive density functional theory study of Fe₂O₃ clusters adsorbed on the anatase TiO₂ (101) surface to investigate the effect of Fe₂O₃ on TiO₂. Our study shows that TiO₂ exhibits improved photocatalytic properties with hematite clusters at low coverage, as evidenced by a systematic study conducted by increasing the number of cluster adsorbates. The adsorption of the clusters generates impurity states in the band gap improving light absorption and consequently affecting the charge transfer dynamics. Furthermore, the presence of hematite clusters enhances the activity of TiO₂ in the hydrogen evolution reaction. The Fe valence mixing present in some clusters leads to a significant increase in H₂ evolution rate compared with the fixed +3 valence of Fe in hematite. We also investigate the effect of oxygen defects and find extensive modifications in the electronic properties and local magnetism of the TiO₂ -Fe₂O₃ system, demonstrating the wide-ranging effect of oxygen defects in the combined system.

Supplementary material for this article is available online

Keywords: density functional theory, photo catalysis, titanium dioxide, hematite clusters, heterostructures

1. Introduction

Photocatalysis emerges as a promising technique to address contemporary energy challenges. In particular, photocatalytic

Original Content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

water splitting represents a highly sustainable approach to produce green hydrogen and oxygen by dissociating water using natural light. This environmentally friendly method enables the conversion of solar energy into chemical energy without contributing to pollution. Semiconductors with band gaps ranging from 2.5 to 3.4 eV are favorable photocatalysts covering visible to ultraviolet (UV) spectra [1]. Consequently, incident photons with energies greater than or equal to the band gap of the material liberate electrons to the conduction band (CB) and holes to the valence band (VB). These photogenerated charge carriers can migrate to the surface of the material participating in oxidation and reduction reactions. Amongst

^{*} Authors to whom any correspondence should be addressed.

the semiconductors suitable for these purposes, TiO_2 has been considered as a premier material since its discovery in 1972 by Fujishima and Honda [2]. It possesses exceptional properties that make it attractive for photocatalysis. These properties include oxidation properties, physical and chemical stability, non-toxicity and abundance [3-6]. Moreover, TiO₂ possesses a band structure suitable for efficient water splitting, as it straddles the reduction (-4.44 eV) and oxidation potentials (-5.67 eV) of water [6]. However, despite the favorable attributes, a large band gap, quick recombination of the electronhole pairs and being inactive for overall water splitting in the absence of sacrificial reagents leads to a performance degradation of TiO_2 [5, 7, 8]. These factors limit the widespread utilization of TiO₂ in photocatalytic applications. Therefore, attempts are made to overcome the shortcomings and enhance the performance of TiO_2 .

TiO₂ exhibits three phases at atmospheric pressure: stable rutile, metastable anatase and brookite. The crystalline structure can strongly affect the photocatalytic activity of a material. Since the synthesis of pure brookite is difficult [9], extant investigations have mainly focused on rutile and anatase phases. Even though anatase possesses a larger band gap than rutile, anatase has been considered to have a superior photocatalytic performance [10-14]. The better performance is generally attributed to indirect band gap and lower effective mass of photogenerated electrons and holes, increasing the lifetime of electron-hole pairs and lowering their recombination rate [15]. However, researchers have also reported a good performance of rutile in special experimental synthesis conditions [16, 17]. Moreover, mixing anatase and rutile phase structures have shown even better activity than pure anatase, attributed to interfacial charge transfer occurring between the two phases [17, 18].

A variety of strategies have been proposed to modify both chemical and physical properties of pure TiO₂, and the construction of heterostructure systems has shown improvements in photocatalytic performance [19]. It is recognized that by combining appropriate photocatalytic materials, heterojunction structures with matching band alignments can be formed. One promising candidate for combination with TiO₂ is hematite (α -Fe₂O₃, hereafter referred to as Fe₂O₃). It is the most stable phase of iron (III) oxide, possessing a narrow band gap of 2.0-2.2 eV [20, 21]. Several studies on TiO₂-Fe₂O₃ interface have been carried out earlier. For instance Mei et al [22] and Singh et al [23] have synthesized TiO₂-Fe₂O₃ heterostructure using deposition methods, where the $TiO_2(Fe_2O_3)$ surface was fully covered and Fe₂O₃ and TiO₂ are in direct contact. The results of Mei et al suggested that Fe₂O₃ concentration plays a key role in light adsorption, and the photoresponse could be engineered by the amount of surface Fe_2O_3 in TiO_2 . However, many studies have found that the increased amount of Fe₂O₃ content is not leading to a superior photocatalytic activity. For instance, in the study of Mei et al, using the photoluminescence spectroscopy (PL), the PL intensity of TH0.5 sample was found to be the lowest, indicating the most efficient charge separation compared to the samples with lower or higher Fe_2O_3 content. Cao *et al* [24] have the same conclusion on Fe₂O₃ coated TiO₂ using atomic layer deposition (ALD) methods. They reported that 400 cycles of Fe₂O₃ coating led to better photocatalytic activity than 200, 600 and/or 800 cycles. In general, at high Fe₂O₃ content iron has been proposed to become a recombination center for the charge carriers, having a negative impact on catalytic activity [25, 26]. Singh et al [23] studied TiO₂-Fe₂O₃ heterostructure over pure Fe₂O₃ surface and a low performance in photoelectrochemical cells (PEC) was attributed to inefficient charge separation in the heterostructure. It is also worth noticing that in their computational investigation, they highlighted that anatase TiO₂ (101) surface placed on top of the Fe₂O₃ surface was reconstructed during the geometry optimization. TiO₂ was reported to exhibit an 'amorphous' structure that resembled none of the stable crystal structures of TiO₂. The notable reconstruction may be attributed to the large lattice mismatch of the two surfaces. Further, investigations focusing on heterostructures with various Fe₂O₃ coverage and content on TiO₂, have shown that finding an optimal Fe₂O₃ content is essential in order to maximize the photocatalytic activity [22, 24-29]. For instance, Sun et al [26] conducted an experimental study on anatase TiO₂ surface modified with the hematite cluster for phenol degradation. They reported that small clusters enhanced the photocatalytic activity of TiO₂ by improving its response to visible light, and charge carrier transfer and separation. In general, the observed enhancement in catalytic activity has been attributed to the formation of a heterojunction between TiO_2 and Fe_2O_3 [24–27, 30–32]. Based on a thorough literature search, we can conclude that increased coverage of Fe₂O₃ is detrimental to photocatalytic performance of the material.

Defect engineering emerges as another effective method to modify the catalytic properties and mechanisms. In metal oxides, including TiO₂, oxygen vacancies are common defects [33]. Resulting from an oxygen vacancy, impurity states are generally observed in the band gap of TiO₂, often manifested as Ti^{3+} species. These impurity states contribute to a shift in the absorption spectrum and increased conductivity of TiO_2 [34, 35]. Consequently, these can lead to enhanced photocatalytic activity, demonstrated by Aschauer et al [36] for example. They reported that oxygen vacancies improved the photocatalytic activity of anatase TiO₂ in water adsorption. Several experiments have also demonstrated an existence of oxygen defect states in Fe₂O₃-TiO₂ and Fe-TiO₂ systems, and the states have been attributed to oxygen vacancies in the TiO₂ lattice [37–40]. Spectroscopy techniques, such as x-ray photoelectron spectroscopy (XPS), have been used to confirm oxygen vacancy defects in the systems. The studies have reported a successful incorporation of Fe³⁺ into the TiO₂ lattice, and due to the charge compensation mechanism, Fe³⁺ species results in the formation of oxygen vacancies. For instance, Zhu et al [40] proposed that the oxygen vacancies could contribute to a reduction in recombination rate. Correspondingly, Bootluck et al [27] suggested that oxygen vacancies contribute to enhanced photocatalytic activity. They reported that resulting from the Ar-plasma treatment, oxygen vacancies were produced in the Fe₂O₃-TiO₂ nanocomposites, contributing to improved photocatalytic activity compared to untreated Fe_2O_3 -TiO₂. It is also demonstrated that Fe_2O_3 -TiO₂ may be suitable material for hydrogen evolution reaction (HER). The improved photocatalytic activity of Fe_2O_3 -TiO₂ nanocomposites was attributed to a lower charge transfer resistance, which has led to better charge separation and reduced recombination rate of electron-hole pairs compared to bare TiO₂. It is worth noting that the study did not provide direct comparison between the HER activity of Fe_2O_3 -TiO₂ and bare TiO₂.

Inspired by the investigations of Sun et al [25], we employ first principles calculations to investigate the adsorption of hematite clusters on anatase TiO₂ (101) surfaces and its effect on photocatalytic properties. The choice of the anatase phase was motivated by its superior photocatalytic activity compared to other polymorphs, as discussed earlier. Moreover, studies have reported that the (101) plane of anatase possesses the highest photocatalytic activity than other crystal orientations [41, 42]. In order to improve the photocatalytic properties of TiO_2 Sun *et al* [26] highlighted the advantage of small Fe₂O₃ cluster size and low Fe₂O₃ coverage on anatase TiO₂. Building upon this, we introduce small hematite clusters, $(Fe_2O_3)_n$ with n = 1, 2, 3 at the TiO₂ surface. We also delve into defect engineering as another effective method to modify the properties of the heterostructures. More precisely, we introduce an oxygen defect in the heterostructure of TiO₂ and (Fe₂O₃)₁. Finally, to assess the photocatalytic performance, we focus on evaluating the suitability of the investigated heterostructures for HER. Our aim is to understand the effects brought about by the hematite clusters and further oxygen defect towards the electronic properties of TiO₂, due to the change in carrier concentration compared to the pristine surface. We also demonstrate that coating the anatase titanium dioxide with mixed-valence iron containing O-ligands using various hematite cluster coverings represents an effective approach to enhance photocatalytic hydrogen production.

2. Computational methodology

First principles calculations based on density functional theory (DFT) were performed using vienna Ab initio simulation package (VASP) [43-45] including the spin polarization. The exchange-correlation potential was described by generalized gradient approximation (GGA) parameterized by Perdew-Burke–Ernzerhof (PBE) functional [46]. The Hubbard correction was employed according to Dudarev et al [47] to describe localized d electrons of titanium and iron in order to obtain more realistic electronic and magnetic properties. Within the GGA+U method we adopted the corrections of $U_{eff} = 4.5$ eV (U=4.5 eV and J=0 eV) [48] for the Ti (table S1) and $U_{eff} = 4.0 \text{ eV} (U = 4.0 \text{ eV} \text{ and } J = 0 \text{ eV})$ [49] for the Fe. In some studies the Hubbard correction has also been applied to O 2p states to further improve the description of Ti-O bonds and obtain a larger opening of the band gap for TiO_2 [50]. Based on our results, in bulk TiO₂, applying the U correction to the O 2p states did not provide a significant improvement in the band gap (table S1), and therefore we chose to consider the Hubbard correction only for Ti 3d states. The 1st Brillouin zone was sampled according to the Monkhorst-Pack scheme [51]. The Projector augmented wave (PAW) method [52] was employed to describe the electron-ion potential with the plane wave energy cutoff of 650 eV (figure S1). The atomic relaxations were performed until the forces and energies were less than 0.001 eV Å⁻¹ and 10⁻⁶ eV, respectively. We used VESTA [53] for visualization and VASPKIT [54] for post-processing of the data from the VASP calculations.

To simulate the pristine anatase TiO_2 (101) surface we constructed a slab of 4 layers containing 192 atoms (64 Ti atoms and 128 O atoms) with lattice parameters of 10.32 Å, 15.25 Å and 35.68 Å in a, b and c directions (figure 2). To prevent interaction between periodic images, a vacuum space of 20 Å was applied along the c-axis. The heterostructures were formed by placing the hematite clusters $(Fe_2O_3)_{1,2,3}$ on the TiO₂ surface. The models were denoted as (Fe₂O₃)₁/TiO₂, (Fe₂O₃)₂/TiO₂ and (Fe₂O₃)₃/TiO₂, and only these three heterostructures were considered in this study. K-point sampling of $3 \times 2 \times 1$ and Gaussian smearing of 0.05 eV were used for the TiO₂ surface and heterostructures. To investigate the effect of an oxygen defect, several defect sites, shown in figure 7, were created in the (Fe₂O₃)₁/TiO₂. An oxygen atom was removed either from the TiO₂ (surface or subsurface vacancy) or from the (Fe₂O₃)₁ cluster. We created an oxygen vacancy in the surface layer of TiO₂ by removing a twofold-coordinated O atom, not forming a bond with the cluster. Three subsurface oxygen atoms were removed at different distances from the cluster in the first subsurface layer. Lastly, two different oxygen defects were created in (Fe₂O₃)₁ cluster. The surface vacancy was labeled as O_v, the subsurface vacancies as O_{sv1}, O_{sv2} and O_{sv3} , and the oxygen defects located in the $(Fe_2O_3)_1$ cluster as O_{c1} and O_{c2}. The defective heterostructures were further denoted as (Fe₂O₃)₁/TiO₂-O_{vac} where O_{vac} specifies the oxygen defect. In addition, to comprehensively investigate the effect of hematite clusters on the HER activity, we also considered the Fe_2O_3 surface in our calculations (figure S2). Thus, the HER activity of heterostructures was compared with both pristine TiO₂ and Fe₂O₃ surfaces. For hydrogen adsorption a supercell of $(2 \times 2 \times 1)$ of Fe₂O₃(0001) surface with a single Fe-termination with a vacuum thickness of around 20 Å was taken, and k-point sampling of $3 \times 3 \times 1$ was used in the calculations.

The adsorption energy of the $(Fe_2O_3)_n$ cluster at the TiO₂ surface was calculated from the formula

$$E^{\text{Ads}} = E\left(\left(\text{Fe}_2\text{O}_3\right)_n/\text{TiO}_2\right) - E\left(\text{TiO}_2\right) - E\left(\left(\text{Fe}_2\text{O}_3\right)_n\right), (1)$$

where $E((\text{Fe}_2\text{O}_3)_n/\text{TiO}_2)$ is the total energy of the heterostructures and $E(\text{TiO}_2)$ and $E((\text{Fe}_2\text{O}_3)_n)$ are the total energies of the pristine TiO₂ surface and (Fe₂O₃)_n cluster, respectively. To investigate the stability of oxygen defects, we calculated the formation energy of the defects using the equation

$$E^{\text{Form}} = E((\text{Fe}_2\text{O}_3)_1/\text{TiO}_2 - \text{O}_{\text{vac}}) - E((\text{Fe}_2\text{O}_3)_1/\text{TiO}_2) - \frac{1}{2}E(\text{O}_2), \qquad (2)$$

where the first term is the total energy of the defective heterostructure, in which the O_{vac} specifies the investigated oxygen defect. $\frac{1}{2}E(O_2)$ is the chemical potential of an oxygen atom that is half of the total energy of an isolated oxygen molecule O_2 . To evaluate the HER activity, we attached a hydrogen atom on the pristine TiO₂ and Fe₂O₃ surfaces, and also on defect-free and defective heterostructures (figures S3 and S4), and calculated the adsorption energy of hydrogen. In general, the free energy of hydrogen adsorption is accepted to be a descriptor for hydrogen-evolving catalysts. We also calculated the work function for the heterostructures. Work function is essentially the energy needed to introduce carriers to the surface and will be affected by doping and the presence of adsorbates. It is an essential parameter in understanding the interaction between the hematite clusters and TiO₂ and the effect of oxygen defect on the surface properties, and it is calculated by subtracting the Fermi energy E_F from the vacuum energy E_V ,

$$\Phi = E_{\rm V} - E_{\rm F}.\tag{3}$$

The electronic structure of the systems investigated was examined through the density of states (DOS). To analyze the charge distribution and charge transfer quantitatively, we performed the Bader analysis [55–58]. A negative Bader charge on an atom refers to electron gain and positive value to electron loss. The charge density differences are also calculated as

$$\Delta \rho \left(\mathbf{r} \right) = \rho_{AB} \left(\mathbf{r} \right) - \rho_{A} \left(\mathbf{r} \right) - \rho_{B} \left(\mathbf{r} \right)$$
(4)

where $\rho_{AB}(\mathbf{r})$ is the total charge density of the heterostructure, and $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ are the total charge densities of the TiO₂ surface and the (Fe₂O₃)_n cluster with atoms in exactly the same sites as they occupy in the heterostructure. Since Fe₂O₃ is a magnetic material, we also calculated the spin density difference. It is calculated from the same equation as charge density difference by replacing charge density $\rho(\mathbf{r})$ by spin density *s*(*r*). In the charge density difference (CDD) plots yellow refers to charge accumulation and cyan refers to charge depletion while in the spin density difference (SDD) plot the orange shows excess spin up polarization and turquoise shows excess spin down polarization. We set the isosurface value of 0.005 *e* Å⁻¹ in all CDD and SDD plots.

3. Results

3.1. Bulk parameters

Initially, we calculated the bulk parameters of Fe_2O_3 and TiO_2 (figure S5). The lattice constants were determined to be a = b = 4.780 Å and c = 13.323 Å and a = b = 3.98 Å and c = 9.56 Å for Fe_2O_3 and TiO_2 , respectively. These results are consistent with experimental measurements [59, 60]. The DOS of the bulk Fe_2O_3 and bulk TiO_2 are in figure S6, showing the electronic structure of the materials. Using the GGA functional Fe_2O_3 was predicted to exhibit metallic behaviour whereas TiO_2 possessed a band gap of 1.7 eV. The results demonstrate that the standard GGA functional is incapable of accurately describing both Fe_2O_3 and TiO_2 because of the localized d electrons. This is a well-known issue in predicting the electronic structure of transition metals oxides [61–65]. Previously, for instance, Labat *et al* [66], Mattioli *et al* [62] and Di Valentin *et al* [67] have reported the band gaps of

2.08 eV, 2.16 eV and 2.19 eV for TiO₂ while Cococcioni and de Gironcol [63] found a zero band gap for Fe₂O₃ with the GGA. Upon employing the Hubbard correction we obtained a band gap of 1.16 eV for Fe₂O₃ and 2.3 eV for TiO₂, which are fairly consistent with the reported theoretical values [62, 68–72], showing improved description of the materials with the GGA+U. Previously, both materials have also been investigated using the hybrid functionals which, however, tend to overestimate the band gap value. Meng et al [73] calculated the band gap of 2.41 eV for Fe₂O₃ using the HSE functional with mixing parameter of a = 0.15, and Yamamoto and Ohno [72] and Deák et al [74] have reported a band gap of 3.37 eV and 3.58 eV using the HSE06 functional. Even though hybrid functionals are generally more accurate for semiconductors, the GGA+U provides a reasonable compromise between the accuracy and computational cost in band gap calculations. Therefore, based on the results, we conclude that the selected methods are sufficient for describing the electronic properties of both materials.

3.2. Freestanding clusters and TiO₂ surface

Before investigating the heterostructures, we simulated the freestanding hematite clusters and pristine TiO₂ surface. The relaxed structures of (Fe₂O₃)₁, (Fe₂O₃)₂ and (Fe₂O₃)₃ are shown in figure 1. The $(Fe_2O_3)_1$ showed a planar structure whereas the $(Fe_2O_3)_2$ and $(Fe_2O_3)_3$ had a cage-like structure. The Fe-O distances were ranging from 1.65 to 1.87 Å in the $(Fe_2O_3)_1$, from 1.73 to 1.83 Å in the $(Fe_2O_3)_2$ and from 1.69 to 1.99 Å in the (Fe₂O₃)₃ (table S2). These geometries and Fe-O distances compared well with previous works [75–79], providing a good starting point for the rest of the calculations. Furthermore, we evaluated the oxidation state of iron in the free-standing clusters. Details of Bader charges and magnetic moments of atoms in the clusters are provided in table S3. According to the Bader analysis, Fe atoms exhibited a gain of charge which was depleted from O atoms. Ferromagnetic configuration was indicated for all the three clusters. The total magnetic moment of the $(Fe_2O_3)_1$ was 9.28 μ_B , and spin magnetic moments of Fe atoms were 3.32 $\mu_{\rm B}$ and 3.60 $\mu_{\rm B}$, suggesting co-existence of Fe^{2+} and Fe^{3+} oxidation states [79]. Bader charges of 1.08 e and 1.46 e supported the presence of mixed-valence Fe [80]. In the (Fe₂O₃)₂ Bader charges of Fe atoms were around 1.30 e for all four Fe atoms whereas magnetic moments of the Fe atoms were 3.70 $\mu_{\rm B}$, 3.32 $\mu_{\rm B}$, 2.89 $\mu_{\rm B}$ and 2.85 $\mu_{\rm B}$. In the (Fe₂O₃)₃ the Bader charge and magnetic moment of Fe atoms varied in the range of 1.03 to 1.53 e, and 2.97 to 4.04 $\mu_{\rm B}$. The reduction in magnetic moment may imply lower oxidation state than Fe^{3+} for Fe in these clusters.

We proceeded with the optimization of anatase TiO₂ (101) surface. There are four types of atoms at the surface: two- and threefold coordinated oxygen atoms (O_{2c} and O_{3c}) and fiveand sixfold coordinated Ti atoms (Ti_{5c} and Ti_{6c}). The calculated O-Ti bond lengths were 1.87 Å for O_{2c}-Ti_{6c}, 1.85 Å for O_{2c}-Ti_{5c} and 2.00 Å for O_{3c}-Ti_{6c}. In addition, we found Ti_{5c}-Ti_{5c} bonds to be 3.81 Å . The calculated lattice parameters were a = b = 3.88 Å and c = 9.52 Å. The electronic structure of the pristine TiO₂ surface, calculated using the GGA+U,



Figure 1. The optimized structure of (a) $(Fe_2O_3)_1$, (b) $(Fe_2O_3)_2$ and (c) $(Fe_2O_3)_3$ clusters.



Figure 2. The surface model and computed DOS of anatase TiO_2 . A reasonable band gap of approximately 2.5 eV was found for the TiO_2 surface. Fermi level is set to zero energy.

is shown in figure 2. The appearance of shoulder features in the CB edge is characteristic of the anatase phase of TiO₂. The valence band maximum (VBM) and conduction band minimum (VBM) were located at -0.05 eV and 2.44 eV, respectively, resulting in a band gap of approximately 2.5 eV. This agrees with the reported results [75, 81]. The band gap energy is in the visible light region indicating that the photoactivation of anatase surface could be achieved by visible light radiation with wavelength up to 500 nm. Due to the dangling bonds the surface band gap of TiO₂ is generally lower than the bulk band gap (3.0–3.3 eV). Moreover, the work function of the surface was calculated to be 7.23 eV. In general, TiO₂ possesses a high work function of 5–6 eV [82, 83]. Compared to this our calculations moderately overestimated the work function.

3.3. Structural and electronic properties of the $(Fe_2O_3)_n/TiO_2$ heterostructures

3.3.1. Structural optimization. The optimized structures of the $(Fe_2O_3)_n/TiO_2$ heterostructures are shown in figure 3. Importantly, the results showed that Fe_2O_3 clusters remained stable on the TiO_2 surface without breaking down. For the $(Fe_2O_3)_1$ the optimization yielded a closed cage-like structure on the surface that resembles a pyramid with a parallelogram shaped base. The (Fe₂O₃)₂ and (Fe₂O₃)₂ maintained a cagelike structure at the TiO₂ surface after the adsorption. The coordination number of the (Fe₂O₃)₁ and (Fe₂O₃)₃ were found to be five and nine, respectively, while the coordination number of the $(Fe_2O_3)_2$ was only two. The adsorption of the clusters resulted in some lattice distortion at the TiO₂ surface primarily limited to the top layer of the surface. The nearest Ti and O atoms at the surface are generally shifted toward the clusters to form new Ti-O and Fe-O bonds between the surface and clusters. The surface Ti-O distances were 1.88 Å, 1.98 Å and in the range of 1.94–2.12 Å, and Fe—surface O distances in the range of 2.04 to 2.14 Å, 1.95 Å and in the range of 1.87 to 2.02 Å in the $(Fe_2O_3)_1/TiO_2$, $(Fe_2O_3)_2/TiO_2$ and (Fe₂O₃)₃/TiO₂, respectively. We also investigated the structure of the clusters after the adsorption. In the adsorbed $(Fe_2O_3)_1$ cluster the Fe-O bond lengths varied from 1.84 to 2.14 Å, showing significant change in the bond lengths when compared with the freestanding $(Fe_2O_3)_1$ cluster. In the adsorbed $(Fe_2O_3)_2$ and $(Fe_2O_3)_3$ clusters the distances lied in the range of 1.69 to 1.91 Å, and 1.69 to 1.94 Å, respectively. These are similar to that of freestanding (Fe₂O₃)₂ and (Fe₂O₃)₃ clusters. Detailed information on structural parameters are listed in table S4. The energetic stability was checked by calculating the adsorption energies of the $(Fe_2O_3)_1$, $(Fe_2O_3)_1$



Figure 3. Optimized structures of (a) $(Fe_2O_3)_1/TiO_2$, (b) $(Fe_2O_3)_2/TiO_2$ and (c) $(Fe_2O_3)_3/TiO_2$. Selected atoms are labeled in the figure.

and $(Fe_2O_3)_3$. The energies were -2.28 eV, -1.72 eV and -3.24 eV, respectively, showing the cluster-surface interaction to be energetically favourable. More negative adsorption energy indicates stronger interaction with TiO₂, and which, in this case, correlates with the number of newly formed bonds between the clusters and TiO₂.

3.3.2. Electronic structure analysis. The electronic structure of the $(Fe_2O_3)_n/TiO_2$ heterostructures are shown in figure 4. The properties of primitive TiO₂ remained unchanged but the results revealed an emergence of spin polarized, both occupied and unoccupied, Fe₂O₃-states within the band gap of TiO₂ due the cluster-surface interaction. The impurity states below the Fermi level led to an upward shift of valence band. The VBM was shifted from -0.05 eV of TiO₂ to -0.70 eV in the $(Fe_2O_3)_1/TiO_2$, -1.60 eV in the $(Fe_2O_3)_2/TiO_2$, and -1.35 eV in the (Fe₂O₃)₃/TiO₂. These newly emerging electronic states resulted in a narrowing in band gap energy compared to the original band gap of TiO2. The unoccupied states in the band gap divided the band gap of $(Fe_2O_3)_1/TiO_2$ into two parts, 0.45 eV and 0.90 eV. In the (Fe₂O₃)₂/TiO₂ the band gap was narrowed down to 0.20 eV. Adsorption of (Fe₂O₃)₃ induced states some of which cross the Fermi level, and thus (Fe₂O₃)₃/TiO₂ exhibited a metallic nature. This is proposed to enable the activation of TiO₂ by visible light. Due to the emerging states the VB of Fe₂O₃ locates above the VB of TiO_2 and the CB of Fe_2O_3 below the CB of TiO_2 . The particular band alignment (VB_{TiO_2} < VB_{Fe_2O_3} < CB_{Fe_2O_3} < CB_{TiO₂}) could generally indicate a formation of type I heterojunction with a straddling gap between Fe_2O_3 and TiO_2 . This is in line with the study of Moniz *et al* [75], and it can affect the charge transfer properties in the heterostructures. Our results showed that the Fe₂O₃ concentration has a significant impact on band gap energy. The decrease in it was more obvious in the presence of larger clusters. Mei et al [22] have synthesized sheet-like TiO₂/Fe₂O₃ nanocomposites with different Fe₂O₃ content on TiO₂ surface. Their results indicated improved light adsorption with Fe₂O₃ content, and by increasing it, the adsorption ability appeared to approach that of pure Fe₂O₃, which showed the highest activity in the visible light region. Our results could imply that the Fe₂O₃ concentration is a determining factor in the photosensitization of TiO₂ surface caused by the adsorbed Fe₂O₃ clusters. Conducting electronic states at the Fermi level induced by (Fe₂O₃)₃ could be advantageous for carrier transfer and contribute to improved photoresponse.

3.3.3. Charge transfer analysis. Efficient charge separation and transfer are essential factors affecting the photocatalytic activity. To gain further insight into the charge transfer properties in the heterostructures we calculated the CDD, shown in figure 5, and performed the Bader analysis. The Bader charge and magnetic moment of selected atoms are listed in table S3. The results indicated a charge redistribution in the



Figure 4. The computed DOS of $(Fe_2O_3)_1/TiO_2$ (a and (b), $(Fe_2O_3)_2/TiO_2$ (c and (d) and $(Fe_2O_3)_3/TiO_2$ (e and (f). Projected DOSs and band gap regions are shown in the left and right, respectively. Fermi level is set to zero energy.

systems after the adsorption of the clusters, localized on the cluster and the top layer of the TiO₂ surface. At the interface the electron accumulation and depletion regions were aligned in the direction of the formed bonds between TiO₂ and Fe₂O₃. This suggests that the bonds can be considered covalent with a polar feature. The blue isosurface around Fe showed charge depletion from Fe, indicating electron donor nature for the clusters. Increased amount of charge accumulation was observed around Fe atoms in case of larger Fe₂O₃ clusters. The work function of TiO₂ was observed to be affected by the clusters. The work function decreased from 7.23 eV to 6.70 eV, 5.90 eV and 6.18 eV in the (Fe₂O₃)₁/TiO₂, (Fe₂O₃)₂/TiO₂ and (Fe₂O₃)₃/TiO₂, respectively, supporting donor nature for Fe₂O₃ clusters. The lower work function can also facilitate electron injection from the TiO₂ surface.

The Bader charge of the $(Fe_2O_3)_1$, $(Fe_2O_3)_2$ and $(Fe_2O_3)_3$ were 0.32 *e*, 0.036 *e* and 0.42 *e*, suggesting an electron transfer from Fe₂O₃ clusters to TiO₂. Bader charges indicated an occurrence of notable charge transfer in the presence of $(Fe_2O_3)_1$ and $(Fe_2O_3)_3$ whereas the adsorption of the $(Fe_2O_3)_2$ induced only a small charge displacement. Nearly 90% of the transferred charge was redistributed to the surface layer of TiO₂. Neither the CDD plots nor Bader charges showed charge localization at the surface, indicating even distribution of charge among surface layer atoms. It should be noted that our results are in conflict with Moniz et al [75] who proposed an electron transfer from TiO2 to Fe2O3 based on their theoretical study on the combined system of TiO₂ and Fe₂O₃ clusters. The difference in the results may result from the use of different methods. Donor nature of Fe atoms was confirmed by the Bader charges. The Bader charges of the Fe1 and Fe2 atoms were 1.61 e and 1.52 e in the $(Fe_2O_3)_1/TiO_2$. The correlation between the Bader charges and oxidation state is still somewhat debuted. However, according to Posysaev et al [80] the particular values suggested Fe^{3+} oxidation state for Fe in the (Fe₂O₃)₁/TiO₂. Larger variation in the Bader charge of Fe atoms was observed in the adsorbed (Fe₂O₃)₂ and $(Fe_2O_3)_3$. In the $(Fe_2O_3)_2/TiO_2$ the Bader charges of Fe1,



Figure 5. The CDD and SDD plot of the $(Fe_2O_3)_1/TiO_2$ (a and (b), $(Fe_2O_3)_2/TiO_2$ (c and (d) and $(Fe_2O_3)_3/TiO_2$ (e and (f). The labels of the atoms are provided in figure 3.

Fe2, Fe3 ad Fe4 were 1.37 *e*, 1.39 *e*, 1.61 *e* and 1.45 *e* while in the $(Fe_2O_3)_3/TiO_2$ the values were 1.63 *e*, 1.51 *e*, 1.32 *e*, 1.20 *e*, 1.56 *e* and 1.30 *e* for Fe1, Fe2, Fe3, Fe4, Fe5 and Fe6, respectively. Reduction in Bader charge could indicate an emergence of Fe²⁺ species [80] and therefore, existence of different valences, Fe²⁺ and Fe³⁺, in these heterostructures. Increased amount of charge accumulation indicated by the CDD plot can support the conclusion.

We were also interested in the magnetism brought by Fe₂O₃ in order to evaluate the oxidation state of Fe. In general, Fe introduces ferromagnetism in the heterostructures which is supported by the positive spin density around Fe in the SDD plots (figures 5). We found a total magnetic moment of 9.61 $\mu_{\rm B}$, 17.2 $\mu_{\rm B}$ and 17.8 $\mu_{\rm B}$ per unit cell for the $(Fe_2O_3)_1/TiO_2$, $(Fe_2O_3)_2/TiO_2$ and $(Fe_2O_3)_3/TiO_2$. In the $(Fe_2O_3)_1/TiO_2$ the magnetic moments of the Fe1 and Fe2 were 4.11 $\mu_{\rm B}$ and 4.06 $\mu_{\rm B}$, respectively, indicating high spin configuration and $3d^5$ occupation [84, 85], that is, Fe³⁺ oxidation state. In the $(Fe_2O_3)_2/TiO_2$ the Fe atoms had an odd contribution to the total magnetic moment. We found a large magnetic moment of 4.02 $\mu_{\rm B}$ and 4.13 $\mu_{\rm B}$ for the Fe2 and Fe3, whereas a reduced magnetic moment of around 3.26 $\mu_{\rm B}$ and 3.36 $\mu_{\rm B}$ for the Fe1 and Fe4, respectively. In the adsorbed $(Fe_2O_3)_3$, Fe1, Fe2 and Fe5 exhibited a magnetic moment of 4.10 $\mu_{\rm B}$, 3.67 $\mu_{\rm B}$ and 3.96 $\mu_{\rm B}$, respectively. The magnetic moment of Fe3 and Fe4 were only around 2.90 $\mu_{\rm B}$, and Fe6 showed antiparallel spin orientation with a magnetic moment of -0.842 $\mu_{\rm B}$. The SDD plot of (Fe₂O₃)₃/TiO₂ also showed an increased amount of spin down components in the cluster. Thus, ferrimagnetism occurred in the $(Fe_2O_3)_3/TiO_2$. With the varying Bader charges, the results can highly suggest mixed-valence state (Fe^{2+}/Fe^{3+}) for Fe in the $(Fe_2O_3)_2/TiO_2$. It is worth noticing that magnetic moments do not directly correlate with the Bader charges. Due to the charge transfer, spin magnetization was also transferred to the atoms nearby Fe. Bader charge and magnetic moment of selected atoms are listed in table S5.

Based on our results, the emerging Fe₂O₃ states in the band gap of TiO₂ have an impact on the charge transfer mechanism in the heterostructures. Induced Fe₂O₃ states in the valence band are proposed to allow visible light excitation of electrons to the CB of TiO₂. Thus, charge accumulation occurs on the TiO₂ surface. At the same time, the holes are found in the Fe₂O₃. This could suggest spatial separation of electrons and hole, which can further imply reduction in recombination rate. In addition, the unoccupied Fe₂O₃-states can act as traps for the conduction band electrons, changing the oxidation state of Fe to Fe²⁺, hindering the charge transfer. However, because Fe²⁺ is relatively unstable and the unoccupied Fe states lie close to the CB of TiO₂, Fe²⁺ might tend to release the trap electrons and change back to Fe^{3+} in the $(Fe_2O_3)_1/TiO_2$. In the $(Fe_2O_3)_2/TiO_2$ the charge transfer between Fe₂O₃ and TiO₂ was almost negligible, which could indicate less efficient charge separation in the system. A type I band alignment with a small band gap energy might facilitate the recombination phenomenon occurring in Fe₂O₃. In the $(Fe_2O_3)_2/TiO_2$, the highest charge transfer could be attributed to the Fe₂O₃ states crossing the Fermi level, enabling direct electron conduction to the CB. The intervalence charge transfer between Fe atoms with different oxidation states can also help to separate the charge in Fe_2O_3 .

3.3.4. Hydrogen evolution reaction activity. After investigating the properties of the heterostructures we evaluate the HER activity by attaching a hydrogen atom on the heterostructures (figures S4) and calculated the adsorption energy



Figure 6. Free energy diagram for hydrogen evolution reaction on the pristine TiO₂ and Fe₂O₃ surfaces and (Fe₂O₃)_n/TiO₂ heterostructures.

(figure 6). An ideal photocatalyst for the HER should have adsorption energy close to zero. Moreover, we incorporated a Fe₂O₃-surface in our investigations for a better comparison. The adsorption energy in the pristine TiO_2 and Fe_2O_3 surfaces were calculated to be 0.65 eV and -0.64 eV. A positive value indicates too weak interaction between TiO₂ and hydrogen, inhibiting the adsorption. On the contrary, the adsorption of hydrogen on the Fe₂O₃ surface is exothermic with negative adsorption energy which facilitates the adsorption but makes the desorption of hydrogen difficult. The presence of the $(Fe_2O_3)_n$ clusters improved the adsorption energy, bringing it closer to the optimal zero energy. In the presence of $(Fe_2O_3)_1$ and $(Fe_2O_3)_2$ the adsorption energy decreased from 0.65 eV to 0.43 eV and 0.29 eV, respectively, showing weakened binding. In the $(Fe_2O_3)_3/TiO_2$ the adsorption was much stronger with an energy value of -0.29. Thus, the Fe₂O₃ clusters facilitate the adsorption of hydrogen and can enhance the HER activity of TiO2. Moreover, the larger cluster size enhanced the HER activity more than the smallest Fe_2O_3 cluster. This was attributed to the co-existence of Fe^{3+} and Fe^{2+} oxidation states for Fe. Interestingly, Zhang *et al* [86] reported similar findings on iron-based metal-organic frameworks, highlighting the mixed-valence of Fe in promoting the hydrogen evolution. Furthermore, these results are in line with that of Sun et al, where they demonstrated that Fe₂O₃ clusters with small size and low coverage on TiO₂ can be beneficial for catalytic reaction.

3.4. Oxygen defect in the (Fe₂O₃)₁/TiO₂ heterostructure

The modeled defect sites and their formation energies are shown in figure 7. Positive formation energies showed that the defect formation is endothermic. The formation energy of the O_{c1} and O_{c2} was the lowest, only 1.59 eV, indicating that the removal of oxygen is easier from the cluster than from the TiO_2 surface. This can be explained by the weaker bonding of oxygen in the adsorbed cluster than at the TiO₂ surface. Considering the relatively high formation energy of 3.41 eV of the surface vacancy O_v, we decided to introduce several subsurface vacancy sites. Based on our findings, a subsurface vacancy is generally more stable in the $(Fe_2O_3)_1/TiO_2$ than a surface vacancy. The O_{sv3} was found to be the most stable, located underneath the cluster, with a formation energy of 2.71 eV. The formation energy of the O_{sv1} and O_{sv2} were 0.41 eV and 0.79 eV larger than that of Osv3, and their transverse distance, perpendicular to the *b*-axis, from the cluster were around 11 Å and 4 Å, respectively. This suggests that the cluster introduces a dependence of the formation energy on the distance from the cluster in the subsurface layer. Previously, Hoh *et al* [87] have reported a distance dependence of oxygen vacancy formation energy from the Au-clusters on hematite surface, proposing that the cluster stabilizes the region underneath and near to it, making it more stable against reduction. We also observed the cluster to enhance the oxygen defect formation at the surface. In the pristine TiO₂ surface the formation energies of the O_v , O_{sv1} , O_{sv2} and O_{sv3} were 5.47 eV, 5.46 eV, 5.12 eV, 5.46 eV, showing that the presence of the cluster can decrease the formation energy even by 50%. A similar observation has been reported in previous studies [88, 89].

Among the modeled defect sites, we chose to further investigate the effect of the O_v , O_{sv3} , and O_{c1} and O_{c2} on the properties of the $(Fe_2O_3)_1/TiO_2$ heterostructure. We employed the same methods to investigate these defective heterostructures as for the defect-free heterostructures.

3.4.1. Structural optimization. The optimized structures of the defective heterostructures are shown in figure 8 while the bond distances between selected atoms are provided in table S6. It is evident that the defects affected the geometry of the cluster adsorbed on the surface. In the presence of the O_v



Figure 7. The modeled defect sites in the $(Fe_2O_3)_1/TiO_2$ and their formation energies, E^{Form} . (a) Surface vacancy O_v and subsurface vacancies (b) O_{sv1} , (c) O_{sv2} , and (d) O_{sv3} . The defects (e) O_{c1} and (f) O_{c2} are located in the $(Fe_2O_3)_1$ cluster. The defect sites are coloured yellow.



Figure 8. The optimized structures of the defective heterostructures: (a) $(Fe_2O_3)_1/TiO_2-O_v$, (b) $(Fe_2O_3)_1/TiO_2-O_{sv3}$ and (c) $(Fe_2O_3)_1/TiO_2-O_c$. The labels correspond to the same atoms in figure 3(a).

and O_{sv3} the structure of the cluster became more open. The structural changes led to the breaking of bonds with TiO₂, thereby reducing the coordination number of the $(Fe_2O_3)_1$ to four in the $(Fe_2O_3)_1/TiO_2$ -O_v and three in the $(Fe_2O_3)_1/TiO_2$ -O_{sv3}. Furthermore, the O_v and O_{sv3} caused local lattice distortion at the TiO₂ surface. The vacancies shifted the adjacent Ti atoms away from the vacancy site while the adjacent oxygen atoms moved closer to it. This is consistent with previous observations [90]. The changes caused by the O_v were

primarily limited to the surface layer whereas the O_{sv3} led to distortion notably extended to the first sublayer. The removal of either of the O_{c1} or O_{c2} resulted in the same geometry with the same total energy for the optimized systems. Therefore, we simply denoted the defective heterostructures simply as $(Fe_2O_3)_1/TiO_2-O_c$. The remaining four atoms of the $(Fe_2O_3)_1$ were re-positioned in a manner that the top of the cluster became planar at the TiO_2 surface, preserving the coordination number of five.



Figure 9. The computed DOS of (a) $(Fe_2O_3)_1/TiO_2-O_v$, (b) $(Fe_2O_3)_1/TiO_2-O_{sv3}$ and (c) $(Fe_2O_3)_1/TiO_2-O_c$. Fermi level is set to zero energy.

3.4.2. Electronic structure analysis. Figure 9 represents the calculated DOS of the (Fe₂O₃)₁/TiO₂-O_y, (Fe₂O₃)₁/TiO₂-O_{sy3} and (Fe₂O₃)₁ /TiO₂-O_c, showing changes in the band gap region. The valence band was further upward-shifted due to the oxygen defects. The VBM positions of TiO₂ were found to be at -0.96 eV in the $(Fe_2O_3)_1/TiO_2-O_v$, -1.8 eV in the $(Fe_2O_3)_1/TiO_2-O_{sv3}$, and -0.93 eV in the $(Fe_2O_3)_1/TiO_2-O_c$, respectively. The properties of primitive TiO₂ remained still unchanged. The presence of defects altered the band gap of the heterostructure. The (Fe₂O₃)₁/TiO₂-O_{sv3} showed a narrow band gap of 0.75 eV. Inversely, the O_v and O_c resulted in an increase in the band gap energy compared to the defect-free (Fe₂O₃)₁/TiO₂. We found a band gap of 1.45 eV for the $(Fe_2O_3)_1/TiO_2-O_v$ and 1.80 eV for the $(Fe_2O_3)_1/TiO_2-O_v$ Oc. Nevertheless, all the three defective heterostructures possessed a narrower band gap than the pristine TiO₂ surface. Interestingly, a localized Ti 3d peak was observed at -0.57 eV, arising from the Ti3 atom (figure 8). This can be evidence of formation of Ti³⁺ species at the TiO₂ surface, which is common phenomenon in $\mathrm{Ti}\mathrm{O}_2$ in the presence of oxygen vacancies.

3.4.3. Charge density analysis. As previously, we investigated the changes in the charge transfer properties via the CDD and Bader analysis, supported by the SDD. The Bader charges and magnetic moments are listed in table S7 for selected atoms. The CDD plots, shown in (figure 10), showed that the main charge redistribution occurred in the cluster and at the interface in the defective heterostructures as well. When a neutral oxygen defect is formed it releases effective excess charge which can generally be transferred either to Fe or Ti. The Bader analysis confirmed the charge gain of Fe, with a yellow isosurface observed around Fe atoms in the CDD plots. The calculated Bader charge of the Fe1 and Fe2 atoms were 1.52 e and 1.30 e in the $(Fe_2O_3)_1/TiO_2-O_v$, 1.26 e and 1.19 *e* in the $(Fe_2O_3)_1/TiO_2-O_{sv3}$, and 1.29 *e* and 1.32 *e* in the $(Fe_2O_3)_1/TiO_2-O_c$, respectively. The corresponding



Figure 10. The CDD (a)–(c) and SDD (d)–(f) of the $(Fe_2O_3)_1/TiO_2-O_v$, $(Fe_2O_3)_1/TiO_2-O_{sv3}$ and $(Fe_2O_3)_1/TiO_2-O_c$.

magnetic moment of the Fe1 and Fe2 were 4.02 $\mu_{\rm B}$ and 3.77 μ_B in the (Fe₂O₃)₁/TiO₂-O_v, 3.26 μ_B and -3.57 μ_B in the $(Fe_2O_3)_1/TiO_2-O_{sv3}$, and 3.67 μ_B and 3.70 μ_B in the (Fe₂O₃)₁/TiO₂-O_c, respectively. A lower magnetic moment supports a charge gain for Fe. To confirm lower spin magnetization of some Fe atoms, we calculated the SDD which showed a larger probability for spin down density (turquoise isosurface) around Fe (figure 10). In the $(Fe_2O_3)_1/TiO_2-O_v$ the total magnetic moment was still 9.66 $\mu_{\rm B}$ per unit cell whereas in the $(Fe_2O_3)_1/TiO_2-O_c$ the total magnetic moment decreased to 7.79 $\mu_{\rm B}$. Surprisingly, the Fe2 atom in the (Fe₂O₃)₁/TiO₂-O_{sv3} experienced a magnetic phase transition. This resulted in a total magnetic moment of 0.09 $\mu_{\rm B}$. Due to the anti-parallel but unequal magnetic moment of Fe atoms, the (Fe₂O₃)₁/TiO₂- O_{sv3} exhibits weak ferrimagnetic behaviour. The magnetic phase transition was attributed to be to the notable lattice distortion at the TiO₂ surface caused by the O_{sv3}. For instance, in their study, Menéndez et al [91] have reported that the lattice distortion caused by oxygen defect can correlate with magnetic behavior and induce a magnetic phase transition.

Our findings suggest that Fe can have the mixed valence state (Fe²⁺/Fe³⁺) in the (Fe₂O₃)₁/TiO₂-O_v [80, 84, 85]. We also observed localized spin density between the Fe atoms (figure 10(d)). This can indicate magnetic coupling between the cations with different oxidation states, supporting the mixed-valence state for Fe. In the (Fe₂O₃)₁/TiO₂-O_{sv3} and (Fe₂O₃)₁/TiO₂-O_c the results indicates the Fe²⁺ oxidation state for Fe [80, 84, 85]. This was supported by the lower Bader charges and even contribution of Fe atoms to the spin magnetization. Additionally, in the (Fe₂O₃)₁/TiO₂-O_v we found the Bader charge of the Ti3 to change notably. It decreased from 2.04 *e* to 1.79 *e*, corresponding to Ti³⁺ species [80]. This is consistent with the findings from the DOS.

As per the Bader charge analysis the direction of the charge transfer remained from the cluster to the surface in the $(Fe_2O_3)_1/TiO_2-O_c$. 0.45 *e* of charge per unit cell was

transferred to the surface, of which approximately 90% e was evenly distributed among Ti and O atoms of the surface layer. The charge transfer was almost 1.5 times larger than in the (Fe₂O₃)₁/TiO₂, showing an increase in the conductivity of TiO₂. This was attributed to the formation of a type II heterojunction. Since no Fe₂O₃-states exist below the CB of TiO₂ electrons from the VB of TiO2 and Fe2O3 can be excited directly to the CB of TiO₂ without trapping. Electron excitation to the unoccupied Fe₂O₃-states can be possible but due to the type II heterojunction electrons can be transferred to the CB of TiO₂. On the contrary, we observed that the direction of the charge transfer reverse in the presence of the $_{v}$ and O_{sv3} . 0.12 e and 0.62 e per unit cell were transferred from the surface to the cluster in the $(Fe_2O_3)_1/TiO_2-O_v$ and $(Fe_2O_3)_1/TiO_2-O_{sv3}$, respectively. A larger charge transfer indicates stronger interaction between TiO_2 and Fe_2O_3 in the $(Fe_2O_3)_1/TiO_2-O_{sv3}$, which is consistent with the lower formation energy of the O_{sv3} compared to that of O_v . For the $(Fe_2O_3)_1/TiO_2-O_{sv3}$ the Bader analysis can support the Z-scheme mechanism, leading to electron accumulation to Fe₂O₃. The lowest unoccupied Fe₂O₃ states started to appear approximately 1.5 eV above the Fermi level, enabling electron excitation using visible light.

The oxygen defects further decreased the work function of the $(Fe_2O_3)_1/TiO_2$. A neutral oxygen defect is a positively charged which makes negatively charged surface more positive, that is, decrease the work function. In the presence of the O_v , O_{sv3} and O_c we found the work function to be 5.27 eV, 5.28 eV and 5.41 eV, respectively. This suggests that an oxygen defect can facilitate electron migration from the TiO₂ surface.

3.4.4. Effect on hydrogen evolution. The results show that oxygen defects enable the engineering of electronic properties of the $(Fe_2O_3)_1/TiO_2$. Finally, we evaluate the HER activity of the defective heterostructures. H-containing structures are

shown in figure S4. Based on the results, oxygen defects have a detrimental effect on the HER activity of the $(Fe_2O_3)_1/TiO_2$. The O_v, O_{sv3} and O_c increased the adsorption energy of hydrogen from 0.43 eV to 0.71 eV, 0.61 eV and 0.60 eV, respectively. Thus, the interaction with hydrogen becomes weaker again, indicating decrease in HER activity. The HER activity of the defective heterostructures is comparable with the pristine TiO₂ surface.

4. Conclusions

First principles DFT calculations were employed to investigate the heterostructure of the TiO₂ surface and $(Fe_2O_3)_n$ (n =1,2,3) clusters, and superior catalytic performance was indicated for the heterostructures. The adsorption of the clusters on the surface was exothermic, thus enabling the modification of the surface properties of TiO₂. The formation of a heterojunction between TiO2 and Fe2O3 was identified to affect band gap energy, charge transfer and charge separation in the heterostructures, leading to enhanced photocatalytic properties. The clusters were observed to improve the HER activity of TiO₂. The existence of mixed-valence Fe (Fe^{2+}/Fe^{3+}) led to greater enhancement in the HER activity. We also incorporated oxygen defects on the $(Fe_2O_3)_1/TiO_2$, and the defect formation was found to be endothermic. The presence of the $(Fe_2O_3)_1$ cluster substantially enhanced the oxygen defect formation at TiO₂ compared to the pristine surface. We found that electronic structure and charge transfer and the local magnetism can be tuned by oxygen defects, which can indirectly affect the oxidation state of Fe. However, it was observed that an oxygen defect was not beneficial in order to improve the HER activity.

Our investigation also suggests variations of the dyesensitized solar cells originally proposed by Grätzel [6]. Here, hematite nanoparticles play the role of dyes used to sensitize TiO_2 in order to produce H_2/O_2 by water photoelectrolysis. The hematite nanoparticles are bound to the nanostructured wide-band-gap TiO_2 semiconductor and can be used as photosensitizers to harvest solar energy and generate excitons needed to fulfill the requirements for a photovoltaic scheme.

In summary, the results of our work reveal three important points. The first point is that +2 and +3 valence-state mixing offers a lot of potential to control the electronic structure of hematite clusters. The second point is that further electronic structure optimization could be achieved by engineering these clusters with various oxygen defects. The third point is that the presence of Fe²⁺-Fe³⁺ intervalence charge transfer implies charge transfer between these non-equivalent Fe sites and could result in broad absorption in the visible or IR region of the electromagnetic spectrum.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgment

This work is supported by the European Union's Horizon Europe research and innovation program under Marie Sklodowska-Curie Actions (Grant No. 101081280), the Finnish cultural foundation (Grant No. 00230235) and the Kvantum Institute. The authors acknowledge the CSC—IT Center for Science, Finland, for computational resources.

Declaration of conflict of interest

The authors declare no competing financial interests

ORCID iDs

- Kati Asikainen b https://orcid.org/0009-0008-2970-6951
- B Barbiellini D https://orcid.org/0000-0002-3309-1362
- S Assa Aravindh D https://orcid.org/0000-0001-9360-3457

References

- Villa K, Galán-Mascarós J R, López N and Palomares E 2021 Sustain. Energy Fuels 5 4560
- [2] Fujishima A and Honda K 1972 Nature 238 37
- [3] Nosaka Y, Nakamura M and Hirakawa T 2002 *Phys. Chem. Chem. Phys.* **4** 1088
- [4] Chen X and Mao S S 2007 Chem. Rev. 107 2891
- [5] Fujishima A, Zhang X and Tryk D A 2008 Surf. Sci. Rep. 63 515
- [6] Grätzel M 2001 Nature 414 338–44
- [7] Bahnemann D W, Hilgendorff M and Memming R 1997 J. Phys. Chem. B 101 4265
- [8] Li R, Weng Y, Zhou X, Wang X, Mi Y, Chong R, Han H and Li C 2015 Energy Environ. Sci. 8 2377
- [9] Di Paola A, Bellardita M and Palmisano L 2013 Catalysts 3 36
- [10] Sclafani A and Herrmann J M 1996 J. Phys. Chem. 100 13655
- [11] Luttrell T, Halpegamage S, Tao J, Kramer A, Sutter E and Batzill M 2014 Sci. Rep. 4 4043
- [12] Žerjav G, Žižek K, Zavašnik J and Pintar A 2022 J. Environ. Chem. Eng. 10 107722
- [13] Augustynski J 1993 Electrochim. Acta 38 43
- [14] Hirano M, Nakahara C, Ota K, Tanaike O and Inagaki M 2003 J. Solid State Chem. 170 39
- [15] Zhang J, Zhou P, Liu J and Yu J 2014 Phys. Chem. Chem. Phys. 16 20382
- [16] Ohno T, Sarukawa K and Matsumura M 2001 Phys. Chem. B 105 2417
- [17] Ohno T, Tokieda K, Higashida S and Matsumura M 2003 Appl. Catal. A 244 383
- [18] Liao Y and Que W 2010 J. Alloys Compd. 505 243
- [19] Wang H, Zhang L, Chen Z, Hu J, Li S, Wang Z, Liu J and Wang X 2014 Chem. Soc. Rev. 43 5234
- [20] Muraro P C L, Mortar S R, Vizzotto B S, Chuy G, Dos Santos C, Brum L F W and da Silva W L 2020 Sci. Rep. 10 3055
- [21] Glasscock J A, Barnes P R F, Plumb I C, Bendavid A and Martin P J 2008 Thin Solid Films 516 1716
- [22] Mei Q, Zhang F, Wang N, Yang Y, Wu R and Wang W 2019 RSC Adv. 9 22764
- [23] Singh A P, Wang R B, Tossi C, Tittonen I, Wickman B and Hellman A 2021 RSC Adv. 11 4297
- [24] Cao Y Q, Zi T Q, Zhao X R, Liu C, Ren Q, Fang J B, Li W M and Li A D 2020 Sci. Rep. 10 13437

- [26] Sun Q, Leng W, Li Z and Xu Y 2012 J. Hazard. Mater. 229-230 224
- [27] Bootluck W, Chittrakarn T, Techato K and Khongnakorn W 2021 J. Environ. Chem. Eng. 9 105660
- [28] Sharma B, Boruah P K, Yadav A and Das M R 2018 J. Environ. Chem. Eng. 6 134
- [29] Abbas N, Shao G N, Haider M S, Imran S M, Park S S and Kim H T 2016 J. Ind. Eng. Chem. 39 112
- [30] Deng J, Zhuo Q and Lv X 2019 *J. Electroanal. Chem.* **835** 287
- [31] Xia Y and Yin L 2013 Phys. Chem. Chem. Phys. 15 18627
- [32] Li X, Lin H, Chen X, Niu H, Liu J, Zhang T and Qu F 2016 Phys. Chem. Chem. Phys. 18 9176
- [33] Pacchioni G 2003 ChemPhysChem 4 1041
- [34] Pan X, Yang M Q, Fu X, Zhang N and Xu Y J 2013 *Nanoscale* 5 3601
- [35] Elahifard M, Sadrian M R, Mirzanejad A, Behjatmanesh-Ardakani R and Ahmadvand S 2020 Catalysts 10 397
- [36] Aschauer U, He Y, Cheng H, Li S, Diebold U and Selloni A 2010 J. Phys. Chem. C 114 1278
- [37] Trenczek-Zajac A, Synowiec M, Zakrzewska K, Zazakowny K, Kowalski K, Dziedzic A and Rabecka M 2022 ACS Appl. Mater. Interfaces 14 33
- [38] Synowiec M, Zákutná D, Trenczek-Zajac A and Rabecka M 2023 Appl. Surf. Sci. 608 155186
- [39] Wu Q, Zheng Q and van de Krol R 2012 J. Phys. Chem. C 116 7219
- [40] Zhu J, Ren J, Huo Y, Bian Z and Li H 2007 J. Phys. Chem. C 111 18965
- [41] Ahmed A Y, Kandiel T A, Oekermann T and Bahnemann D 2011 J. Phys. Chem. Lett. 2 2461
- [42] Günnemann C, Haisch C, Fleisch M, Schneider J, Emeline A V and Bahnemann D W 2019 ACS Catal. 9 1001
- [43] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558
- [44] Kresse G and Furthmüller J 1996 Comput. Mater. Sci. 6 15
- [45] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
- [46] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
- [47] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Phys. Rev. B 57 1505
- [48] Kumaravel V et al 2019 J. Phys. Chem. C 123 21083
- [49] Rollmann G, Rohrbach A, Entel P and Hafner J 2004 Phys. Rev. B 69 165107
- [50] Ataei S S, Mohammadizadeh M R and Seriani N 2016 J. Phys. Chem. C 120 8421
- [51] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
- [52] Blöchl P E 1994 *Phys. Rev.* B **50** 17953
- [53] Momma K and Izumi F 2008 J. Appl. Cryst. 41 653
- [54] Wang V, Xu N, Liu J C, Tang G and Geng W T 2021 Comput. Phys. Commun. 267 108033
- [55] Tang W, Sanville E and Henkelman G 2009 J. Phys.: Condens. Matter 21 084204
- [56] Sanville E, Kenny S D, Smith R and Henkelman G 2007 J. Comp. Chem. 28 899
- [57] Henkelman G, Arnaldsson A and Jónsson H 2006 Comput. Mater. Sci. 36 354
- [58] Yu M and Trinkle D R 2011 J. Chem. Phys. 134 064111

- [59] Finger W and Hazen R M 1980 J. Appl. Phys. 51 5362
- [60] Burdett J K, Hughbanks T, Miller G J, Richardson J W Jr and Smith J V 1987 J. Am. Chem. Soc. 109 3639
- [61] Morgan B J and Watson G W 2007 Surf. Sci. 601 5034
- [62] Mattioli G, Alippi P, Filippone F, Caminiti R and Bonapasta A A 2010 J. Phys. Chem. C 114 21694
- [63] Cococcioni M and de Gironcoli S 2005 *Phys. Rev.* B 71 035105
- [64] Erhart P, Albe K and Klein A 2006 Phys. Rev. B 73 205203
- [65] Ghosal S, Dutta K, Chowdhury S and Jana D 2022 J. Phys.D: Appl. Phys. 55 375303
- [66] Labat F, Baranek P, Domain C, Minot C and Adamo C 2007 J. Chem. Phys. 126 154703
- [67] Di Valentin C, Pacchioni G and Selloni A 2004 Phys. Rev. B 70 085116
- [68] Rivera R, Pinto H P, Stashans A and Piedra L 2012 Phys. Scr. 85 015602
- [69] Huda M N, Walsh A, Yan Y, Wei S H and Al-Jassim M M 2010 J. Appl. Phys. 107 123712
- [70] Fujimori A, Saeki M, Kimizuka N, Taniguchi M and Suga S 1986 Phys. Rev. B 34 7318
- [71] Mo S D and Ching W Y 1995 Phys. Rev. B 51 13023
- [72] Yamamoto T and Ohno T 2012 Phys. Chem. Chem. Phys. 14 589
- [73] Meng Y et al 2016 J. Chem. Theory Comput. 12 5132
- [74] Deák P, Aradi B and Frauenheim T 2011 *Phys. Rev.* B 83 155207
- [75] Moniz S J A, Shevlin S A, An X, Guo Z X and Tang J 2014 Chem. Eur. J. 20 15571
- [76] Erlebach A, Hühn C, Jana R and Sierka M 2014 Phys. Chem. Chem. Phys. 16 26461
- [77] Peters L, Sasioglu E, Rossen S, Friedrich C, Blügel S and Katsnelson M I 2017 Phys. Rev. B 95 155119
- [78] Reilly N M, Reveles J U, Johnson G E, del Campo M, Khanna S N, Ko A M and Castleman A W 2007 J. Phys. Chem. C 111 19086
- [79] Majid A, Zahid S, Khan S U D and Khan S U D 2020 J. Nanoparticle Res. 22 145
- [80] Posysaev S, Miroshnichenko O, Alatalo M, Le D and Rahman T S 2019 Comput. Mater. Sci. 161 403
- [81] Wang J, Huang J, Meng J, Li Q and Yang J 2017 RSC Adv. 7 39877
- [82] Kashiwaya S, Morasch J, Streibel V, Toupance T, Jaegermann W and Klein A 2018 Surfaces 1 73
- [83] Borodin A and Reichling M 2011 Phys. Chem. Chem. Phys. 13 15442
- [84] Neufeld O and Toroker M C 2015 J. Phys. Chem. C 119 5836
- [85] Geneste G, Paillard C and Dkhil B 2019 Phys. Rev. B 99 024104
- [86] Zhang X, Ma X, Ye Y, Guo C, Xu X, Zhou J and Wang B 2023 Chem. Eng. J. 456 140939
- [87] Hoh S W, Thomas L, Jones G and Willock D J 2015 Res. Chem. Intermediates 41 9587
- [88] Giordano L, Goniakowski J and Pacchioni G 2001 Phys. Rev. B 64 075417
- [89] Yang Z, Lu Z, Luo G and Hermansson K 2007 Phys. Lett. A 369 132
- [90] Li H, Guo Y and Robertson J 2015 J. Chem. Phys. C 119 18160
- [91] Menéndez C, Chu D and Carzola C 2020 Comput. Mater. 6 76