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# Photoelectrochemical water splitting using TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> heterojunction films produced by chemical vapour deposition

 Abdullah M. Alotaibi, \* Hussam M. Alzahrani, Saud M. Alosaimi, Abdullah M. Alqahtani, Mohammed A. Alhajji and Mohammed J. Alotaibi

This study reports the enhanced photoelectrochemical (PEC) performance of TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> heterostructure films fabricated *via* a sequential aerosol-assisted chemical vapour deposition (AACVD) of hematite at 450 °C, followed by atmospheric pressure CVD (APCVD) of anatase TiO<sub>2</sub> with controlled thickness. Structural analyses (XRD, Raman, XPS) confirmed phase purity and oxidation states, while UV-vis spectroscopy revealed a narrowed bandgap and extended visible light absorption for the heterostructures compared to pristine films. The optimized TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> (8 min) photoanode achieved a photocurrent density of 1.75 mA cm<sup>-2</sup> at 1.23 V vs. RHE in 1.0 M NaOH under AM 1.5G illumination, representing a ~150% improvement over pure α-Fe<sub>2</sub>O<sub>3</sub>. Incident-photon-to-current efficiency (IPCE) reached 7.47% at 420 nm, with enhanced performance sustained across the visible range. Transient absorption spectroscopy (TAS) revealed prolonged charge carrier lifetimes, indicating suppressed electron-hole recombination. The heterojunction design also improved stability, maintaining performance for over 16 h compared to 6.5 h for hematite alone. These synergistic effects including narrowed bandgap, efficient charge separation, and enhanced light harvesting highlight the novelty of combining AACVD and APCVD in fabricating TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> heterostructures as durable, high-performance photoanodes for scalable solar hydrogen generation.

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## 1. Introduction

Photoelectrochemical water splitting is a promising approach for sustainable energy production.<sup>1–5</sup> Generating electricity from hydrogen is highly desirable since it serves as an eco-friendly energy carrier and helps reduce reliance on fossil fuels. However, conventional hydrogen production methods using oil, coal, and methane have detrimental environmental effects, especially regarding climate change, due to the significant carbon dioxide emissions they generate.<sup>6–8</sup> The application of photoanodes in water splitting has garnered significant interest since the work of Fujishima and Honda (1972).<sup>9</sup> Since that time, numerous studies have focused on enhancing PEC efficiency and improving catalyst stability.

TiO<sub>2</sub> naturally occurs in three crystalline forms, anatase, rutile, and brookite, and possesses a wide band gap (>3.0 eV), which limits its photo-absorption to the UV range.<sup>10–12</sup> However, hematite α-Fe<sub>2</sub>O<sub>3</sub> features a lower bandgap (2.0–2.2 eV), enabling enhanced visible light absorption. Additionally, it is relatively non-toxic, chemically stable, cost-effective, and possesses a suitable valence band edge position.<sup>13–18</sup> These

combined attributes establish hematite as one of the most promising metal oxides for water splitting.

Nevertheless, hematite has some notable limitations, one of which is its conduction band edge being positioned below the reversible hydrogen potential.<sup>19</sup> Additionally, the photogenerated holes in Fe<sub>2</sub>O<sub>3</sub> exhibit limited efficiency in driving the water oxidation process, this is attributed to the short hole diffusion length in Fe<sub>2</sub>O<sub>3</sub>,<sup>20</sup> in contrast to the high penetration depth.<sup>21</sup> Several studies have employed hematite as a photoanode for oxygen evolution in water splitting; however, these materials require an external electrical bias to generate hydrogen.

It is important to note that, despite its theoretical potential, the actual efficiency of hematite for water splitting remains negligible in practice when compared to theoretical calculations (16.8%),<sup>19,22</sup> this is due to high charge recombination, limited hole diffusion length, and low electrical conductivity.

To enhance the efficiency of Fe<sub>2</sub>O<sub>3</sub> in water splitting, various strategies have been employed, including doping it with different elements or combining α-Fe<sub>2</sub>O<sub>3</sub> with other metal oxide semiconductors like TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, and WO<sub>3</sub>.<sup>19,23–27</sup> In fact, the exploration of Fe<sub>2</sub>O<sub>3</sub> for water splitting dates back quite a while, with the first paper on its use being published by Hardee and Bard.<sup>28</sup> They discovered that when Fe<sub>2</sub>O<sub>3</sub> was placed on a Ti and Pt substrate, the photocurrent under 500 nm illumination in KCl was 0.8 V *versus* the saturated calomel electrode (*V*<sub>SCE</sub>). In

King Abdulaziz City for Science and Technology (KACST), Hydrogen Technologies Institute, Saudi Arabia. E-mail: [abalotaibi@kacst.gov.sa](mailto:abalotaibi@kacst.gov.sa)



the same year, another study by Quinn *et al.* reported that on Fe<sub>2</sub>O<sub>3</sub> single crystals under 475 nm illumination in 0.5 M NaOH, the photocurrent density reached 1.57 mA cm<sup>-2</sup> versus the reversible hydrogen electrode ( $V_{\text{RHE}}$ ).<sup>29</sup>

However, as mentioned, the PEC performance of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be enhanced through surface treatment and/or metal ion doping, which helps reduce electron-hole recombination<sup>30</sup> and increases donor density.<sup>31</sup> Surface treatment also leads to accelerated solar water oxidation.<sup>32-34</sup> It was found that heterojunction systems enhance PEC performance by facilitating efficient charge separation and reducing recombination of photogenerated electron-hole pairs. This leads to improved light absorption and higher photocurrent, boosting overall PEC water splitting efficiency. The study reports on WO<sub>3</sub>/TiO<sub>2</sub> core/shell heterojunction photoanodes with a dendritic TiO<sub>2</sub> shell that significantly enhances photoelectrochemical water splitting performance.<sup>35</sup> The dendritic TiO<sub>2</sub> increases surface area and active sites, while the heterojunction improves charge separation and reduces recombination. This architecture leads to higher photocurrent density, better light absorption, and improved stability compared to individual WO<sub>3</sub> or TiO<sub>2</sub> electrodes, demonstrating the important role of dendritic TiO<sub>2</sub> in optimizing PEC efficiency. Another study focuses on surface engineering of CuO-Cu<sub>2</sub>O heterojunction thin films to enhance their photoelectrochemical water splitting performance.<sup>36</sup> By optimizing the interface and surface properties, the heterojunction facilitates better charge separation and transport. As a result, the films exhibit increased photocurrent and improved stability during water splitting. In addition, the paper reports the fabrication of WO<sub>3</sub>/BiVO<sub>4</sub> heterojunction photoanodes with nanostructured WO<sub>3</sub> to boost photoelectrochemical performance.<sup>37</sup> The nanostructuring enhances light absorption, charge separation, and interfacial charge transfer. Consequently, the photoanodes achieve higher photocurrent density and improved efficiency in water splitting.

In this paper, we present, for the first time,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> deposited by AACVD on an FTO substrate at 450 °C, followed by anatase TiO<sub>2</sub> deposited as a second layer by APCVD and annealed at 500 °C to remove carbon contamination. This TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> layered approach enhanced both the water splitting efficiency and stability compared to pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films. Additionally, TiO<sub>2</sub> films deposited using this method demonstrated excellent water splitting performance under sunlight. A pure Fe<sub>2</sub>O<sub>3</sub> film, deposited *via* AACVD, proved effective for water splitting (0.8 mA cm<sup>-2</sup> at 1.23 V vs. RHE) and remained stable for about 6.5 hours. A notable improvement in photocurrent density was observed for the heterojunction after coupling with TiO<sub>2</sub> (1.75 mA cm<sup>-2</sup> at 1.23 V vs. RHE), which increased the stability to 16 hours. Transient absorption spectroscopy (TAS) was used to investigate charge carrier recombination dynamics and carrier lifetimes of the TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films. A correlation between PEC efficiency and carrier lifetimes measured by TAS was identified.

## 2. Experimental section

### 2.1. General procedure

All chemicals used in these experiments were provided by Sigma-Aldrich Chemical Co. and were used without further

purification. Deposition was carried out on a 10 × 20 mm<sup>2</sup> fluorine-doped tin oxide (FTO) glass. Before use, the FTO substrates were meticulously cleaned with acetone (99%), isopropanol (99.9%), and distilled water, and then dried in air.

### 2.2. Deposition conditions

[0.23 g, 0.905 mmol] of iron(II) acetylacetonate Fe[CH<sub>3</sub>COCH=C(O)CH<sub>3</sub>]<sub>2</sub> was dissolved in 60 mL of ethyl acetate in a glass bubbler. Aerosol-assisted chemical vapor deposition (AACVD) was then employed to deposit  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin films onto FTO glass substrate. The mist was transferred into the reactor using nitrogen (BOC Ltd, 99.99%) at a flow rate of 1.4 L min<sup>-1</sup>, and deposition was carried out for 40 minutes at 450 °C. Afterward, the reactor was allowed to cool to room temperature under nitrogen before the films were removed and annealed at 500 °C in nitrogen at 2 L min<sup>-1</sup> for 30 minutes to eliminate carbon contamination.

At this point, 40 mL of titanium(IV) isopropoxide [Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] was introduced into a glass bubbler. Atmospheric pressure chemical vapor deposition (APCVD) was used to deposit TiO<sub>2</sub> films on the FTO glass substrate, with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films forming as the second layer. Concurrently, titanium(IV) isopropoxide was heated in the bubbler to around 120 °C, and the vapor was transferred to the reactor *via* nitrogen (BOC Ltd, 99.99%) at a flow rate of 4 L min<sup>-1</sup>. Deposition took place at 450 °C for TiO<sub>2</sub> and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films for different time intervals (4, 8, and 12 minutes) on the glass substrate, followed by annealing at 500 °C for 30 minutes (Fig. S1).

## 3. Photoelectrochemical performance (PEC)

PEC measurements were carried out using a 1 M NaOH electrolyte (Fluka, in ID water, pH = 13.6) in a three-electrode electrochemical cell under simulated sunlight (100 mW cm<sup>-2</sup>, AM 1.5G). A platinum wire served as the counter electrode, and an Ag/AgCl electrode in saturated KCl was used as the reference. The photoelectrode was controlled by a potentiostat (Ivium Technology), with the reversible hydrogen electrode (RHE) potential given by the equation:

$$E_{\text{RHE}} = E_{\text{AgCl}} + 0.059\text{pH} + E_{\text{AgCl}}^{\circ}$$

$$\text{where } E_{\text{AgCl}}^{\circ} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C}$$

The potential was scanned from -1.0 to 1.23 V at a rate of 50 mV s<sup>-1</sup>, and sunlight was simulated using an Ivium CompactStat (IVIUM Technologies) Lamp at an intensity of 100 mW cm<sup>-2</sup> (AM 1.5G). The illumination intensity was calibrated using a silicon reference cell and optical meter (Newport, Model 1918-R). Incident-photon-to-current efficiency (IPCE) measurements were performed with 1.0 M NaOH electrolyte and a 200 W Xe lamp at 1.23 V vs. RHE. IPCE values were calculated using the formula:

$$\text{IPCE}\% = \frac{12\,400 \times I_{\text{SC}} \text{ (A cm}^{-2}\text{)}}{\lambda \text{ (nm)} \times P_{\text{in}} \text{ (W cm}^{-2}\text{)}} \times 100$$



where  $I_{SC}$  is the current density at 1.23 V vs. RHE,  $\lambda$  is the wavelength of the incident monochromatic light, and  $P_{in}$  is the light intensity at a specific wavelength. Mott–Schottky measurements were conducted in the dark at a 1 kHz frequency, using the same electrolyte as for IPCE.

The Applied Bias Photon-to-Current Efficiency (ABPE) was calculated according to the following equation:

$$\text{ABPE (\%)} = \frac{J \times (1.23 - V_b)}{P_{\text{light}}}$$

where  $J$  is the photocurrent density ( $\text{mA cm}^{-2}$ ) measured by the electrochemical workstation,  $V_b$  is the applied bias versus RHE (V), and  $P_{\text{light}}$  is the incident light intensity under AM 1.5G ( $100 \text{ mW cm}^{-2}$ ) illumination.

## 4. Transient absorption spectroscopy (TAS)

Transient absorption measurements were conducted using a custom-built pump–probe setup. The monochromatic pump pulse was generated by a Q-switched laser system (InnoLAS, Picolo AOT MOPA, Picosecond Nd:YVO<sub>4</sub> Laser System), where the fundamental frequency was tripled to produce a 355 nm output, with the pulse energy adjusted to  $300 \mu\text{J cm}^{-2}$  using a reflective neutral medium filter. The broadband probe pulse, spanning from 420 nm to 1100 nm, was generated through

a supercontinuum process by focusing a 1300 nm seed pulse onto a 3 mm *c*-cut sapphire crystal. This seed pulse was produced by an optical parametric amplifier (Light Conversion, TOPAS Prime) after being pumped by a commercial Ti:sapphire amplifier (Coherent Legend Elite Duo, 4.5 mJ, 3 kHz, 100 fs). The delay time between the pump and probe pulses was controlled by an electronic delay generator (Stanford Research System DG535) with a jitter of approximately 100 ps. The spot sizes of the laser pulses were determined by transmissivity through a 75 nm precision laser pinhole, with 20% for the pump and 50% for the probe, resulting in the pump pulse being over three times larger than the probe pulse. In the experiments, the pump and probe pulses were overlapped on the front surface of the samples. All measurements were performed at room temperature, and the samples were kept in a nitrogen-filled chamber.

## 5. Results and discussion

### 5.1. X-ray diffraction (XRD) and Raman spectroscopy

Powder X-ray diffraction (PXRD) was employed to examine the TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and pure TiO<sub>2</sub> films (Fig. 1a). The analysis revealed that the iron oxide was in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase, with diffraction peaks corresponding to the (012), (104), (110), (113), (024), (116), and (214) planes at  $2\theta$  values of 24.2°, 33.1°, 35.5°, 40.8°, 49.4°, 54.1°, and 62.5°, respectively. These findings

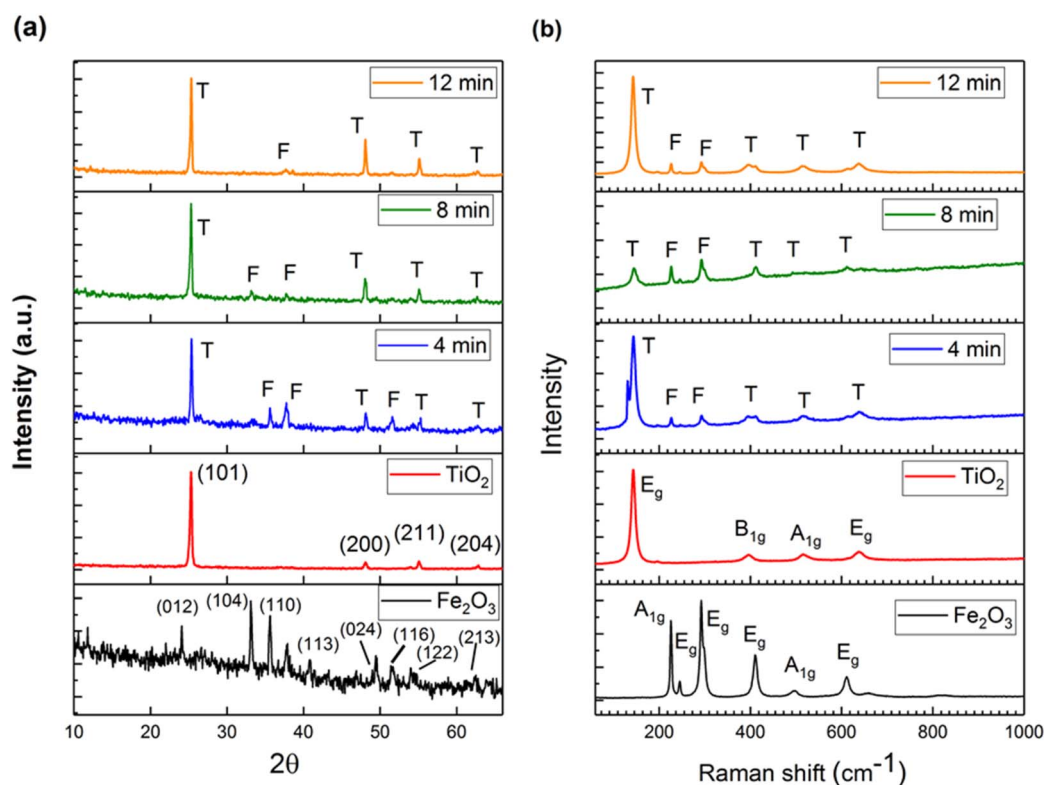


Fig. 1 (a) Shows the powder X-ray diffraction (PXRD) patterns of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> layer films with varying TiO<sub>2</sub> thicknesses. (b) Displays the Raman spectra (recorded using a 633 nm laser wavelength) for all these films. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film was deposited via AACVD at 450 °C on a glass substrate and annealed at 500 °C, while the pure TiO<sub>2</sub> and TiO<sub>2</sub> on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films were deposited using APCVD at 450 °C and annealed at 500 °C with different deposition durations (4, 8, and 12 minutes).



align well with the reference data for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase.<sup>38,39</sup> No peaks corresponding to other iron oxide phases were detected. The PXRD patterns for pure TiO<sub>2</sub> revealed a typical anatase phase, with diffraction peaks at (101), (112), (200), and (204) corresponding to  $2\theta$  values of 25.3°, 38.6°, 48.0°, 55.1°, and 62.8°, respectively.<sup>40</sup> The TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films, with varying TiO<sub>2</sub> thicknesses, exhibited the anatase phase of TiO<sub>2</sub>. However, for the films with a deposition time of 4, 8 and 12 minutes, a peak for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was observed, as the TiO<sub>2</sub> layer was thin enough to reveal the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> peak. Fig. 1b presents the Raman spectra of TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and pure TiO<sub>2</sub> films. The Raman peaks for the Fe<sub>2</sub>O<sub>3</sub> films appeared at 225 cm<sup>-1</sup> (A<sub>1g</sub>), 245 cm<sup>-1</sup> (E<sub>g</sub>), 292 cm<sup>-1</sup> (E<sub>g</sub>), 410 cm<sup>-1</sup> (E<sub>g</sub>), 502 cm<sup>-1</sup> (A<sub>1g</sub>), 497 cm<sup>-1</sup> (E<sub>g</sub>), and 612 cm<sup>-1</sup> (E<sub>g</sub>). The TiO<sub>2</sub> films in the anatase phase exhibited peaks at 141.5 cm<sup>-1</sup> (E<sub>g</sub>), 397 cm<sup>-1</sup> (B<sub>1g</sub>), 514 cm<sup>-1</sup> (A<sub>1g</sub>), and 635 cm<sup>-1</sup> (E<sub>g</sub>). The TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films displayed peaks corresponding to both TiO<sub>2</sub> in the anatase phase and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. These Raman spectra align with the XRD results, confirming the presence of iron oxide in the hematite phase and TiO<sub>2</sub> in the anatase phase.

## 5.2. UV-vis spectroscopy

The optical properties of TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films, as well as pure Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films, were examined using UV-vis spectroscopy. Fig. 2a presents the absorption spectra of all the films. Pure TiO<sub>2</sub> exhibits absorption around 380 nm, as expected, while pure Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films with deposition times of 4 and 8 minutes absorb near 600 nm, with absorption extending into the visible spectrum. The absorption of the TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> film (12 minutes) shows a slight shift towards the visible region, around 650 nm. Fig. 2a also shows the bandgaps of these films, which were calculated using Tauc plots.<sup>41</sup> The bandgaps of pure Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are approximately 1.95 eV and 3.2 eV, respectively. For the TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films, the bandgaps are 2.1 eV, 2.1 eV, and 1.78 eV for deposition times of 4, 8, and 12 minutes, respectively.

Fig. 3 presents the UV-vis transmission spectra for all samples, displaying the characteristic interference fringes for TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> based films. The transmission of TiO<sub>2</sub> films is approximately 72% for wavelengths between 380 and 780 nm, increasing to around 83% in the near-infrared region. In contrast, the transparency of hematite films deposited by AACVD is lower than that of TiO<sub>2</sub> films in the visible range, but fluctuates between 72% and 63% in the near-infrared. The transmission spectra of TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films with a 12 minutes deposition time exhibit the lowest transparency in the visible range (500–760 nm), while the TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films with a 4 minutes deposition time show a slight increase in transparency in the 700–2500 nm range compared to pure TiO<sub>2</sub> films.

## 5.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface-level chemical states and valence band characteristics of all iron (Fe) and titanium (Ti) films. The 2p<sub>2/3</sub> peaks corresponding to high-spin Fe<sup>2+</sup> and Fe<sup>3+</sup> ions displayed a notably broader profile compared to those observed in low-spin Fe<sup>2+</sup> or metallic Fe<sup>(0)</sup>.<sup>42</sup> Gupta and Sen have demonstrated that the broadening arises from three factors:

- (1) The presence of unpaired 3d electrons in the photo-ionized Fe cation.
- (2) Spin-orbit coupling involving the 2p core hole state.
- (3) The incorporation of crystal field effects and electrostatic interactions.<sup>43,44</sup>

According to the study by Gupta and Sen, corroborated by additional research,<sup>45,46</sup> the Fe 2p<sub>3/2</sub> peaks were analyzed using multiplet structure calculations. It was determined that the Fe 2p<sub>3/2</sub> spectrum in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> consists of four distinct components at 709.8, 710.7, 711.4, and 712.3 eV. Additionally, a satellite peak appears around 719 eV due to charge transfer processes and shake-up effects. Another peak, associated with surface structure, is observed at approximately 715 eV.<sup>45</sup>

The Fe spectrum was fitted using a Gaussian-Lorentzian function, revealing Fe 2p binding energies characteristic of Fe<sup>3+</sup>.

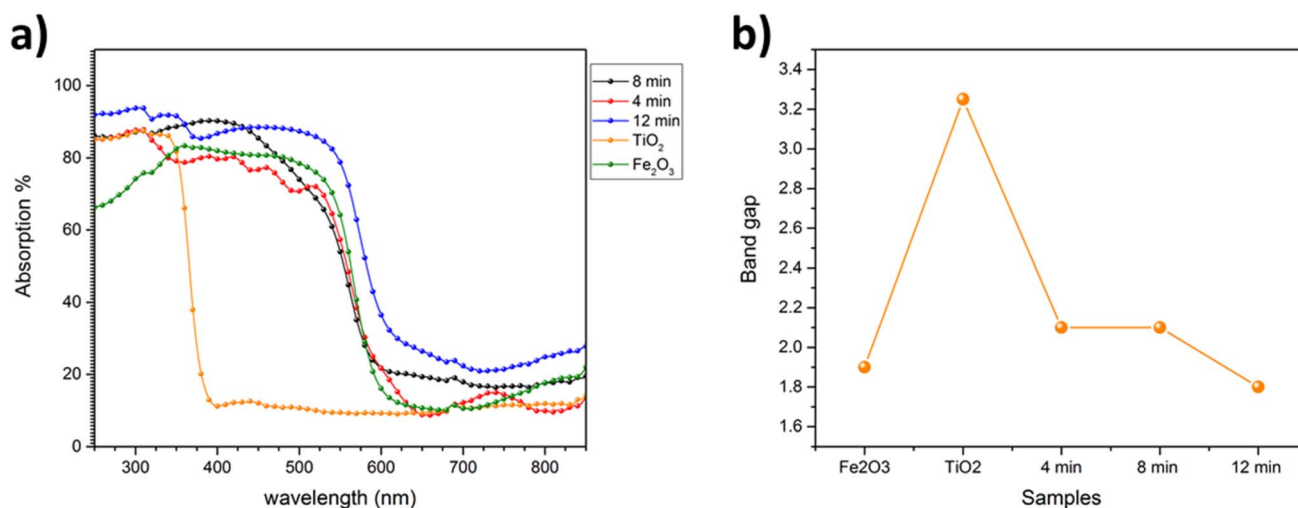


Fig. 2 (a) UV-vis absorption spectra of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films. (b) Displays the absorption spectra for all films, where pure TiO<sub>2</sub> absorbs around 380 nm and pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film absorbs near 600 nm. The bandgaps, calculated using Tauc plots, are also shown in (b).



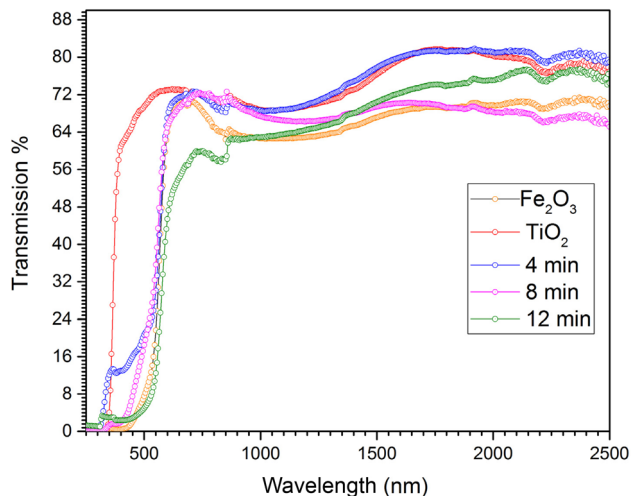


Fig. 3 Transmission spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films deposited on glass substrate.

The 2p<sub>3/2</sub> peaks were centered at 709.2, 710.1, 710.6, 711.7, and 712.7 eV, with a pre-peak at 708.1 eV and a satellite peak at 719.1 eV. These results closely align with our samples, as illustrated in (Fig. 4a).

The XPS analysis of Ti 2p in pure TiO<sub>2</sub> and the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> series revealed peaks at binding energies of 458.9 eV and 464.6 eV, corresponding to Ti–O bonds of Ti<sup>4+</sup> within the TiO<sub>2</sub> lattice (Fig. 4b). The 2p<sub>3/2</sub> peaks were more intense than the 2p<sub>1/2</sub> peaks due to the greater degeneracy of 2p<sub>3/2</sub> (four states) compared to 2p<sub>1/2</sub> (two states) in spin–orbit (*j-j*) coupling. Additionally, no Ti<sup>3+</sup> peak was detected in any of the samples.

Fig. 5 presents the XPS spectra of the valence band (VB) region for Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films with varying TiO<sub>2</sub> thicknesses. While all VB spectra exhibit a main band spanning from 0 to approximately 10 eV, the VB spectrum of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film also features three distinct bands at around 2.3, 4.8, and

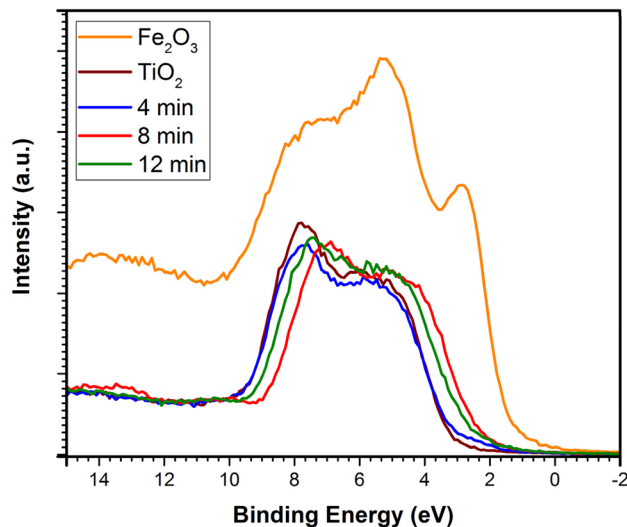


Fig. 5 Valence band XPS spectra of pure Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films with deposition times of 4, 8, and 12 minutes. The VB spectra reveal a decrease in the band onset as the TiO<sub>2</sub> thickness increases.

7.5 eV, aligning well with the characteristic VB structure of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>46</sup> The valence band (VB) spectra of TiO<sub>2</sub> and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films, deposited at different durations (4, 8, and 12 minutes), exhibit two primary peaks at approximately 4.2 and 7.5 eV. A slight shift in binding energy is observed as the TiO<sub>2</sub> film thickness increases compared to the pure TiO<sub>2</sub> film. The most significant distinction among the VB spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> samples is their intensity. The VB intensity of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is notably higher than that of TiO<sub>2</sub> or TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This is attributed to the presence of Fe 3d (*t*<sub>2g</sub> and *e*<sub>g</sub> orbital symmetry) and O 2p hybridized states, along with the O 2p valence state. Additionally, the two lowest-energy peaks, at 2.3 and 4.8 eV, correspond to excitations of the 3e<sub>g</sub> and 2t<sub>2g</sub> orbitals, respectively. A third peak, located around 7.5 eV, is associated

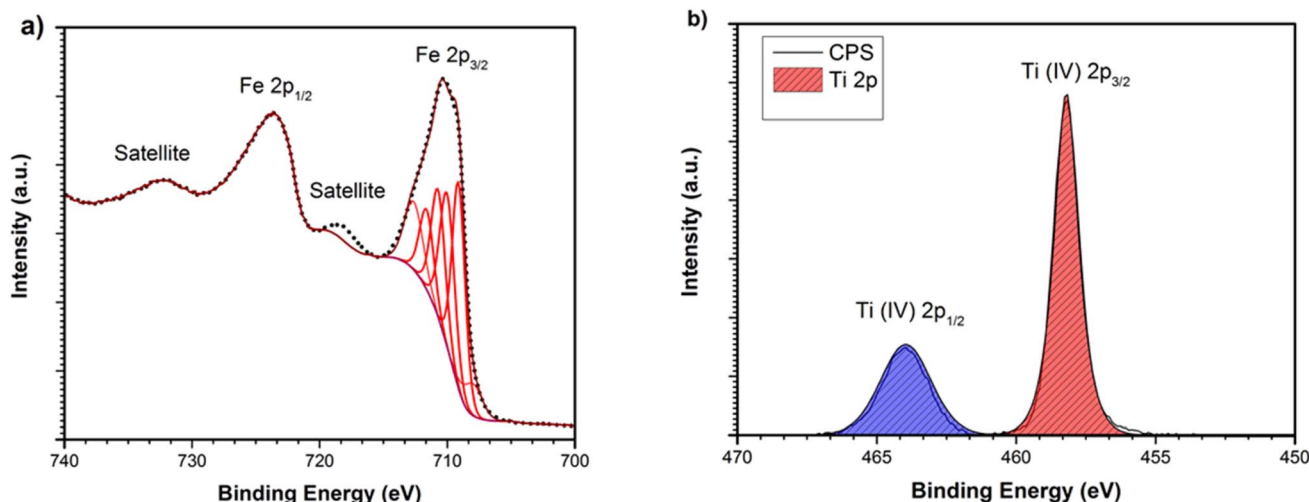


Fig. 4 Surface X-ray photoelectron spectra (XPS) of the Fe 2p region for: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and (b) Ti, which remained in the +4 oxidation state across all films, with 2p<sub>3/2</sub> peaks centered around 458.3 eV.



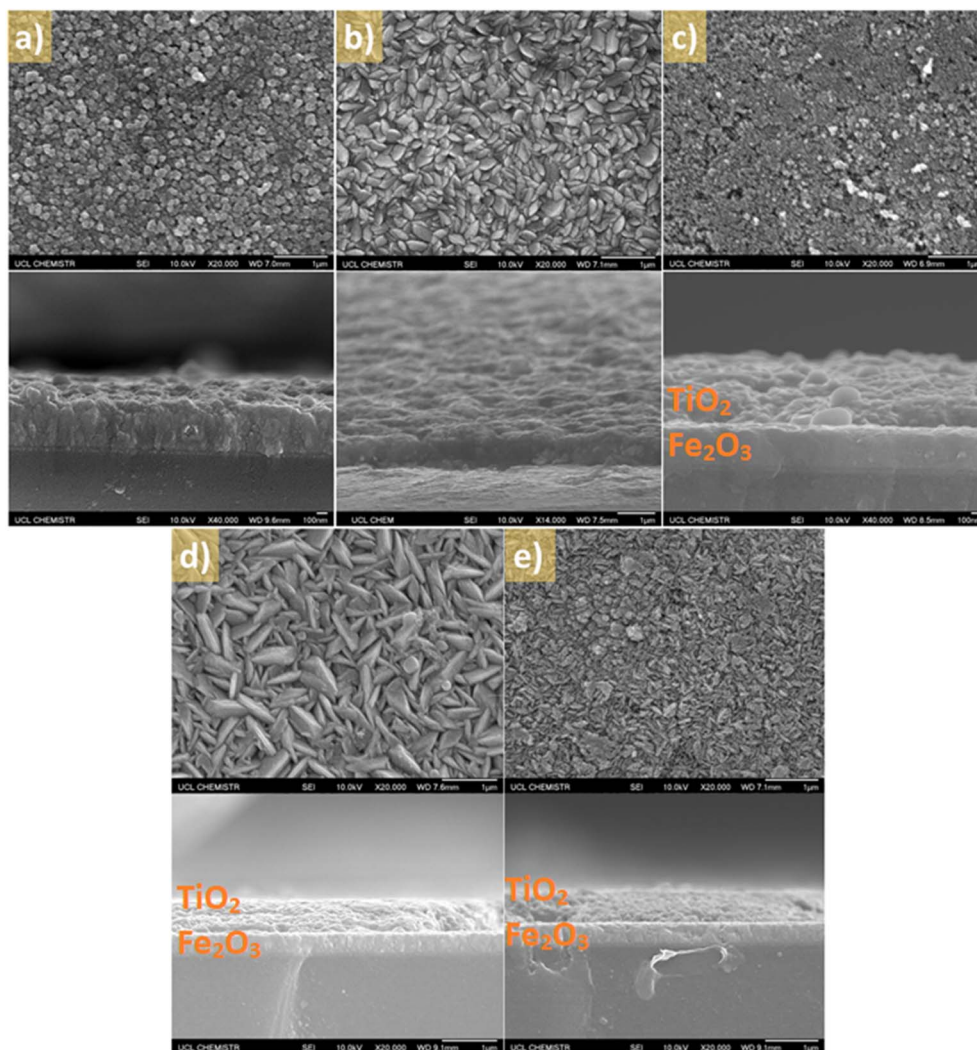


Fig. 6 SEM images of: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) pure TiO<sub>2</sub>, (c) TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (4 min), (d) TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (8 min), and (e) TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (12 min) films grown by AACVD and APCVD on FTO at 450 °C and then annealed at 500 °C. The thicknesses are shown in side-view SEM images.

with the 2e<sub>g</sub> orbital.<sup>46</sup> Additionally, the O 2p peaks overlap with the 4d orbitals, with the O 2p state appearing around 7.0 eV. Furthermore, the O 2p  $\sigma$  states overlap with the e<sub>g</sub> peaks.<sup>47</sup>

Conversely, the valence band (VB) spectra of TiO<sub>2</sub> films feature e<sub>g</sub> and t<sub>2g</sub> states at approximately 7.5 eV and 4.2 eV, respectively, arising from O 2p orbitals.<sup>48</sup>

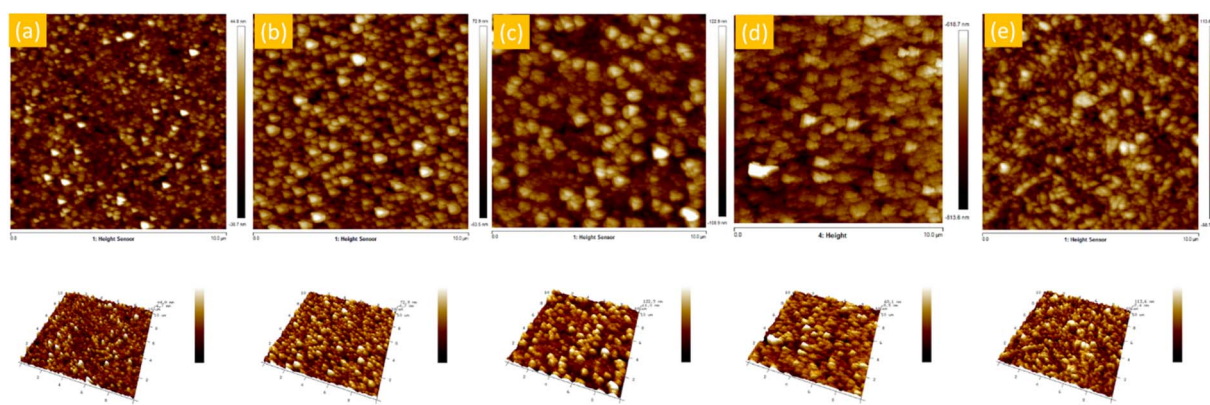


Fig. 7 2D (top) and 3D (bottom) surface images of: (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) TiO<sub>2</sub>, and (c, d, and e) TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films with deposition times of 4, 8, and 12 minutes, respectively, at a scale of 10 × 10  $\mu$ m.



#### 5.4. Scanning electron microscopy (SEM)

The morphology of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  films was analyzed using SEM (Fig. 6). The  $\alpha\text{-Fe}_2\text{O}_3$  films exhibited approximately spherical particles with an average diameter of 100–200 nm (Fig. 6a), while the pure  $\text{TiO}_2$  films featured densely packed particles ranging from 200 to 400 nm in diameter (Fig. 6b).

The morphology of the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  films differed from that of the pure  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{TiO}_2$  films. The  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  film with a deposition time of 4 minutes displayed particles with diameters ranging from 50 to 100 nm (Fig. 6c). The film deposited for 8 minutes had a similar morphology to pure  $\text{TiO}_2$ , consisting of densely packed particles approximately 500 nm wide (Fig. 6d). The  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  film with a deposition time of 12 minutes featured densely packed, needle-like particles, typically 200–400 nm in length (Fig. 6e).

Side-view micrographs revealed that the thickness of the pure  $\alpha\text{-Fe}_2\text{O}_3$  film on the substrate ranged from 368 to 422 nm (Fig. 6a), while the  $\text{TiO}_2$  film was approximately 470 nm thick (Fig. 6b). The thicknesses of the  $\text{TiO}_2$  layers in the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  films with deposition times of 4, 8, and 12 minutes were around 438, 500, and 633 nm, respectively (Fig. 6c, d, and e).

#### 5.5. Atomic force microscopy (AFM)

To further investigate the film morphology, AFM was employed to analyze the surface topography of all samples in this study (Fig. 7). AFM measurements were performed at a  $10 \times 10 \mu\text{m}$  scale. The resulting images reveal that the particles are similar, closely packed, pseudo-spherical grains. However, as shown in Fig. 6a,  $\text{Fe}_2\text{O}_3$  appears to consist of smaller grains and has a flatter surface compared to the other samples. AFM images of  $\text{TiO}_2$  and the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  series showed particle aggregates, with varying surface roughness. This variation was quantified by measuring the RMS (root mean square) roughness of all samples at the  $10 \times 10 \mu\text{m}$  scale. The roughness of  $\text{TiO}_2$  was 20.3 nm, nearly twice that of  $\alpha\text{-Fe}_2\text{O}_3$  (10.2 nm). The roughness values for the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (4 min) and  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (12 min) samples were relatively similar, at 36.7 nm and 31.7 nm, respectively. In contrast, the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (8 min) sample exhibited a significantly lower surface roughness of about 19.8 nm. Additionally, the surface area of all samples was similar, with  $\alpha\text{-Fe}_2\text{O}_3$  having an area of  $101 \mu\text{m}^2$ , and  $\text{TiO}_2$ ,  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (4 min, 8 min, and 12 min) having areas of 103, 104, 102, and  $105 \mu\text{m}^2$ , respectively.

## 6. Photoelectrochemical (PEC) performances

Fig. 8 displays the current–voltage ( $I$ – $V$ ) curves for (a)  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  layers and pure  $\alpha\text{-Fe}_2\text{O}_3$ , and (b)  $\text{TiO}_2$  films, under both dark and simulated sunlight conditions (AM 1.5G,  $100 \text{ mW cm}^{-2}$ ). As seen in Fig. 8a, the photocurrent of hematite in the dark increases sharply at a voltage of approximately  $1.70 V_{\text{RHE}}$ . Under simulated sunlight, the onset potential shifts to around  $0.4 V_{\text{RHE}}$ , with the photocurrent rising until about  $1.4 V_{\text{RHE}}$ . The  $\text{Fe}_2\text{O}_3$  photocurrent peaks at approximately  $0.7 \text{ mA cm}^{-2}$  at  $1.23 V_{\text{RHE}}$ ,

where the RHE corresponds to the potential of the reversible oxygen electrode.

Fig. 8a also presents the photocurrent graphs for  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  films with varying  $\text{TiO}_2$  thicknesses under sunlight conditions. It is evident that the  $\text{TiO}_2$  layer, deposited by APCVD, not only enhances the photocurrent of  $\alpha\text{-Fe}_2\text{O}_3$  but also improves the onset potential. Specifically, the photocurrents of  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (4 and 8 min) show onset potentials at 0.1 and  $0.5 V_{\text{RHE}}$ , respectively, with currents increasing to approximately  $1.2$  and  $1.75 \text{ mA cm}^{-2}$  at  $1.23 V_{\text{RHE}}$ . The sample with an 8-minute deposition time achieves a photocurrent of around  $2.3 \text{ mA cm}^{-2}$  at  $1.45 V_{\text{RHE}}$ . However, for the thicker  $\text{TiO}_2$  layer (12 min deposition time), the photocurrent decreased compared to pure

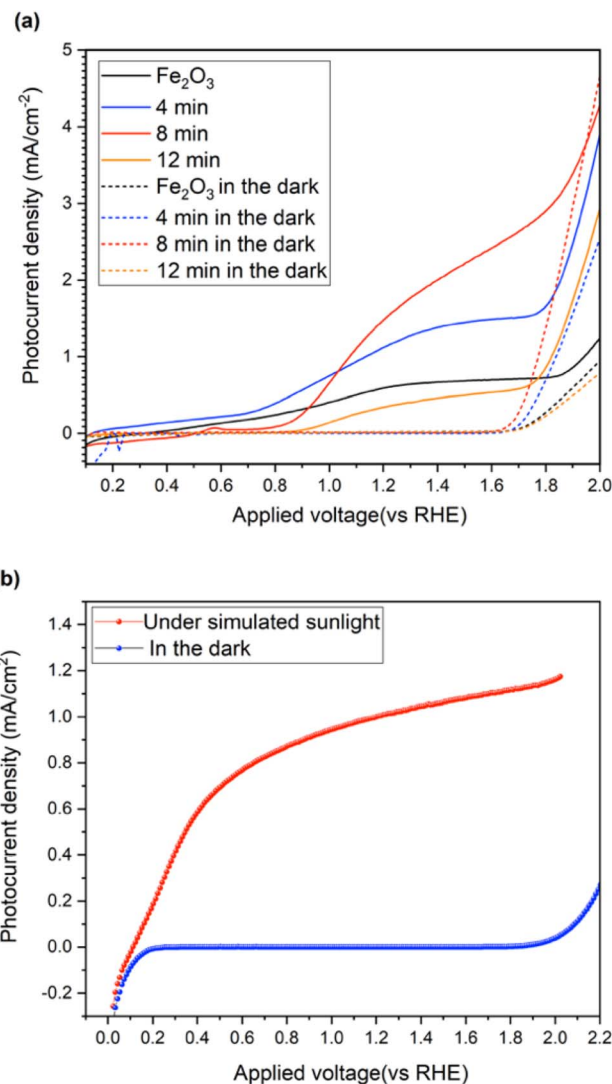


Fig. 8 PEC performance of (a) hematite and  $\text{TiO}_2/\text{hematite}$  films with varying deposition times (4, 8, and 12 minutes); (b)  $\text{TiO}_2$  films. All films were deposited on FTO glass. Hematite was deposited using AACVD at  $450^\circ\text{C}$  with  $\text{Fe}(\text{II})$  acetylacetonate dissolved in ethyl acetate.  $\text{TiO}_2$  films were prepared via APCVD using titanium isopropoxide at  $450^\circ\text{C}$ , followed by a 1-hour annealing under nitrogen to eliminate carbon contamination. Water oxidation was tested in 1.0 M NaOH (pH 13.7) under both dark and AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ).



Table 1 Comparing the photocurrents of some  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> heterojunction photoanodes obtained from the literature with our work

Photocathode	Electrolyte	Photocurrent density (mA cm <sup>-2</sup> )	References
TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub> core/shell nanostructure	1 M KOH	0.91 mA cm <sup>-2</sup> at 1.23 V vs. RHE	50
Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> heterojunction	1 M KOH	1.02 mA cm <sup>-2</sup> at 1.23 V vs. RHE	51
CQDs modified TiO <sub>2</sub> /Sn-Fe <sub>2</sub> O <sub>3-x</sub> heterojunction	1 M KOH	1.47 mA cm <sup>-2</sup> at 1.23 V vs. RHE	52
WO <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub> nanocomposite	0.5 M Na <sub>2</sub> SO <sub>4</sub>	2.34 mA cm <sup>-2</sup> at 1.4 V vs. RHE	53
BiVO <sub>4</sub> /WO <sub>3</sub> /W heterojunction	0.1 M KH <sub>2</sub> PO <sub>4</sub>	2.01 mA cm <sup>-1-2</sup> at 0.6 V (vs. Ag/AgCl)	54
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /CuO	0.05 M Na <sub>2</sub> SO <sub>4</sub>	0.53 mA cm <sup>-2</sup> at 1.0 V vs. RHE	55
ZnO/Fe <sub>2</sub> O <sub>3</sub> core-shell nanowires	1 M NaOH	1.5 mA cm <sup>-2</sup> at 0.6 V vs. Ag/AgCl	56
TiO <sub>2</sub> / $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	1 M NaOH	1.7 mA cm <sup>-2</sup> at 1.23 V vs. RHE	This work

hematite, reaching approximately 0.3 mA cm<sup>-2</sup> at 1.2 V<sub>RHE</sub>. For all samples, the  $J$ - $V$  curves in the dark conditions increased up to 1.67 V<sub>RHE</sub>.

The highest photocurrent recorded for Fe<sub>2</sub>O<sub>3</sub> to date was reported by Michael Grätzel *et al.* in 2011, reaching approximately 2.3 mA cm<sup>-2</sup> at 1.23 RHE.<sup>15</sup> Guo *et al.*<sup>49</sup> enhanced the performance of the hematite photoanode by doping hematite nanorod films with Ru, resulting in the best performance to date, achieving approximately 5.7 mA cm<sup>-2</sup> at 1.23 RHE. The pure TiO<sub>2</sub> (with an 8-minute deposition time) was fabricated onto PEC photoanodes, and its performance was evaluated in 1.0 M NaOH under both dark and simulated sunlight (AM 1.5G, 100 mW cm<sup>-2</sup>) conditions. As shown in Fig. 8b, the photocurrent density of this TiO<sub>2</sub> sample under sunlight conditions was approximately 1.0 mA cm<sup>-2</sup> at 1.23 V<sub>RHE</sub>, which is higher than previously reported for undoped TiO<sub>2</sub>. Under dark conditions, the photocurrent of the same sample increased rapidly at around 1.9 V<sub>RHE</sub>. However, an optimal TiO<sub>2</sub> thickness on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can enhance hole injection through surface contact with the solution, thereby reducing electron-hole recombination – a phenomenon confirmed by transient absorption spectroscopy (TAS) (see the TAS section). Although the optimized TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> heterojunction achieved a photocurrent density (1.75 mA cm<sup>-2</sup> at 1.23 V vs. RHE) slightly lower than the record value reported for hematite nanostructures, the present work demonstrates a scalable, low-temperature AACVD-APCVD fabrication route that delivers competitive efficiency,

significantly enhanced operational stability, and mechanistic insight *via* TAS into charge carrier dynamics. These combined advances highlight the practical potential of TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanodes for durable, large-area solar hydrogen generation. However, Table 1 provides a comparison of photocurrents reported for various Fe<sub>2</sub>O<sub>3</sub> photoanodes in previous studies with our TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photoanode.

The positions of the valence and conduction band edges of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> films in contact with an electrolyte at pH 13.7, relative to the reversible hydrogen electrode (RHE) potential, were determined from the flat band measurements (Fig. 9). The band gaps of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were found to be 3.2 eV and 1.95 eV, respectively. The conduction band of TiO<sub>2</sub> is positioned at 0.16 eV, while hematite shows a conduction band at 0.46 eV. Both of these conduction band edges are below the H<sub>2</sub>O/H<sub>2</sub> electrochemical level for water reduction, meaning they cannot reduce H<sub>2</sub>O without the application of an external bias (Fig. 9). Additionally, the conduction band of the Fe<sub>2</sub>O<sub>3</sub> film is more positive than that of anatase TiO<sub>2</sub>, which aligns with the photocurrent onset potential observed in Fig. 8. The valence band of the TiO<sub>2</sub> film lies significantly deeper than that of the Fe<sub>2</sub>O<sub>3</sub> film and even falls below the water oxidation potential of 1.23 V vs. NHE, making it capable of oxidizing H<sub>2</sub>O to O<sub>2</sub> (Fig. 9).

However, the heterogeneous system consisting of TiO<sub>2</sub> deposited on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film, which is itself on a FTO glass

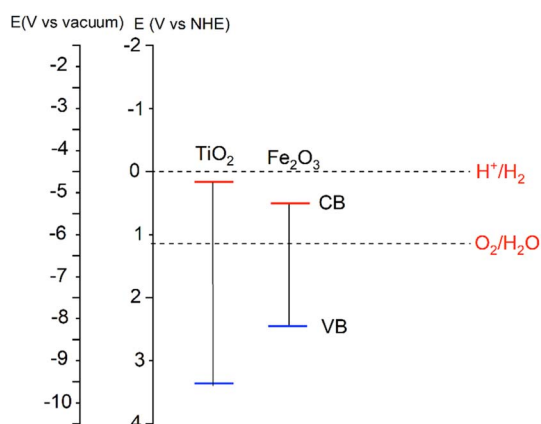


Fig. 9 Positions of the valence and conduction bands of TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> thin films at pH = 13.7.

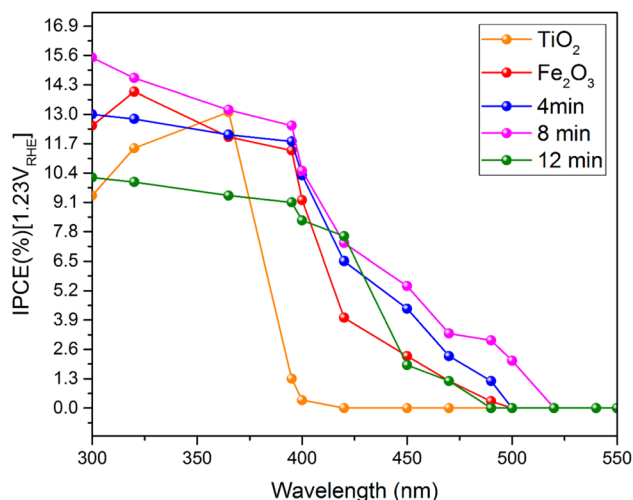


Fig. 10 Incident-photon-to-current efficiency (IPCE) of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films.



substrate, exhibits a type-II staggered band alignment in the 1.0 M NaOH electrolyte (pH 14). This specific alignment is critical for efficient charge separation and is depicted in the energy diagram. Upon illumination, both semiconductors absorb photons and generate electron-hole pairs. At the interface, the unique band alignment drives the photogenerated electrons from the higher-energy conduction band of  $\text{Fe}_2\text{O}_3$  into the lower-energy conduction band of  $\text{TiO}_2$ . Simultaneously, holes from the higher-energy valence band of  $\text{TiO}_2$  transfer to the lower-energy valence band of  $\text{Fe}_2\text{O}_3$ . This spatial separation prevents the recombination of electrons and holes. The electrons that accumulate in the  $\text{TiO}_2$  conduction band travel through the external circuit to the Pt counter electrode to facilitate the hydrogen evolution reaction (HER). Meanwhile, the holes accumulated in the  $\text{Fe}_2\text{O}_3$  valence band migrate to the semiconductor-electrolyte interface to participate in the oxygen evolution reaction (OER), completing the water-splitting process.<sup>57,58</sup>

For all samples, the incident-photon-to-current efficiency (IPCE) at 1.23 V vs. RHE was measured as a function of various incident light wavelengths to compare the behavior of  $\text{TiO}_2$  films with  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  films. The results are presented in Fig. 10. The  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  samples showed enhanced IPCE values compared to pure  $\text{Fe}_2\text{O}_3$  across the wavelength range of 300–550 nm, especially in the visible region. For instance, the IPCE of  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  (8 min) at 420 nm increased to 7.47%, up from 3.9% for  $\text{Fe}_2\text{O}_3$  alone. A similar improvement was observed for  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  (4 min), which reached 6.5%. In the UV region, IPCE values for  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  (4 min) were comparable to pure  $\text{Fe}_2\text{O}_3$ , while the values for  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  (12 min) decreased. Notably, at 500 nm, the IPCE of  $\text{Fe}_2\text{O}_3$  dropped to zero, whereas  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  (8 min) maintained an IPCE value of 1.95% at this wavelength.

These results align with previous studies, which have reported a greater increase in IPCE values in the visible region compared to the UV region.<sup>59</sup> In contrast, studies on Zr, Sn, and

Ti doping show that these elements have a minimal impact on the IPCE values of hematite in the visible region but a significant effect in the UV region.<sup>25,30,60</sup>

Mott-Schottky (M-S) calculations were employed to determine the flat band potential ( $V_{\text{fb}}$ ) and donor density ( $N_{\text{d}}$ ) of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  samples. Measurements were taken in the dark at a frequency of 1 kHz, using the equation:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_{\text{d}} A^2} \left( E - V_{\text{fb}} - \frac{k_{\text{B}} T}{e} \right) \quad (1)$$

where  $A$  is the active area,  $e$  is electron charge,  $\epsilon_0$  is the permittivity of a vacuum,  $\epsilon$  is the dielectric constant,  $T$  is the absolute temperature,  $k$  is the Boltzmann constant and  $E$  is the applied potential.<sup>61,62</sup> The results are shown in Fig. 11.

All films exhibited a positive gradient, confirming that  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  are n-type semiconductors. As shown in Fig. 11a, the  $\text{Fe}_2\text{O}_3$  films have a flat band potential around 0.48 V<sub>RHE</sub> and a donor density of approximately  $3.27 \times 10^{19} \text{ cm}^{-3}$ . The  $\text{TiO}_2$  thin films display a  $V_{\text{fb}}$  of about 0.16 V vs. RHE and a donor density of  $1.68 \times 10^{18} \text{ cm}^{-3}$ , as seen in Fig. 11b. Fig. 11a also shows that  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  films (4, 8, and 12 min) exhibit  $V_{\text{fb}}$  values of approximately 0.06, 0.52, and 0.74 V<sub>RHE</sub>, with corresponding donor densities of  $2.24 \times 10^{19}$ ,  $4.66 \times 10^{19}$ , and  $1.75 \times 10^{19} \text{ cm}^{-3}$ , respectively. The shift in the  $V_{\text{fb}}$  values for  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  films could be attributed to efficient hole transport from hematite to  $\text{TiO}_2$ , leading to enhanced water oxidation reactions at the surface.<sup>59</sup> However, since the  $V_{\text{fb}}$  of  $\text{Fe}_2\text{O}_3$  typically ranges between 0.4 and 0.8 V<sub>RHE</sub>, our results for  $\text{Fe}_2\text{O}_3$  are generally consistent with those reported by Dotan *et al.*<sup>63</sup>

The photoconversion efficiencies of the various photoanodes were assessed using the applied bias photon-to-current conversion efficiency (ABPE), derived from the LSV curves. As illustrated in Fig. 12a, the  $\alpha\text{-Fe}_2\text{O}_3$  photoanode exhibits a maximum ABPE of only 0.1% at 0.86 V *versus* RHE. The photoanodes prepared for 4 and 12 minutes show ABPE peaks of 0.19% (at 0.9 V vs. RHE) and 0.04% (at 1.0 V vs. RHE),

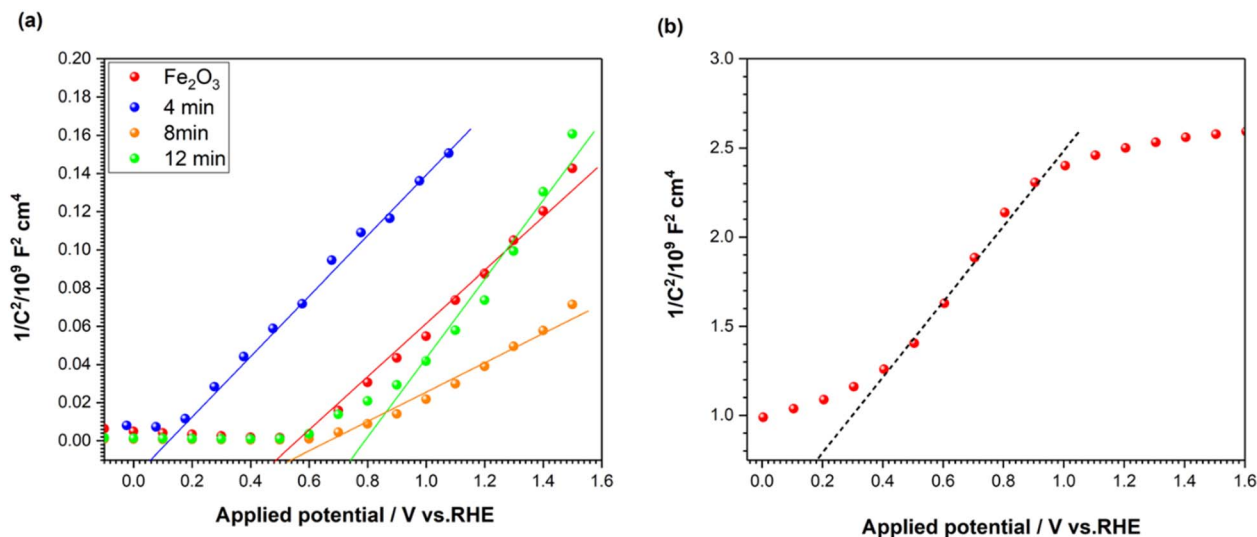


Fig. 11 Mott-Schottky plots for three electrodes: (a)  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  films, and (b) anatase  $\text{TiO}_2$  as the photoanode. The flat band potential and donor density of the samples were determined from this analysis.



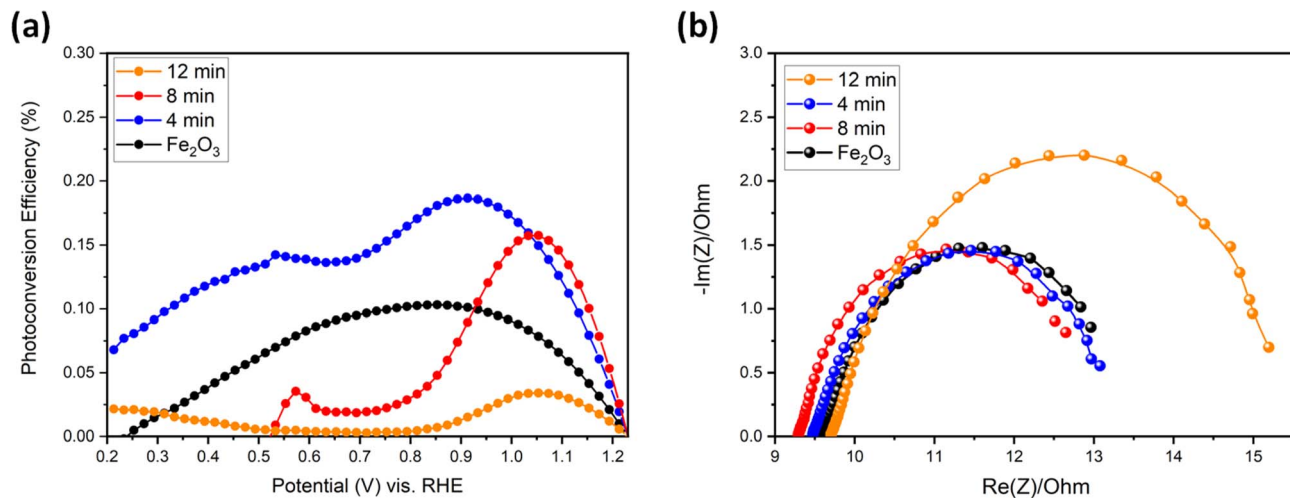


Fig. 12 (a) Applied bias photon-to-current efficiency (ABPE) curves for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with varying deposition times (4, 8, and 12 minutes). (b) Electrochemical impedance spectroscopy (EIS) for all samples in 1.0 M NaOH electrolyte.

respectively. Notably, the 8-minute photoanode displays a ABPE peak of 0.16% near 1.1 V vs. RHE, surpassing that of the bare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and occurring at a more practically relevant bias for PEC applications.

However, the electrochemical impedance spectroscopy (EIS) measurements provide clear insight into the influence of coating duration on the interfacial charge transfer properties of the photoanodes. The Nyquist plots, which represent the imaginary and real components of the EIS plots ( $Z'$  versus  $-Z''$ ), were measured at 1.23 V<sub>RHE</sub> under simulated sunlight conditions (AM 1.5G, 100 mW cm<sup>-2</sup>) (Fig. 12b). The bare Fe<sub>2</sub>O<sub>3</sub> electrode exhibits a semicircle with moderate diameter, reflecting relatively high charge transfer resistance ( $R_{ct}$ ) due to its intrinsically poor conductivity and high recombination rates. Upon coating for 4 min, the semicircle diameter decreases slightly, suggesting reduced interfacial resistance and improved charge transfer kinetics, likely due to the formation of a thin layer that facilitates more efficient electron transport. The 8 min coated sample shows a comparable semicircle to Fe<sub>2</sub>O<sub>3</sub>, indicating only moderate improvement, as increased thickness can introduce additional scattering centers or recombination pathways. In contrast, the 12 min coated sample displays the largest semicircle, corresponding to the highest  $R_{ct}$ , which can be attributed to excessive coating thickness that hinders charge mobility, blocks active sites, and limits effective interaction with the electrolyte.

### 6.1. Long-term stability

The stability of photoelectrodes is crucial for the generation and commercial viability of PEC hydrogen production devices. As a result, enhancing the stability of semiconductors has been a focus of recent research. Fig. 13 illustrates the stability of hematite and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (8 min) films under simulated sunlight at an intensity of 100 mW cm<sup>-2</sup>. The Fe<sub>2</sub>O<sub>3</sub> film, deposited *via* AACVD, remained stable for over 6.5 hours, the photocurrent response measured at 1.0 V vs. RHE. Remarkably,

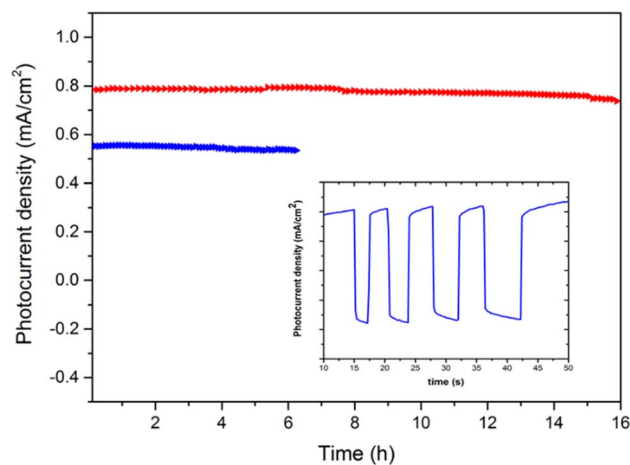


Fig. 13 Polarization curves of the Fe<sub>2</sub>O<sub>3</sub> films (blue) and TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films (red) recorded under simulated solar illumination (100 mW cm<sup>-2</sup>) with a fixed bias of 1 mA cm<sup>-2</sup>. The measurements were conducted in a 1.0 M NaOH electrolyte under sunlight.

the incorporation of a TiO<sub>2</sub> layer improved the stability of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film, extending its performance to over 16 hours.

The morphology of the TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (8 min) film was analyzed using SEM before and after PEC and stability tests. As shown in Fig. 14, the initial morphology featured densely packed particles approximately 500 nm in width (Fig. 14a). However, after undergoing prolonged testing (over 16 hours), the structure transformed into irregular shapes with visible pinholes, voids, and cracks (Fig. 14b). These morphological changes suggest that the sample's stability is influenced by the TiO<sub>2</sub> surface, as TiO<sub>2</sub> exhibits greater stability compared to Fe<sub>2</sub>O<sub>3</sub>.

Fig. 15 presents the XPS analysis of the TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (8 min) sample before and after stability tests. The results reveal a reduction in XPS intensity for Ti 2p and Fe 2p following the



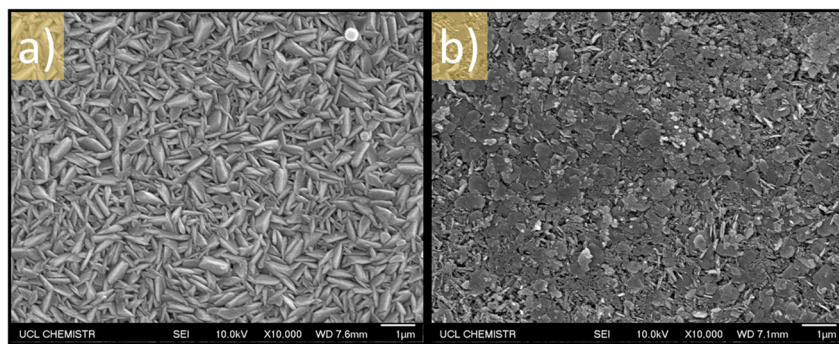


Fig. 14 SEM images of the  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  (8 min) anode captured (a) before and (b) after stability tests. The photocurrent stability test was conducted for over 16 hours under simulated solar illumination ( $100 \text{ mW cm}^{-2}$ ) with a constant bias of  $1.0 \text{ mA cm}^{-2}$ .

test, indicating that both  $\text{TiO}_2$  and  $\alpha\text{-Fe}_2\text{O}_3$  underwent decomposition.

## 7. Transient absorption spectroscopy (TAS)

Transient absorption spectroscopy (TAS) was employed to study the charge carrier dynamics in  $\text{TiO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  films over a nanosecond to microsecond timescale at room temperature ( $25^\circ\text{C}$ ). Previous studies have demonstrated that varying the thickness of  $\text{TiO}_2$  on  $\alpha\text{-Fe}_2\text{O}_3$  enhances photocurrent generation in water-splitting reactions. In this work, TAS was utilized to examine how coupling hematite with  $\text{TiO}_2$  influences the dynamics and lifetime of photo-generated charge carriers. Fig. 16 presents the transient absorption spectra of  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2/\alpha\text{-Fe}_2\text{O}_3$  samples. Pristine  $\text{TiO}_2$  films exhibit a broad and structured photo-induced absorption (PIA) band with peaks at 630 and 770 nm, aligning with previously reported findings.<sup>64</sup> As reported by Akihiro Furube *et al.*,<sup>64</sup> the broad PIA band comprises multiple components: the 630 nm PIA band is

primarily associated with trapped holes, while the 770 nm PIA band corresponds to trapped electrons. Our findings confirm that photogenerated hole absorption occurs around 630 nm, though other studies have suggested a spectral range of 450–570 nm with a lifetime spanning microseconds to milliseconds. However, this interpretation remains a topic of ongoing discussion.<sup>64</sup> The transient absorption data also reveal that the 770 nm PIA band disappears after 100 ns, whereas the 630 nm PIA band remains even beyond 1  $\mu\text{s}$ . This indicates that the electrons have a shorter lifespan than the holes. The TA spectra of  $\text{Fe}_2\text{O}_3$  sample exhibited an absorption peak at 560 nm, accompanied by a slight tail at 680 nm. This could be linked to trapped photo-generated holes and electrons, or potentially result from reactive oxygen species on the surface.<sup>65–67</sup> Moreover, the signal intensity of pure hematite is twice that of pure  $\text{TiO}_2$ , as shown in Fig. 16. The behavior of photo-generated holes in  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  has been studied before using different hole scavengers, such as methanol for  $\text{TiO}_2$ , and thiocyanate, isopropanol, and iodide for  $\text{Fe}_2\text{O}_3$ .<sup>67,68</sup> The decay dynamics of photo-generated holes in  $\text{Fe}_2\text{O}_3$  showed no dependence on the chemical environment when measured with

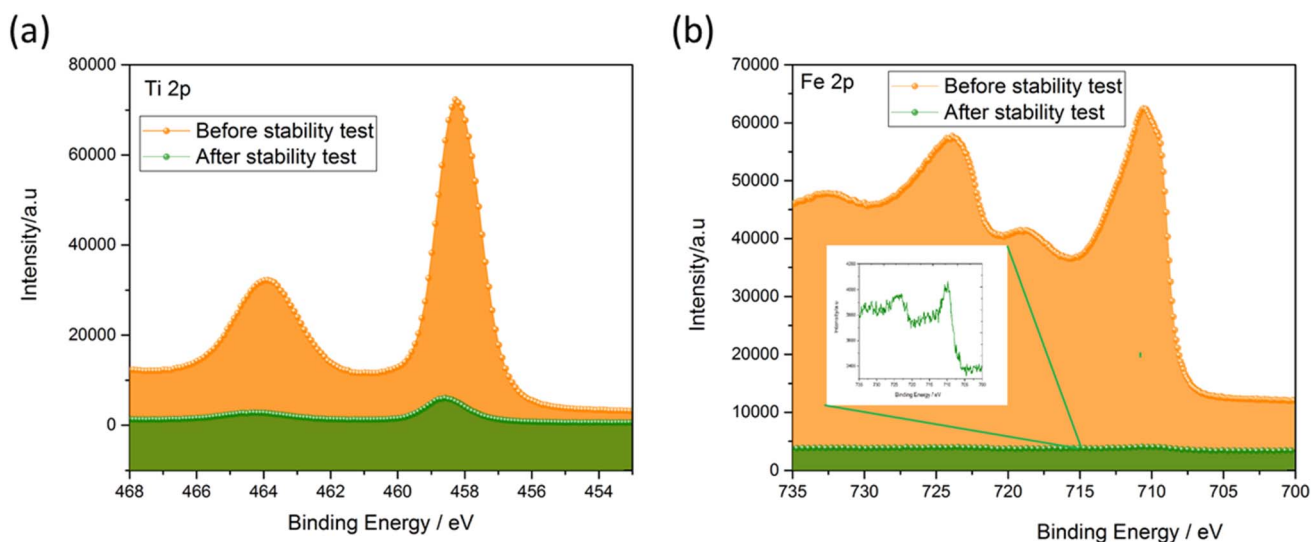


Fig. 15 X-ray photoelectron spectroscopy (XPS) analysis of the surface for (a) Ti 2p and (b) Fe 2p, conducted before and after the stability test.

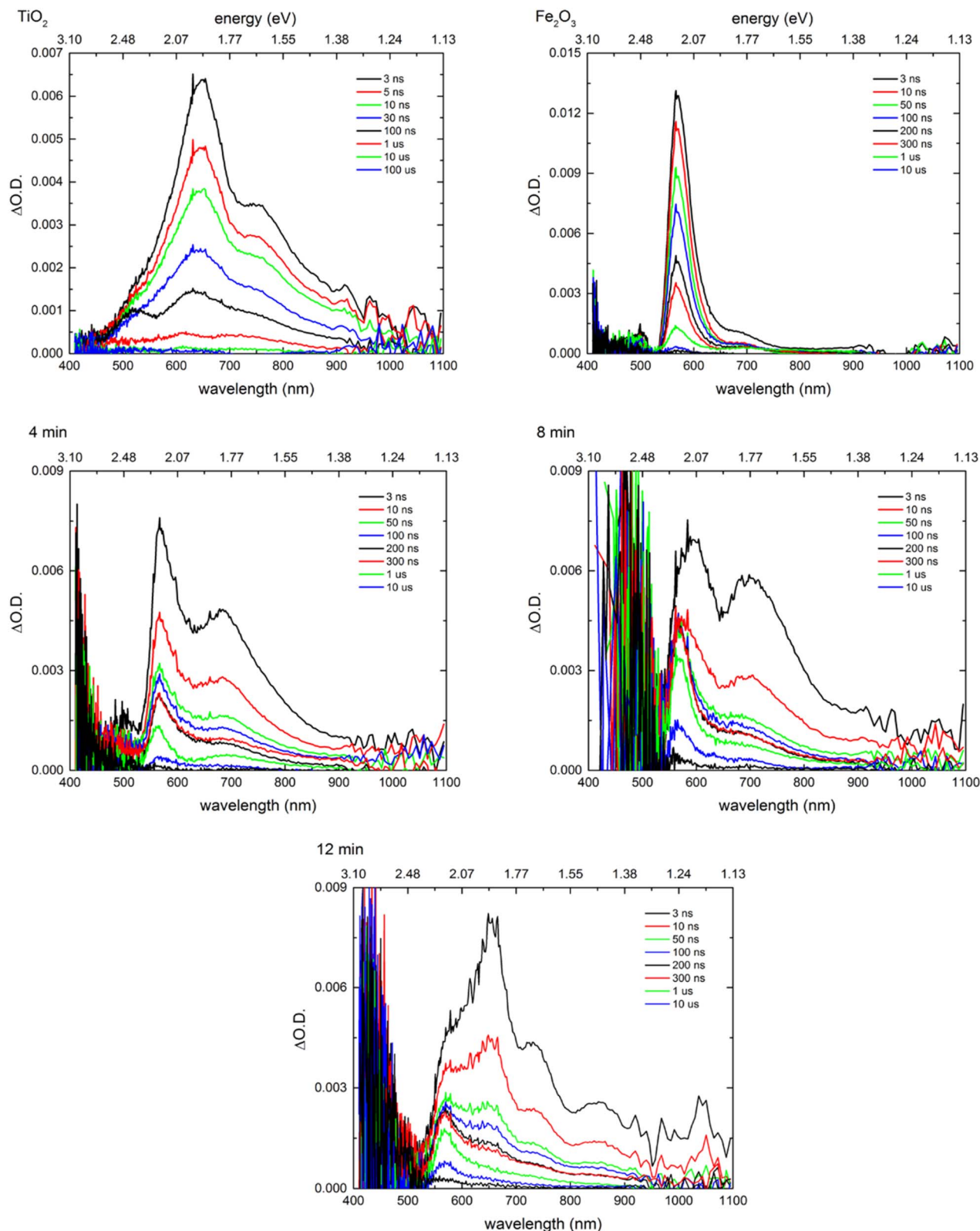


Fig. 16 Transient absorption spectra at various delay times for pure  $\text{TiO}_2$ , pure  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  thin films. The pump wavelength is 355 nm, with a fluence density of  $300 \mu\text{J cm}^{-2}$ .

TAS at 580 nm over a time scale of  $\mu\text{s}$ –ms. In contrast, the decay dynamics of photo-generated holes in  $\text{TiO}_2$  exhibited a significant sensitivity to methanol at 460 nm.<sup>68</sup>

In our experiments, the  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  samples exhibit absorption at 560 and 700 nm, which we attribute to trapped photogenerated holes in  $\text{Fe}_2\text{O}_3$ , as the holes in  $\text{Fe}_2\text{O}_3$  absorb



significantly more strongly than those in  $\text{TiO}_2$ . This may cause a spectral overlap of trapped holes in  $\text{Fe}_2\text{O}_3$  with those in  $\text{TiO}_2$ . However, when the  $\text{TiO}_2$  thickness is increased (as in the 12-minute sample), absorption bands at 560 and 650 nm are

observed for  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ , respectively, along with a band at 770 nm for electrons.

The TA spectra of the series of  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  films illustrate how the spectra change as the  $\text{TiO}_2$  layer thickness increases

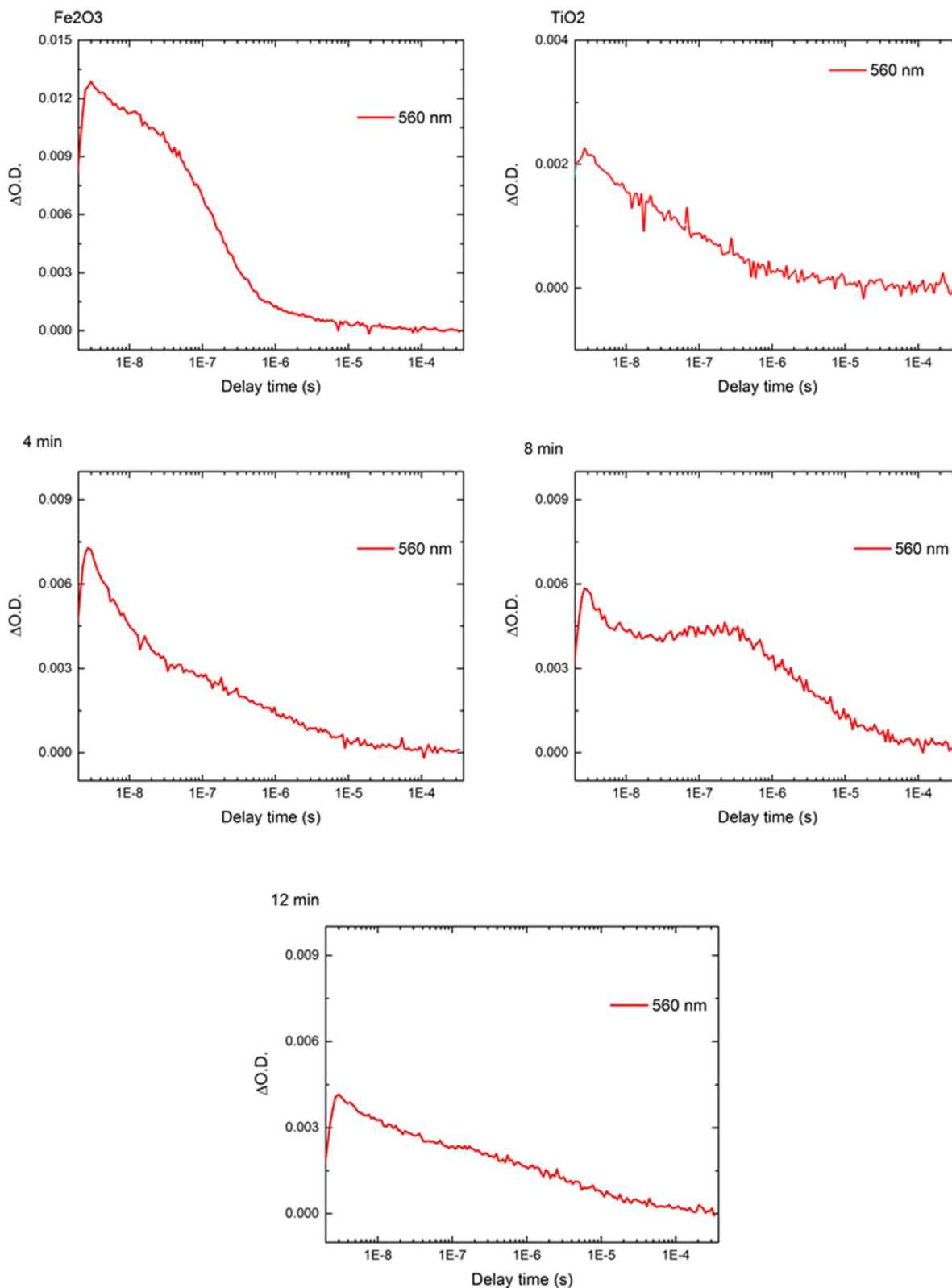


Fig. 17 Transient absorption decay profiles at 560 nm for pure  $\text{TiO}_2$ , pure  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2/\text{Fe}_2\text{O}_3$  thin films.



(i.e., with longer reaction times). For the thinnest TiO<sub>2</sub> layer, the TA spectra show a larger contribution from Fe<sub>2</sub>O<sub>3</sub>, with a prominent PIA band peaking around 560 nm. As the TiO<sub>2</sub> layer thickness grows, the contribution from TiO<sub>2</sub> gradually increases, and the 650 nm PIA band becomes more prominent than the 560 nm PIA band.

The temporal evolution of the transient absorption decay was measured at 560 nm for TiO<sub>2</sub> excited at 355 nm with pulse energy densities of 300 μJ cm<sup>-2</sup> in the sub-nanosecond range. For TiO<sub>2</sub>, the fastest TA decay occurred at 560 nm with a lifetime of  $t_{50\%} = 85$  ns, where  $t_{50\%}$  represents the time for the signal to decay to 50% of its initial amplitude. For hematite, the TA decay at 560 nm showed an initial signal intensity of about 0.013 ΔO.D. with a lifetime of  $t_{50\%} = 112$  ns. The TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> (4, 8, 12 min) samples exhibited initial signal intensities of 0.075, 0.006, and 0.0045 ΔO.D. at 560 nm, respectively, with lifetimes of  $t_{50\%} = 66$  ns, 1200 ns, and 880 ns. Notably, the TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> (8 min) sample showed slower decays and a significant increase in signal intensity at 560 nm compared to pure Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. These findings align with the photocurrent data obtained during water oxidation (Fig. 17), suggesting that the low efficiency of pure Fe<sub>2</sub>O<sub>3</sub> is due to rapid electron-hole recombination. However, at 560 nm, single-layer TiO<sub>2</sub> shows a lower signal intensity than Fe<sub>2</sub>O<sub>3</sub> because the valence band of Fe<sub>2</sub>O<sub>3</sub> is higher than that of TiO<sub>2</sub>. In contrast, TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films, particularly the TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> (8 min) sample, exhibit much slower recombination, which could be attributed to the transfer of photogenerated holes from Fe<sub>2</sub>O<sub>3</sub> to TiO<sub>2</sub>. Additionally, photogenerated electrons in TiO<sub>2</sub> may be transferred to Fe<sub>2</sub>O<sub>3</sub>, extending the photo hole lifetime in the TiO<sub>2</sub> films.

## 8. Conclusion

Fe<sub>2</sub>O<sub>3</sub> film was deposited on FTO glass using aerosol-assisted chemical vapor deposition (AACVD) at 450 °C, employing iron(II) acetylacetonate [Fe(CH<sub>3</sub>COCH=C(O)CH<sub>3</sub>)<sub>2</sub>] as the precursor. Subsequently, titanium isopropoxide [Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] was used in atmospheric pressure chemical vapor deposition (APCVD) to deposit TiO<sub>2</sub> on the Fe<sub>2</sub>O<sub>3</sub> films, with deposition times of 4, 8, and 12 minutes. XRD and Raman spectroscopy confirmed the phase formation of the resulting samples, with Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> present only in the hematite and anatase phases, respectively. XPS studies indicated that Fe and Ti were in the Fe<sup>3+</sup> and Ti<sup>4+</sup> oxidation states. The bandgap of TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films was found to be smaller than that of Fe<sub>2</sub>O<sub>3</sub> films, and a significant increase in photocurrent was observed in TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films compared to pure Fe<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> films. PEC measurements of TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films deposited on FTO showed a photocurrent of 1.7 mA cm<sup>-2</sup> at 1.23 V vs. NHE in 1.0 M NaOH, under AM 1.5 sunlight conditions. Transient absorption spectroscopy (TAS) revealed that TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> had a longer lifetime compared to pure hematite, which could be due to reduced electron-hole recombination, contributing to the improved photocurrent.

This study highlights the potential of TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> films as a promising material for water splitting with high stability.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Additional datasets available upon reasonable request.

The supporting data are available within the article and its SI. See DOI: <https://doi.org/10.1039/d5ra05064b>.

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