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Enhanced photocatalytic water splitting of a SILAR deposited α -Fe₂O₃ film on TiO₂ nanoparticles

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We have investigated the effect of deposition of a α -Fe₂O₃ thin layer on a substrate of TiO₂ nanoparticles for photoelectrochemical (PEC) water splitting. The TiO₂ layer was coated on an FTO substrate using the paste of TiO₂ nanoparticles. The α -Fe₂O₃ layer was deposited on the TiO₂ thin film, using the method of Successive Ionic Layer Adsorption and Reaction (SILAR) with different cycles. Various characterizations including XRD, EDX and FE-SEM confirm the formation of α -Fe₂O₃ and TiO₂ nanoparticles on the electrode. The UV-visible absorption spectrum confirms a remarkable enhancement of the absorption of the α -Fe₂O₃/TiO₂/FTO composite relative to the bare TiO₂/FTO. In addition, the photocurrents of the composite samples are remarkably higher than the bare TiO₂/FTO. This is mainly due to the low band gap of α -Fe₂O₃, which extends the absorption spectrum of the α -Fe₂O₃/TiO₂ composite toward the visible region. In addition, the impedance spectroscopy analysis shows that the recombination rate of the charge carriers in the α -Fe₂O₃/TiO₂ is lower than that for the bare TiO₂. The best PEC performance of the α -Fe₂O₃/TiO₂ sample was achieved by the sample of 70 cycles of α -Fe₂O₃ deposition with about 7.5 times higher photocurrent relative to the bare TiO₂.

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Introduction

Fossil fuels are currently the main non-renewable energy resource in the world, and have negative effects on the environment like greenhouse gas production and global temperature rise. These unclean fuels cannot meet the continuously increasing future demands for energy resources.^{1–4} Hydrogen as a non-polluting fuel can be considered as a good candidate of sustainable energy resources.⁵ Of various methods to produce hydrogen, efficient photoelectrochemical (PEC) water splitting provides a promising pathway for solar-to-hydrogen conversion using cost-effective semiconductor materials.^{6–9}

In PEC water splitting, hydrogen is generated by the absorption of light in a semiconductor, which must have a suitable bandgap and suitable energies of conduction and valence bands relative to the oxidation and reduction potentials of water. Also, it should be chemically stable in the electrolyte of the PEC process.^{10–12}

In recent years, TiO₂ nanoparticles have been extensively studied for PEC water splitting due to their low cost, simple preparation, non-toxicity and chemical stability. However, the high bandgap of TiO₂ (3.2 eV for the anatase and 3.0 eV for the rutile phase) only allows absorption of the ultraviolet region of

sun light, which covers only 5% of the solar spectrum. This significantly decreases the efficiency of PEC using the TiO₂ nanostructures. To improve the PEC properties of TiO₂, many methods such as sensitization to the sunlight with doping of nitrogen or heavy metals^{13–17} and incorporating plasmonic nanoparticles such as Ag, Au, Pt^{18–20} have been investigated in the literatures. Most of these approaches have the drawback of increasing crystal deformations or introducing defects that act as additional electron–hole recombination centers.^{21–26} In addition, combining TiO₂ with another semiconductor with suitable band alignments has been reported to achieve larger electron/hole separation due to the movement of charge carriers between the different semiconductors. With this regard, Fe₂O₃ with a bandgap of about 1.9–2.2 eV, which can absorb photons of visible light spectrum,^{27,28} is a suitable semiconductor to be mixed with TiO₂ to extend the adsorption spectrum of the composite efficiency.²⁹ However, two main disadvantages of Fe₂O₃ are the low conductivity and a short diffusion length of excitons (2–20 nm), which significantly diminish its photocatalytic efficiency.^{30,31} However, these deficiencies of Fe₂O₃ can be resolved by combining TiO₂ with Fe₂O₃, due to a strong electric field at the interface of Fe₂O₃/TiO₂.^{30–32} Accordingly, the combination of these two semiconductors has attracted many attentions recently.^{33–43}

In this work, a composite electrode of α -Fe₂O₃/TiO₂ was introduced as a photoanode for PEC cells. The SILAR method was used for the deposition of α -Fe₂O₃ on the TiO₂ substrate. Fig. 1 shows a schematic of the composite electrode in the

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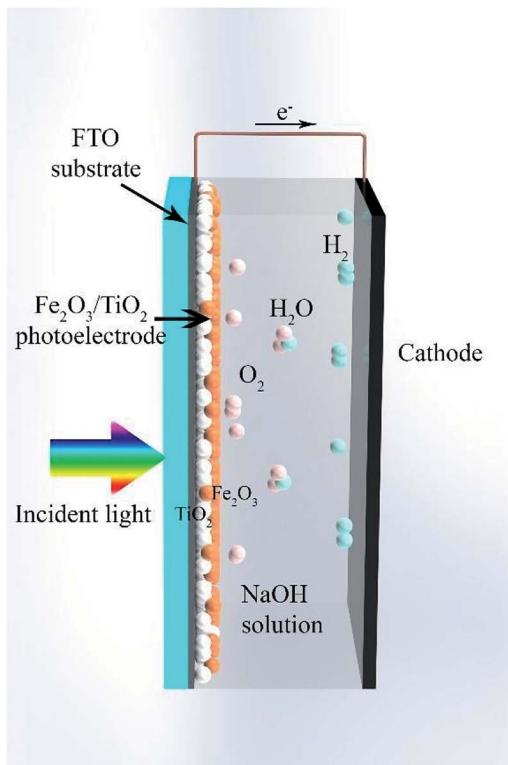


Fig. 1 Schematic of the composite electrode of α -Fe₂O₃/TiO₂ in the water splitting process.

water-splitting process. Under visible light irradiation, the composite electrode produces electron–hole pairs and the holes oxidize water at the electrode surface to generate oxygen. The produced electrons migrate to the counter electrode and take part in the reduction of water to produce hydrogen. We studied the optimum thickness of α -Fe₂O₃ on the TiO₂ substrate to obtain the best water-splitting activity. We found that under 70-cycle deposition of α -Fe₂O₃, the best PEC water-splitting activity occurs, which corresponds to about 7.5 times photocurrent improvement relative to the bare TiO₂ electrode. This result is mainly due to extension of the absorption spectrum of the sample into the visible light, due to incorporating α -Fe₂O₃. In addition, the recombination of charge carriers greatly decreases by using the α -Fe₂O₃/TiO₂ composite.

Experimental section

The TiO₂ layer was deposited on an area of 1 cm × 1 cm of the FTO substrate (with the sizes of 1 cm × 2 cm) by the doctor blade method,⁴⁴ using the paste of TiO₂ (Degussa, P-25) purchased from Sharif solar. Then, a thin film of α -Fe₂O₃ nanoparticles was deposited on the TiO₂ layer by the SILAR method, which provides a strong control over the film thickness. In this method, 0.05 M FeCl₃ and 0.1 M NaOH, were used as iron and hydroxide precursors.⁴² The synthesis process is shown in Fig. 2, in which each immersion stage lasted 10 seconds. After depositing 30 cycles, the solutions of FeCl₃ and NaOH were renewed by the fresh ones. The deposition of Fe₂O₃

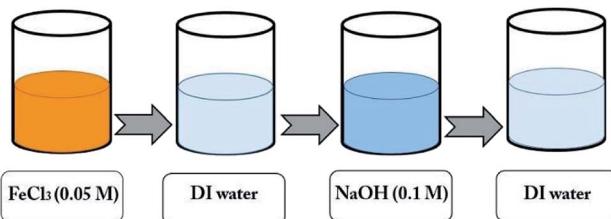


Fig. 2 A schematic of the SILAR process for deposition of α -Fe₂O₃ nanoparticles on a sample for one cycle.

on the samples by the SILAR method was done with various cycles of 50, 60, 70 and 80th. After finishing the SILAR deposition, we completely remove the tiny layer of α -Fe₂O₃ on the back of FTO by ethanol. Then the composite samples were placed inside a furnace for annealing at 550 °C for 4 hours. Fig. 3 shows a photo of the samples fabricated by the SILAR method with different cycles.

For the electrochemical measurements, the entire substrate was illuminated by a 100 W Xe lamp, so the illumination area of the α -Fe₂O₃/TiO₂ layer was 1 cm × 1 cm. In addition, the illumination was frontside.

Results and discussion

Characterization

The X-ray diffraction pattern of a sample of α -Fe₂O₃/TiO₂/FTO prepared with 70 SILAR cycles is shown in Fig. 4, using an X-ray diffractometer (Xpert, Philips) with Cu K α radiation ($\lambda = 1.54$ Å). According to the reference cards of (JCPD-01-083-2243) and (JCPD-01-073-2224), the peaks of the crystalline phases of anatase and rutile of TiO₂ are clearly seen at the 2 θ angles of 29.5°, 44.2°, 56.4°, 63.5°, 74.4°, 31.9°, 77.8° relating to the planes of (101), (004), (200), (105), (204), (110), and (221), respectively. The substrate peaks of SnO₂ are identified, in the pattern, according to the card of (JCPD-01-077-0450). On the other hand, the diffraction peaks of α -Fe₂O₃ nanoparticles are characterized at the angles of 38.8°, 41.7°, 47.9°, 58.2° and 74.1°, relating to the planes of (104), (110), (113), (024), (116) and (214), according to the card of (JCPD-01-086-0550).

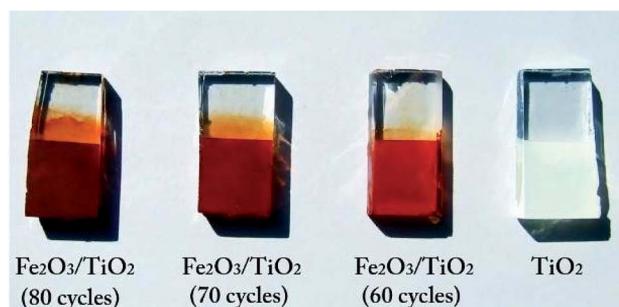


Fig. 3 A photograph of the samples of α -Fe₂O₃/TiO₂/FTO with different SILAR deposition cycles of α -Fe₂O₃.



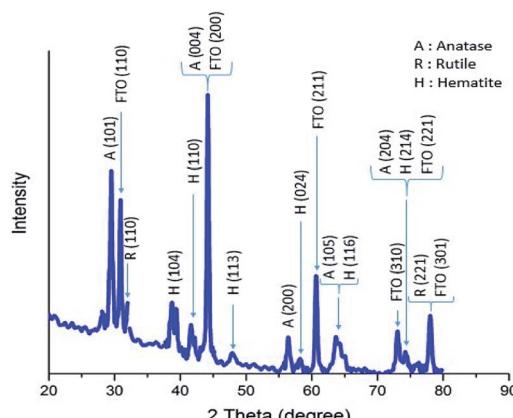


Fig. 4 XRD diffraction pattern of a sample of α -Fe₂O₃/TiO₂/FTO prepared with 70 SILAR cycles.

In order to investigate the morphology of the samples, the Field Emission Scanning Electron Microscopy (FESEM) of the samples was taken using the MIRA3 TESCAN microscope. The top and the cross-section images of the TiO₂ samples are shown in Fig. 5. We see that the thickness of the TiO₂ layer on the surface is around 400 nm. While a very thick layer of Fe₂O₃ (about 18 μ m) is produced on the sample by the 70-cycle SILAR deposition.

The EDX analysis was used for elemental determination of the samples. The weight percentages of the elements Ti, O, Fe and Au (which is used for preparation of the layers for EDX/

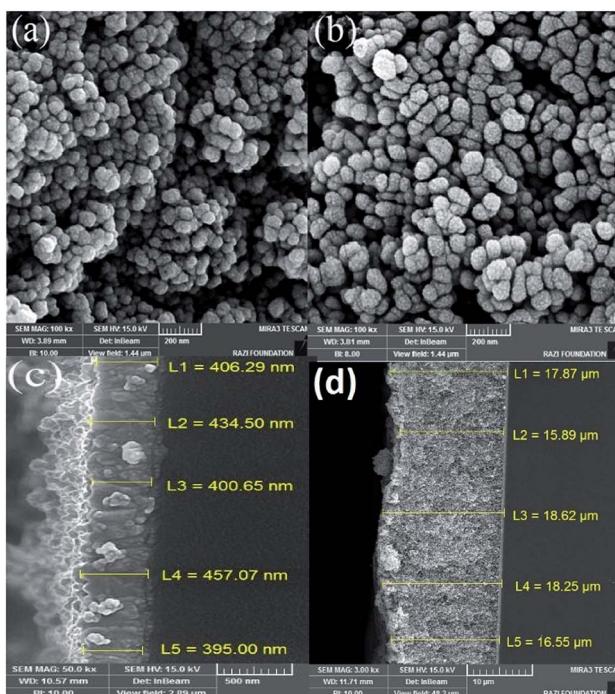


Fig. 5 FE-SEM images from various samples of (a) TiO₂/FTO, (b) α -Fe₂O₃/TiO₂/FTO with 70 SILAR cycles, (c) cross-sectional image of TiO₂/FTO, (d) cross-sectional image of α -Fe₂O₃/TiO₂/FTO with 70 SILAR cycles.

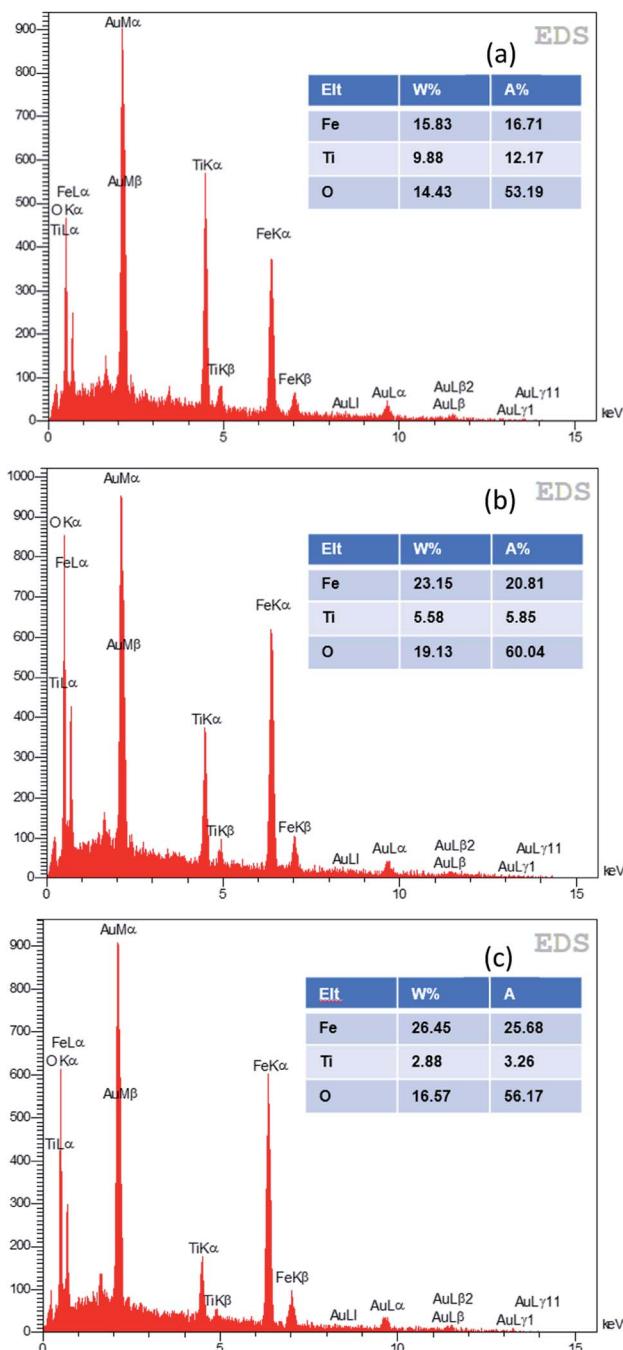


Fig. 6 EDX analysis of various samples of α -Fe₂O₃/TiO₂/FTO with (a) 60, (b) 70, (c) 80 SILAR cycles.

FESEM) for the samples with different SILAR cycles are shown in Fig. 6. It is seen that the iron percentage of the best α -Fe₂O₃/TiO₂ sample for the PEC application (which is the 70-cycle sample) was about 23.15% (wt).

Fig. 7 shows the UV-vis absorption spectrums of the bare TiO₂ and the α -Fe₂O₃/TiO₂ sample with the 70-cycle. The bare TiO₂ has an absorption edge around 390 nm (\sim 3.13 eV), which is related to its wide bandgap. The absorption edge of α -Fe₂O₃/TiO₂ has been transferred to the visible range with a much



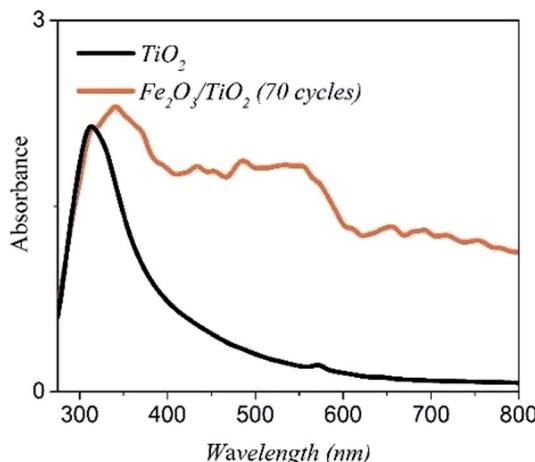


Fig. 7 The UV-vis spectra of the samples of TiO_2/FTO and $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2/\text{FTO}$ with 70-cycle.

higher absorption intensity than the bare TiO_2 in the range of 400–800 nm.

The bandgaps of the fabricate TiO_2 and $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ film are calculated using the Tauc plot. As it showed in Fig. 8, the tangent lines indicates that the $\alpha\text{-Fe}_2\text{O}_3$ has an indirect band gap of about 2.04 eV and direct band gap of TiO_2 is about 3.35 eV for our sample; which is agreed with other observations.^{42,45}

Photoelectrochemical characterization

Fig. 9 shows the results of PEC measurements for the $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ samples. The photoelectrochemical properties were

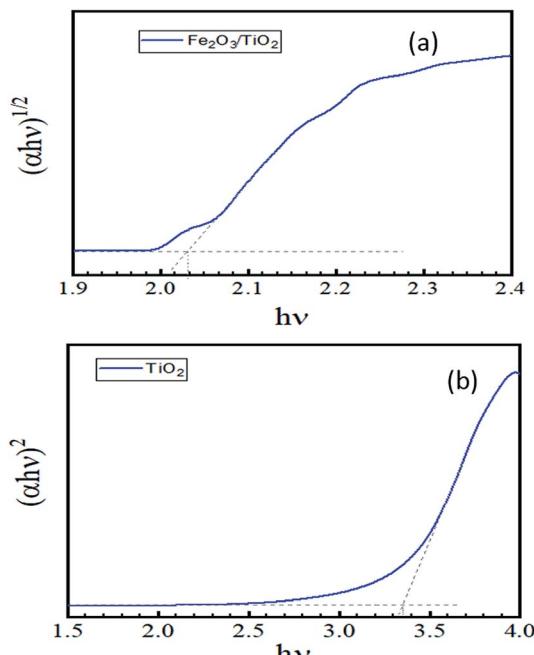


Fig. 8 Tauc plot calculated to find the band gap of the layer from the UV-vis spectrum (a) $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$ (b) pure TiO_2 .

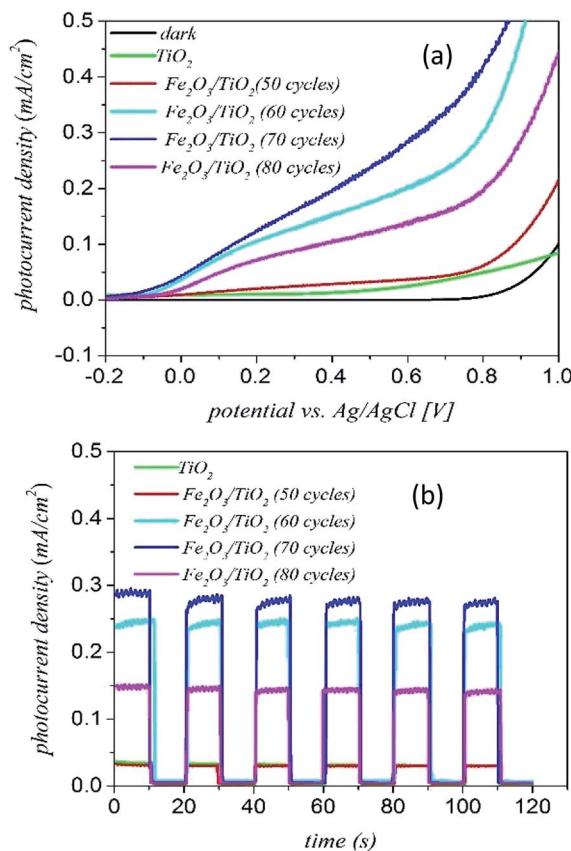


Fig. 9 (a) The J - V measurement curves and (b) chronoamperometry measurements of the $\alpha\text{-Fe}_2\text{O}_3$ loaded TiO_2/FTO samples with different deposition cycles.

carried out using a three-electrode cell with the sample as the working electrode, a Pt wire as the counter electrode and the Ag/AgCl electrode saturated with 3 M KCl as the reference electrode. The electrolyte was 1 M NaOH solution.

Fig. 9(a) shows the photocurrent–voltage (J - V) curves of various samples for both dark and light illuminations. The dark current curves of all samples are close to zero with no photoelectrochemical activity under the dark condition. The bare sample of TiO_2 has a small photocurrent density of around 0.04 mA cm⁻². The J - V curves of the samples confirm that the current density of the 70 cycles deposition of $\alpha\text{-Fe}_2\text{O}_3$ gives the highest photocurrent (around 0.3 mA cm⁻²). With increasing the number of deposition cycles to 80 cycles, the current density of the sample decreases. In fact, the 70-cycle deposition of $\alpha\text{-Fe}_2\text{O}_3$ is the optimum thickness for getting the best water-splitting properties from the composite sample.

Fig. 9(b) shows the transient photocurrent curves of various samples for the ON-OFF period of 20 s. We see that the photocurrent rapidly increases when the light is turned on and it immediately decreased to zero when the light is turned off. According to the results of Fig. 9(b), after about 80 seconds, the photocurrent becomes stable and repeatable. In addition, there is a small slope for the current curve under the light ON



condition indicating that the electron–hole recombination is small in the complex of α -Fe₂O₃/TiO₂/FTO.

The main reason for increment of the photocurrent density of the α -Fe₂O₃/TiO₂/FTO electrode relative to the bare TiO₂ goes back to the higher absorption of the composite material. As shown in Fig. 7, TiO₂ mainly absorb short wavelength photons below 400 nm. However, adding α -Fe₂O₃ to the electrode can extend the optical absorption to the visible spectrum.⁴⁶ As a result, the low energy photons can be absorbed by the α -Fe₂O₃ part of the photoelectrode and more photoelectrons can be produced by the composite electrode.⁴⁷

The next reason is the location of the α -Fe₂O₃ edge conduction band compare to TiO₂ (as shown in Fig. 10). Under UV-vis illumination, electrons can be excited from the valence band (VB) to the conduction band (CB) of the anatase, creating a charge vacancy in the VB. In the absence of the α -Fe₂O₃, most of electron–holes are combined quickly.^{39,47}

Increasing the coating cycles of hematite (from 50 to 70 cycles), had a significant improvement in current density. According to the results of Fig. 9, the sample of 70-cycle represents the best photocurrent. However, with increasing the number of cycles to 80 cycles, the photocurrent density decreases. Therefore, it is indicated that there was an optimal amount of deposition layer. By increasing the amount of α -Fe₂O₃ nanoparticles on the surface of the TiO₂ nanoparticles, the surface was blocked and light access was greatly reduced, and the production of the electron–hole decreased, so the photocurrent was reduced. So when the amount of α -Fe₂O₃ was increased from an optimal amount, because photoelectrons accumulated on α -Fe₂O₃, the recombination probability of the electron–holes increased.⁴⁸ So α -Fe₂O₃ being as an electron–hole recombination center, and resulted a reduction in optical activity.⁴⁹

In order to investigate the charge transport properties of the bare TiO₂ and α -Fe₂O₃/TiO₂ samples, the electrical impedance spectroscopy measurements (EIS) were performed for various samples. The applied frequency range was from 100 mHz to 100 kHz (in a 0.1 M Na₂SO₄ electrolyte at the potential of $V = 0.7$ V *versus* the Ag/AgCl reference). The Nyquist plots obtained by the EIS measurements in addition to the equivalent RC circuit for

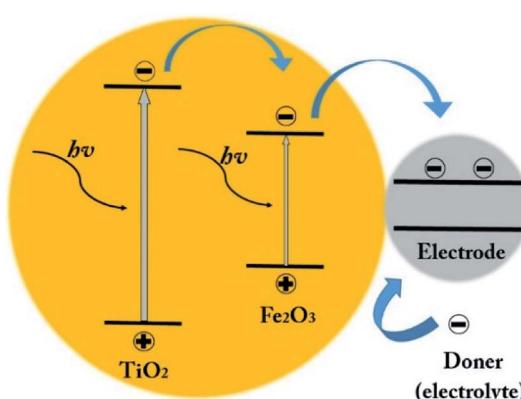


Fig. 10 Schematic of the electron–hole generation and the transferring of the photogenerated charges into the photoanode under the visible light illumination.

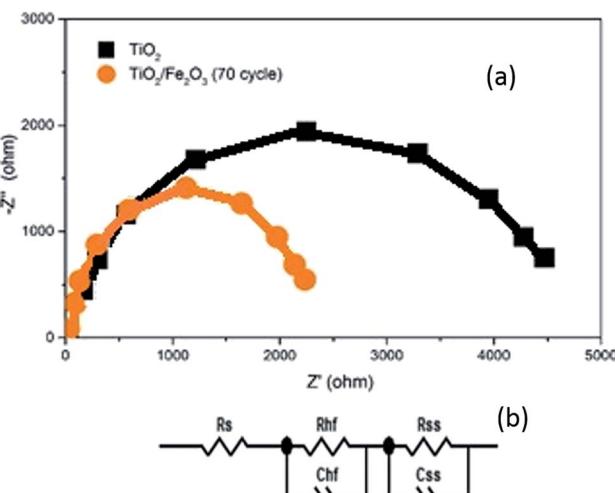


Fig. 11 (a) Nyquist plots of TiO₂/FTO and the sample of α -Fe₂O₃/TiO₂/FTO with 70 cycles. (b) The equivalent circuit used for the fitting of EIS results.

fitting the EIS data are shown in Fig. 11. In the equivalent circuit, R_s indicates a serial resistance between the FTO substrate and the TiO₂ layer. R_{hf} demonstrates the high frequency resistance due to accumulation and trapping of fast charges throughout the α -Fe₂O₃/TiO₂ composite. R_{ss} represents the resistance of charge transfer between the photoanode and the electrolyte. The capacitances C_{hf} and C_{ss} are relating to the space charge capacitance of the sample and the capacitance associated with the surface states of the photoanode, respectively.

As shown in Fig. 11, the curve of α -Fe₂O₃/TiO₂ photoanode has a smaller semicircle radius than the bare TiO₂, which indicates that both R_{hf} and R_{ss} are lower for the α -Fe₂O₃/TiO₂ relative to the bare TiO₂. This result completely confirms the improvement of charge transfer kinetics of the bare TiO₂ sample after the Fe₂O₃ modification. The faster charge transfer of the 70-cycle sample leads to less surface recombination and improving the photocatalytic activity of this sample relative to all other ones.

It should be mentioned that TiO₂ has better charge transport properties relative to Fe₂O₃, considering the mobility of electrons and the holes in both semiconductors. Therefore, deposition of a thin layer of TiO₂ under Fe₂O₃ in the samples causes that the electrons are better transmitted to the external circuit relative to the case of blank Fe₂O₃ on FTO. In fact, the recombination between electron and holes at the interface of TiO₂/FTO is less than that of Fe₂O₃/FTO. Consequently, a higher photocurrent is expected from the stack of Fe₂O₃/TiO₂/FTO relative to that of Fe₂O₃/FTO. This issue has clearly been confirmed by other researchers.⁴²

Conclusions

In this work, we reported on the effect of deposition of a thin layer of α -Fe₂O₃ on TiO₂ nanoparticles by the SILAR method for



photoelectrochemical water splitting. The formation of α -Fe₂O₃ was confirmed by various characterizations including XRD, EDX and FE-SEM spectroscopy. The UV-visible absorption spectrum showed a remarkable enhancement in the absorption of α -Fe₂O₃/TiO₂ relative to the bare TiO₂. The photoelectrochemical characterizations indicate that all samples of α -Fe₂O₃/TiO₂ have an improved photocurrent compared to the bare TiO₂. This result is mainly due to the proper bandgap of α -Fe₂O₃, which extended the absorption spectrum of the sample into the visible light. Also, the recombination of charge carriers greatly decreased by using α -Fe₂O₃ on TiO₂. We found that there is an optimum number of cycles for the SILAR deposition of α -Fe₂O₃, on TiO₂, which is the 70-cycle exhibiting much better photoelectrochemical activity from α -Fe₂O₃/TiO₂ relative to the bare TiO₂, with about 7.5 times photocurrent improvement.

Conflicts of interest

There are no conflicts to declare.

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