Fe₂TiO₅-Incorporated Hematite with Surface P-Modification for High-Efficiency Solar Water Splitting

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Abstract: Hematite is a promising photocatalyst for solar water splitting while its performance has been severely limited by various factors. Recently surface Fe_2TiO_5 layer was widely reported to enhance the performance of hematite with a favorable band position to facilitate hole transport. Here we further show that **the Fe_2TiO_5 -incorporation in bulk hematite** can also improve the performance with faster charge separation. Moreover, it can be well coupled with surface P-modification to simultaneously improve charge separation and hole transfer with a synergetic effect. The Ti and P co-modified hematite shows a significantly enhanced photocurrent of 2.37 mA/cm^2 at 1.23 V vs. RHE when compared to the pristine value of 0.85 mA/cm^2 . After coupling with Co-Pi catalysts, the hematite sample can even achieve a stable, high photocurrent of 2.90 mA/cm^2 at 1.23 V vs. RHE . The design of Ti and P co-modified hematite hollow nanostructures can be used as a promising candidate for solar water splitting applications. The **discrete Fe_2TiO_5 -incorporation** also provides a good insight on the mechanism to understand other Ti-based treatments of hematite.

KEYWORDS: Hematite, Fe_2TiO_5 -incorporation, hollow nanostructures, P-modification, solar water splitting

Introduction

Hematite has been attracting intense interest as a good photocatalyst for photoelectrochemical (PEC) water splitting due to its suitable band gap, good stability in solution, and earth abundance [1-6]. However, the practical performance of hematite is far below its theoretical limit due to various problems in the PEC process. For example, the photo-induced electron-hole pairs may quickly recombine because of short lifetime (10^{-12} s); the low conductivity of hematite severely limits the carrier transfer to the surface; and the photo-induced hole at the surface also suffers from poor oxygen evolution reaction (OER) kinetics and recombination [1-10]. To overcome these problems, various methods including morphology control, elemental doping, surface modification and surface co-catalysts, have been developed to improve the performance [1-10].

The exotic elemental modification has been considered to be an effective way to enhance the performance of hematite [11-18]. Especially, Ti-based treatments have been used with great success [19-23]. Ti-doping in hematite *via* various approaches has been widely reported [12,19-21]. Ti-based material coating on hematite was also shown to effectively enhance the performance [24]. Although numerous mechanisms have been proposed to understand the Ti-based treatments, by now the role of Ti in hematite is still an open question [12,19,22]. Recently, a Fe_2TiO_5 thin layer deposited on the surface of hematite by Ti-treatment was reported, which could form a heterojunction and offer a favorable valence band position to facilitate hole transport for enhanced performance [13]. The effect of Fe_2TiO_5 on hematite was then widely discussed in some recent literatures [22,23,25,26]. However, all the reports were limited to the surface coating of Fe_2TiO_5 on hematite, while the bulk effect of Fe_2TiO_5 in hematite has never been investigated [22,23,25,26]. The excellent property of Fe_2TiO_5 may also be expected useful in the bulk of hematite for fast hole transport to benefit charge separation. When the photo-induced hole is collected at the Fe_2TiO_5 site in hematite, quick transfer of the hole to the surface is also required for efficient water oxidation. According to the literatures, a surface P-treatment (as FePO_4) can form a gradient electric field and accelerate hole transfer from the bulk to the surface [9,17,18]. Thus the

coupling of discrete Fe_2TiO_5 and surface P (FePO_4) in hematite may simultaneously improve charge separation and hole transfer to improve the performance, as illustrated in Fig. 1a.

Here we prepared the Ti and P co-modified hematite nanostructures by a simple hydrothermal synthesis on the fluorine-doped SnO_2 (FTO) substrate pretreated simultaneously with Ti and P precursors. Transmission electron microscopy (TEM) and synchrotron-based X-ray absorption spectroscopy (XAS) results clearly reveal the discrete Fe_2TiO_5 -incorporation in bulk hematite and the surface P-modification (as FePO_4). The co-modification also leads to a hollow structure. The co-modified hematite shows a greatly enhanced photocurrent of 2.37 mA/cm^2 at 1.23 V vs. RHE which is more than 2.5 times higher than that of the pristine sample (0.85 mA) and also significantly higher than those of the hematite samples modified by Ti or P alone. The co-modified hematite can be further coupled with Co-Pi catalysts to achieve an even higher photocurrent of 2.90 mA/cm^2 at 1.23 V vs. RHE , which is comparable to the high photocurrent values reported for hematite [6,17,25]. To the best of our knowledge, it is the first time to report a discrete Fe_2TiO_5 -incorporation in bulk hematite to accelerate charge separation, which can be further coupled with surface P-modification to achieve higher performance with the faster hole transfer. It also provides a good insight on the mechanism to understand some Ti-based treatments of hematite in the literatures.

Experimental

Photoanodes preparation. A modified hydrothermal method was used to prepare the pristine hematite photoanodes grown on a fluorine-doped SnO_2 (FTO, Nippon Sheet Glass, Japan, 14 ohm/sq) glass substrate [11,13]. Briefly, A teflon-lined stainless steel autoclave was filled with 70 mL aqueous solution containing 75 mM ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd.) and 75 mM sodium nitrate (NaNO_3 , Sinopharm Chemical Reagent Co., Ltd). Then the autoclave with cleaned FTO glass slide ($50 \text{ mm} \times 30 \text{ mm} \times 2 \text{ mm}$) was heated at $95 \text{ }^\circ\text{C}$ for 4 h to produce FeOOH on FTO [11,13].

The FeOOH-coated substrate was washed with deionized water and subsequently sintered in air at 550 °C for 2 h and at 750 °C for additional 15 min. The product was labeled as the pristine hematite (Fe₂O₃).

To prepare Ti and P co-modified (TiP-treated) hematite, the FTO substrate was pre-treated by a hydrothermal method to decorate Ti and P based materials. Typically, 10 mg titanium oxysulfate-sulfuric acid hydrate (TiOSO₄ • xH₂SO₄ • xH₂O, Aladdin, synthesis grade) and 3.5 mL phosphoric acid (H₃PO₄, Sinopharm Chemical Reagent Co., Ltd) were dispersed in deionized water by ultrasonication. Then the 70 mL aqueous solution was filled in a teflon-lined stainless steel autoclave with cleaned FTO glass slide and heated at 100 °C for 4 h. The FTO thus prepared was washed and then used in the same process to produce hematite as described for the pristine hematite. The hematite thus prepared was labeled as Fe₂O₃-TiP. For Ti-treated hematite, HCl (100 µL) was also used to replace H₃PO₄ in the whole process and the final product was labeled as Fe₂O₃-Ti. For P-treated hematite, the FeOOH prepared by hydrothermal method was immersed in H₃PO₄ and then annealed by the same way [18]. For the combination of Ti and P treatments, the Ti-treated FeOOH (using Ti-treated FTO) was immersed in H₃PO₄ and then annealed by the same process. The FTO substrates treated by Ti and P or only Ti were also annealed for XAS experiments, which were labeled as FTO-TiP and FTO-Ti, respectively. The experimental process can be described in Fig. 1b. Cobalt phosphate (Co-Pi) catalyst was deposited on the Fe₂O₃-TiP sample by photo-assisted electrodeposition in a three-electrode system [4].

Structural characterization. Scanning Electron Microscope (SEM, Zeiss-supra 55), Transmission Electron Microscopy (TEM, FEI Tecnai G2 F20 S-TIWN), X-ray photoelectron Spectrometer (XPS, Kratos AXIS UltraDLD) and X-ray Diffraction (XRD, PANalytical, Zmpyrean) were used for the morphology and structural characterization. X-ray absorption spectra were collected at the XMCD endstation of the National Synchrotron Radiation Laboratory (NSRL) and the BL8.0.1 (wet-RIXS endstation) of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory.

Photoelectrochemical (PEC) experiments. The working area of hematite photoanodes was about 0.1 cm² with the left part covered by non-conductive hysol epoxy. An electrochemical workstation (CHI 660D) was used for the PEC and electrochemical impedance spectra (EIS) measurements. The pH value

of the electrolyte (1 M NaOH) was controlled at 13.6. The measured voltage was converted into the potential vs. reversible hydrogen electrode (RHE). The light source was a Xenon High Brightness Cold Light Sources (XD-300) equipped with AM 1.5 filter and the light power density was 100 mW/cm². A Xenon lamp (CEL-HXF300/CEL-HXBF300, 300W) coupled with a monochromator (Omni- λ 3005) was used to measure the IPCE data.

Results and discussion

The preparation of Ti and P co-modified hematite hollow nanostructures involved firstly pre-treating the FTO substrate in a hydrothermal process using TiOSO₄ and H₃PO₄ as the Ti and P precursors, respectively. Afterwards, the hematite nanostructures were grown on the modified FTO substrate (labeled as TiP-treatment) with Ti and P co-modification. The detailed experimental process can be found in the experimental section and is illustrated in Fig. 1b. The Ti and P elements were added in the initial growth process of FeOOH to allow homogeneous modification. The hematite nanostructures prepared by only TiOSO₄ were also prepared for comparison (labeled as Ti-treatment). The hematite prepared by only H₃PO₄ cannot obviously modify the FTO substrate, and it shows a performance similar to the pristine sample. We thus immersed the FeOOH in H₃PO₄ as the pure P-treated hematite for comparison [18]. The SEM images in the Supporting Information Fig. S1 show the FTO substrates after various treatments. Small nanoparticles (a few nm) can be observed on the pristine FTO substrate after Ti-treatment, while larger particles (about 1 μ m) can be found after TiP-treatment, revealing the different treating processes. Both SEM images show the successful modification of the FTO substrates by Ti and TiP pre-treatments.

Fig. 1 (a) Illustration of the Ti and P co-modified hematite nanostructure. The **discrete Fe_2TiO_5 in bulk hematite** facilitates the charge separation (step 1) while the surface FePO_4 accelerates the hole transfer (step 2). The Co-Pi catalysts improve the OER kinetics (step 3). (b) Experimental illustration of the Ti and P co-modified hematite. (c-e): SEM images of the pristine, Ti-treated, and TiP-treated hematite nanostructures, respectively.

The SEM images of the pristine, Ti-treated, and TiP-treated hematite samples are shown in Fig. 1c-e, respectively. Both the pristine hematite (Fig. 1c) and the Ti-treated hematite (Fig. 1d) show a nanorod-like morphology similar to the literature reports [11,13]. However, the TiP-treated hematite (Fig. 1e) shows a hollow-rod structure. The different hematite morphology can be attributed to the use of different modified FTO substrates which will lead to different nucleation and growth processes [27]. SEM cross section images for the vertical morphology are also shown in the Supporting Information Fig. S2. Both the pristine and Ti-treated hematite samples show a vertically aligned structure with a thickness around

250 nm. However, the TiP-treated sample (Fe_2O_3 -TiP75, with a FeCl_3 concentration of 75 mM) in Fig. S2c shows an obviously larger thickness (about 800 nm). The thickness effect has been carefully investigated while the results show that the increased thickness in Fe_2O_3 -TiP75 doesn't contribute to the enhanced performance. XRD data of the samples shown in the Supporting Information Fig. S3 confirm the hematite structure. No additional XRD peaks for Ti and P based materials in hematite can be found.

Fig. 2 shows the TEM images and elemental mappings of the TiP-treated hematite nanostructures. The hollow-rod structure can be clearly observed in Fig. 2a with a hollow core and a thin shell (the thickness about 25 nm). Hollow structure was reported to shorten the charge transfer length for enhanced performance [28]. However, here the end of the hollow nanostructure is not open and the electrolyte can not penetrate through the shell to contact the inner surface. Thus the hollow structure will not contribute to the performance. More hollow structures can be observed under TEM as shown in the Supporting Information Fig. S4. The high-resolution TEM image in Fig. 2b clearly exhibits the single crystalline structure of hematite. To reveal the existence of Ti and P in hematite, elemental mappings of the hollow-rod structure are shown in Fig. 2c. Ti and P can be clearly observed in hematite. The elemental line scans are also shown in the Supporting Information Fig. S5. The distribution of Ti is almost identical to that of Fe and O, suggesting **the Ti-incorporation in bulk hematite**. The hollow structure can also be identified in the line scan of Ti, confirming Ti-incorporation is in the bulk instead of at the surface. The P signal in hematite can also be identified in the line scan. However, as the P signal is much weaker than that of Ti, it cannot reflect the hollow structure. The TEM images and elemental line scan of hematite only Ti-treated are also shown in the Supporting Information Fig. S6, confirming the Ti-incorporation in Ti-treated hematite.

Fig. 2 (a) and (b): TEM images of the TiP-treated (Fe_2O_3 -TiP75) hematite nanostructures. (c): Dark field image and the corresponding TEM elemental mappings of Fe_2O_3 -TiP75: O (red), Fe (blue), Ti (green), and P (yellow) distribution in the selected area.

The performance of variously-treated hematite samples is shown in Fig. 3 by the photocurrent density *versus* applied potential (J - V) scans. In Fig. 3a the pristine hematite sample (Fe_2O_3) shows a photocurrent of 0.85 mA/cm^2 at 1.23 V vs. RHE , while the Ti-treated hematite (Fe_2O_3 -Ti) exhibits an increased photocurrent of 1.58 mA/cm^2 indicating the benefit of Ti-treatment. Moreover, the TiP-treated hematite (Fe_2O_3 -TiP75) shows a significantly enhanced photocurrent of 2.37 mA/cm^2 at 1.23 V vs. RHE ,

which is over 2.5 times that of the pristine hematite and 1.5 times that of the Ti-treated hematite. The enhanced performance can be attributed to the synergetic and collective effect of Ti and P to simultaneously improve charge separation and accelerate hole transport as illustrated in Fig. 1a. For comparison, Fig. 3b also shows the performance of pure P-treated hematite ($\text{Fe}_2\text{O}_3+\text{H}_3\text{PO}_4$, by immersing FeOOH in H_3PO_4) and the sample treated by the simple combination of Ti and P ($\text{Fe}_2\text{O}_3\text{-Ti}+\text{H}_3\text{PO}_4$, by immersing the Ti-treated FeOOH in H_3PO_4). Although the Ti-treatment and the P-treatment alone can significantly enhance the performance, the simple combination of these two processes ($\text{Fe}_2\text{O}_3\text{-Ti}+\text{H}_3\text{PO}_4$) seems to show only weak cumulative effect for enhanced performance (from 1.58 to 1.80 mA/cm^2 at 1.23 V *vs.* RHE). The simultaneous Ti and P treatment to modify hematite is thus important and effective to obtain the high performance with a synergetic effect. When coupling with Co-Pi catalysts, the photocurrent of the TiP-treated hematite can be further improved to achieve a remarkable value of 2.90 mA/cm^2 at 1.23 V *vs.* RHE, which is comparable to the high performance hematite photoanodes in recent reports [6,17,25]. It also represents the highest photocurrent ever reported for the Fe_2TiO_5 -related hematite photoanodes [13,22,23,25]. Although the value of 2.9 mA/cm^2 is slightly lower than the best one ever reported for the P-modified hematite photoanodes (3.1 mA/cm^2) [17], yet the present photoanode shows very stable performance in 6 hours (see the Supporting Information Fig. S7) in contrast to the sharp decay from 3.1 to 2.65 mA/cm^2 in 1 hour in the literature [17].

The performance of Ti-treated hematite ($\text{Fe}_2\text{O}_3\text{-Ti}$) sample was optimized in terms of HCl concentration and shown in the Supporting Information Fig. S8a, while the performance of $\text{Fe}_2\text{O}_3\text{-Ti}+\text{H}_3\text{PO}_4$ sample was optimized in terms of H_3PO_4 concentration in Fig. S8b. The $\text{Fe}_2\text{O}_3\text{-TiP}$ samples were also optimized by controlling the solution concentrations and temperature, and the results are shown in the Supporting Information Fig. S9 and Fig. S10. Fig. S11 shows the incident photon-to-current conversion efficiencies (IPCE) of Fe_2O_3 , $\text{Fe}_2\text{O}_3\text{-Ti}$ and $\text{Fe}_2\text{O}_3\text{-TiP75}$ (at 1.23 V *vs.* RHE). Significant improvement in the IPCE was observed for the $\text{Fe}_2\text{O}_3\text{-TiP75}$ sample, which is consistent with the high photocurrent value.

Fig. 3 (a) J - V curves of the pristine hematite (Fe_2O_3), Fe_2O_3 -Ti, Fe_2O_3 -TiP75 and Fe_2O_3 -TiP75-Co-Pi. (b) J - V curves of Fe_2O_3 , Fe_2O_3 -Ti, Fe_2O_3 + H_3PO_4 and Fe_2O_3 -Ti+ H_3PO_4 .

X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy were employed to probe the electronic structure of the hematite samples. XPS data are shown in the Supporting Information Fig. S12. Ti and P signals can be clearly observed in the TiP-treated samples, confirming the effective co-modification. Ti 2p XPS spectra show an energy position similar to that of TiO_2 , indicating an oxidation state of Ti^{4+} [20]. P 2p XPS spectra with a strong peak around 137 eV suggest the existence of P^{5+} (similar to that of FePO_4) in hematite [17].

The exact chemical compositions of Ti and P in hematite were investigated by XAS to characterize the electronic states [12]. Fig. 4a and 4b show the Ti *L*-edge XAS spectra in total electron yield (TEY) and total fluorescence yield (TFY) detection modes, respectively. TEY is a surface-sensitive method with the detection depth about 5-10 nm, while TFY is a bulk-sensitive (about 1 μm) method. Fig. 4a shows the Ti *L*-edge XAS spectra (TEY) of the pristine and TiP-treated samples. The reference spectrum of Fe_2TiO_5 and the spectra of FTO substrates treated by Ti and TiP (the same annealing process but without hematite) are also shown. Without hematite, the Ti-treated FTO (FTO-Ti) shows a spectral shape similar to that of rutile TiO_2 with two separated peaks B1 and B2 (the e_g related peak splitting, B2 is strong than B1 indicating the rutile structure). The TiP-treated FTO (FTO-TiP) also shows a rutile TiO_2 structure with separated peaks B1 and B2, while a new feature A1 and an increased B2 can be observed indicating the titanium phosphate (TiP_2O_7) structure (The TiP_2O_7 structure is confirmed by XRD spectra, data not shown). The successful deposition of Ti- and TiP-based materials on the FTO substrates may reduce the interfacial recombination and then improve the performance [21,27]. When hematite was prepared on the modified FTO, the Ti-related materials can be different due to the participation of Fe. For Fe_2O_3 -Ti, a single feature B at the center position of B1 and B2 can be observed, offering the fingerprint evidence of Fe_2TiO_5 structure [13]. The TiP-treated sample (Fe_2O_3 -TiP75) also shows a single feature B indicating the Fe_2TiO_5 structure [13]. The TiP_2O_7 structure disappears suggesting the strong interaction between Ti and Fe to form Fe_2TiO_5 structure. The bulk information of Ti is also measured by the bulk-sensitive TFY mode in Fig. 4b. Interestingly, The XAS spectra of Fe_2O_3 -TiP75 and Fe_2O_3 -Ti in TFY mode show almost identical spectral features to those in

the surface-sensitive TEY mode, confirming the existence of Fe_2TiO_5 in the bulk of hematite. The results are consistent with the TEM results in Fig. 2 and Fig. S5. Fe_2TiO_5 can exist as discrete clusters over the Fe_2O_3 host while it is hard to be directly observed due to the small size (less than 1 nm). Fe_2TiO_5 thin layer on the surface of hematite was widely reported, which had a favorable band structure for the photo-induced hole transfer to enhance charge separation [13,15,22]. Here the discrete Fe_2TiO_5 in bulk hematite may also be expected useful to benefit charge separation with a favorable band structure. However, the charge transfer mechanism of the discrete Fe_2TiO_5 can be different from that of the thin layer Fe_2TiO_5 on hematite. The discrete Fe_2TiO_5 sites in bulk hematite may quickly collect photo-induced holes and this process can be stopped due to accumulated holes. Quick transfer of the hole to the surface is thus required for further water oxidation. The surface $\text{Fe}_2\text{TiO}_5/\text{Fe}_2\text{O}_3$ heterojunction may partly accelerate the hole transfer with faster surface hole transfer to the electrolyte [13]. A gradient electric field by P-modification can further accelerate hole transfer from the Fe_2TiO_5 sites (discrete clusters) to the surface for effective water oxidation [9,17,18]. Note that all previous works reported that the Fe_2TiO_5 layer was formed on the surface, whereas the distribution of discrete Fe_2TiO_5 in bulk hematite to facilitate the charge separation for enhanced performance has not been reported. Here, we report for the first time a discrete Fe_2TiO_5 -incorporation in bulk hematite to improve the performance. Fig. 4c shows the Fe *L*-edge XAS spectra in TEY and TFY modes. There is no obvious Fe^{2+} signal in Fe_2O_3 -TiP75 and Fe_2O_3 -Ti in both detection modes, indicating no FeTiO_3 in the Ti-treated samples. The formation of Fe_2TiO_5 with Fe^{3+} and Ti^{4+} could be a good form for Ti-modification in hematite, which can be used to understand the mechanism of some other Ti-based treatment of hematite.

The P-based compositions in hematite are also probed by P *L*-edge XAS spectra in Fig. 4d (TEY and TFY modes). The TEY spectrum of Fe_2O_3 -TiP75 clearly shows P *L*-edge signal indicating the P-modification. The peak position also suggests that the P exists as FePO_4 (similar to the standard sample), which is different from that of TiP_2O_7 without the participation of Fe. The result is also consistent with the XPS data. Interestingly, the bulk-sensitive TFY signal of Fe_2O_3 -TiP75 is much weaker than the surface-sensitive TEY signal (normalized to the incident beam and calibrated by using the FTO-TiP

sample in the two modes), suggesting that P element mainly resides at the surface region instead of in the bulk. To investigate the different distribution of Ti and P in hematite, we performed DFT calculation by using VASP package. The configuration with Ti in the bulk and P at the surface was used, compared with another one with Ti at the surface and P in the bulk (Fig. S13). The results show that the first configuration has a lower energy (1.4 eV) than the second one, supporting the distribution of Ti in the bulk and P at the surface. The surface P-modification as electron-rich FePO_4 can accelerate hole transfer with a gradient electric field [9,18]. To reveal the surface chemical state, Fe 2p XPS spectra of the pristine hematite and $\text{Fe}_2\text{O}_3\text{-TiP75}$ are shown in the Supporting Information Fig. S14. XPS is a more surface-sensitive method (1-2 nm) than XAS (TEY mode: 5-10 nm). Interestingly, $\text{Fe}_2\text{O}_3\text{-TiP75}$ shows an enhanced feature at 716 eV for Fe^{2+} , indicating an electron-rich environment at the surface. The existence of Fe^{2+} strongly supports the surface P-modification effect to improve performance. The co-modification of Ti in the bulk and P at the surface of hematite leads to the synergetic effect as illustrated in Fig. 1a.

Fig. 4 (a) and (b): Ti *L*-edge XAS spectra of the samples in TEY and TFY modes, respectively. (c): Fe *L*-edge XAS spectra of the samples in TEY and TFY modes. (d): P *L*-edge XAS spectra of the samples in TEY and TFY modes.

To confirm the working mechanism of the co-modified sample, the electrochemical impedance spectroscopy (EIS) was measured, and the results are shown in Fig. 5a as Nyquist plots. The inset in Fig. 5a shows the equivalent circuit (EC) to simulate the Nyquist plot and Fig. 5b shows the parameters of EC elements in EIS. Compared to the pristine hematite, the Fe₂O₃-Ti sample exhibits a curve with

obviously a smaller diameter indicating faster charge transfer kinetics at the electrode interface [18]. It can be attributed to the existence of Fe_2TiO_5 with a favorable band position to facilitate charge separation [13,22]. The curve diameter for the Ti and P co-modified sample ($\text{Fe}_2\text{O}_3\text{-TiP75}$) is even smaller, suggesting an even faster charge transfer with the outer surface P to accelerate hole transport [9,18]. More information can be found from the fitting parameters of EC elements in Fig. 5b. The R_{ct} or the resistance for the interfacial charge transfer decreases significantly from Fe_2O_3 to $\text{Fe}_2\text{O}_3\text{-Ti}$ and then $\text{Fe}_2\text{O}_3\text{-TiP75}$, confirming the faster charge transfer in $\text{Fe}_2\text{O}_3\text{-TiP75}$ due to concurrent improvement of charge separation and transport by Ti and P, respectively [18]. Compared to the $\text{Fe}_2\text{O}_3\text{-Ti}$ sample, $\text{Fe}_2\text{O}_3\text{-TiP75}$ shows a larger C_{trap} indicating an increased amount of active sites in surface states, strongly confirming the effective surface P-modification to improve the performance [18]. The R_{trap} or the resistance for trapping holes by surface states of $\text{Fe}_2\text{O}_3\text{-TiP75}$ also sharply decreases suggesting that the surface P (in the form of FePO_4) can effectively affect the surface region to accelerate the reaction [18]. The co-modified Ti in the bulk and P at the surface regions show the synergetic and collective effect to enhance performance for solar water splitting.

Fig. 5 (a) EIS spectra of Fe_2O_3 , $\text{Fe}_2\text{O}_3\text{-Ti}$, and $\text{Fe}_2\text{O}_3\text{-TiP75}$ measured at 1.23 V vs. RHE under illumination. The inset shows the equivalent circuit. (b) Parameters of equivalent circuit elements. R_s is the series resistances. C_{bulk} is the capacitance of the space charge depletion region at the electrode surface. R_{trap} is the resistance for trapping holes by surface states. C_{trap} shows the amount of active sites in surface states. R_{ct} is the resistance for charge transfer across the interface.

Conclusion

Ti and P co-modified hematite hollow nanostructures have been prepared by using a FTO substrate pre-treated with Ti and P precursors. TEM and synchrotron-based XAS analyses clearly reveal the discrete Fe_2TiO_5 -incorporation and the surface FePO_4 -modification in the hematite nanostructures. The discrete Fe_2TiO_5 -incorporation in bulk hematite has been firstly reported to facilitate charge separation with a favorable band position, while the surface FePO_4 improves hole transfer to the surface by a gradient electric field. The synergetic effect of Fe_2TiO_5 and FePO_4 in hematite nanostructures significantly enhances the performance with a photocurrent of 2.37 mA/cm^2 at 1.23 V vs. RHE , which is much higher than that of the hematite samples treated by Ti or P alone. The photocurrent can be further improved by coupling the hematite with Co-Pi catalysts to achieve a high value of 2.90 mA/cm^2 at 1.23 V vs. RHE with a stable performance. The facile method to prepare Ti and P co-modified hematite hollow nanostructures to concurrently improve charge separation and transport can facilitate practical solar water splitting applications.

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Appendix A. Supporting Information Available

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/>.

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Graphical Abstract