KCl flux suppresses surface recombinations of hematite photoanode for water oxidation

Huanhuan Cao BE

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China

Wenping Si PhD

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China

Wenlei Guo MSc

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China

Tao Zhang BE

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China

Yonghuan Han BE

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China

Feng Hou PhD

Key Laboratory of Advanced Ceramics and Machining Technology of the Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin, China (corresponding author: houf@tju.edu.cn)

Ji Liang PhD

Institute for Superconducting and Electronic Materials, Australian Institute of Innovative Materials, University of Wollongong, Innovation Campus, Wollongong, Australia

Hematite is a promising photoanode for solar water splitting because of its favorable bandgap, excellent chemical stability and low cost. However, it suffers from both severe bulk and surface-charge recombinations, resulting in photoactivities much lower than the theoretical value. In this work, a facile new strategy is proposed by annealing hematite in the presence of potassium chloride (KCl) flux at 800°C. The photocurrent density of the annealed hematite, denoted 'KCl-hematite', increases from 0.34 mA/cm² for pristine hematite to 0.54 mA/cm² at 1.23 V_{RHE} and further to 0.90 mA/cm² after cobalt-phosphate (Co-Pi) deposition. Moreover, the photocurrent onset potential of KCl-hematite shows a cathodic shift of 120 mV compared with that of pristine hematite. It is demonstrated that potassium chloride flux can enhance the crystallinity and orderliness of hematite on the surface, reducing surface recombinations. This facile strategy by a flux offers a new insight to passivate surface recombinations of photoelectrodes and can be easily extended to other materials to enhance their photoactivities.

Notation

A	electrochemical active surface area
C_{ct}	capacitance of the space-charge layer
C_{sc}	space-charge layer capacitance
e	elementary charge
E_{fb}	flat-band potential
J_{H_2O}	overall water-splitting photocurrent
$J_{H_2O_2}$	photocurrent measured with hydrogen peroxide in the electrolyte
k_B	Boltzmann constant
N_D	donor density
$P_{charge\ injection}$	yield of the holes that have reached the electrode/electrolyte interface and that are injected into the electrolyte to oxidize the water
$P_{charge\ separation}$	yield of the photogenerated holes that reach the electrode/electrolyte interface
R_{bulk}	resistance of bulk electron transport
R_{ct}	charge-transfer resistance
R_s	resistance of the electrolyte
$(RC)_{bulk}$	bulk electron transport time constant
$(RC)_{ct}$	charge-transfer time constant
T	absolute temperature
V	applied potential
ϵ_0	vacuum dielectric constant

ϵ_r	hematite dielectric constant
$\eta_{charge\ injection}$	charge injection into water

1. Introduction

The growing population and environmental pollution demand clean, renewable alternative energy resources. Solar energy plays an important role in supplying renewable energy, which can be converted into electricity through photovoltaics or chemical fuels through photo(electro)chemical conversion.¹ Hydrogen (H₂), as an attractive clean fuel, can be directly obtained by photoelectrochemical (PEC) water (H₂O) splitting,^{2,3} in which the oxygen (O₂) evolution reaction and the hydrogen evolution reaction occur on separate electrodes.⁴ Metal oxide materials are of great interest to function as photoanodes for the solar water-splitting process due to their favorable band positions and peculiar physicochemical properties; such materials include hematite,^{5–8} titanium dioxide (TiO₂),^{9–12} zinc peroxide (ZnO₂),^{13–15} tungsten trioxide (WO₃)^{16–18} and bismuth vanadate (BiVO₄).¹⁹ Hematite has a favorable bandgap (1.9–2.1 eV) for light absorption, excellent chemical stability in alkaline solutions and, most importantly, low cost.^{5,20,21} However, the photocurrent densities reported for hematite photoanodes are often much lower than the theoretical value,²² mainly due to the inefficient electron–hole separation and a short hole diffusion length (2–4 nm) in the bulk,^{6,23} as well as the severe charge recombinations at the

surface. Various strategies have been proposed to improve the bulk properties, such as element doping with tin (Sn) or titanium (Ti),^{23–26} electrochemical reduction by applying a reduction potential^{27–29} and the formation of a heterojunction with another light absorber.³⁰

Furthermore, the surface properties play a significant role in determining the hole transfer efficiency of hematite due to the presence of surface states, which have been categorized into two types. One type of surface states is considered as electron–hole recombination centers, and the other serve as hole collectors that facilitate charge accumulation and transfer.^{31–33} The presence of recombination centers is one of the reasons responsible for the late onset potential (typically 0.8–1.0 V against reversible hydrogen electrode (V_{RHE})) and low photocurrents of hematite photoanodes.^{6,34} Proper surface treatments can effectively passivate the surface recombination centers and promote charge transfer, thus lowering the onset potentials and improving the photocurrents.^{35–37} Common strategies for enhancing the surface properties include the passivation of surface recombination centers by very thin layers of aluminum oxide (Al_2O_3),³⁸ titanium dioxide or gallium (I) oxide (Ga_2O_3)^{39,40} and the introduction of cocatalysts, such as cobalt phosphate (Co-Pi), FeOOH and CoOOH, into the surface of hematite to boost water oxidation reaction.^{6,8,41–43}

In this paper, the authors propose a new strategy of annealing hematite in the presence of a potassium chloride (KCl) flux to passivate the surface recombination centers and enhance the photoactivity of hematite. Potassium chloride flux, which would be in molten salt status at high temperatures, was usually used as a sinter aid to lower the sintering temperature and improve crystallinity.^{44,45} Usually, in the synthesis process for a ceramic, chloride is added and heated to elevated temperatures above the melting point of the chloride, which promote the destabilization of reactants, as well as the mass transfer of constituents to form the ceramic.^{44,45} Thus, the high temperatures required to synthesize ceramic materials can be reduced in the presence of chloride salts. It is expected that potassium chloride flux could improve crystallinity and orderliness and increase the donor density of hematite by promoting tin diffusion from the fluorine (F)-doped tin (IV) oxide (SnO_2) (FTO) substrate into hematite. The crystallinity, morphology, PEC performances and impedance spectra, as well as the Mott–Schottky plots, were examined to understand the effect of potassium chloride flux on the hematite. It is confirmed that potassium chloride indeed passivates the surface recombination centers of hematite, leading to an earlier onset potential and higher photoactivity.

2. Experimental procedure

2.1 Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2 ; 30%) were purchased from Tianjin Yuanli Chemical Reagent Co., Ltd. Sodium nitrate (NaNO_3) was bought from Sinopharm Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH) was obtained from Tianjin Guangfu Chemical Reagent Co., Ltd.

Potassium chloride was purchased from Tianjin Jiangtian Chemical Reagent Co., Ltd. Potassium phosphate monobasic (KH_2PO_4) was obtained from Aladdin. All the chemicals were of analytical grade and used as received in the experiments without further purification.

2.2 Preparation of hematite photoelectrodes

FTO glass substrates ($\sim 7 \Omega/\text{sq}$) were ultrasonically cleaned by using deionized water, acetone and isopropanol. $\beta\text{-FeOOH}$ nanorods were grown at 100°C on FTO for 3 h in a 30 ml solution containing 0.15 M iron (III) chloride and 1 M sodium nitrate adjusted by 60 μl hydrochloric acid (HCl) (37 wt.%). The optimization of the hydrochloric acid amount is described in Figure S1 in the online supplementary material. Four different amounts of hydrochloric acid were tested, and the highest photocurrent density was achieved when the hydrochloric acid amount was 60 μl . In this process, Kapton tape was used to define the area for hematite growth and isolate the back side of the glass from the growing solution, with an exposed area of $1 \times 1 \text{ cm}^2$. After being cleaned with deionized water and dried in air, $\beta\text{-FeOOH}$ was firstly annealed at 250°C for 8 min to remove hydroxyl rapidly. Hematite was subsequently obtained after annealing at 550°C for 2 h. Afterward, a thin layer of solid potassium chloride flux was carefully spread using a weighing spoon on the surface of hematite ($1 \times 1 \text{ cm}^2$) but leaving the bare FTO glass blank, which was then annealed at 800°C for 10 min in a tube furnace. The hematite annealed in the presence of potassium chloride flux is denoted as ‘KCl-hematite’. The KCl-hematite photoelectrodes were cleaned to remove the excess potassium chloride with deionized water before PEC measurements.

2.3 Co-Pi cocatalyst deposition

To prepare the Co-Pi cocatalyst on a hematite photoanode, a photo-assisted electrodeposition under AM 1.5 G illumination was conducted in an electrolyte containing 0.5 mM cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1 M potassium phosphate monobasic at pH = 7 adjusted with sodium hydroxide. The photo-assisted electrodeposition was carried out at a constant potential of 0.1 $V_{\text{Ag}/\text{AgCl}}$ for 20 s.

2.4 PEC measurements

All the PEC measurements were performed using a CHI 650E workstation in a three-electrode system in an argon (Ar)-saturated 1 M sodium hydroxide (pH = 14.0) electrolyte at room temperature. The light source was a 150 W xenon (Xe) arc lamp equipped with an AM 1.5 G filter ($100 \text{ mW}/\text{cm}^2$). In this experiment, the prepared hematite/FTO ($1 \times 1 \text{ cm}^2$) was used as the working electrode, a platinum (Pt) plate was used the counter electrode and silver (Ag)/silver chloride (AgCl) was used the reference electrode. The linear sweep voltage (LSV) was used to characterize the PEC performances at a scan rate of 10 mV/s in the potential window of 0.4–1.6 V_{RHE} .

2.5 Impedance spectroscopy and Mott–Schottky plots

Impedance spectroscopy measurements were carried out in an oxygen-saturated 1 M sodium hydroxide electrolyte on a CHI 650E workstation in the frequency range between 1 Hz and

100 kHz using a 5 mV alternating-current amplitude between 1.1 and 1.3 V_{RHE} under AM 1.5 G illumination (100 mW/cm^2). Mott–Schottky plots were obtained at a fixed frequency of 1000 Hz in the potential range 0.7–1.1 V_{RHE} in an oxygen-saturated 1 M sodium hydroxide electrolyte in the dark.

2.6 Material characterizations

The morphology of the samples was characterized using field-emission scanning electron microscopy (FESEM; Hitachi S-4800). The crystal structure of the materials was analyzed by X-ray diffraction (XRD; Bruker D8) with copper (Cu) $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in the 2θ range between 10 and 70° .

3. Results and discussion

The XRD patterns of the FTO substrate, hematite/FTO annealed at 550 and 800°C and KCl-hematite annealed at 800°C are shown in Figure 1. As previously reported, the peaks at 2θ of 36° , 54° and 63° belong to hematite (Joint Committee on Powder Diffraction Standards 33-066). The dominant peak at 36° , corresponding to (110) reflexes, indicates a preferential growth direction along [110].²³ Compared with the hematite annealed at 550°C , high-temperature annealing at 800°C can significantly improve the crystallinity of hematite. In addition, the intensity of the (110) diffraction for KCl-hematite is higher than that for the pristine hematite, confirming that KCl-hematite has improved crystallinity, which is beneficial to the enhancement of photoactivity of hematite. Moreover, the (110) peak of KCl-hematite shifts toward smaller 2θ values compared with that of the pristine hematite, indicating a larger lattice spacing, which could be due to more tin in the lattice. Also, the hematite was then investigated with X-ray photoelectron spectroscopy (XPS) analysis, and the result is shown in Figure S2 in the online supplementary material. The XPS survey confirms that the peaks at 710.6, 530.4 and 496.2 eV correspond to iron (Fe) 2p, oxygen (O) 1s and tin 3d in hematite, respectively.²³ Moreover, the atomic percentage of tin is around

2.54%. In addition, the ultraviolet–visible spectra of hematite and KCl-hematite are shown in Figure S3 in the online supplementary material, and the optical bandgaps for these two samples are determined to be both 2.09 eV.

To explore the effect of potassium chloride on the morphology of hematite, the microstructures of the $\beta\text{-FeOOH}$ precursor, hematite annealed at 550 and 800°C and KCl-hematite annealed at 800°C were characterized by FESEM, as shown in Figure 2. $\beta\text{-FeOOH}$, hematite and KCl-hematite all exhibited nanorod morphologies. The diameter of nanorods grew continuously with increased annealing temperature. It can be clearly observed that each nanorod of hematite in Figures 2(b) and 2(c) were composed of several smaller nanorods or nanowires originating from the $\beta\text{-FeOOH}$ precursors, which exhibited many cavities or defects on the surfaces. Interestingly, compared with its counterparts annealed without potassium chloride, the KCl-hematite annealed at 800°C in Figure 2(d) exhibited very different morphologies, with more rounded nanorods and smooth homogenous surfaces, while the smaller ‘components’ were no longer observable. The same phenomena were also observed on KCl-hematite annealed at 770°C , as shown in Figures S4(b) and S4(c) in the online supplementary material. Together with the observation from XRD results in Figure 1, it would be justified to conclude that the presence of potassium chloride, which would be in a molten status at 800°C , indeed enhanced the surface orderliness of hematite, similar to the observation of the regrowth strategy for hematite reported by Jang *et al.*³⁷ It is thus expected that hematite would have better photoactivity.

To investigate the PEC performances of these materials toward solar water splitting, PEC measurements were carried out in a three-electrode configuration, in which hematite or KCl-hematite was used as the working electrode and platinum and silver/silver chloride as the counter electrode and reference electrode,

Figure 1. XRD patterns of FTO glass, pristine hematite annealed at 550°C for 2 h, pristine hematite and KCl-hematite annealed at 800°C . The right panel shows the enlarged patterns for the peak around 2θ of 36°

Figure 2. SEM images of (a) $\beta\text{-FeOOH}$, (b) pristine hematite annealed at 550°C , (c) pristine hematite annealed at 800°C and (d) KCl-hematite annealed at 800°C

respectively. The photocurrent densities of these photoanodes were examined by LSV mode. KCl-hematite had a photocurrent density of 0.54 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$, which is obviously higher than 0.34 mA/cm^2 for pristine hematite, as shown in Figure 3(a). Moreover, the photocurrent onset potential of KCl-hematite showed a cathodic shift of 120 mV compared with that of the pristine hematite, which was probably due to the reduction of surface recombination through the orderliness enhancement of nanorods for KCl-hematite.³⁷ To improve further the photocurrent density, a Co-Pi layer was deposited on the KCl-hematite by photo-assisted electrodeposition. The photocurrent density of Co-Pi-coated KCl-hematite is shown in Figure 3(a); it increased from 0.54 to 0.90 mA/cm^2 at $1.23 \text{ V}_{\text{RHE}}$ after the loading of Co-Pi.

Furthermore, the comparisons of the photocurrent densities measured with and without the presence of hydrogen peroxide in sodium hydroxide are shown in Figures 3(b) and 3(c) for pristine hematite and KCl-hematite, respectively. Hydrogen peroxide usually can be used as a hole scavenger in electrolyte due to the

thermodynamically more facile oxidation of hydrogen peroxide, which has a rate constant 10–100 times higher than that of water.⁴⁶ Thus, the photocurrent for hydrogen peroxide oxidation can be considered as a maximum value utilizing all the photoinduced holes that reach the surface, reflecting mainly the bulk charge separation efficiency of a material. A smaller gap between the photocurrents of hydrogen peroxide and water oxidations indicates fewer recombinations of charge carriers on the surface – that is, good surface properties. The gap between the water and hydrogen peroxide oxidation photocurrents for KCl-hematite in Figure 3(c) is smaller than that for pristine hematite in Figure 3(b), indicating fewer recombinations on the surface of KCl-hematite.

The overall water-splitting photocurrent ($J_{\text{H}_2\text{O}}$) can be described by the following equation⁴⁶

$$1. \quad J_{\text{H}_2\text{O}} = J_{\text{absorbed}} \times P_{\text{charge separation}} \times P_{\text{charge injection}}$$

Figure 3. (a) Photocurrent densities of hematite and KCl-hematite in argon-saturated 1 M sodium hydroxide electrolyte (pH = 14.0) under AM 1.5 G illumination of 100 mW/cm^2 ; photocurrent densities of (b) hematite and (c) KCl-hematite in 1 M sodium hydroxide with and without the presence of 0.5 M hydrogen peroxide under AM 1.5 G illumination of 100 mW/cm^2 ; (d) charge injection efficiencies of hematite and KCl-hematite for water oxidation

$P_{\text{charge separation}}$ is the yield of the photogenerated holes that reach the electrode/electrolyte interface or, in other words, the fraction of photogenerated holes that do not recombine with electrons in the bulk. $P_{\text{charge injection}}$ is the yield of those holes that have reached the electrode/electrolyte interface and that are injected into the electrolyte to oxidize the water or, in other words, do not recombine with electrons at surface traps. When a hole scavenger (hydrogen peroxide) is added in the electrolyte, all holes that reach the electrode/electrolyte interface will participate in the oxidation of hydrogen peroxide.⁴⁷ Since the oxidation of hydrogen peroxide is facile and fast, $P_{\text{charge injection}}$ can be considered as 100% for this process; the photocurrent measured with hydrogen peroxide in the electrolyte ($J_{\text{H}_2\text{O}_2}$) is thus a product of J_{absorbed} and $P_{\text{charge separation}}$

$$2. \quad J_{\text{H}_2\text{O}_2} = J_{\text{absorbed}} \times P_{\text{charge separation}}$$

The charge injection into water yield can be obtained by dividing $J_{\text{H}_2\text{O}}$ with $J_{\text{H}_2\text{O}_2}$

$$3. \quad \eta_{\text{charge injection}} = \frac{J_{\text{H}_2\text{O}}}{J_{\text{H}_2\text{O}_2}}$$

Figure 3(d) shows the comparison of $\eta_{\text{charge injection}}$ for hematite and KCl-hematite toward solar water oxidation. KCl-hematite showed a significantly enhanced charge injection efficiency throughout the scanned potential window, indicating improved surface properties, which is most probably due to the higher crystalline orderliness, as discussed in the XRD and SEM sections.

It is noteworthy that the water oxidation photocurrent for KCl-hematite was higher than that for the pristine hematite, while the hydrogen peroxide oxidation photocurrent for KCl-hematite was lower than that for the pristine hematite. These observations indicate a complicated scenario induced by the presence of potassium chloride, which includes a surface improvement and a worsened bulk charge separation for KCl-hematite. Although KCl-hematite has a worse bulk property, it still has a higher photocurrent density for water oxidation than pristine hematite due to the substantial improvement of the surface. In order to understand more about the underlying mechanisms responsible for the variations in the bulk and surface properties of KCl-hematite, Mott–Schottky plots and impedance Nyquist plots were measured and are discussed.

The Mott–Schottky plots (Figure 4(a)) were obtained by measuring the impedance with a fixed frequency of 1000 Hz within a potential window of 0.7–1.1 V_{RHE} in oxygen-saturated 1 M sodium hydroxide electrolyte in the dark. Obviously, the slopes of hematite and KCl-hematite plots are positive, confirming the n-type semiconductor feature of hematite. The flat-band potential and donor density can be obtained from the intercept and slope of Mott–Schottky curves through the following equation²⁷

Sample	$V_{\text{fb}}/V_{\text{RHE}}$	Donor density: $\times 10^{19} \text{ cm}^{-3}$
Hematite	0.54	0.43
KCl-hematite	0.57	1.23

Figure 4. (a) Mott–Schottky plots obtained by measuring the impedance spectroscopy in 1 M sodium hydroxide electrolyte saturated with oxygen in the dark for hematite and KCl-hematite; (b) flat-band potential, donor density at 1.23 V_{RHE}

$$4. \quad \left(\frac{A}{C_{\text{sc}}} \right)^2 = \frac{2}{\epsilon_r \epsilon_0 N_D} \left(V - E_{\text{fb}} - \frac{k_B T}{e} \right)$$

where V is the applied potential; E_{fb} is the flat-band potential; C_{sc} is the space-charge layer capacitance; A is the electrochemical active surface area (determined by cyclic voltammetry measurement in the dark assuming a specific capacitance of 20 μF/cm² for the Helmholtz layer); ϵ_0 is the vacuum dielectric constant (8.854 × 10^{−14} F/cm); a value of 80 is taken for the hematite dielectric constant ϵ_r ; e is the elementary charge (1.6 × 10^{−19} C); k_B is the Boltzmann constant; and T is the absolute temperature.

The calculated flat-band potentials and donor densities for pristine hematite and KCl-hematite are displayed in Figure 4(b). Pristine hematite had a donor density of 0.42 × 10¹⁹ cm^{−3}, which is comparable with literature reports on tin-doped hematite.^{23,27,47} Furthermore, the donor density rose up to 1.23 × 10¹⁹ cm^{−3} for KCl-hematite. The increased carrier density was considered the result of more tin diffusion in KCl-hematite. This confirms that the presence of potassium chloride indeed promotes tin diffusion into hematite,²³ also consistent with the observations from XRD patterns. The flat-band potential was 0.54 V_{RHE} for hematite and 0.57 V_{RHE} for KCl-hematite. These very close values of V_{fb} indicate similar Fermi levels for these two materials.

The impedance measurements were performed under AM 1.5 G illumination at 1.1 V_{RHE} to understand the bulk charge separation and solid–electrolyte charge-transfer processes for pristine hematite and KCl-hematite. An equivalent circuit model^{5,48,49} (inset in Figure 5(a)) was adopted to interpret the impedance. R_s is the resistance of the electrolyte, C_{ct} is the capacitance of the space-charge layer, R_{ct} represents the charge-transfer resistance in the interface between the photoanode surface and the electrolyte and $(RC)_{ct}$ is the time constant, R_{bulk} is the resistance of bulk electron transport and $(RC)_{bulk}$ is the bulk transport time constant.^{50,51} The fitted R_{bulk} , R_{ct} and time constants for bulk charge separation and interface charge transfer are listed in Figure 5(b). Compared with pristine hematite, KCl-hematite had a smaller charge-transfer resistance but a higher bulk transport resistance. The $(RC)_{ct}$ of KCl-hematite was smaller than that of pristine hematite, indicating a more facile charge-transfer kinetics for KCl-hematite. The presence of potassium chloride flux during annealing improved the orderliness and suppressed the surface defects of hematite, leading to fewer surface recombinations and thus an enhanced photocurrent for water oxidation. This result is also consistent with the observations from the photocurrent measurements for water and hydrogen peroxide oxidation.

However, the R_{bulk} and $(RC)_{bulk}$ of KCl-hematite were larger than those of pristine hematite, indicating a worsened bulk charge

separation efficiency. Potassium chloride improved the orderliness of hematite but also caused the FTO to deform, leading to higher R_{bulk} . Figure S5 in the online supplementary material shows the photographs of pristine hematite, KCl-hematite annealed at 800°C for 10 min and KCl-hematite annealed at 800°C for 20 min. Observable wave-like fluctuations of the FTO layer appeared on the substrate for KCl-hematite-10 min, while in the case of KCl-hematite-20 min, the FTO glass was very severely deformed or even broken in extreme cases.

Although the presence of potassium chloride promoted the diffusion of tin into hematite and suppressed surface defects, the deformation of the FTO layer introduced a negative effect on the total PEC performances. The FTO substrate lost its good electrical conductivity owing to the deformation, inhibiting charge transport at the interface of FTO and hematite. This could be due to an excessive usage of potassium chloride in the current work. It is envisioned that an optimized amount of potassium chloride or the use of eutectic mixture of chloride salts is very promising to overcome this issue and both bulk and surface properties of hematite can be improved.

4. Conclusions

In conclusion, a new strategy is proposed to reduce the surface defects by simply annealing hematite in the presence of potassium chloride flux at 800°C. Compared with the photocurrent density of pristine hematite, the photocurrent density of KCl-hematite improved from 0.34 to 0.54 mA/cm² and further increased to 0.90 mA/cm² at 1.23 V_{RHE} after the loading of Co-Pi. Significantly, KCl-hematite showed better crystallinity and orderliness on the surface, as evidenced by the analysis of XRD and SEM. The comparison of hydrogen peroxide and water oxidation confirms enhanced surface properties for KCl-hematite. Impedance measurements demonstrated that potassium chloride flux indeed could passivate surface-charge recombinations of hematite and boost the charge transfer across the hematite surface and electrolyte interface. On the other hand, the bulk charge transport efficiency of KCl-hematite worsened compared with that of pristine hematite, although KCl-hematite had a higher donor density as evidenced by Mott–Schottky plots due to more tin diffusion from the FTO substrate into hematite. It is most probably due to the more severe deformation of the FTO layer in the presence of excessive potassium chloride. It is expected that potassium chloride with an optimized amount or the use of eutectic mixture of chloride salts could probably improve both the surface and bulk of hematite photoanodes. This facile method of annealing photoelectrodes in the presence of a flux to passivate surface recombinations can be easily extended to other photoelectrodes, promoting their PEC performances toward solar water splitting.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (numbers 51072130 and 51502045) and the Australian Research Council through the Discovery Early Career Researcher Award (number DE170100871) program. Authors H. Cao and W. Si contributed equally to this paper.

Figure 5. (a) Nyquist plots measured under AM 1.5 G illumination at 1.1 V_{RHE} for hematite and KCl-hematite in 1 M sodium hydroxide electrolyte saturated with oxygen and fitted with the equivalent circuit shown as the inset. (b) R_{bulk} , R_{ct} , $(RC)_{bulk}$ and $(RC)_{ct}$ obtained by fitting the impedance spectroscopy data

REFERENCES

- Kun W, Gao YZ and Qi X (2019) Amorphous SiO₂ nanofiber@CuO quantum dots with enhanced photocatalytic activity. *Surface Innovations* **7**(1): 44–50, <https://doi.org/10.1680/jsuin.18.00031>.
- Thomson J (2019) Viewpoint: Hydrogen storage for energy applications in future cities. *Nanomaterials and Energy* **8**(2): 1–3, <https://doi.org/10.1680/jnaen.19.00045>.
- Pandiyan A, Uthayakumar A, Subrayan R et al. (2019) Review of solid oxide electrolysis cells: a clean energy strategy for hydrogen generation. *Nanomaterials and Energy* **8**(1): 2–22, <https://doi.org/10.1680/jnaen.18.00009>.
- Zhang J and Eslava S (2019) Understanding charge transfer, defects and surface states at hematite photoanodes. *Sustainable Energy & Fuels* **3**(6): 1351–1364.
- Sivula K, Le Formal F and Grätzel M (2011) Solar water splitting: progress using hematite (α -Fe₂O₃) photoelectrodes. *ChemSusChem* **4**(4): 432–449.
- Tang C, Sun B, Li M et al. (2019) Surface hydroxylated hematite promotes photoinduced hole transfer for water oxidation. *Journal of Materials Chemistry A* **7**(14): 8050–8054.
- Jansi Rani B, Ravi G, Yuvakkumar R et al. (2019) Sn doped α -Fe₂O₃ (Sn=0,10,20,30 wt%) photoanodes for photoelectrochemical water splitting applications. *Renewable Energy* **133**: 566–574.
- Liu C, Xu Y, Luo H et al. (2019) Synthesis and photoelectrochemical properties of CoOOH/phosphorus-doped hematite photoanodes for solar water oxidation. *Chemical Engineering Journal* **363**: 23–32.
- Mondal K, Kumar J and Sharma A (2013) TiO₂-nanoparticles-impregnated photocatalytic macroporous carbon films by spin coating. *Nanomaterials and Energy* **2**(3): 121–133, <https://doi.org/10.1680/nme.12.00034>.
- Xie SL, Zhai T, Li W et al. (2013) Hydrogen production from solar driven glucose oxidation over Ni(OH)₂ functionalized electroreduced-TiO₂ nanowire arrays. *Green Chemistry* **15**(9): 2434–2440.
- Wang Y, Wu B, Liu Z and Gu H (2018) The first-principle study of oleic acid/hydrazine exciting the growth of TiO₂ (100) crystal face. *Surface Innovations* **6**(1–2): 31–36, <http://doi.org/10.1680/jsuin.17.00043>.
- Dinc DO, Yilmaz M, Cetin SS, Turk M and Piskin E (2019) Gold-nanoisland-decorated titanium nanorod arrays fabricated by thermal dewetting approach. *Surface Innovations* **7**(5): 249–259, <https://doi.org/10.1680/jsuin.19.00013>.
- Mao YC, Yang H, Chen JX et al. (2014) Significant performance enhancement of ZnO photoanodes from Ni(OH)₂ electrocatalyst nanosheets overcoating. *Nano Energy* **6**: 10–18.
- Game O, Singh U, Gupta AA et al. (2012) Concurrent synthetic control of dopant (nitrogen) and defect complexes to realize broadband (UV–650 nm) absorption in ZnO nanorods for superior photo-electrochemical performance. *Journal of Materials Chemistry* **22**(33): 17302–17310.
- Wang GM, Yang XY, Qian F, Zhang JZ and Li Y (2010) Double-sided CdS and CdSe quantum dot Co-sensitized ZnO nanowire arrays for photoelectrochemical hydrogen generation. *Nano Letters* **10**(3): 1088–1092.
- Chen S, Zeng L, Tian H, Li XY and Gong JL (2017) Enhanced lattice oxygen reactivity over Ni-modified WO₃-based redox catalysts for chemical looping partial oxidation of methane. *ACS Catalysis* **7**(5): 3548–3559.
- Li MY, Yang Y, Ling YC et al. (2017) Morphology and doping engineering of Sn-doped hematite nanowire photoanodes. *Nano Letters* **17**(4): 2490–2495.
- Li G, Chen J, Wu S et al. (2017) The relationship between the mesostructure of WO₃/TiO₂ hollow microsphere and its property. *Surface Innovations* **6**(1–2): 37–46, <https://doi.org/10.1680/jsuin.17.00039>.
- Kim TW and Choi KS (2014) Nanoporous BiVO₄ photoanodes with dual-layer oxygen evolution catalysts for solar water splitting. *Science* **343**(6174): 990–994.
- Grave DA, Yatom N, Ellis DS, Toroker MC and Rothschild A (2018) The ‘rust’ challenge: on the correlations between electronic structure, excited state dynamics, and photoelectrochemical performance of hematite photoanodes for solar water splitting. *Advanced Materials* **30**(41): article e1706577.
- Bora DK, Braun A and Constable EC (2013) ‘In rust we trust’. Hematite – the prospective inorganic backbone for artificial photosynthesis. *Energy & Environmental Science* **6**(2): 407–425.
- Ryzhkov NV, Brezhneva N and Skorb EV (2019) Feedback mechanisms at inorganic–polyelectrolyte interfaces for applied materials. *Surface Innovations* **7**(3–4): 145–167, <https://doi.org/10.1680/jsuin.19.00006>.
- Ling YC, Wang GM, Wheeler DA, Zhang JZ and Li Y (2011) Sn-doped hematite nanostructures for photoelectrochemical water splitting. *Nano Letters* **11**(5): 2119–2125.
- Mazzaro R, Bibi SB, Natali M et al. (2019) Hematite nanostructures: an old material for a new story. simultaneous photoelectrochemical oxidation of benzylamine and hydrogen production through Ti doping. *Nano Energy* **61**: 36–46.
- Li HB, Zhao FY, Zhang JC et al. (2017) A g-C₃N₄/WO₃ photoanode with exceptional ability for photoelectrochemical water splitting. *Materials Chemistry Frontiers* **1**(2): 338–342.
- Jansi Rani B, Praveen Kumar M, Ravi G et al. (2019) Electrochemical and photoelectrochemical water oxidation of solvothermally synthesized Zr-doped α -Fe₂O₃ nanostructures. *Applied Surface Science* **471**: 733–744.
- Si W, Haydous F, Babic U, Pergolesi D and Lippert T (2019) Suppressed charge recombination in hematite photoanode via protonation and annealing. *ACS Applied Energy Materials* **2**(8): 5438–5445.
- Tang J and Wang J (2017) Fe-based metal organic framework/graphene oxide composite as an efficient catalyst for Fenton-like degradation of methyl orange. *RSC Advances* **7**(80): 50829–50837.
- Cibrev D, Tallarida M, Das C et al. (2017) New insights into water photooxidation on reductively pretreated hematite photoanodes. *Physical Chemistry Chemical Physics* **19**(32): 21807–21817.
- Zhou ZY, Wu SL, Qin LL et al. (2018) Modulating oxygen vacancies in Sn-doped hematite film grown on silicon microwires for photoelectrochemical water oxidation. *Journal of Materials Chemistry A* **6**(32): 15593–15602.
- Li ZS, Luo WJ, Zhang ML, Feng JY and Zou ZG (2013) Photoelectrochemical cells for solar hydrogen production: current state of promising photoelectrodes, methods to improve their properties, and outlook. *Energy & Environmental Science* **6**(2): 347–370.
- Zandi O and Hamann TW (2014) Enhanced water splitting efficiency through selective surface state removal. *Journal of Physical Chemistry Letters* **5**(9): 1522–1526.
- Liang Y and Messinger J (2014) Improving BiVO₄ photoanodes for solar water splitting through surface passivation. *Physical Chemistry Chemical Physics* **16**(24): 12014–12020.
- Li CC, Luo ZB, Wang T and Gong JL (2018) Surface, bulk, and interface: rational design of hematite architecture toward efficient photo-electrochemical water splitting. *Advanced Materials* **30**(30): article 1707502.
- Xi L, Chiam SY, Mak WF et al. (2013) A novel strategy for surface treatment on hematite photoanode for efficient water oxidation. *Chemical Science* **4**(1): 164–169.
- Barroso M, Pendlebury SR, Cowan AJ and Durrant JR (2013) Charge carrier trapping, recombination and transfer in hematite (α -Fe₂O₃) water splitting photoanodes. *Chemical Science* **4**(7): 2724–2734.
- Jang JW, Du C, Ye Y et al. (2015) Enabling unassisted solar water splitting by iron oxide and silicon. *Nature Communications* **6**: article 7447.

38. Tailor S, Rakoch AG, Gladkova AA *et al.* (2017) Kinetic features of wear-resistant coating growth by plasma electrolytic oxidation. *Surface Innovations* **6**(3): 150–158, <https://doi.org/10.1680/jsuin.17.00054>.
39. Xi L and Lange K (2018) Surface modification of hematite photoanodes for improvement of photoelectrochemical performance. *Catalysts* **8**(11): 497.
40. Yang X, Liu R, Du C *et al.* (2014) Improving hematite-based photoelectrochemical water splitting with ultrathin TiO₂ by atomic layer deposition. *ACS Applied Materials & Interfaces* **6**(15): 12005–12011.
41. Ye KH, Wang Z, Li H *et al.* (2018) A novel CoOOH/(Ti, C)-Fe₂O₃ nanorod photoanode for photoelectrochemical water splitting. *Science China Materials* **61**(6): 887–894.
42. Kim JY, Youn DH, Kang K and Lee JS (2016) Highly conformal deposition of an ultrathin FeOOH layer on a hematite nanostructure for efficient solar water splitting. *Angewandte Chemie International Edition in English* **55**(36): 10854–10858.
43. Zhang Y, Ji H, Ma W *et al.* (2016) Doping-promoted solar water oxidation on hematite photoanodes. *Molecules* **21**(7): 868.
44. Örnek M, Wang K, Xiang S *et al.* (2019) Molten salt synthesis of highly ordered and nanostructured hexagonal boron nitride. *Diamond and Related Materials* **93**: 179–186.
45. Jai Shree K and Das D (2019) Molten salt assisted growth of lead-free BCZT crystals: effects of synthesis conditions and sintering on structural and electrical properties. *Journal of Materials Science: Materials in Electronics* **30**(12): 11094–11107.
46. Dotan H, Sivula K, Gratzel M, Rothschild A and Warren SC (2011) Probing the photoelectrochemical properties of hematite (α -Fe₂O₃) electrodes using hydrogen peroxide as a hole scavenger. *Energy & Environmental Science* **4**(3): 958–964.
47. Gurudayal, Chee PM, Boix PP *et al.* (2015) Core-shell hematite nanorods: a simple method to improve the charge transfer in the photoanode for photoelectrochemical water splitting. *ACS Applied Materials & Interfaces* **7**(12): 6852–6859.
48. Zieliński A (2015) Application of different modes of nanoscale impedance microscopy in materials research. *Surface Innovations* **3**(3): 181–189, <https://doi.org/10.1680/jsuin.15.00006>.
49. Wen L, Wang X, Liu G *et al.* (2018) Novel surface coating strategies for better battery materials. *Surface Innovations* **6**(1–2): 13–18, <https://doi.org/10.1680/jsuin.17.00056>.
50. Song D, Guo WL, Zhang T *et al.* (2019) A free-standing CNTs film fabricated by pyrrole-modified chemical vapor deposition for capacitive deionization. *Surface Innovations* **7**(1): 10–17, <https://doi.org/10.1680/jsuin.18.00036>.
51. Szociński M and Darowicki K (2018) Impedance evaluation of coatings from biobased material. *Surface Innovations* **6**(4–5): 286–294, <https://doi.org/10.1680/jsuin.18.00016>.

How can you contribute?

To discuss this paper, please submit up to 500 words to the journal office at journals@ice.org.uk. Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editor-in-chief, it will be published as a discussion in a future issue of the journal.

ICE Science journals rely entirely on contributions from the field of materials science and engineering. Information about how to submit your paper online is available at www.icevirtuallibrary.com/page/authors, where you will also find detailed author guidelines.