Direct Z scheme-fashioned photoanode systems consisting of Fe$_2$O$_3$ nanorod arrays and underlying thin Sb$_2$Se$_3$ layers toward enhanced photoelectrochemical water splitting performance†

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An elegant Z-scheme-fashioned photoanode consisting of Fe$_2$O$_3$ nanorod arrays and underlying thin Sb$_2$Se$_3$ layers was rationally constructed. The photocurrent density of the Sb$_2$Se$_3$–Fe$_2$O$_3$ Z-scheme photoanode reached 3.07 mA cm$^{-2}$ at 1.23 V vs. RHE, three times higher than that of pristine Fe$_2$O$_3$ at 1.03 mA cm$^{-2}$. An obvious cathodic shift of the photocurrent onset potential of about 200 mV was also observed. The transient photovoltage response demonstrates that the suitable band edges ($E_{CB} \approx -0.4$ eV and $E_{VB} \approx 0.8$ eV) of Sb$_2$Se$_3$, match well with Fe$_2$O$_3$ ($E_{CB} \approx 0.29$ eV and $E_{VB} \approx 2.65$ eV), permitting the photoexcited electrons on the conduction band of the Fe$_2$O$_3$ to transfer to the valence band of Sb$_2$Se$_3$, and recombine with the holes therein, thus allowing a high concentration of holes to collect in the Fe$_2$O$_3$ for water oxidation. The transient absorption spectra further corroborate that the built-in electric field in the p–n heterojunction leads to a more effective separation and a longer lifetime of the charge carriers.

Introduction

Solar water splitting in photoelectrochemical (PEC) cells has drawn much attention for sustainable hydrogen production, owing to the limited reserve of fossil fuels and the increasing concern of environmental pollution.$^{1-3}$ Photoanodes for water oxidation are the rate-limiting step for the PEC overall water splitting efficiency. Hematite ($\alpha$-Fe$_2$O$_3$), an n-type semiconductor with a suitable narrow band gap (2.2 eV), has emerged as one of the most attractive photoanode candidates because of its low cost, (photo)-electrochemical stability, non-toxicity, and earth-abundance.$^{4-7}$ However, $\alpha$-Fe$_2$O$_3$ suffers from sluggish water oxidation kinetics, severe surface recombination, poor lifetimes of carriers, and short hole migration distance.$^{8-10}$ Great efforts such as surface passivation, nanostructure engineering, selective doping, and oxygen evolution cocatalysts have been made to improve its PEC performance.$^{11-17}$ However, the $\alpha$-Fe$_2$O$_3$ photoanode developed so far still shows a lower photocurrent density relative to its theoretical maximum of 12.6 mA cm$^{-2}$ at 1.23 V versus the reversible hydrogen electrode (vs. RHE) under AM 1.5G illumination (100 mW cm$^{-2}$).$^{11,12}$ Obviously, a single Fe$_2$O$_3$ component cannot satisfy the requirement of efficiently steering the spatial separation/transfer of electron–hole pairs for high PEC performance. The conjugation of coupling with other semiconductors has been proven an efficient method for solving the weaknesses above by providing a built-in electric field and optimal transportation path.$^{17}$ Type II heterostructures have been commonly built, allowing photogenerated electrons (holes) to be transferred from one semiconductor with a higher conduction (lower valence) band (CB) to that with a lower conduction (higher valence) band (VB).$^{18}$ However, the redox ability of this type of heterojunction is dynamically lowered after charge flowing, compared to individual components.

Z-scheme photocatalyst systems by mimicking natural photosynthesis in green plants are designed to employ two semiconductors with one H$_2$ production photocatalyst and one O$_2$ production photocatalyst.$^{19}$ The Z-scheme semiconductor heterojunction possesses a vectorial charge transfer feature,
i.e. the photo-induced electrons on the semiconductor with a lower conduction band (CB) potential will combine with the holes on another semiconductor with a higher valence band (VB) potential, and leave the electrons and holes in reduction-evolving and oxidation-evolving semiconductors, respectively. It simultaneously leads to superior charge separation and perseveration of the strong redox ability of each component. A direct Z-scheme free of electron mediators provides energetically favorable band alignment for facile migration of charge across the interface in the heterojunction region. While many \( \alpha \text{-Fe}_2\text{O}_3 \)-based Z-schemes of powder systems have been established, such as with \( \text{g-C}_3\text{N}_4 \), \( \text{Sb}_2\text{Se}_3 \), \( \text{Fe}_2\text{O}_3 \), they have well-constructed \( \text{Fe}_2\text{O}_3 \)-Z-scheme photoanodes been used for the PEC reaction, especially \( \text{Fe}_2\text{O}_3 \) nanorod array-based ones, which are beneficial for direct charge transfer to conductive substrates.

\( \text{Sb}_2\text{Se}_3 \) is a direct band gap \( (1.0 \text{--} 1.3 \text{ eV}), \) low-cost, and p-type semiconductor composed of non-toxic and earth-abundant elements, which possesses wide applications in solar selective and decorative coatings, as well as optical and thermoelectric cooling devices. \( \text{Sb}_2\text{Se}_3 \) possesses a high absorption coefficient of \( 10^5 \text{ cm}^{-1} \) in the visible range and has been selected as a promising photocathode for water splitting into \( \text{H}_2 \).

In this work, a direct Z-scheme-fashioned photocathode consisting of \( \text{Fe}_2\text{O}_3 \) nanorod arrays and underlining thin \( \text{Sb}_2\text{Se}_3 \) layers free of electron mediators was for the first time rationally constructed. The photocurrent density of the elegant \( \text{Sb}_2\text{Se}_3 \)-\( \text{Fe}_2\text{O}_3 \) Z-scheme photoanode reaches \( 3.07 \text{ mA cm}^{-2} \) at \( 1.23 \text{ V} \) vs. RHE, three times higher than that of pristine \( \text{Fe}_2\text{O}_3 \) at \( 1.03 \text{ mA cm}^{-2} \). An obvious cathodic shift of the photocurrent onset potential of about \( 200 \text{ mV} \) is also observed. The transient photocurrent (TPV) response demonstrates that the photoexcited electrons on the CB of the \( \text{Fe}_2\text{O}_3 \) transfer to the VB of \( \text{Sb}_2\text{Se}_3 \), and recombine with the holes therein, allowing a high concentration of the holes to be collected in the \( \text{Fe}_2\text{O}_3 \) for water oxidation. The transient absorption (TA) spectra corroborate that the built-in electric field in the p-n heterojunction leads to a more effective separation and longer lifetimes of the charge carriers. The selection of \( \text{Sb}_2\text{Se}_3 \) for the construction of the present Z-scheme photoanode system has several advantages: (1) the band edges \( (E_{\text{CB}} \sim \sim -0.4 \text{ eV} \text{ and } E_{\text{VB}} \sim -0.8 \text{ eV}) \) of \( \text{Sb}_2\text{Se}_3 \) match well with \( \text{Fe}_2\text{O}_3 \) \( (E_{\text{CB}} \sim -0.29 \text{ eV} \text{ and } E_{\text{VB}} \sim -2.65 \text{ eV}) \) for the Z-scheme; (2) \( \text{Sb}_2\text{Se}_3 \) is a promising light-absorbing material with the property of efficient charge separation; (3) the narrow bandgap allows the material to absorb as much as possible near-infrared light, extending the range of the light absorption; (4) \( \text{Sb}_2\text{Se}_3 \) possesses a much higher hole mobility up to \( 42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) compared to \( 0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) of \( \text{Fe}_2\text{O}_3 \). It allows the holes of \( \text{Sb}_2\text{Se}_3 \) to move fast and arrive on the interface of the \( \text{Sb}_2\text{Se}_3 \)-\( \text{Fe}_2\text{O}_3 \) prior to those of \( \text{Fe}_2\text{O}_3 \) recombining with the electrons of the \( \text{Fe}_2\text{O}_3 \), thus reducing the intrinsic charge recombination of \( \text{Fe}_2\text{O}_3 \); (5) \( \text{Sb}_2\text{Se}_3 \) shows an Ohmic junction with the underlying \( \text{FTO} \) with a small interface resistance, which allows the electrons from the \( \text{Sb}_2\text{Se}_3 \)-\( \text{Fe}_2\text{O}_3 \) to smoothly flow to the \( \text{FTO} \) substrate, in contrast to the high resistance of the pristine \( \text{Fe}_2\text{O}_3 \) with \( \text{FTO} \) due to the Schottky junction.

### Experimental section

#### Preparation of the \( \text{Fe}_2\text{O}_3/\text{Sb}_2\text{Se}_3 \) photoanode

The fabrication of the \( \text{Sb}_2\text{Se}_3/\text{Fe}_2\text{O}_3 \) Z-scheme photoanode starts with the deposition of a thin \( \text{Sb}_2\text{Se}_3 \) layer on a fluorine-doped tin oxide (FTO) substrate through thermal evaporation. The evaporator source is commercially available \( \text{Sb}_2\text{Se}_3 \) powder (antimony(III) selenide, AR, 99.9\%). The details of the process are as follows, the FTO glass (1 cm \( \times \) 2 cm) was cleaned with deionized (DI) water, acetone, and ethanol, and then was placed a few cm apart from the \( \text{Sb}_2\text{Se}_3 \) powder, inside a quartz tube. With \( \sim \approx 200 \text{ sccm} \) of high-purity Ar gas, the furnace temperature was raised to \( 550 \text{ °C} \). After 30 min of deposition, the furnace was allowed to cool to room temperature under the argon flow, resulting in a successfully uniform coating of \( \text{Sb}_2\text{Se}_3 \) on the FTO substrate. \( \text{FeOOH} \) nanorods were then vertically aligned on the \( \text{Sb}_2\text{Se}_3 \) nanosheets according to the reported methods by our group. More details were described previously. Finally, the \( \text{Sb}_2\text{Se}_3/\text{FeOOH} \) was heated at \( 550 \text{ °C} \) for 120 minutes in Ar atmosphere, and subsequently at \( 650 \text{ °C} \) for 15 min resulting in the formation of \( \text{Sb}_2\text{Se}_3/\text{Fe}_2\text{O}_3 \). As a comparison, the \( \text{Fe}_2\text{O}_3 \) nanorods were synthesized under the same growth conditions, except for the step of deposition of a thin \( \text{Sb}_2\text{Se}_3 \) layer on a FTO substrate through thermal evaporation.

#### Sample characterization

A FEI NOVA NanoSEM230 scanning electron microscope is employed to investigate the morphology of the samples. The crystal structure of the samples is identified by X-ray diffraction (XRD) (Ultima III, Rigaku) with Cu K\( \alpha \) radiation \( (k = 0.154 \text{ nm}) \). Transmission electron microscope (TEM) images are taken on a JEM 200CX TEM apparatus. X-ray photoelectron spectroscopy (XPS) is carried out on a Thermo Scientific K-Alpha instrument operating with an unmonochromatized Al K\( \alpha \) X-ray source, and the data are calibrated by the binding energy of the C 1s line at 283.6 eV. A Shimadzu UV-2550 spectrometer equipped with an integrating sphere is used to investigate the absorption properties of the samples. Electrochemical impedance spectroscopic (EIS) curves are measured by a PAR2273 workstation (Princeton Applied Research, USA) under a forward bias of 0.2 V and AM 1.5G illumination. Transient photovoltage (TPV) based on the lock-in amplifier measurement were carried out on a home-made system of Tengfeng Xie’s group of Jilin University, which researches the separation and kinetic behaviors of photogenerated charge carriers. The TPV measurement was performed under the illumination of a 355 nm laser pulse.

#### Photoelectrochemical property measurements

The photoelectrochemical (PEC) performance of the photoanodes is investigated in a three-electrode cell using an electrochemical analyzer (CHI-630D, Shanghai Chenhua) under AM 1.5G illumination. The electrolyte is a 1 M NaOH aqueous solution \( (pH 13.6) \). The \( \text{Fe}_2\text{O}_3 \) sample is used as the working electrode. A Pt foil and a saturated Ag/AgCl electrode are used
as the counter and reference electrode. The RHE potential is calculated following the formula $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \ pH + E_{\text{Ag/AgCl}}$, where $V_{\text{RHE}}$ is the converted potential versus RHE, and $E_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25^\circ \text{C}$. The active area of the Fe$_2$O$_3$ sample is fixed to 0.28 cm$^2$ using a black mask. A cyclic voltammetry method is adopted with a scan rate of 10 mV s$^{-1}$.

**Results and discussion**

The fabrication of the Sb$_2$Se$_3$/Fe$_2$O$_3$ Z-scheme photoanode starts with the deposition of a thin Sb$_2$Se$_3$ layer on a fluorine-doped tin oxide (FTO) substrate through thermal evaporation (Scheme 1). The FeOOH nanorod array was then hydrothermally grown onto the surface of the Sb$_2$Se$_3$/FTO, and subsequently annealed in an inert atmosphere to transfer into Fe$_2$O$_3$. The FE-SEM image from the top view of the FTO/Sb$_2$Se$_3$ film clearly shows the apparent difference of the surface of the FTO substrate before (Fig. 1a) and after (Fig. 1b and Fig. S1a†) deposition of the Sb$_2$Se$_3$. The formed Sb$_2$Se$_3$ layer consists of nanosheet-like particles with full coverage of the FTO substrate. FE-SEM elemental mapping and the EDX spectrum demonstrate the presence of Sb and Se elements (Fig. S2†).

The corresponding cross-sectional FE-SEM image reveals the thickness of the Sb$_2$Se$_3$ layer to be approximately 120 nm (Fig. 1c). Fig. 1d and e show the cross-section and top view of the vertical growth of the Fe$_2$O$_3$ nanorods on the surface of the Sb$_2$Se$_3$ layer, respectively. No morphological differences of the Fe$_2$O$_3$ nanorod array were observed between the Sb$_2$Se$_3$/FTO and the FTO (Fig. S1b and S1c†), which indicates that the presence of the Sb$_2$Se$_3$ layer has no effect on the rod-like crystal growth of Fe$_2$O$_3$. Fig. S3† shows the UV-Vis absorption spectra of Sb$_2$Se$_3$, Fe$_2$O$_3$, and the Sb$_2$Se$_3$/Fe$_2$O$_3$ film.

The XRD patterns clearly show the characteristic diffraction peaks of hematite (Fe$_2$O$_3$; JCPDS 79-0007) and FTO (Fig. S4†). No Sb$_2$Se$_3$ diffraction peaks are identified in the composite film, possibly due to the thinness of the Sb$_2$Se$_3$. The high-resolution XPS profiles of the Sb$_2$Se$_3$ film display the peak positions at binding energies of 530.1 and 538.5 eV, corresponding to Sb 3d$_{5/2}$ and Sb 3d$_{3/2}$, respectively (Fig. 2a). The Se 3d spectrum exhibits two peaks of Se 3d$_{5/2}$ and Se 3d$_{3/2}$ (Fig. 2b), consistent with Se$^{2-}$ in the case of Sb$_2$Se$_3$. The Fe 2p high-resolution XPS of both Fe$_2$O$_3$ and the Sb$_2$Se$_3$/Fe$_2$O$_3$ films can be fitted into Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ peaks, centered at binding energies of 723.5 eV and 711.4 eV, respectively, typical values for Fe$^{3+}$ in Fe$_2$O$_3$. Satellite peaks at 717.2 eV indexable to Fe$^{2+}$ were observed in both pristine Fe$_2$O$_3$ and Sb$_2$Se$_3$/Fe$_2$O$_3$, originating from the annealing process-inducing oxygen vacancy (Fig. 2c). The O 1s peak can be assigned to two main constituent peaks at 528.9 and 530.4 eV, corresponding to the Fe–O band and OH$^-$, respectively (Fig. 2d).

The PEC performance of the Sb$_2$Se$_3$/Fe$_2$O$_3$ photoanode is dependent on the film thickness of the Sb$_2$Se$_3$ layer (Fig. S5†). 15 min deposition cannot obtain an observable film due to its too thin thickness (Fig. S5b†). It may result in a non-consecutive Sb$_2$Se$_3$ layer, incompletely covering the FTO substrate, and subsequently leading to the reverse reaction, decreasing the PEC performance. 60 and 90 min deposition generates ~300 nm and ~500 nm thick Sb$_2$Se$_3$ films (Fig. S5d and S5e†), in which the holes need to move down a long pathway to recombine with the electrons of Fe$_2$O$_3$, also depressing the

![Scheme 1](image1.png) Schematic illustration of the fabrication process of Sb$_2$Se$_3$/Fe$_2$O$_3$.

![Fig. 1](image2.png) (a) FE-SEM image of FTO. (b and c) Top- and cross-sectional view FE-SEM images of Sb$_2$Se$_3$ with 30 min deposition on the FTO substrate, respectively. (d and e) Cross-sectional and top-view SEM images of Sb$_2$Se$_3$/Fe$_2$O$_3$, respectively.

![Fig. 2](image3.png) High-resolution XPS (a) Sb 3d, (b) Se 3d signal peak of Sb$_2$Se$_3$, (c) Fe 2p, and (d) O 1s spectra of Fe$_2$O$_3$ and Sb$_2$Se$_3$/Fe$_2$O$_3$. 

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PEC performance. The Sb$_2$Se$_3$/Fe$_2$O$_3$ with 30 min deposition of about 120 nm thickness exhibits a maximum photocurrent density of 3.03 mA cm$^{-2}$ at 1.23 V vs. RHE, about three times higher than pristine Fe$_2$O$_3$ (1.09 mA cm$^{-2}$ at 1.23 V vs. RHE) (Fig. S5c† and Fig. 3a). The corresponding onset potential also obviously cathodically-shifts about 200 mV from 1.00 to 0.80 V. In addition, the Sb$_2$Se$_3$/Fe$_2$O$_3$ photoanode displays a significantly enhanced incident photon-to-current conversion efficiency (IPCE) of 48.5% at 380 nm, double that of pristine Fe$_2$O$_3$ at 22.9% (Fig. 3b). While the Sb$_2$Se$_3$ film alone is a p-type semiconductor which behaves as an insulator under positive bias, the increase of the PEC performance can be ascribed to the unique charge separation mechanism of the Z-scheme system. Furthermore, the Sb$_2$Se$_3$/Fe$_2$O$_3$ photoanode exhibits considerable stability, and the photocurrent only decreased by 12% after 5.6 h of continuous illumination (Fig. S6f).

The TPV responses for the Sb$_2$Se$_3$/Fe$_2$O$_3$ and Fe$_2$O$_3$ with 355 nm laser illumination were detected with a logarithmical time scale through light illumination from top to bottom electrodes (Fig. 4). The TPV spectra of both photoanodes reveal a positive sign response, implying that the holes move toward and accumulate on the top electrode, i.e. the Fe$_2$O$_3$ side. The Sb$_2$Se$_3$/Fe$_2$O$_3$ displays an almost three-times stronger intensity of TPV signal than the pristine Fe$_2$O$_3$, which can be ascribed to the strong charge carrier separation ability of this structure and high concentration of holes collected in the Fe$_2$O$_3$ with a long surviving time. The Z-scheme mode of the Sb$_2$Se$_3$/Fe$_2$O$_3$ can be schematically illustrated (Fig. 4b). Under light illumination, both Sb$_2$Se$_3$ and Fe$_2$O$_3$ are photoexcited to generate electron–hole pairs. The electrons in the CB of the Fe$_2$O$_3$ shift to the VB of the Sb$_2$Se$_3$ and recombine with the holes therein. The depletion of the electrons of Fe$_2$O$_3$ restrains the intrinsic charge recombination of the Fe$_2$O$_3$, allowing the longer survival time of the holes, which are highly oxidative, and can readily perform oxygen evolution reactions at the electrode/electrolyte interface. Meanwhile, the concentrated electrons in the Sb$_2$Se$_3$ side are highly reductive, which then transfer to the counter electrode to efficiently drive hydrogen production.

To explore the impact of Sb$_2$Se$_3$ on the photogenerated charge carrier dynamics, the TA spectra of the pristine Fe$_2$O$_3$ and Sb$_2$Se$_3$/Fe$_2$O$_3$ on a 0–6393 ps time scale were probed after 350 nm laser excitation (Fig. 5a and b). Across the probed wavelength range, both the films display two excited state absorption (ESA) signal peaks, a weak one at ~500 nm and a strong one at ~575 nm. Two peaks showing a similar time-decay tendency derive from the absorption of photo-generated holes with different energy levels. The ESA signal at the latter was the main spectroscopic feature in the hematite sample, which can be attributed to the absorption of photo-generated holes. The TA spectrum of Sb$_2$Se$_3$/Fe$_2$O$_3$ exhibits a higher intensity and a slow time-dependent decay rate within the monitored time range, compared with the Fe$_2$O$_3$. It suggests that the Sb$_2$Se$_3$/Fe$_2$O$_3$ possesses more photogenerated holes and a lower recombination rate of carriers, further confirming the Z-scheme structure. The time profiles of the TA probed at 575 nm were fitted by a two-exponential function in Fig. 5c. The Sb$_2$Se$_3$/Fe$_2$O$_3$ shows a relatively slower decay than the Fe$_2$O$_3$ in the 9–18 ps windows, and the lifetimes for the Fe$_2$O$_3$ and Sb$_2$Se$_3$/Fe$_2$O$_3$ were detected 2.1 ps and 3.7 ps, respectively, indicating that the Z-scheme heterostructure is beneficial for separation of the photogenerated charges, and maintaining the separation long enough for the surface reaction of water oxidation. The open-circuit photovoltage (OCPV) calculated from the difference of the open-circuit potentials between dark and illumination reveals that the OCPV values of Sb$_2$Se$_3$/Fe$_2$O$_3$ was higher in comparison with the pristine Fe$_2$O$_3$, additionally demonstrating the improvement of the charge separation efficiency (Fig. S7f).
Solid-state current–voltage ($J-V$) characterization was conducted. FTO and Ag were used as the front and back contacts, respectively. While the pristine Fe$_2$O$_3$ film displays rectifying characteristics to form a Schottky junction with FTO, the linear $J-V$ feature of the FTO/Sb$_2$Se$_3$ indicates an Ohmic junction formation of the Sb$_2$Se$_3$ with FTO. The steep slope close to that of the FTO implies a small contact resistance at the interface of the Sb$_2$Se$_3$/FTO, which allows the electrons from the Sb$_2$Se$_3$ to smoothly flow to the FTO substrate. The increased slope of the Sb$_2$Se$_3$/Fe$_2$O$_3$ compared with pristine Fe$_2$O$_3$ clearly states that more electrons in the former transfer to the FTO substrate in comparison with the latter. The electrochemical impedance spectroscopy (EIS) semicircle for the Sb$_2$Se$_3$/Fe$_2$O$_3$ photoanode displays a smaller diameter than Fe$_2$O$_3$, also demonstrating that the interface charge transfer rate increases after combination of the thin Sb$_2$Se$_3$ layer (Fig. 6b).

Conclusion

A novel direct Sb$_2$Se$_3$/Fe$_2$O$_3$ Z-scheme system was successfully constructed through a vapor deposition process of a thin layer of Sb$_2$Se$_3$ on a FTO substrate, followed by growth of Fe$_2$O$_3$. The elegant Z-scheme Sb$_2$Se$_3$/Fe$_2$O$_3$ reaches a photocurrent density of 3.03 mA cm$^{-2}$ at 1.23 V vs. RHE, and shows an extraordinary cathodic shift of the onset potential of about 200 mV. The enhanced PEC performance is ascribed to the unique charge separation and transfer mechanism. This study may not only inspire further development of new direct solid-state Z-scheme systems for solar water splitting with superior performance, but also could be significant in meeting the demands of environmental domains.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by 973 Programs (No. 2014CB239302), NSF of China (No. 21773114 and 21473091), NSF of Jiangsu Province (No. BK20171246). Additionally, the TPV measurement was greatly supported by Prof. Tengfeng Xie of Jilin University, China.

Notes and references


