TiO₂ Nanosheet Arrays with Layered SnS₂ and CoOₓ Nanoparticles for Efficient Photoelectrochemical Water Splitting

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Abstract
Converting solar energy into sustainable hydrogen fuel by photoelectrochemical (PEC) water splitting is a promising technology to solve increasingly serious global energy supply and environmental issues. However, the PEC performance based on TiO₂ nanomaterials is hindered by the limited sunlight-harvesting ability and its high recombination rate of photogenerated charge carriers. In this work, layered SnS₂ absorbers and CoOₓ nanoparticles decorated two-dimensional (2D) TiO₂ nanosheet array photoelectrode have been rationally designed and successfully synthesized, which remarkably enhanced the PEC performance for water splitting. As the result, photoconversion efficiency of TiO₂/SnS₂/CoOₓ and TiO₂/SnS₂ hybrid photoanodes increases by 3.6 and 2.0 times under simulated sunlight illumination, compared with the bare TiO₂ nanosheet arrays photoanode. Furthermore, the TiO₂/SnS₂/CoOₓ photoanode also presented higher PEC stability owing to CoOₓ catalyst served as efficient water oxidation catalyst as well as an effective protectant for preventing absorber photocorrosion.

Keywords: TiO₂ nanosheet arrays, Tin sulfide, Heterojunction, Photocatalysis, Photoelectrochemical water splitting

Background
Nowadays, with the emergence of non-renewable fossil fuel concerns and environmental pollutions caused by conventional fossil fuel combustion, there is an urgent need to seek a sustainable clean, high photostability, non-toxicity, low cost, and environmental strategy for the generation of clean fuels [1–4]. Photoelectrochemical (PEC) water splitting is well recognized as an ideal alternative to explore attractive sustainable energy sources and technologies since the initial report on PEC water splitting in 1972 [5–7]. Photogenerated electron-hole pairs are spatially separated and transferred and subsequently participates in the water-splitting processes. Titanium dioxide (TiO₂) is a promising semiconductor material candidate owing to its intrinsic advantages of high chemical stability, favorable band edge positions, earth-abundant, and nontoxicity [8–11]. However, TiO₂, as a large band-gap semiconductor (ca. 3.2 eV), only absorb the ultraviolet (UV) light. Moreover, its high rate of photoinduced charge carrier recombination and low photoelectric-conversion efficiency limit substantially the practical photocatalytic activity [12–15]. It is highly desirable to construct the efficient geometric nanostructures for improving photoconversion efficiency of PEC water splitting, such as nanowires [16], nanorods [17], nanotubes [18], nanobelts [19], and nanofibers [20]. Recently, different morphological TiO₂ materials have been applied to drive water splitting by using sunlight [21–23]. However, the water-splitting efficiency is unsatisfactory owing to the accompaniment of grain boundary effect and deficient specific surface area in these nanostructures. Therefore, two-dimensional (2D) vertically aligned TiO₂ nanosheet array structure has attracted intense interest in the PEC water splitting. Compared to other one-dimensional (1D) nanostructures, anatase TiO₂ nanosheet arrays with high proportion of exposed [001] facets have been proven to be an active phase when used as a photocatalyst [24–27]. Besides, the vertically grown TiO₂ nanosheet arrays

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provide an unobstructed transportation pathway for electron transfer to substrates, and the high photocatalytic activity [001] facet-dominated anatase TiO2 has an extraordinary advantage on the separation of photogenerated charge carriers.

Nevertheless, the practical applications of TiO2-based water splitting systems are limited because not only the narrow light absorption region resulted from large bandgap, but also its low quantum efficiency and high photogenerated charge carriers recombination rate. Therefore, considerable efforts have been paid to improve the solar light absorption ability and conversion efficiency, for instance, ions doping [28, 29], coupling metal plasmonic nanostructures [30–32], or photosensitization of semiconductors with small bandgap [33–35]. Alternatively, heterogeneous junction constructed with narrow-bandgap photosensitizer has been widely recognized to be an available method to promote efficiently charge carrier separation and extend light absorption ability of the photocatalytic materials [36–39]. Typically, tin (IV) disulfide (SnS2) with a suitable bandgap energy of 2.4 eV has attracted significant attention for its remarkable optical and electrical properties. As a member of the layered metal chalcogenide semiconductor, 2D SnS2 nanosheets have been demonstrated as an attractive photocatalyst in PEC solar water splitting because of the effective light absorption ability, short carrier transport distances, and large specific surface area [40–43]. Alternatively, the type II heterojunction combined SnS2 with TiO2 has been considered as an efficient route to enhance significantly the light absorption ability as well as improve charge separation efficiency [44, 45]. Furthermore, oxygen evolution, which is the four electrons transfer reaction, is usually considered to be a kinetics controlling step. The water-splitting efficiency can be further enhanced through the integration of cobalt-based catalysts; the catalyst acts as active sites for water oxidation, provides a lower over-potential, and prevents photocorrosion in the water-splitting process [46–48].

In this work, vertically aligned TiO2 nanosheet arrays were applied in TiO2/SnS2/CoOx heterojunction photoelectrodes for PEC water splitting. CoOx nanoparticles, which are known to be excellent water oxidation catalysts, were loaded on TiO2/SnS2 nanosheet arrays to construct triple hybrid photoanodes. The hybrid semiconducting photoanodes were fabricated by simple hydrothermal or solvothermal process, and the detailed prepared method characterization was discussed subsequently. With CoOx loading, the performance of TiO2/SnS2 photoanode was improved markedly. TiO2/SnS2/CoOx composite nanosheet array photoanode exhibits remarkably improved performances for the PEC water splitting.

Methods

Chemicals and Reagents

Tetrabutyl titanate (C16H36O4Ti, Aladdin Chemistry Co., Ltd., ≥ 99%), ammonium hexafluorotitanate ((NH4)2TiF6, Sinopharm Chemical Reagent Co., Ltd., AR), tin (IV) chloride pentahydrate (SnCl4·5H2O, Sinopharm Chemical Reagent Co., Ltd., ≥ 99%), thioacetamide (CH3CSNH2, Sinopharm Chemical Reagent Co., Ltd., ≥ 99%), cobalt (II) acetate tetrahydrate (Co (CH3COO)2·4H2O, Sinopharm Chemical Reagent Co., Ltd., ≥ 99.5%), ammonium solution (NH2H2O, 25 wt%), concentrated hydrochloric acid (36–38 wt%), acetone (AR), and ethanol (AR) were obtained from Tianjin Chemical Reagents Plant, China. All chemicals were used as received without any further purification.

Preparation of TiO2 Nanosheet Arrays

TiO2 nanosheet array photoelectrodes were fabricated onto fluorine-doped tin oxide (FTO)-coated conductive glass substrates using a facile hydrothermal process [49]. In a typical procedure, 10 ml of concentrated hydrochloric acid and 10 ml of deionized (DI) water (18.25 MΩ cm) were mixed under strong stirring at room temperature. Subsequently, 0.4 ml of tetrabutyl titanate was dropped to the mixed solution and stirred vigorously for 5 min to obtain a transparent solution. Next, 0.2 g of ammonium hexafluorotitanate ((NH4)2TiF6) was added and further stirred for 10 min. The as-prepared mixture precursor solution was transferred to a Teflon-lined autoclave (100 ml in volume). The FTO substrates (14 Ω/square) were ultrasonically cleaned with acetone, ethanol, and DI water in sequence and dried prior to the experiment. Then, the conductive FTO substrate was placed facing down into the autoclave obliquely. The autoclave was conducted at 170 °C for 10 h and then naturally cooled down. After the synthesis, the sample was washed with DI water and air-dried at room temperature. To increase the crystallinity of TiO2 nanosheet arrays, the as-prepared samples were annealed in air atmosphere at 550 °C for 3 h.

Fabrication of TiO2/SnS2 Hybrid

The hybrid TiO2/SnS2 nanosheet arrays can be fabricated as described in the following preparation details; 2D SnS2 were grown on TiO2 nanosheet arrays by low-temperature solvothermal method. A mixture solution containing 10 ml absolute ethanol, 10 mM SnCl4, and 30 mM thioacetamide was magnetically stirred and prepared in the solvothermal process. Then FTO substrates covered with TiO2 nanosheet arrays were vertically inserted into the precursor solution. During the deposition, the temperature was heated at 80 °C for 1 h. After cooling down, the fabricated samples were rinsed by
absolute ethanol and DI water several times and annealed in Ar atmosphere at 250 °C for 2 h.

Synthesis of TiO$_2$/SnS$_2$/CoO$_x$ Photoelectrodes

Finally, CoO$_x$ nanoparticles were loaded on TiO$_2$/SnS$_2$ nanosheet arrays by a modified solvothermal method reported previously [50, 51]. In detail, 0.25 ml ammonium solution was dropwise added into 18 ml ethanol solution containing 5 mM cobalt acetate under vigorous stirring. Subsequently, the as-prepared solution was transferred into a 25-ml autoclave and two pieces of TiO$_2$/SnS$_2$ electrodes were obliquely placed into the bottom of the autoclave. Next, the autoclave was heated and kept at 120 °C for 1 h. After the solvothermal process finished, the obtained TiO$_2$/SnS$_2$/CoO$_x$ photoelectrodes were thoroughly rinsed with DI water and dried in air.

Characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Discover X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). Scanning electron microscopic images were obtained using a FEI NovaSEM-450 field emission scanning electron microscope (SEM) equipped with an Oxford X-max20 energy dispersive X-ray spectrometer (EDS). The optical absorption spectra were recorded on a Perkin Elmer Lambda 750 coupled with a 60-mm integrating sphere attachment. Transmission electron microscopy (TEM) images were recorded in a FEI Tecnai F20 transmission electron microscope with operating voltage 200 kV. Raman spectra were recorded on a LabRAM HR Evolution Horiba JY high-resolution Raman spectrometer with a wavelength of 633 nm as the excitation source. X-ray photoelectron spectroscopy (XPS) was recorded by a Thermo Fisher Scientific- Escalab 250Xi X-ray photoelectron spectrometer with a monochromatic Al Kα irradiation.

PEC Measurements

PEC measurements were carried out using a standard three-electrode cell with the fabricated electrode used as a working electrode, a Pt wire used as a counter electrode, and Ag/AgCl used as reference electrode at an electrochemical workstation (CorrTest, CS350). All PEC measurements were performed with the effective surface area of the working electrode kept as 2 cm$^2$ and illuminated in 0.5 M Na$_2$SO$_4$ (pH = 6.8) electrolyte. The electrode potential of the working electrodes (vs. Ag/AgCl) can be converted to the reversible hydrogen electrode (RHE) potential by the Nernst equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{pH} + E^\theta_{\text{Ag/AgCl}}$, where $E_{\text{RHE}}$ is the converted potential vs. RHE, $E^\theta_{\text{Ag/AgCl}}$ is 0.1976 V at 25 °C, and $E_{\text{Ag/AgCl}}$ is the applied potential against the Ag/AgCl reference electrode. The photocurrent density-potential ($i$-$v$) measurements were carried out at a scan rate of 10 mV/s under the solar simulator (71S0503A) using a 150 W xenon lamp equipped with an AM 1.5G filter as illumination source (100 mW/cm$^2$). The amperometric photocurrent-time ($i$-$t$) curves were evaluated with light irradiation on/off cycles under an applied potential of 1.23 V vs. RHE. Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range of 0.01–100 kHz and an AC voltage amplitude of 5 mV at an open-circuit potential.

Results and Discussion

The process for fabrication of the TiO$_2$/SnS$_2$/CoO$_x$ nanosheet array photoanode is illustrated (Additional file 1: Scheme S1). The morphology and structure images of the pristine TiO$_2$ and hybrid nanosheet array photoelectrodes are displayed in Fig. 1 by SEM and TEM observation. In order to ensure that each photo-electrode has an equal density of nanosheet arrays, the pristine TiO$_2$ nanosheet array photoelectrode was prepared in one-pot hydrothermal synthesis. Obviously, the surface of FTO substrate is uniformly covered with smooth TiO$_2$ nanosheet arrays and the thickness of nanosheet is typically about 280 nm as observed from Fig. 1a. In addition, the cross-section image shows that the film is composed of vertically aligned TiO$_2$ nanosheet arrays and the height of nanosheet arrays is about 1 μm (Additional file 1: Figure S1). It is apparent that the entire surfaces of TiO$_2$ nanosheet arrays become rough after the deposition of SnS$_2$ layer (Fig. 1b). With the loading of CoO$_x$ nanoparticles, the SEM picture of the nanosheet arrays has almost no significant difference owing to CoO$_x$ nanoparticle high dispersion and low concentration, as shown in Fig. 1c. However, EDS reflect the presence of CoO$_x$ nanoparticles on the surface of hybrid (Additional file 1: Figure S2). As revealed by Fig. 1d, HRTEM images further reveal that the nanosheets have a single-crystalline structure, which clearly shows the lattice fringes of 0.23 nm, corresponding to the $d$-spacing values of the anatase TiO$_2$ (001) planes. In the TEM image in Fig. 1e of an individual TiO$_2$/SnS$_2$ heterojunction nanosheet, it clearly illustrates that the TiO$_2$ nanosheets are covered by the SnS$_2$ outlayer. As can be seen in the HRTEM images, the lattice $d$-spacing is 0.32 nm, corresponding to (100) fringe plane of hexagonal SnS$_2$. As seen in Fig. 1f, the HRTEM image shows that CoO$_x$ nanoparticles are evenly dispersed on the surface of TiO$_2$/SnS$_2$ nanosheet arrays.

XRD measurement was used to identify the crystallinity and crystal structure of hybrid photoelectrodes. As described in Fig. 2a, all of the diffraction peaks are readily indexed to the typical anatase TiO$_2$ (JCPDS 21-1272) and hexagonal SnS$_2$ (JCPDS 21-1231) apart from the FTO substrate peaks, which revealed the coexistence of

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TiO$_2$ and SnS$_2$ in the hybrid electrodes. However, diffraction peaks corresponding to CoO$_x$ (CoO or Co$_3$O$_4$) were not evidently detected, probably because of their low concentration and high dispersion on the hybrid electrode surface. To further verify the crystalline phase of hybrid photoelectrodes, an additional Raman spectrum was performed (Additional file 1: Figure S3). The Raman spectrum for the TiO$_2$ nanosheet arrays shows characteristic bands at around 144, 394, 514, and 637 cm$^{-1}$, corresponding to the Raman active modes in anatase TiO$_2$ with the O–Ti–O vibration of $E_g$, $B_{1g}$, $A_{1g}$, and $E_g$, respectively [52–54]. The same Raman scattering peaks are observed for the TiO$_2$/SnS$_2$ sample. After the formation of TiO$_2$/SnS$_2$ heterojunction, the $A_{1g}$ mode Raman peak of hexagonal SnS$_2$ at 314 cm$^{-1}$ is observed, verifying the successful introduction of SnS$_2$ layers in the hybrid electrode [55, 56]. The optical absorption spectra of bare TiO$_2$, TiO$_2$/SnS$_2$, and TiO$_2$/SnS$_2$/CoO$_x$
nanosheet arrays are presented in Fig. 2b. The pristine TiO₂ nanosheet array sample shows the characteristic absorption band located at 380 nm, while the TiO₂/SnS₂ hybrid appears a wide visible light absorption edge, which was attributed to the excellent light absorption ability of SnS₂ layer. The corresponding optical energy gap can be subsequently calculated using the following equation: $\alpha h\nu = A(h\nu - E_g)^n$, where $\alpha$, $A$, $h\nu$, and $E_g$ are the optical absorption coefficient, a constant, incident photon energy, and the bandgap, respectively. In addition, $n$ is equal to 1/2 for direct bandgap semiconductors while $n$ is equal to 2 for indirect bandgap semiconductors. The energy gap for the bare TiO₂ and pristine SnS₂ was estimated to be 3.2 and 2.4 eV (Additional file 1: Figure S4), respectively [57–60]. After decorating with CoOₓ, the absorption spectra of TiO₂/SnS₂/CoOₓ nanosheet arrays display similar light absorption bands (ca. 560 nm) to TiO₂/SnS₂ hybrid, which implies absent additional bandgap transition resulted from the introduction of CoOₓ catalysts.

To further investigate the valence state and chemical environment, XPS characterization of all the photoelectrodes was measured. As illustrated in Fig. 3a, XPS survey spectrum of the TiO₂/SnS₂/CoOₓ hybrid proves the presence of Ti, O, Sn, S, and Co elements. Figure 3b shows the high-resolution XPS spectrum of Ti 2p. The two peaks located at 458.6 and 464.2 eV are ascribed to Ti 2p₃/₂ and Ti 2p₁/₂, respectively, indicating the presence of Ti⁴⁺ species. Figure 3c shows the binding energy of the O 1s core level around 531.4 eV, which is corresponding to the lattice oxygen atoms of Ti–O–Ti bond. Two symmetric peaks at the binding energy of 486.47 (Sn 3d₅/₂) and 494.88 eV (Sn 3d₃/₂) are shown in Fig. 3d, which confirmed the existence of Sn⁴⁺ in the hybrid electrodes. Meanwhile, the peaks located at 161.2 and 162.3 eV are corresponding to S 2p₃/₂ and S 2p₁/₂ states (Fig. 3e), demonstrating the formation of the SnS₂ outer layer. Furthermore, two distinct peaks located at 796.5 (Co 2p₁/₂) and 780.6 eV (Co 2p₃/₂) with the satellite peaks are presented in Fig. 3f, which is ascribed to the coordination of both the Co³⁺ and Co²⁺. That is a demonstration, in fact, that the water oxidation catalyst CoOₓ (CoO and Co₃O₄) is definitely assembled on the surface of hybrid photoelectrodes. In addition, the atomic percentage of Co element was estimated to be about 4.3 at% based on XPS analysis in the TiO₂/SnS₂/CoOₓ nanosheet arrays. As a result, the diffraction peak performed on the previous XRD measurement is not detected because of the low concentration of CoOₓ nanoparticles in the hybrid photoelectrodes.

To investigate the PEC performance of these photoelectrodes, the nanosheet arrays were fabricated into the working electrode in a standard three-electrode electrochemical system. Linear sweep voltammetry (LSV) curves of the pristine TiO₂, TiO₂/SnS₂, and TiO₂/SnS₂/CoOₓ nanosheet array photoelectrodes are shown in Fig. 4a, in an applied potential range of 0.2 to 1.3 V vs. RHE. Obviously, dark scan LSV curves show an almost
negligible current density for all samples. Nevertheless, the photocurrent of TiO$_2$ electrode is remarkably enhanced after coated with SnS$_2$ photosensitizer and then further improved when deposited CoO$_x$ catalysts under simulated sunlight illumination. Furthermore, the onset potential of photocurrent for TiO$_2$ nanosheet arrays is negatively shifted for TiO$_2$/SnS$_2$ and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet array electrodes, due to the negative shift of Fermi level and low carrier recombination rate by SnS$_2$ outlayer and CoO$_x$ catalysts. In addition, the photoconversion efficiency ($\eta$) of pristine TiO$_2$ and TiO$_2$/SnS$_2$ and TiO$_2$/SnS$_2$/CoO$_x$ photoelectrodes are calculated using the following equation:

$$\eta = \frac{I (E_\text{rev} - V)}{J_{\text{light}}}$$

where $I$ is the photocurrent density (mA/cm$^2$), $E_\text{rev}$ is 1.23 V vs. RHE for the water splitting, $V$ is the measured potential vs. RHE, and $J_{\text{light}}$ is the irradiance intensity of incident light (100 mW/cm$^2$). Figure 4b displays the photoconversion efficiency plots with applied potential from 0.2 to 1.3 V vs. RHE under light radiation. The pristine TiO$_2$ photoelectrode displays the optimal photoconversion efficiency of 0.12% at 0.70 V vs. RHE. Remarkably, TiO$_2$/SnS$_2$/CoO$_x$ and TiO$_2$/SnS$_2$ nanosheet array photoelectrodes exhibit the highest efficiency of 0.44% and 0.24%, about 3.6 and 2.0 times higher compared with pristine TiO$_2$ nanosheet arrays, respectively. The chopped light photoresponse ($i-t$) curves of the photoanodes measured at 1.23 V vs. RHE, as shown in Fig. 4c. The fast rise-fall changing of the photocurrent density indicates that the charge transport in the photoelectrodes is very quick. In contrast, TiO$_2$/SnS$_2$/CoO$_x$ photoelectrode exhibits a higher photocurrent density of 1.05 mA/cm$^2$, 3.38-fold enhancement compared to bare TiO$_2$ nanosheet arrays at the same applied bias potential. This is mainly due to the fact that SnS$_2$ outlayer and CoO$_x$ catalysts would effectively extend the optical
absorption range, accelerate the effective transfer of charge carriers and reduce the charge carrier recombination, thus enhanced photocurrent density. In order to further study the interface charge transport process of photoanodes, electrochemical impedance spectrum (EIS) investigations of the TiO$_2$, TiO$_2$/SnS$_2$, and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays are shown in Fig. 4d, measured at open circuit potential under light illumination (100 mW/cm$^2$). Here, $R_s$ denotes the contact resistances of the electrochemical device, CPE denotes the capacitance phase element, and $R_{ct}$ denotes the interfacial charge transfer resistance. The values of $R_{ct}$ are calculated to be 3780, 2460, and 1650 $\Omega$ for TiO$_2$, TiO$_2$/SnS$_2$, and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet array electrodes, respectively. Clearly, a smaller arc radius was observed for TiO$_2$/SnS$_2$/CoO$_x$ as compared to those of TiO$_2$ and TiO$_2$/SnS$_2$ hybrid photoelectrodes. It is noteworthy that the reduction of Nyquist arc radius reflects that an effective separation and fast charge transfer of photoinduced charge carriers have occurred at the hetero-junction interface. These results significantly indicate that the introduction of SnS$_2$ and CoO$_x$ obviously improve the TiO$_2$ PEC properties.

On the other hand, the photocurrent stability is also very important to further confirm the PEC performance of water splitting. In order to show the photostability of these photoelectrodes, the long-term stability photostability measurements for TiO$_2$/SnS$_2$ and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays were carried out for 2 h under the continuous simulated sunlight illumination. As presented in Fig. 5, the decrease in photocurrent density of TiO$_2$/SnS$_2$ and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet array photoanode is about 54.0% and 18.3% in the following measurement period, respectively. The achieved good stability indicates that the photocorrosion process was restrained after the decoration of CoO$_x$ catalysts, and TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays still retain the primitive structure under simulated sunlight illumination after long-term PEC water splitting process.

Based on the above results, a possible charge transfer mechanism for the hybrid TiO$_2$/SnS$_2$/CoO$_x$ nanosheet array photoelectrode is proposed in Fig. 6. When the hybrid heterojunction is irradiated by sunlight, as a narrow photosensitizer with excellently high absorption, SnS$_2$ is readily excited to generate photoinduced charge carriers under illumination. Eventually, photoinduced electrons on the conduction band (CB) of SnS$_2$ can be efficiently transferred to the CB of TiO$_2$ nanosheets by the use of the type-II band alignment (Additional file 1: Figure S5), subsequently transmitted to counter electrode through the extra circuit to drive water splitting reactions. Simultaneously, photogenerated holes are transported to the opposite direction from the valence band (VB) of TiO$_2$. 

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**Fig. 5** Steady-state photocurrent density curves of the TiO$_2$/SnS$_2$ and TiO$_2$/SnS$_2$/CoO$_x$ photoelectrodes measured at 1.23 V vs. RHE

**Fig. 6** Schematic illustration of device configuration and proposed energy band structure mechanism of TiO$_2$/SnS$_2$/CoO$_x$ photoelectrode
Conclusions

In summary, we have successfully fabricated a novel 2D architecture heterojunction TiO$_2$/SnS$_2$/CoO$_x$ photoanode for PEC water splitting. This ternary hybrid TiO$_2$/SnS$_2$/CoO$_x$ photoanode exhibits significantly enhanced photocurrent density. The photoconversion efficiency of TiO$_2$/SnS$_2$/CoO$_x$ is about 1.8 and 3.6 times higher than that of the TiO$_2$/SnS$_2$ and pristine TiO$_2$ photoelectrodes, respectively. The enhanced PEC performance can be attributable to improve light absorption ability and reduce photo-generated carrier recombination as a result of the type-II heterojunction constructed between TiO$_2$ nanosheet and layered SnS$_2$. Furthermore, CoO$_x$ catalysts further accelerate surface water oxidation kinetics, promote efficient charge separation, and improve PEC stability. This work provides new insight and potential construct of efficient PEC practical applications toward sustainable solar-driven water splitting systems.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s11671-019-3168-7.

Additional file 1: Scheme S1. A schematic illustration of the formation process for the TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays on FTO substrates. Figure S1. Cross-sectional SEM images of (a) pristine TiO$_2$, (b) TiO$_2$/SnS$_2$, and (c) TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays on FTO substrates, respectively. Figure S2. EDS pattern of the TiO$_2$/SnS$_2$/CoO$_x$ nanosheet arrays. Figure S3. Raman spectra of pristine TiO$_2$ and TiO$_2$/SnS$_2$ nanosheet arrays. Figure S4. Optical bandgap of (a) bare TiO$_2$ nanosheet arrays and (b) pristine SnS$_2$ samples calculated from the Kubelka-Munk equation. Figure S5. (a) UPS spectra of SnS$_2$ and (b) XPS valence band spectra of the TiO$_2$/SnS$_2$ photoanode. (DOCX 23095 kb)

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Funding

This work was supported by the National Natural Science Foundation of China (Grant No. 11574081), and the Changsha Planning Project of Science and Technology (kq1901089).

Availability of Data and Materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Competing Interests

The authors declare that they have no competing interests.

Received: 24 June 2019 Accepted: 30 September 2019
Published online: 11 November 2019
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