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# TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanorods vertically aligned on carbon fiber papers for enhanced photoelectrochemical performance

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Semiconductor heterostructures are regarded as an efficient way to improve the photocurrent in photoelectrochemical cell-type (PEC) photodetectors. To better utilize solar energy, TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> arrays vertically aligned on carbon fiber papers were synthesized *via* a hydrothermal route with a two-step method and used as photoanodes in a self-powered photoelectrochemical cell-type (PEC) photodetector under visible light. TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> heterostructures exhibit a stable photocurrent of 180 μA, which is a 4-fold increase with respect to that of the Sn<sub>3</sub>O<sub>4</sub> nanoflakes on carbon paper, and a two-order increase with respect to that of the TiO<sub>2</sub> NRs arrays. The evolution of hydrogen according to the photo-catalytic water-splitting process showed that Sn<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> heterostructures have a good photocatalytic hydrogen evolution activity with the rate of 5.23 μmol h<sup>-1</sup>, which is significantly larger than that of Sn<sub>3</sub>O<sub>4</sub> nanoflakes (0.40 μmol h<sup>-1</sup>) and TiO<sub>2</sub> nanorods (1.13 μmol h<sup>-1</sup>). Furthermore, the mechanism behind this was discussed. The detector has reproducible and flexible properties, as well as an enhanced photosensitive performance.

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## Introduction

TiO<sub>2</sub>, as one of the widest band gap semiconductors (~3.0 eV), is widely used in photocatalysts and photoelectrodes due to its strong optical absorption, favorable band edge positions, and abundant availability.<sup>1</sup> For example, oriented, single-crystalline rutile TiO<sub>2</sub> nanorod films on transparent conductive fluorine-doped tin oxide (FTO) substrates or carbon fiber were used as dye-sensitized solar cells (DSSCs) and exhibited an improved cell performance due to a direct connection of the point of photo-generation with the collection electrode.<sup>2,3</sup> However, the energy unitization efficiency of TiO<sub>2</sub> is limited because of its wide band gap and the rapid recombination of photogenerated electron-hole pairs. Metal/nonmetal element doping or decoration was developed to increase its photoactivity, for example, TiO<sub>2</sub> modification with carbon nanolayers used as a photocatalyst led to an enhanced efficiency due to the increased substrate adsorption in the vicinity of the photocatalytic sites and high migration efficiency of photoinduced electrons at the carbon/TiO<sub>2</sub> interface.<sup>4,5</sup> And metal modification of TiO<sub>2</sub> to increase photocatalytic properties of nanoparticles were reported also.<sup>6,7</sup>

Among their methods, heterogeneous photocatalysts were regarded as an effective way to improve photocatalytic activity,

since heterojunctions can promote charge migration across both the semiconductor/electrolyte and the semiconductor/photoelectrode interface effectively separating photogenerated electrons and holes.<sup>8-10</sup> P-SnO/*n*-TiO<sub>2</sub> composite electrodes revealed a better PEC performance as reported by Naeem *et al.*<sup>11</sup> And tree-like TiO<sub>2</sub> architectures assembled with CdS and reduced graphene oxide can improve photoelectrochemical performance as reported by Pathak *et al.*<sup>12</sup>

On the other hand, a mixed-valence tin oxide (Sn<sup>2+</sup> and Sn<sup>4+</sup>) has a strong resistance against acidic/alkaline solutions and exhibits a good photocatalytic activity without generating secondary pollutants under irradiation with visible light. It is a desirable material for PEC-type photodetectors and an efficient visible-light-driven photocatalyst.<sup>13-16</sup> To improve the photoelectric properties, Sn<sub>3</sub>O<sub>4</sub> nanomaterials combined with others have been used as electrodes and photocatalysts. For example, integrated Sn<sub>3</sub>O<sub>4</sub> nanosheets and rGO nanosheets as hybrid nanostructures were used as high-performance photocatalysts.<sup>17</sup> With the combination of visible light active Sn<sub>3</sub>O<sub>4</sub> and ultraviolet (UV) light active TiO<sub>2</sub>, this composite can be a broad spectrum photocatalytic material from the UV to visible region as well as having enhanced separation of photogenerated electrons and holes,<sup>18</sup> therefore people paid more attention to TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanostructures. For example, 3D lupinus-like TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanostructures on a transparent F-doped SnO<sub>2</sub> (FTO) glass substrate were prepared and used as photoanode for PEC water splitting as reported by Zhu *et al.*<sup>19</sup> TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hybrid nanobelts exhibited markedly enhanced photoelectrochemical (PEC) response, which caused higher

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photocatalytic hydrogen evolution even without the assistance of Pt as a co-catalyst, and enhanced the degradation ability of organic pollutants under both UV and visible light irradiation.<sup>20</sup>

Recently, self-powered photodetectors (SPPD) are becoming a promising candidate for application in high-sensitivity and high-speed SPPDs because they do not require batteries as an external power source.<sup>21,22</sup> For example, TiO<sub>2</sub> based self-powered photochemical UV detectors have been reported, but they are restricted to UV light.<sup>23–25</sup> To better use solar light for energy conversion, it is very important to extend the spectrum to the visible region. Although there are some discussions on the TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> electrodes, flexible SPPDs based on TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> haven't been reported yet.

Herein, TiO<sub>2</sub> nanorod arrays (NRs) vertically aligned on the carbon fiber papers were synthesized *via* a hydrothermal route, where TiO<sub>2</sub> nanorods have a diameter of about 500–1000 nm; then Sn<sub>3</sub>O<sub>4</sub> nanoflakes (NFs) with a thickness of less than 100 nm and width of 100–300 nm were grown on the surface of TiO<sub>2</sub> nanorod. Furthermore, hybrid PEC-type photodetectors were designed using three prepared 3-D (three dimensional) hierarchical arrays, TiO<sub>2</sub>, Sn<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> as photoanodes, respectively. As a visible light SPPD device, TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> heterostructures exhibit a stable photocurrent of 180 μA, which is a 4-fold increase with respect to that of Sn<sub>3</sub>O<sub>4</sub> NFs on carbon paper, and a two-order increase with respect to that of TiO<sub>2</sub> NRs on carbon paper. The detector exhibits reproducible and flexible properties, as well as an enhanced photosensitive performance. Finally, the photocatalytic properties of the pure Sn<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub> NRs and their combinations have been studied, where the evolution of hydrogen was measured according to the photocatalytic water-splitting process. The results show that Sn<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> heterostructures have hydrogen evolution activity with the rate of 5.23 μmol h<sup>-1</sup>, significantly larger than that of others. The mechanism behind has been discussed.

## Experimental section

### Materials

All chemicals were analytical-grade and used without further purification. Titanium butoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>), tin dichloride dehydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O), sodium citrate dihydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, 99%), ethanol, and hydrochloric acid (HCl, 36.5–38% by weight) were purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial carbon fiber papers were provided by FuelCellStore.

### Synthesis of TiO<sub>2</sub> NRs

TiO<sub>2</sub> nanorod arrays (NRs) were prepared on the carbon fiber papers by the one-step hydrothermal method. Firstly, the commercial carbon fiber papers were cut into the desired sizes and ultrasonically washed using deionized water and ethanol. Then, 12 mL of deionized water was mixed with 12 mL of hydrogen chloride (36.5–38% by weight). The mixture was stirred for 5 min before the addition of 400 μL of titanium butoxide (97% Aldrich). After stirring for another 5 min, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave

with the treated carbon fiber paper vertically immersed in the reaction solution. The hydrothermal reaction was carried out at 180 °C for 18 h and cooled naturally to room temperature. Finally, the carbon fiber paper substrates covered by TiO<sub>2</sub> NRs were washed with deionized water.

### Synthesis of Sn<sub>3</sub>O<sub>4</sub> NFs

Sn<sub>3</sub>O<sub>4</sub> nanoflakes (NFs) were prepared on the carbon fiber papers by a modified hydrothermal approach, which is similar to the reported in our previous study.<sup>26</sup> In detail, 1.073 g of SnCl<sub>2</sub>·2H<sub>2</sub>O and 2.940 g Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O were dissolved in the mixture of 20 mL de-ionized water and 20 mL alcohol under constant magnetic stirring for approximately 60 min. The obtained homogeneous solution was transferred into a Teflon liner of 50 mL capacity with the carbon fiber paper vertical immersed into the reaction solution and keeping sealed under 180 °C for 18 h. After the reaction, the carbon fiber paper coated with a brown product was further washed with deionized water and absolute ethanol for several times. The final sample dried in an oven before characterization.

### Synthesis of TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical heterostructured arrays

Details of growth process of the TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical heterostructured arrays were described previously. 0.35 g of SnCl<sub>2</sub>·2H<sub>2</sub>O and 1.14 g of Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O were dissolved in a mixture of 25 mL of deionized water and 25 mL of alcohol under constant magnetic stirring for approximately 60 min. Then, the mixture was transferred to a Teflon-lined autoclave (50 mL). Subsequently, the carbon fiber paper covered by TiO<sub>2</sub> NRs was vertically immersed into the aforementioned mixture. The hydrothermal reaction was carried out at 180 °C for 18 h and cooled naturally to room temperature. Finally, the resulting carbon fiber papers with TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical heterostructured arrays were rinsed with deionized water and dried at 60 °C in air.

### Characterization

The morphology and microstructure of the TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> heterostructured nanowire arrays on carbon fiber papers were examined by a Hitachi S-4800 field emission scanning electron microscope (FESEM) and a Tecnanai G2 F30 field emission transmission electron microscope (TEM) operated at an accelerating voltage of 300 kV. The phase and composition of samples were analyzed by powder X-ray diffraction (XRD, Bruker D8 advance) with Cu Kα (λ = 1.5406 Å). UV-visible absorption spectra (200–1200 nm) were measured using a Varian Cary 50 UV-visible spectrophotometer. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB-250Xi photoelectron spectroscopy to obtain information on the valence state of the Ti and O ions.

### PEC measurements

To perform the PEC tests, the Zanner CIMPS electrochemical workstation (Germany) was used to examine the photocurrent densities' curves and electrochemical impedance spectroscopy

(EIS) plots in a three-electrode mode. PEC measurements were performed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> using Pt wire as the counter electrode and Ag/AgCl in saturated KCl as a reference electrode. The carbon fiber papers with TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical heterostructured arrays were acted as the working electrode and placed in the cell with an area of 1 × 1 cm<sup>2</sup> exposed to the electrolyte. A 500 W Xe lamp (CEL-HXF 300, Beijing Au-light, China) was employed as incident light source to study the PEC response of the samples. The H<sub>2</sub> evolution experiments were carried out in a gas-closed circulation system under a 300 W Xe lamp.

## Results and discussion

### Morphology and structure

The schematic diagram of the formation process of the TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical heterostructured nanowire arrays on carbon fiber papers is shown in Fig. 1a, which involves two major steps. In the first step, large-scale well-aligned TiO<sub>2</sub> nanowires are grown on the carbon fiber papers by the one-step hydrothermal method. High-density TiO<sub>2</sub> NRs are grown uniformly on the carbon fiber papers, which also serve as stems to provide a platform for later Sn<sub>3</sub>O<sub>4</sub> NFs growth. In the second step, the Sn<sub>3</sub>O<sub>4</sub> NFs were conformably coated onto TiO<sub>2</sub> nanowire stems by a facile and effective hydrothermal method. Fig. 1b reveals the crystal structure of the as-synthesized TiO<sub>2</sub>, Sn<sub>3</sub>O<sub>4</sub> and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanowires heterostructure arrays on carbon fiber papers. The diffraction peaks in each pattern at 26.22° and 54.72° are indexed to the carbon fiber paper substrate. For TiO<sub>2</sub> NRs on the carbon fiber paper substrate, the diffraction peaks at 2θ values of 27.45°, 36.08°, 41.22°, 44.05°, 56.64°, 62.74°, 64.04°, 69.01° and 69.79° can be well identified as (110), (101), (111), (210), (220), (002), (310), (301) and (112) planes of the tetragonal rutile TiO<sub>2</sub> phase (JCPDS 21-1276). Diffraction peaks at about 33.01°, 37.07° and 51.69° can be indexed to (210), (130) and ( $\bar{1}\bar{3}2$ ) phases of Sn<sub>3</sub>O<sub>4</sub> (JCPDS 16-0737). Besides, the XRD pattern of as-synthesized TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical nanowire arrays on carbon fiber papers is also shown in Fig. 1c. All the major diffraction peaks of TiO<sub>2</sub> and

Sn<sub>3</sub>O<sub>4</sub> can also be identified in the pattern of TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure and no extra peak was detected.

To observe the morphology and microstructure of the samples, the FESEM images of TiO<sub>2</sub> NRs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure are shown in Fig. 2. Fig. 2a–c show FESEM images of TiO<sub>2</sub> NRs on carbon fiber paper substrate with different magnifications. With the hydrothermal synthesis, TiO<sub>2</sub> NRs with a size of 500–1000 nm grow vertically along the surface of the carbon fiber paper substrate forming nanowire arrays with good uniformity, each TiO<sub>2</sub> NR has a square shape. After the growth of Sn<sub>3</sub>O<sub>4</sub> nanoflake branches by the followed hydrothermal method, it can be obviously noted that high-density secondary Sn<sub>3</sub>O<sub>4</sub> nanoflake branches are successfully grown on the surface of the TiO<sub>2</sub> nanowires with good uniformity, which lead to a thicker and rougher surface of TiO<sub>2</sub> nanowires. The magnified image (Fig. 2f) reveals that Sn<sub>3</sub>O<sub>4</sub> NFs have a thickness of less than 100 nm and width of 100–300 nm. Because of the existence of convenient diffusion pathways, these TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanowire array hierarchical structures are extraordinarily accessible to electrolytes during the electrochemical measurement process. In addition, the compact nanoflakes interlaced with each other can also greatly increase the capture of light. Further morphological and structural characterizations of the TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure are performed using HRTEM. The low-magnification TEM image (Fig. 3a) reveals the typical heterostructured nanowire taken from hierarchical TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanowire arrays, which can be evidently observed that the individual TiO<sub>2</sub> nanowire with a length of several micrometers is covered by compact Sn<sub>3</sub>O<sub>4</sub> nanoflake branches. A close examination of the exposed profile (inset of Fig. 3a) reveals that thickness of the outer Sn<sub>3</sub>O<sub>4</sub> NFs is around several tens nm. The high resolution TEM examination shown in Fig. 3b reveals a distinct set of visible lattice fringes of 0.33 nm, corresponding to the (111) plane of triclinic Sn<sub>3</sub>O<sub>4</sub> (JCPDS 16-0737). To determine the atomic distribution in TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure, EDS element mapping analysis of the individual hybrid nanowire was performed (Fig. 3c–f), Ti, Sn and O elements are found clearly in the hierarchical heterostructure of TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> nanowire.

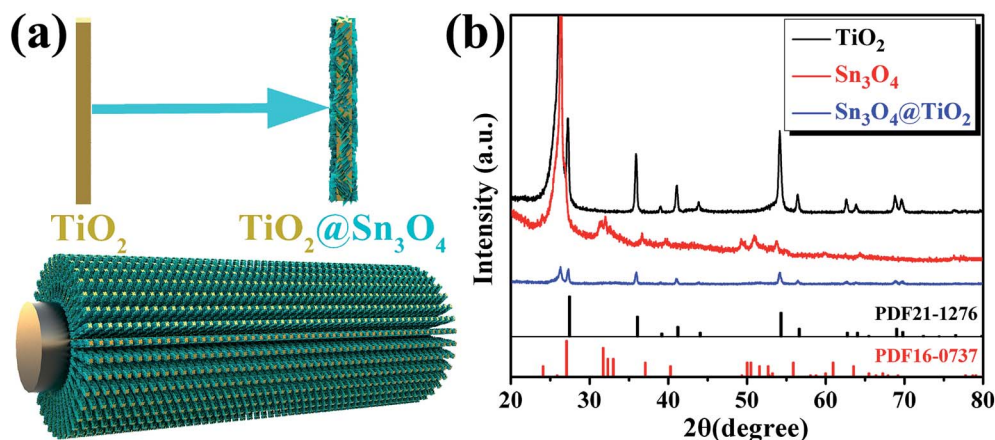


Fig. 1 (a) Schematic of fabrication process and (b) XRD patterns of TiO<sub>2</sub> NRs, Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> heterostructure arrays grown on carbon fiber papers.

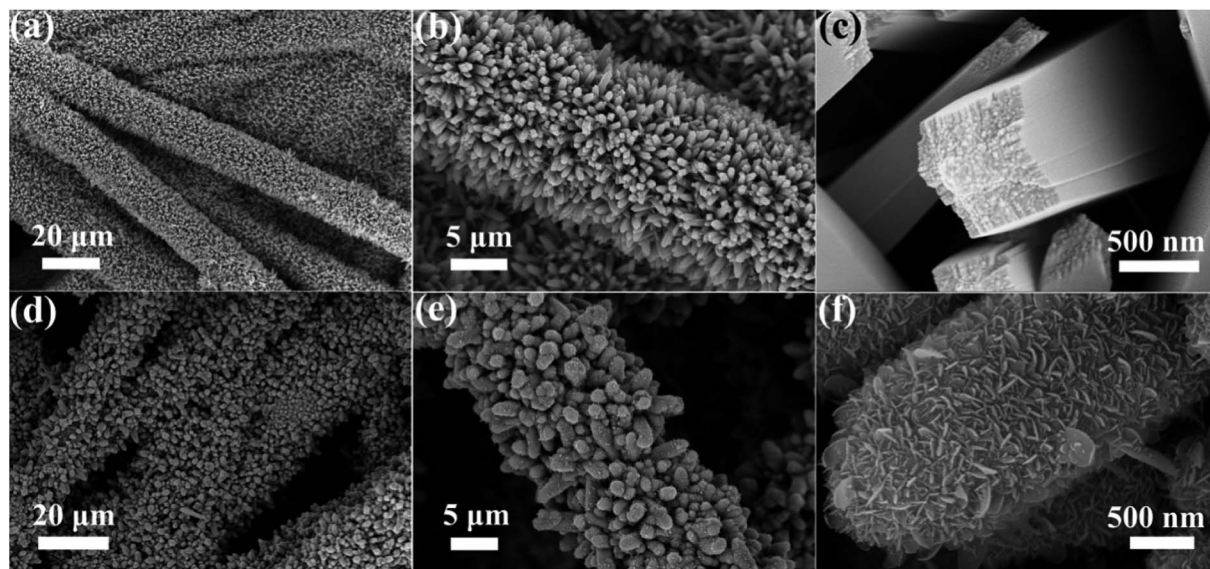


Fig. 2 FESEM images of (a–c)  $\text{TiO}_2$  NRs and (d–f)  $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  hierarchical structure grown on carbon fiber paper.

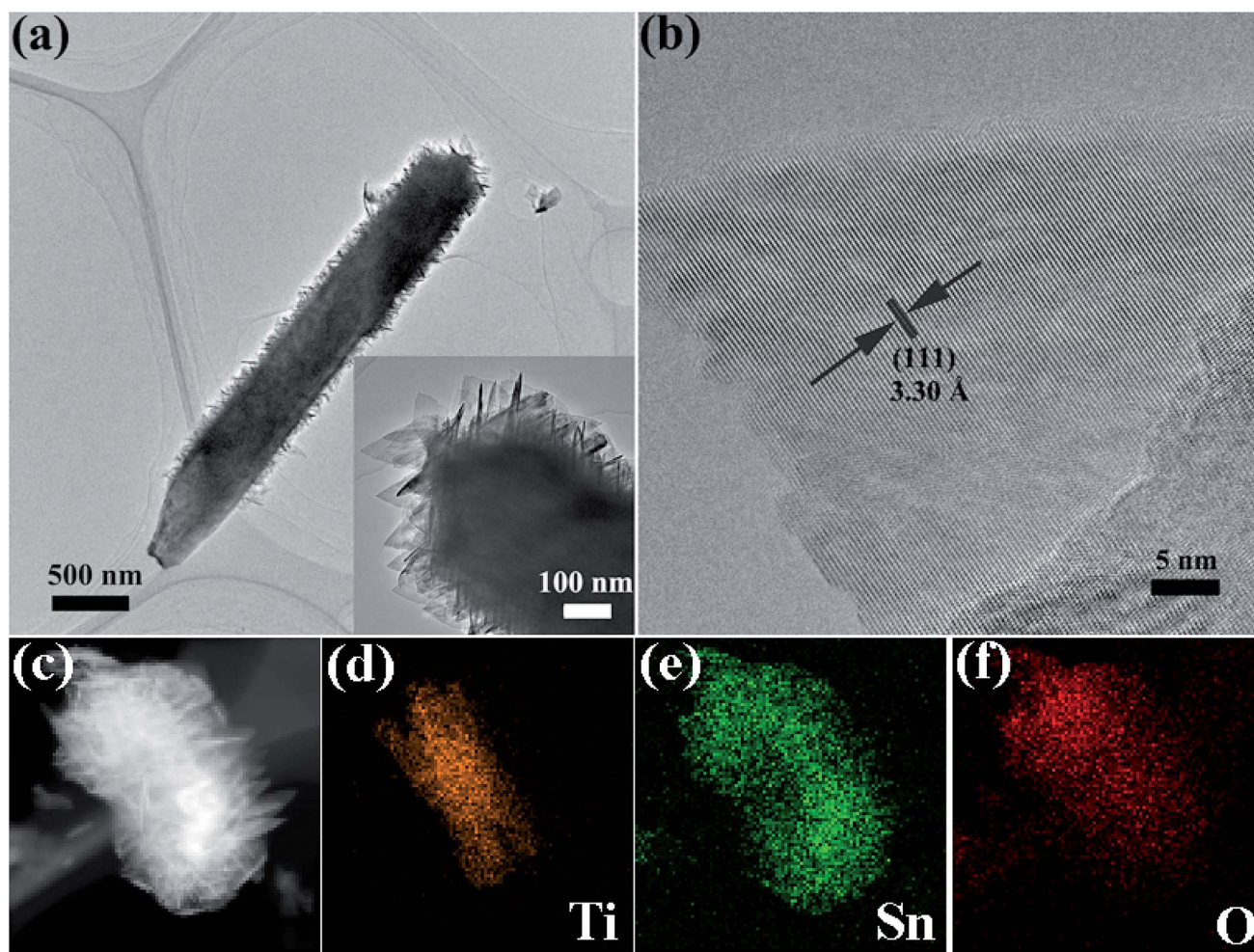


Fig. 3 TEM image (a) and HRTEM image (b) of a representative  $\text{TiO}_2$ @ $\text{Sn}_3\text{O}_4$  heterostructured nanowire. (c–f) Elemental mapping images of an individual hybrid nanowire.

Optical properties of the as-prepared TiO<sub>2</sub> NRs, Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure grown on carbon fiber paper were investigated by diffuse reflectance UV-vis spectra (ultraviolet-visible spectroscopy) (Fig. 4a). Compared with bare TiO<sub>2</sub> NRs, TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure shows significantly increased light absorption in the visible-light region. The absorption edge of the TiO<sub>2</sub> NRs (black line) is located at 408 nm, which indicates the energy gap is 3.04 eV. The absorption band edge of the Sn<sub>3</sub>O<sub>4</sub> NFs (red) is closed to 435 nm (with the energy gap of 2.85 eV), which can absorb the visible light. For the 3D TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure (blue line), its absorption band edge is at ~558 nm, showing a significant redshift compared with the bare TiO<sub>2</sub> NRs. Therefore, coupling TiO<sub>2</sub> NRs with Sn<sub>3</sub>O<sub>4</sub> NFs can significantly broaden the range of photo-response, which can result in an enhancement of utilization of solar light and improved PEC performance. XPS measurements were used to investigate the surface composition of the as-synthesized products. Fig. 4b shows the XPS survey spectra of Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure. Chemical state binding energy of Sn 3d in the Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure was carried by XPS measurements as shown in Fig. 4c. Consistent with our previous study, the binding energies of Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> peaks in the pure Sn<sub>3</sub>O<sub>4</sub> NFs locate at 494.64 eV and 486.15 eV, respectively. After growing onto the TiO<sub>2</sub> NRs, however, the Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> peaks of TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure obviously shifted to higher binding energies by 0.46 and 0.47 eV, respectively. Therefore, the observed peak shift indicates that the electrons are injected from Sn<sub>3</sub>O<sub>4</sub> NFs to the TiO<sub>2</sub> NRs in TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure. This result can be

Table 1 Energy level

Samples	$E_g$ (eV)	$E_C$ (eV) vs. vacuum)	$E_F$ (eV) vs. vacuum)	$E_V$ (eV) vs. vacuum)
TiO <sub>2</sub>	3.04	4.43	5.20	7.47
Sn <sub>3</sub> O <sub>4</sub>	2.85	3.7	3.9	6.55

further supported by the shift by 0.4 eV of the Ti 2p<sub>3/2</sub> peak in Fig. 4d. The TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure is possibly advantageous because of their electronic band structure.

UPS measurements were carried out to study the surface electron behavior of TiO<sub>2</sub> NRs, as shown in Fig. 4e and f. Fig. 4e is a view of the secondary electron edge (SEE) energy corresponding to the left spectra in UPS data. The work function ( $\phi$ ) can be by observing the low energy secondary electron cutoff, which is ~5.20 eV for TiO<sub>2</sub> NRs. Fig. 4f is a view of the valence band maximum (VBM) region corresponding to the right spectra in UPS data and the VBM can be extracted from the Fig. 4f, which is about 2.2 eV for TiO<sub>2</sub> NRs. The energy band of Sn<sub>3</sub>O<sub>4</sub> NFs has been discussed previously.<sup>22</sup> Then, the conduction band and valence band (vs. vacuum) of TiO<sub>2</sub> NRs and Sn<sub>3</sub>O<sub>4</sub> NF scan be obtained, as shown in Table 1.

The PEC measurements were carried out in a three-electrode configuration in 0.1 M Na<sub>2</sub>SO<sub>4</sub> using Pt wire as a counter electrode, Ag/AgCl in saturated KCl as a reference electrode, and carbon-paper-supported Sn<sub>3</sub>O<sub>4</sub> NFs, TiO<sub>2</sub> NRs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structures as active photoanodes, respectively, as shown in the Fig. 5a. The incident radiation is switched with an on/off interval of 20 s. Twenty repeated cycles are displayed in

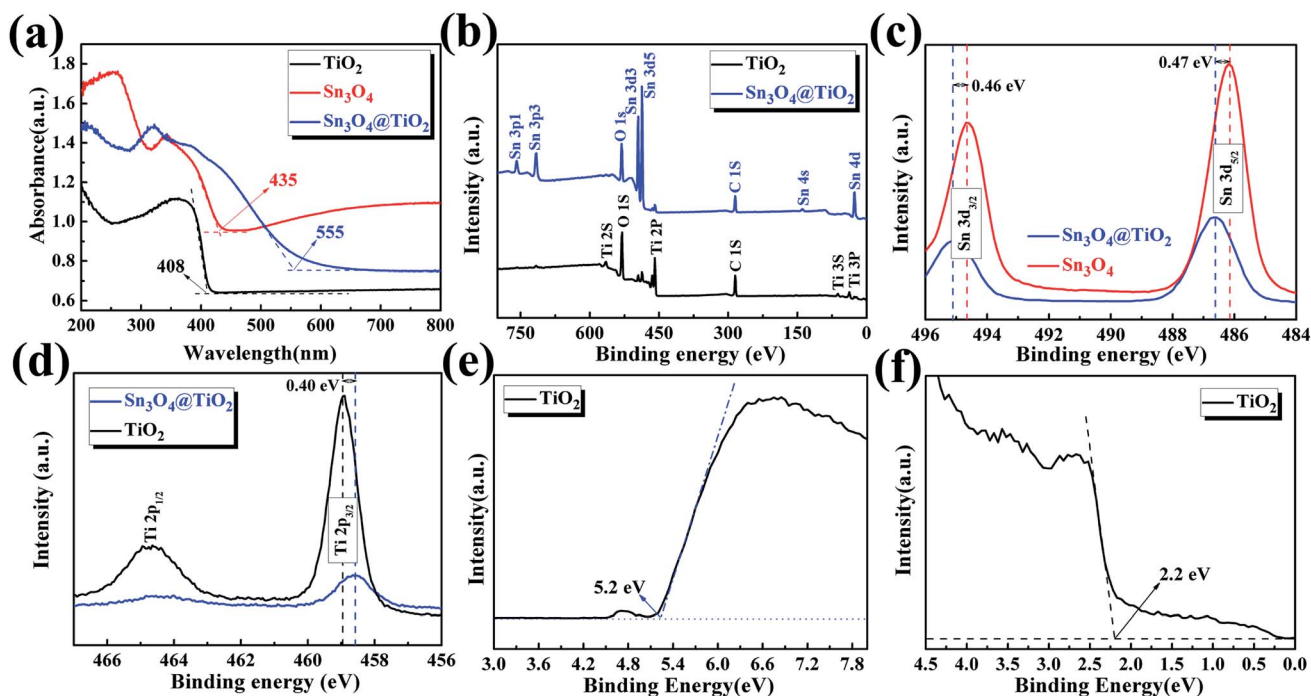


Fig. 4 (a) UV-vis spectra of the TiO<sub>2</sub> NRs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical structure. (b) Survey XPS spectra of TiO<sub>2</sub> NRs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub>. (c) XPS spectra of Sn 3d for Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub>. (d) XPS spectra of Ti 2p for Sn<sub>3</sub>O<sub>4</sub> NFs and TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub>. (e) UPS secondary edge spectrum and (f) view of the valence band maximum (VBM) region.

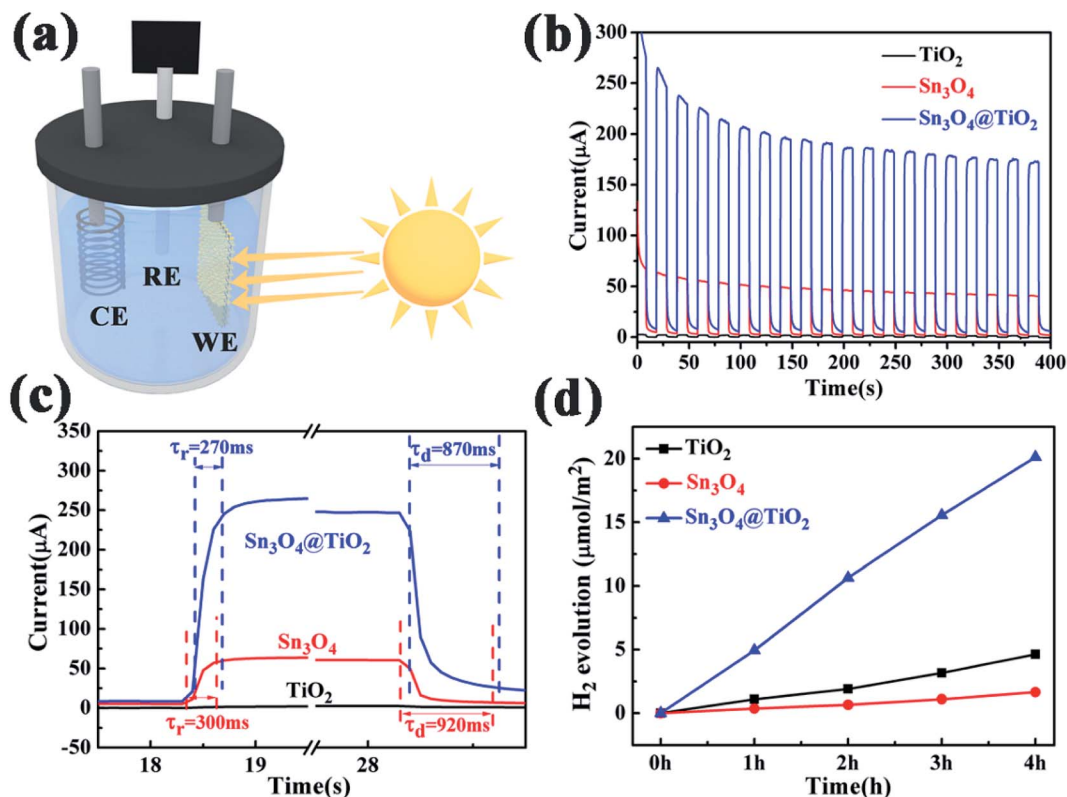


Fig. 5 (a) Schematic illustration of self-powered PEC type detector; (b) photocurrent responses under on/off of 20 s for 20 cycles at 0.0 V versus Ag/AgCl with illumination of 500 W Xe lamp; (c) enlarged rising and decaying edges of the photocurrent response; (d) H<sub>2</sub> evolutions as a function of time under irradiation of the 500 W Xe arc lamp.

Fig. 5b, in which TiO<sub>2</sub> NRs display a quite weak photocurrent under visible-light irradiation. The as-obtained Sn<sub>3</sub>O<sub>4</sub> NFs exhibit a much enhanced photocurrent density of  $\sim 40 \mu\text{A cm}^{-2}$  in the visible-light spectral region. However, the photocurrent exhibited nearly 40% decrease after 20 cycles. The TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical electrode shows the highest photocurrent and a decrease of 30% compared with the initial photocurrent. From the magnified rising and decaying edges of photocurrent shown in Fig. 5c, a fast photo-response can be seen clearly. The rising time ( $\tau_r$ , defined as the time to increase from 10% to 90% of the maximum photocurrent) and the decaying time ( $\tau_d$ , defined as the time to recover from 90% to 10% of the maximum photocurrent) of TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> hierarchical electrodes are about 0.27 s and 0.87 s, respectively, faster than 0.30 s and 0.92 s for Sn<sub>3</sub>O<sub>4</sub> NFs. The mechanism of reason for enhanced PEC performance will be explained in detail later. PEC measurements that the 3D TiO<sub>2</sub>@Sn<sub>3</sub>O<sub>4</sub> photoelectrode exhibited a stable photocurrent of 180  $\mu\text{A}$ , which is 4-fold increase with respect to that of Sn<sub>3</sub>O<sub>4</sub> NFs, and two-order increase respect to that of TiO<sub>2</sub> NRs. In comparison to the report of ref. 19, the formation of the heterostructure on the photocurrent is much larger without external power source.

Furthermore, the photocatalytic property of the pure Sn<sub>3</sub>O<sub>4</sub>, TiO<sub>2</sub> NRs and their combinations have been studied under visible light, where the evolution of hydrogen was measured according to the photo-catalytic water-splitting process, as shown in Fig. 5d. The results show that Sn<sub>3</sub>O<sub>4</sub> NFs show

negligible photocatalytic hydrogen evolution activity with the rate of  $0.40 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and the rate of the TiO<sub>2</sub> NRs is  $1.13 \mu\text{mol h}^{-1}$ . TiO<sub>2</sub> NRs, which is much lower than that of Sn<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> heterostructures of  $5.23 \mu\text{mol h}^{-1}$ , this value is comparable with the results reported by Kodiyath *et al.*<sup>27</sup> Contrary to the photocurrents, the H<sub>2</sub> generation of Sn<sub>3</sub>O<sub>4</sub> is less than that of TiO<sub>2</sub>. Several aspects, such as the density of the photoanode catalysts, electron transportation and carrier's concentration *etc.*, will influence the H<sub>2</sub> generation. In the further work we will study them.

To further understand the reasons of the charge transfer process occurring at the interface of photoelectrode/electrolyte, electrochemical impedance spectroscopy (EIS)<sup>28,29</sup> was carried out and presented in Fig. 6a and b. The equivalent RC circuit was used to interpret the EIS results (see inset of Fig. 6b). As shown in Fig. 6a and b, each Nyquist plots are composed of one semicircle and a slope line. For deeper analysis, all Nyquist plots display a semicircle at high frequencies whose diameter represents the charge-transfer resistance ( $R_{ct}$ ), which reflects the electron transfer kinetics of the redox probe at the interface. The slope line at low frequency is related to the diffusion process. The corresponding equivalent circuit is depicted in the inset of Fig. 6b, where  $R_s$  denotes the series resistance at the interface of the photoelectrode material and the carbon fiber paper substrate,  $C_{dl}$  reflects the constant phase element that models capacitance of the double layer, and  $Z_w$  stands for the Warburg impedance originated from the diffusion process at

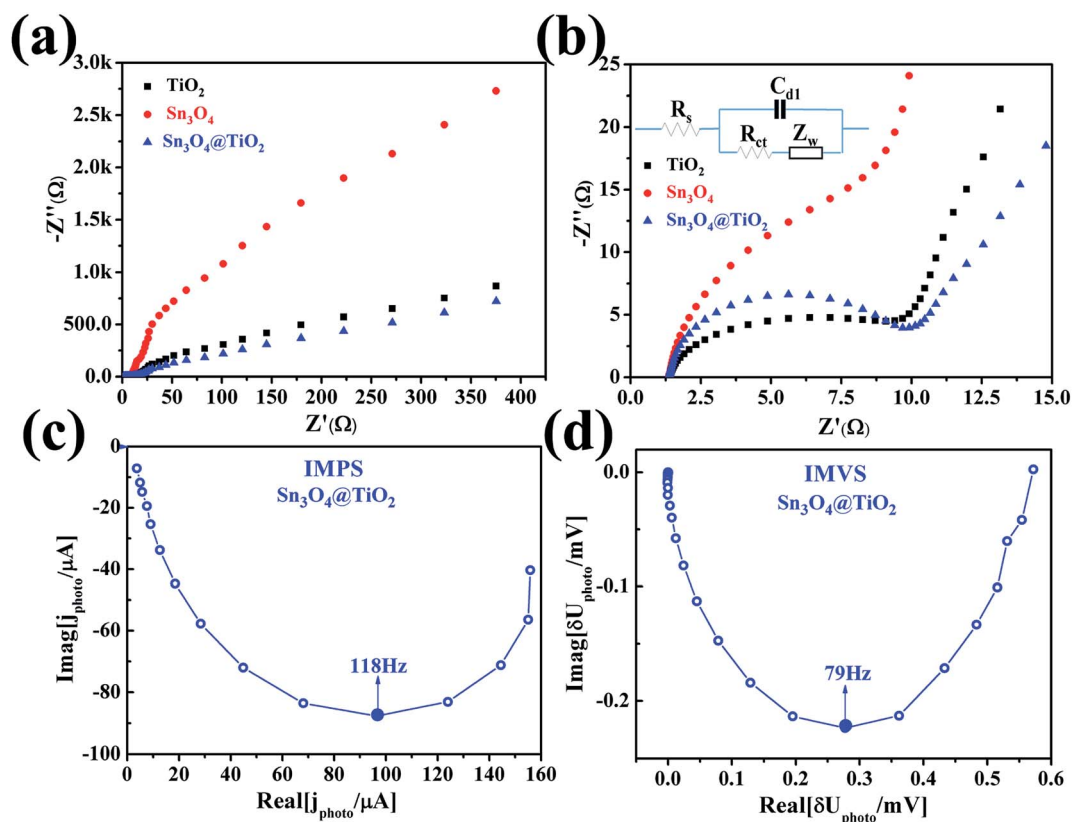


Fig. 6 (a) Nyquist plots of  $\text{TiO}_2$  NRs,  $\text{Sn}_3\text{O}_4$  NFs and  $\text{TiO}_2@Sn_3O_4$  heterostructure arrays grown on carbon fiber papers; (b) plots in the expanded high-frequency region and the inset represents the equivalent circuit applied to fit the impedance data; (c) typical IMPS and (d) IMVS plot of  $\text{TiO}_2@Sn_3O_4$  heterostructure arrays.

the electrode surface. After being decorated with  $\text{Sn}_3\text{O}_4$  NFs, the value  $R_{ct}$  of  $\text{TiO}_2@Sn_3O_4$  hierarchical photoelectrode is almost the same, which is smaller than the corresponding value of  $\text{Sn}_3\text{O}_4$  NFs. The above result demonstrates that  $\text{TiO}_2$  NRs provide a conduction path and rapidly transfer the photoelectrons coming from  $\text{Sn}_3\text{O}_4$  NFs to the carbon fiber paper substrate along the vertically oriented  $\text{TiO}_2$  NRs, which is also correlated to the enhanced PEC performance. To obtain deep insights into the enhanced PEC properties of the  $\text{TiO}_2@Sn_3O_4$  hierarchical electrodes, intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) have been employed to investigate further the electron transport and recombination process, as shown in Fig. 6c and d. The IMPS and IMVS plots display a semicircle in the complex plane under the incident light source was an LED with a wavelength of  $564 \pm 60$  nm. From the IMPS measurement (Fig. 6c), the transport time ( $\tau_d$ ) of injected electrons from  $\text{Sn}_3\text{O}_4$  NFs to  $\text{TiO}_2$  NRs can be calculated from the following equation:

$$\tau_d = 1/(2\pi f_{d,\min}),$$

where  $f_{d,\min}$  is characteristic frequency at the minimum of the IMPS imaginary component. Thus,  $\tau_d$  value is estimated to be 1.35 ms. In addition, from the IMVS measurement (Fig. 6d), the recombination lifetime ( $\tau_n$ ) was determined using the following equation:

$$\tau_n = 1/(2\pi f_{n,\min}),$$

where  $f_{n,\min}$  is the characteristic frequency at the minimum of IMVS imaginary component. The  $\tau_n$  can be calculated to be 2.0 ms for  $\text{TiO}_2@Sn_3O_4$  hierarchical photoelectrode. All the above results indicate that vertically oriented  $\text{TiO}_2$  NRs can serve as fast electron transport and  $\text{TiO}_2@Sn_3O_4$  heterostructure can increase electron lifetime and result in the enhanced PEC performance.

Based on the above measurements and analyses, by combining both the band gap estimated from optical absorption and the conduction band and valence band (vs. vacuum) obtained by UPS, the energy band alignment of  $\text{TiO}_2$  NRs and  $\text{Sn}_3\text{O}_4$  NFs is displayed in Fig. 7a. When  $\text{Sn}_3\text{O}_4$  NFs contact with  $\text{TiO}_2$  NRs to form a heterojunction, the band structure of  $\text{TiO}_2@Sn_3O_4$  is reconfigured. The bandgap energy of  $\text{Sn}_3\text{O}_4$  (2.85 eV) is smaller than  $\text{TiO}_2$  (3.04 eV) and both the potentials of VB and CB of  $\text{Sn}_3\text{O}_4$  are higher than those of  $\text{TiO}_2$ , so  $\text{TiO}_2@Sn_3O_4$  heterostructure belongs to a typical type-II heterojunction. Under visible-light irradiation, photogenerated holes and electrons appear in the VB and CB of  $\text{Sn}_3\text{O}_4$  NFs. Due to type-II heterostructure, the photogenerated electrons in  $\text{Sn}_3\text{O}_4$  CB were easily injected into the  $\text{TiO}_2$  CB. Effective separation of photoexcited electron-hole pairs could be accomplished by a longer electron lifetime. To explain the enhanced PEC performance of  $\text{TiO}_2@Sn_3O_4$  photoelectrode in the visible-light

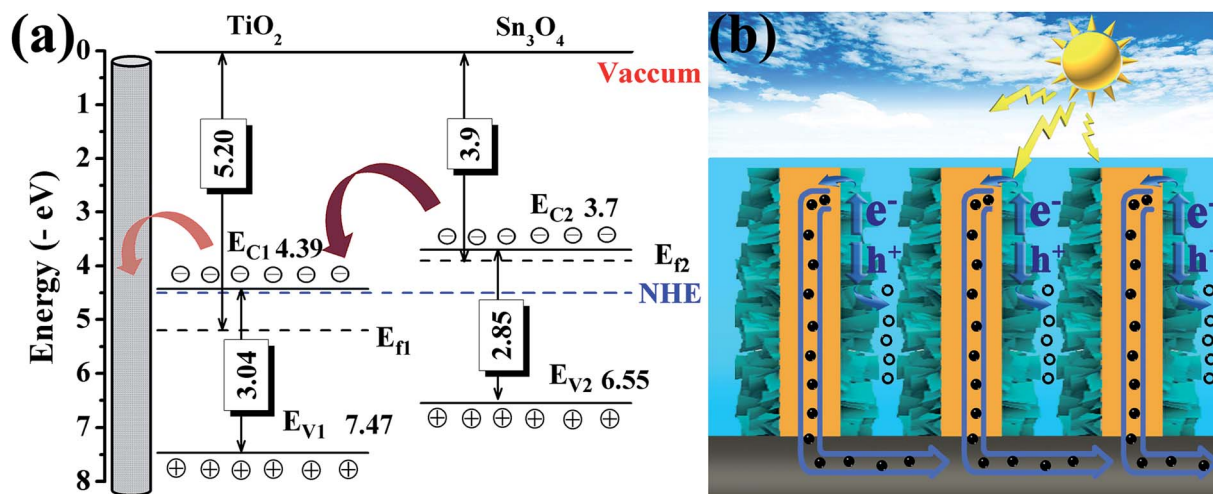


Fig. 7 (a) Proposed energy band alignment and (b) scheme of the electron–hole pair separation and the transfer process in  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  photoelectrode.

spectral region, we present the scheme of the electron–hole pair separation and the transfer process in  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  hierarchical photoelectrode (Fig. 7b). Generally, enhanced PEC performance of  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  photoelectrode may be attributed to the reasonable design of  $\text{TiO}_2\text{NRs}@\text{Sn}_3\text{O}_4\text{NFs}$  heterostructure. On one hand, the aligned  $\text{TiO}_2$  NRs can provide a conduction path and rapidly transfer electrons to carbon fiber paper substrate along the vertically oriented  $\text{TiO}_2$  NRs. On the other hand, the type-II heterojunction of  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  heterostructure can drive photoexcited electron transfer from  $\text{Sn}_3\text{O}_4$  NFs to  $\text{TiO}_2$  NRs. In one word, for our  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  photoelectrode under the synergistic effects between unique band structures and morphology, which is crucial for the enhancement of PEC performance.

## Conclusion

In this paper,  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  arrays vertically aligned on the carbon fiber papers were synthesized and used as photoanodes to improve the photocurrent performance under visible light. Because of the 3-D structure, the  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  arrays can absorb more incident lights which have been reflected among  $\text{Sn}_3\text{O}_4$  NFs, at same time there are more interfacial states to adsorb electrolyte molecules. The  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  arrays not only extend the spectra from UV to visible region with respect to  $\text{TiO}_2$ , but also increase the separation of photogenerated electrons and hole due to the good band alignment of type-II heterostructure for  $\text{TiO}_2@\text{Sn}_3\text{O}_4$ . Therefore, as photoanodes in self-powered photoelectrochemical cell-type (PEC) photodetector under visible light,  $\text{TiO}_2@\text{Sn}_3\text{O}_4$  heterostructures exhibit a stable photocurrent of  $180 \mu\text{A}$ , which is 4-fold increase with respect to that of  $\text{Sn}_3\text{O}_4$  NFs, and two-order increase respect to that of  $\text{TiO}_2$  NRs arrays.  $\text{Sn}_3\text{O}_4/\text{TiO}_2$  heterostructures also have a good photocatalytic hydrogen evolution activity with the rate of  $5.23 \mu\text{mol h}^{-1}$ , which is quite larger than that of  $\text{Sn}_3\text{O}_4$  nanoflakes ( $0.40 \mu\text{mol h}^{-1}$ ) and  $\text{TiO}_2$  NRs ( $1.13 \mu\text{mol h}^{-1}$ ). By the way, the detector exhibits reproducible and flexible properties, as well as

an enhanced photosensitive performance. The results will be helpful for the construction of hierarchical structures used in the PEC detectors.

## Conflicts of interest

The authors declare no competing financial interest.

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