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# Seed layer-free hydrothermal synthesis of porous tungsten trioxide nanoflake arrays for photoelectrochemical water splitting

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The simple preparation of efficient nano-photoanodes has been a key issue in the development of photoelectrochemical water splitting. In this work, a convenient and seed layer-free hydrothermal approach has been developed to synthesize vertically aligned porous WO<sub>3</sub> nanoflakes on a fluorine-doped tin oxide conductive glass substrate. The morphology of WO<sub>3</sub> nanoflakes could be manipulated by changing the annealing time, which further affected the performance of WO<sub>3</sub> nanoflakes as photoanodes. Under optimum conditions, the obtained photoanode can lead to a high photocurrent density of 2.34 mA cm<sup>-2</sup> at 1.4 V vs. Ag/AgCl under one sun irradiation (100 mW cm<sup>-2</sup>) and an incident photon to current conversion efficiency of 60% at 300 nm. The excellent photoelectrochemical performance can be mainly attributed to the larger active surface area, single crystal structure with an optimum thickness and the exposed highly active facets.

## 1. Introduction

Unlike fossil fuels, hydrogen (H<sub>2</sub>) is one of the most attractive and environmentally friendly fuels for energy application.<sup>1</sup> Photoelectrochemical (PEC) water splitting is a scalable and cost-effective approach for the generation of H<sub>2</sub>, which converts solar energy into chemical energy and stores it in H<sub>2</sub>.<sup>2,3</sup> In the PEC reaction, a semiconductor with a suitable band gap is used as the photoelectrode, which can harvest solar energy by absorbing photons and produce photogenerated carriers to realize water splitting.<sup>4–6</sup> Among them, the water reduction reaction for the extraction of H<sub>2</sub> and the water oxidation reaction for the extraction of O<sub>2</sub> occur in the photocathode and photoanode, respectively. Moreover, because the water oxidation reaction is an energetically uphill reaction with the four-electron and four-proton transfer process, the exploration of an efficient photoanode material is key for high performance PEC water splitting. Metal oxides such as TiO<sub>2</sub>, ZnO, BiVO<sub>4</sub> and WO<sub>3</sub> have been investigated as photoelectrodes owing to their favorable band gap and excellent chemical stability.<sup>7–15</sup> Among them, WO<sub>3</sub> is a prospective photoanode material, which has a higher oxidizing capacity because of its higher valence band potential (3.1–3.2 eV vs. NHE),<sup>16,17</sup> suitable bandgap (2.6–2.8 eV),<sup>18</sup> moderate hole diffusion length (~150 nm),<sup>19,20</sup> good

electron mobility (~12 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)<sup>21</sup> and low cost. However, although WO<sub>3</sub> possesses impressive advantages as a photoanode material, its practical conversion efficiency is lower than the theoretical value (approximately 10%).<sup>22</sup> The reason is that WO<sub>3</sub> is an indirect bandgap semiconductor, and a relatively thick film is needed for adequate light absorption. However, the thicker WO<sub>3</sub> film usually causes significant recombination of electron-hole pairs.

Compared with the bulk materials, the nanostructured WO<sub>3</sub> photoanode has the advantages of greatly increasing the density of active redox sites, enlarging the semiconductor-electrolyte interface and enhancing the kinetics parameters of the water oxidation reactions through the reduction of bulk recombinations.<sup>22</sup> For example, based on the seed layer-assisted solvothermal growth, Grimes *et al.* synthesized WO<sub>3</sub> nanowire arrays on a fluorine-doped tin oxide (FTO) substrate as a photoanode, which showed the saturation photocurrent of 1.43 mA cm<sup>-2</sup> under AM 1.5 G illumination.<sup>23</sup> Zhang *et al.* proposed a postgrowth modification method of the WO<sub>3</sub> nanoflakes by a simultaneous solution etching and reducing process, and the modified WO<sub>3</sub> photoanodes showed enhanced PEC performance with a photocurrent density of 1.10 mA cm<sup>-2</sup> at 1.0 V vs. Ag/AgCl.<sup>24</sup> Moreover, Gong *et al.* synthesized the monoclinic multilayered WO<sub>3</sub> photoanode with a photocurrent density of 1.62 mA cm<sup>-2</sup> at 1.25 V versus Ag/AgCl via the seed layer-assisted growth.<sup>25</sup> Recently, by employing the 2-step hydrothermal process, Wang *et al.* prepared WO<sub>3</sub> plate-like arrays on a FTO substrate with an unprecedented photocurrent density of 3.7 mA cm<sup>-2</sup> at 1.23 V vs. RHE under AM 1.5 G illumination.<sup>26</sup> However, although great progress in the nanostructured WO<sub>3</sub> photoanode has been made in recent years, the common

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synthesis method refers to either the seed layer-assisted growth or multi-step hydrothermal reaction, which is time-consuming and energy-consuming. Moreover, the seed layer containing a large number of nanocrystalline particles can introduce numerous grain boundaries, which eventually results in the increase of interfacial carrier recombination.<sup>27,28</sup> Thus, it is crucial for the development of a simple and seed layer-free synthetic method to grow a nanostructured WO<sub>3</sub> photoanode for PEC water splitting.

Herein, we demonstrate a seed layer-free, one-step hydrothermal synthesis method to grow vertically aligned porous WO<sub>3</sub> nanoflakes on a FTO substrate. The WO<sub>3</sub> nanoflakes comprise a single crystal structure with a thickness of ~45 nm. The surface morphology and crystalline oriented facets of the WO<sub>3</sub> nanoflakes will evolve with different annealing times. More importantly, the optimal WO<sub>3</sub> nanoflakes exhibit excellent PEC performance without the use of oxygen evolution cocatalysts, which may open up new opportunities in the design of practical photoanodes for PEC water splitting.

## 2. Experimental

### Materials

All chemicals were used without further purification. H<sub>2</sub>WO<sub>4</sub> (Sinopharm Chemical Reagent Co., Ltd, GR, ≥99.5%) was used as a tungsten source. H<sub>2</sub>O<sub>2</sub> (AR, 30%), HCl (AR, 35%), acetonitrile (AR, ≥99.0%), urea (AR, ≥99.0%), and oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O) (AR, ≥99.5%), were used in the precursor solution. The FTO conductive glasses (14 Ω, light transmission rate is 90%) were used as substrates that had been cleaned with acetone, ethanol and deionized water in an ultrasonic bath for 15 min and dried in a nitrogen stream. A Na<sub>2</sub>SO<sub>4</sub> solution of 0.1 M (pH 6.8) was used as the electrolyte for testing the photocurrent density, incident-photon-to-current conversion efficiency (IPCE), and the electrochemical impedance spectroscopy (EIS) measurements.

### Preparation of the precursor for the hydrothermal reaction

A H<sub>2</sub>WO<sub>4</sub> solution as one of the components of the precursor solution was prepared by means of dissolving 1.25 g H<sub>2</sub>WO<sub>4</sub> into 20 ml deionized water by adding 20 ml H<sub>2</sub>O<sub>2</sub> (30 wt%), which was stirred until it became clear in a hot-water-bath at 95 °C. Then, the H<sub>2</sub>WO<sub>4</sub> solution was cooled to room temperature in air. The transparent H<sub>2</sub>WO<sub>4</sub> solution was then diluted by deionized water to 100 ml with a molar concentration of 0.05 M. The precursor consists of 3 ml of the above H<sub>2</sub>WO<sub>4</sub> solution (0.05 M), 0.15 ml HCl (35%), 0.35 ml deionized water, and 12.5 ml acetonitrile with 0.02 g oxalic acid and 0.02 g urea. Then, the mixture was evenly stirred using a magnetic stirring apparatus until there were no longer solid grains of oxalic acid or urea.

### Hydrothermal growth of the WO<sub>3</sub> films

The mixture was placed into a teflon-lined stainless-steel autoclave with a volume of 25 ml. A piece of bare FTO-glass substrate with the conductive layer facing down was immersed and

leaned against the wall of the teflon-vessel, which had been previously cleaned. Then, the stainless-steel autoclave was sealed and maintained at 180 °C for 2 h. The as-prepared sample was then rinsed with ethanol and dried in a nitrogen stream. Subsequently, the as-prepared sample was annealed at 500 °C for a certain time in air. In order to study the relationship between the performance and annealing time, the as-prepared samples were annealed for 1 hour, 2 hours and 4 hours in this work, and named as 1 H-WO<sub>3</sub>, 2 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub>, respectively.

### Photoelectrochemical test

The photoelectrochemical (PEC) performance was tested at room temperature by using the typical three-electrode PEC cell with a round flat quartz window. A FTO-glass with the as-prepared samples (1.5 × 1.5 cm<sup>2</sup>) was clamped with a Pt electrode holder as the working electrode and a saturated-potassium-chloride silver chloride electrode (Ag/AgCl) as a reference electrode. A platinum foil (1.5 × 1.5 cm<sup>2</sup>) as a counter electrode was fixed in the PEC cell with a 0.1 M of Na<sub>2</sub>SO<sub>4</sub> solution (pH 6.8). A 300 W Xenon arc lamp (Newport, MODEL 67005) as a light-source simulator provided an illumination intensity of one sun (AM 1.5 G, 100 mW cm<sup>-2</sup>). The current/potential curves were scanned from -0.2 V to +1.4 V (vs. Ag/AgCl @ 25 °C) at a scan rate of 50 mV s<sup>-1</sup> using an electrochemical station (IVIUM). During the test, the light was vertically illuminated on the working electrode through a quartz window that was parallel with the working electrode and the counter electrode.

In the whole test process, the potential conversion between the Ag/AgCl electrode and reversible hydrogen electrode (RHE) can be expressed by the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\text{Ag/AgCl}}^0$$

where  $E_{\text{Ag/AgCl}}^0 = 0.197 \text{ V} (@ 25^\circ\text{C})$ . All of the electrochemical analysis was completed in the Na<sub>2</sub>SO<sub>4</sub> solution (pH 6.8) at room temperature, so the equation can be converted to:

$$E_{\text{Ag/AgCl}} = E_{\text{RHE}} - 0.5982$$

IPCE was measured in a Na<sub>2</sub>SO<sub>4</sub> solution. A simulator (Newport 69 911 300 W Xenon lamp) coupled to an aligned monochromator (Oriel Cornerstone 260 1/4 m) was used as a simulated light source to provide light at a certain wavelength. A power meter was used to obtain the power density at the certain wavelength, and an electrochemical workstation was used to apply a constant potential (0.63 V vs. Ag/AgCl @ 25 °C). IPCE can be expressed as:<sup>29–32</sup>

$$\text{IPCE}(\%) = \frac{J(\text{mA cm}^{-2}) \times 1240(\text{V nm})}{\lambda(\text{nm}) \times J_{\text{light}}(\text{nW cm}^{-2})} \times 100$$

where  $J$  is the photocurrent density (mA cm<sup>-2</sup>) that had been deducted dark current,  $\lambda$  is the incident light wavelength (nm), and  $J_{\text{light}}$  is the power density measured at a specific wavelength (mW cm<sup>-2</sup>).



The EIS spectral measurements of the annealed as-prepared samples were performed under an illumination intensity of one sun (AM 1.5 G,  $100 \text{ mW cm}^{-2}$ ) between the frequency of 0.01 Hz to 10 MHz in  $\text{Na}_2\text{SO}_4$  solution with an AC 0.63 V vs. Ag/AgCl bias.

### 3. Results and discussion

#### Morphology and characterization

The typical XRD pattern of the unannealed as-prepared sample is given in Fig. 1(a). Peaks marked with an asterisk originate from the FTO substrate. The other diffraction peaks agree well with those of  $\text{H}_{0.23}\text{WO}_3$  with the lattice spacing of  $a = 7.546 \text{ \AA}$ ,  $b = 7.546 \text{ \AA}$ ,  $c = 7.546 \text{ \AA}$  ( $\alpha = 90^\circ$ ) (PDF#42-1260). The typical SEM of the unannealed as-prepared sample is shown in Fig. 1(b). It can be seen that the nanoflakes vertically grew on the FTO substrate with the uniform thickness of  $\sim 45 \text{ nm}$ .

After annealing, the XRD pattern of the as-prepared sample changed, as shown in Fig. 2(a). All of the diffraction peaks agree well with those of the monoclinic  $\text{WO}_3$  with the lattice spacing of  $a = 7.297 \text{ \AA}$ ,  $b = 7.539 \text{ \AA}$ ,  $c = 7.688 \text{ \AA}$  ( $\alpha = 88.83^\circ$ ,  $\beta = 90.91^\circ$ ,  $\gamma = 90.93^\circ$ ) (PDF#43-1305). According to the XRD patterns of the three samples, the (002), (020) and (200) planes are exposed in  $\gamma$ -monoclinic  $\text{WO}_3$ . In addition to the FTO signals, no other

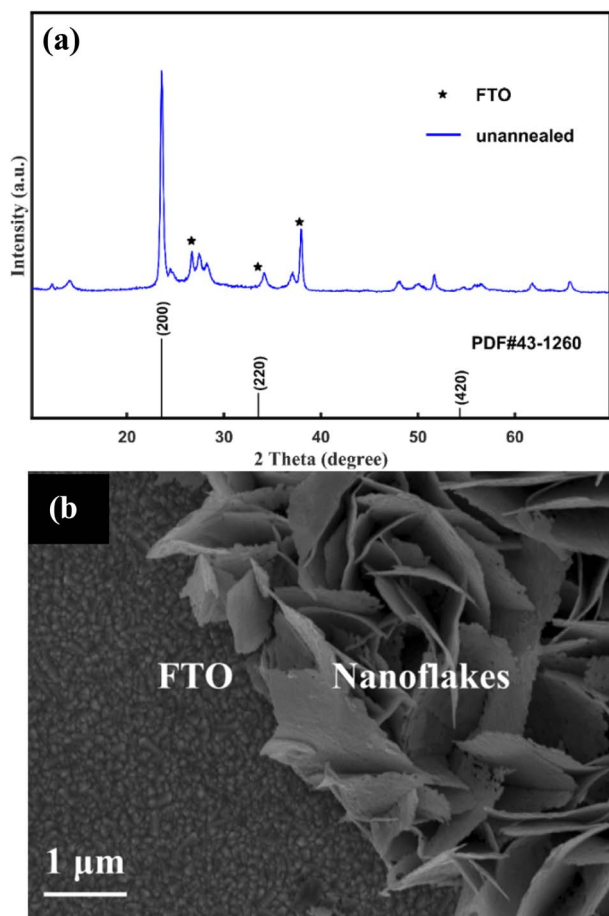


Fig. 1 XRD pattern (a) and SEM image (b) of the unannealed samples. Peaks marked with an asterisk originate from the FTO substrate.

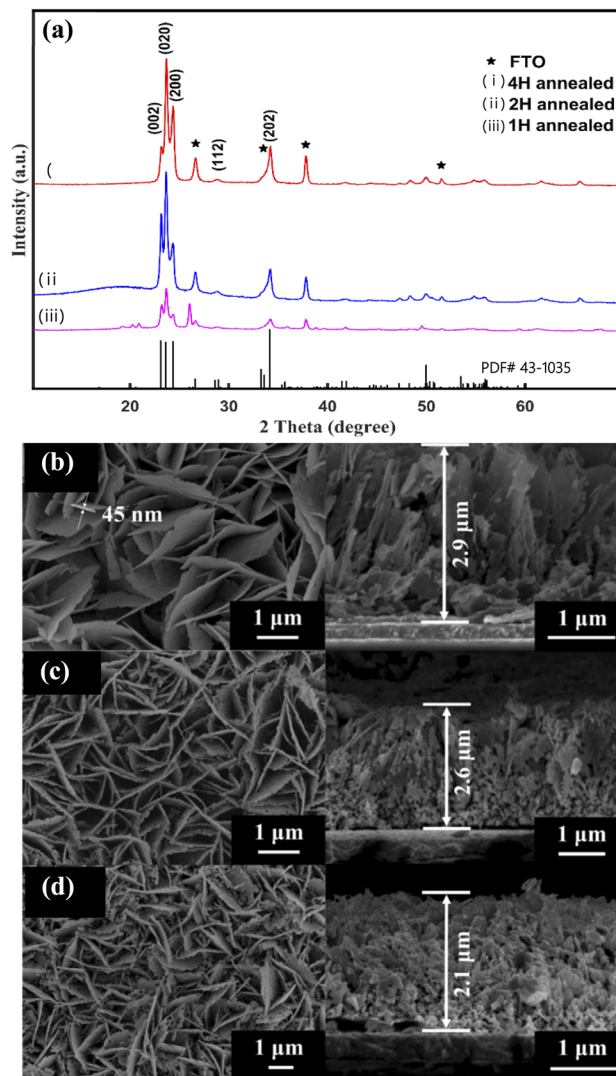


Fig. 2 XRD patterns of the annealed  $\text{WO}_3$  nanoflakes (a). SEM images of the  $\text{WO}_3$  nanoflakes for different annealed times: (b) 1 hour, (c) 2 hours, (d) 4 hours.

peak can be observed, indicating that all samples consisted of pure  $\text{WO}_3$ . Moreover, the X-ray diffraction peaks become sharper and more intense through increasing the annealed time, which indicated that the 2 H- $\text{WO}_3$  and 4 H- $\text{WO}_3$  samples had better crystallinity than the 1 H- $\text{WO}_3$  sample. The peak of the (002) facets was strengthened with the annealing time increasing from 1 hour to 2 hours, but it almost disappeared when the annealing time was increased to 4 hours. It has been reported that the (002) facets are the most active facets when compared with the other facets of  $\gamma$ -monoclinic  $\text{WO}_3$ , and have superior activity in the PEC reaction.<sup>25</sup> Therefore, the above results of the XRD patterns suggest that the 2 H- $\text{WO}_3$  sample could be a promising photoanode in PEC water splitting, owing to it having more active facets than the other two as-prepared samples.

Furthermore, the SEM images revealed that the annealing as-prepared sample is composed of well-aligned  $\text{WO}_3$  nanoflakes,



as shown in Fig. 2(b–d). The morphology of the nanoflakes is obviously different with different annealing times. The 1 H-WO<sub>3</sub> sample has an intact flake-like morphology, which is the same as that of the as-prepared sample before annealing (Fig. 2(b)). When the annealing time increased to 2 hours, numerous pores were observed in the nanoflakes (Fig. 2(c)). The size and number of the pores increased with increasing annealing time. Furthermore, even the nanoflakes of the 4 H-WO<sub>3</sub> sample were smashed (Fig. 2(d)). The porous structure obtained by annealing is favorable to high PEC performance because the porous structure can afford a higher specific surface area and active sites for electrochemical energy conversion.<sup>33</sup> The thickness of the nanofilms of the 1 H-WO<sub>3</sub>, 2 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub> samples also gradually decreased with the annealing time from 2.9  $\mu\text{m}$  to 2.1  $\mu\text{m}$ . Combined with the above XRD results, the crystal transformation may be responsible for the morphological changes of the as-prepared sample *via* annealing in air.<sup>34</sup> The dehydration will result in volume shrinkage, which causes the decrease of the nanofilm thickness and the formation of a porous structure.

Fig. 3 presents the TEM images and SAED patterns of the 2 H-WO<sub>3</sub> nanoflakes. The porous structure was further confirmed by the low-magnification TEM image. The clear SAED patterns reveal that the porous nanoflake is a single crystalline with high crystallinity. Furthermore, the HRTEM image of the nanoflake shows fringe spacings of 0.3764 nm and 0.3838 nm with an angle of 90°, which is consistent with the d-spacing values of the (020) and (002) facets of the monoclinic WO<sub>3</sub>, respectively. This excellent single-crystallinity structure of the 2 H-WO<sub>3</sub> nanoflakes can offer direct conduction paths for the photogenerated electrons, which is beneficial for the PEC performance of the sample.<sup>22</sup>

### Photoelectrochemical properties

The PEC performances of the WO<sub>3</sub> nanoflakes electrode were investigated using linear sweep voltammetry conducted from −0.2 to +1.4 V *vs.* Ag/AgCl in a Na<sub>2</sub>SO<sub>4</sub> solution (pH 6.8) at room temperature. Fig. 4(a) shows the current density *vs.* potential (*I*–*V*) curves of 1 H-WO<sub>3</sub>, 2 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub>. As expected, the 2 H-WO<sub>3</sub> sample exhibits the best PEC performance with the photocurrent density of 2.34 mA cm<sup>−2</sup> at 1.4 V *vs.* Ag/AgCl at

room temperature. Meanwhile, the 1 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub> samples only could reach to 1.65 mA cm<sup>−2</sup> and 1.54 mA cm<sup>−2</sup> at the same potential, respectively. Compared with the other reported works,<sup>22–25</sup> our WO<sub>3</sub> nanoflakes synthesized by simple seed layer-free and one-step hydrothermal method have comparable or even better photocurrent density than the other nanostructured WO<sub>3</sub> synthesized by other complex methods. Here, the morphology of the as-prepared sample is suggested to have an important impact on the overall PEC performance. As to the 2H-WO<sub>3</sub> sample, it is a porous structure and more pores exist in the nanoflakes, which can afford higher specific surface area and more reactive active sites for electrochemical energy conversion. The well-aligned WO<sub>3</sub> nanoflakes facilitate the random reflection of light in the array, which further promotes the absorption of solar energy. As to the 1H-WO<sub>3</sub> sample, there are fewer pores in it, so it has fewer reactive active sites compared to the 2H-WO<sub>3</sub> samples. For the 4H-WO<sub>3</sub> sample, due to the long annealing time, its structure was smashed and collapsed. The flakes appeared to be damaged, and then its PEC performance was weakened. In addition, the more active facet (002) of the 2H-WO<sub>3</sub> samples plays a crucial role in its excellent PEC performance.

To obtain a quantitative correlation of the nanoflakes, we performed IPCE measurements as a means of studying the photoactive wavelength regime for the nanostructured WO<sub>3</sub> films. As shown in Fig. 4(b), the IPCE results of the three types of films were consistent with the *I*–*V* curves, with the 2 H-WO<sub>3</sub> sample giving the highest efficiency value. At 300 nm, the 2 H-WO<sub>3</sub> sample gave IPCE values higher than 60%. However, the 1 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub> samples gave IPCE values of about 48% and 24%, respectively. The data reveal that the 2 H-WO<sub>3</sub> sample had the most outstanding conversion efficiency.

To further explore the origin of the excellent photocatalytic activity, the light absorption of the WO<sub>3</sub> nanoflakes photoanodes was investigated, as shown in Fig. 4(c). The absorption edges of 1 H-WO<sub>3</sub>, 2 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub> are located at 340 nm, 380 nm and 360 nm, respectively. The 2 H-WO<sub>3</sub> sample had higher light absorption intensities compared to the other two samples, which indicates the superior PEC efficiency. The optical band gap, *E<sub>g</sub>*, can be estimated using the following equation:<sup>35</sup>

$$\alpha h\nu = A(h\nu - E_g)^n$$

where *h* is Planck's constant, *v* is the frequency of light, *A* is a constant, and *n* is equal to 2 for an indirect semiconductor or 1/2 for a direct semiconductor. For WO<sub>3</sub>, the transition is indirect. Therefore, ( $\alpha h\nu$ )<sup>1/2</sup> is plotted as a function of *hν*, from which the band gap energy is obtained. The *E<sub>g</sub>* values of 1 H-WO<sub>3</sub>, 2 H-WO<sub>3</sub> and 4 H-WO<sub>3</sub> were calculated to be 2.90, 2.80 and 2.87 eV, respectively. Combined with the SEM images as shown in Fig. 2, after annealing for 2 hours, more pores were generated in the nanoflakes. Many defects were also introduced in the structures. The shallower defect level in the band structure extended the spectral response region of its photocatalytic activity to a certain extent, which further promoted the absorption of solar energy and improved its photocatalytic

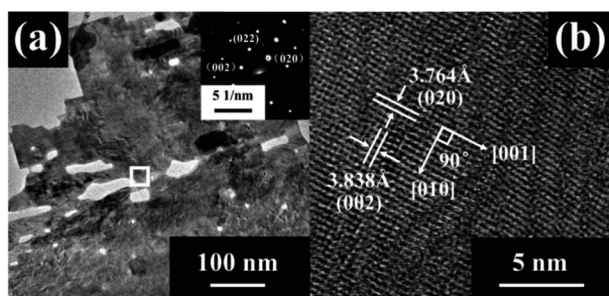


Fig. 3 (a) Low-magnification TEM image of the 2 H-WO<sub>3</sub> nanoflake (the inset shows the corresponding SAED pattern). (b) HRTEM images of the 2 H-WO<sub>3</sub> nanoflake taken from the area marked by a white square in (a).



efficiency. After annealing for 4 hours, the structures of the 4H-WO<sub>3</sub> nanoflakes were smashed and collapsed. The poor crystal quality led to the degradation of its optical absorption performance, which resulted in the weaker PEC efficiency.

The EIS Nyquist curves of the samples consist of two semi-circles and a line, which are assigned to the electrochemical reaction at the Pt counter electrode at high frequencies ( $R_{ct1}$ ), charge transfer at the WO<sub>3</sub>/electrolyte interface at medium frequencies ( $R_{ct2}$ ), and the Warburg diffusion process of the electrolyte at low frequencies ( $Z_w$ ).<sup>36</sup> As shown in Fig. 4(d), the arc radii of the three samples at high frequencies are similar, which means they have the same electrochemical reaction at the Pt counter electrode. However, 2 H-WO<sub>3</sub> has the smallest arc radius at medium frequencies, indicating a faster interfacial charge transfer and a more effective separation of the photo-generated electron-hole pairs during light illumination.<sup>37</sup> The result clearly demonstrates that the 2 H-WO<sub>3</sub> photoanode with a modest pore density and more exposure of the (002) and (020) facets remarkably increases the electron mobility by reducing the recombination of electron-hole pairs, which results in a higher reaction efficiency.

Finally, the photocurrent-time curves were measured using the typical three-electrode PEC cell at 0.63 V vs. Ag/AgCl in

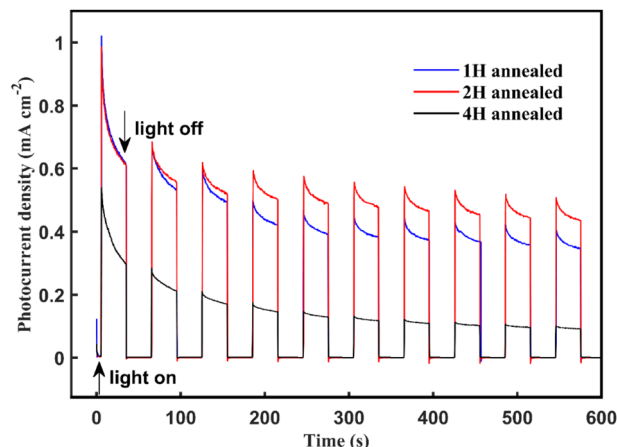


Fig. 5 Photocurrent density vs. time curves of the annealing WO<sub>3</sub> nanoflakes at 0.63 V vs. Ag/AgCl bias in the Na<sub>2</sub>SO<sub>4</sub> solution under AM 1.5 G illumination at room temperature.

a Na<sub>2</sub>SO<sub>4</sub> solution (pH 6.8) under AM 1.5 G illumination for 600 s. The 4 H-WO<sub>3</sub> and 1 H-WO<sub>3</sub> samples exhibit poor stability, and the initial photocurrent density eventually decreased by 83% and 66%, respectively. The photocurrent density of the 2 H-

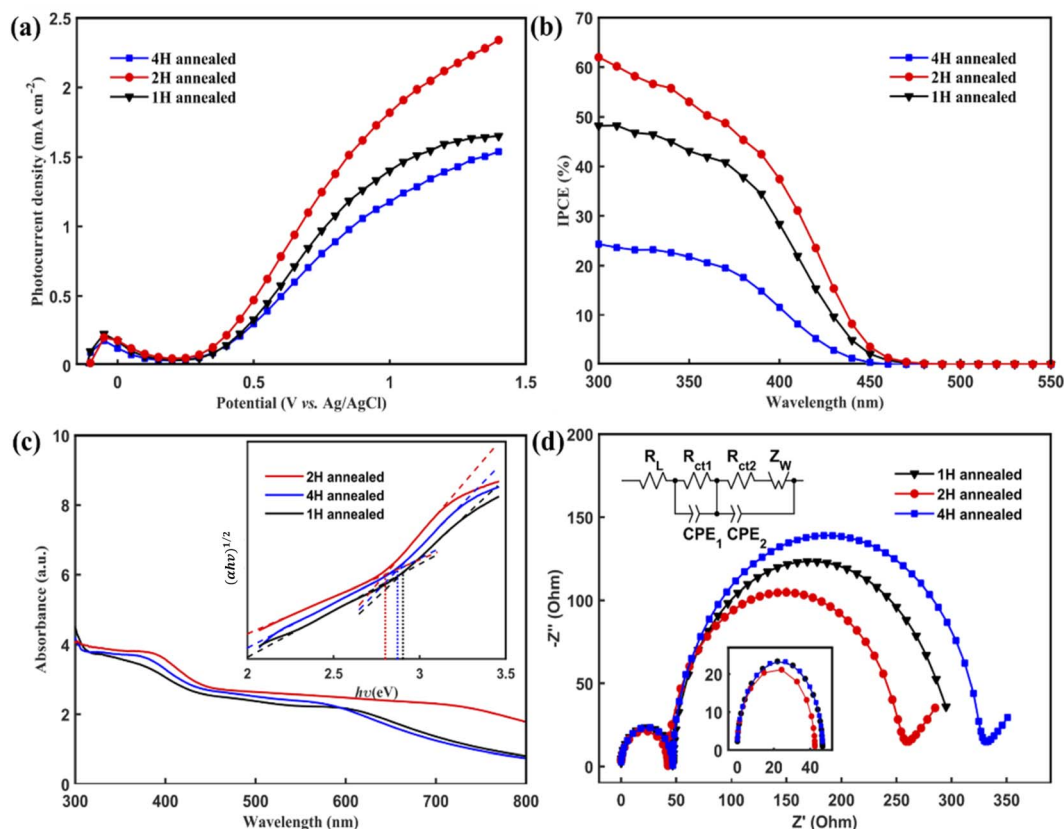


Fig. 4 (a) Current density vs. potential ( $J/V$ ) curves of the photoelectrodes prepared in a Na<sub>2</sub>SO<sub>4</sub> solution were scanned from  $-0.2$  V to  $+1.4$  V (vs. Ag/AgCl @  $25^\circ\text{C}$ ) with a scan rate of  $50\text{ mV s}^{-1}$  using linear sweep voltammetry. (b) Incident-photon-to-current efficiency (IPCE) vs. wavelength curves were collected at  $0.63$  V (vs. Ag/AgCl @  $25^\circ\text{C}$ ) in Na<sub>2</sub>SO<sub>4</sub> solution. (c) UV-visible absorption spectra of the WO<sub>3</sub> samples (the inset show the Tauc curves converted from the UV-vis absorption spectra). (d) Electrochemical impedance spectroscopy (EIS) Nyquist curves using a typical three-electrode PEC cell (@  $0.63$  V vs. Ag/AgCl bias) under AM 1.5 G illumination in the Na<sub>2</sub>SO<sub>4</sub> solution at room temperature (the inset show the equivalent and magnification magnifying profile of the EIS curves).

WO<sub>3</sub> sample only decreased by 56% for the initial value, and the enhanced stability can be attributed to the good crystallinity and stable crystal exposed facet.<sup>21</sup> Fig. 5 shows that all photo-current densities had a rapid jump between zero and saturation values following the light being switched on and off, which indicates that all samples had an efficient charge separation, migration and surface reaction, *i.e.*, high sensitivity.

## 4. Conclusion

The vertically aligned porous WO<sub>3</sub> nanoflakes have been synthesized by a convenient and seed layer-free hydrothermal approach. The morphology and crystal facet can be manipulated by adjusting the annealing time. The sample with 2 hours annealing time exhibited much better PEC performance, which shows an enhanced photocurrent density of 2.34 mA cm<sup>-2</sup> at 1.4 V *vs.* Ag/AgCl under AM 1.5 G light irradiation and an IPCE value of more than 60% at 300 nm wavelength without the use of any cocatalyst. The synergistic effect of the porous morphology, good crystallinity and the exposure of high activity (002) facets obtained under 2 hours annealing process effectively enhances the charge transfer efficiency, thereby improving the PEC performance with better photostability.

## Conflicts of interest

There are no conflicts of interest to declare.

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