Sacrificial Template Synthesis of Copper Tungstate: Influence of Preparing Conditions on Morphology and Photoactivity

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Received: 14 October 2018 / Accepted: 10 December 2018 / Published: 7 February 2019

Morphology-controlled synthesis of ternary transition metal oxides is very important for their application in many fields. As a typical n-type semiconductor ternary oxide, CuWO₄ finds application in solar water splitting as a photoanode material. In this work, we successfully prepared the CuWO₄ nanoflakes (NFs), nanoneedles (NNs) and nanoparticles (NPs) films via a thermal solid-state reaction using different WO₃ as sacrificial templates. We systematically investigated the effect of the morphology, size, and crystal type of the WO₃ templates on the resulting CuWO₄. We found that the morphology and size of WO₃ templates and the reaction temperature were crucial factors that dominated the formation and morphology of CuWO₄. The well-crystallized CuWO₄ NFs and NPs were obtained at 550 °C, whereas, the crystalline CuWO₄ samples exhibited activity and good stability for photoelectrochemical (PEC) water oxidation. Among the CuWO₄ samples, the NFs exhibited the highest activity, which was attributed to (1) the high light absorption efficiency obtained from the perpendicularly oriented NF structure and (2) the large electron density. This work reveals the dependence of morphology, crystallinity, and photoactivity of CuWO₄ on the preparation conditions during sacrificial template synthesis.

Keywords: Copper tungstate; Sacrificial template synthesis; Photoelectrochemical water splitting.

1. INTRODUCTION

Copper tungstate (CuWO₄) has attracted extensive attention as a photoanode material in the field of solar water splitting [1-4]. As a n-type semiconductor and a typical ternary oxide, CuWO₄ has

a wolframite structure with an indirect band gap of ca. 2.4 eV [5-7], which ensures that a larger portion of the visible spectrum can be utilized to generate electron-hole pairs as compared to TiO₂ and WO₃ [8,9]. Moreover, the valence band edge of CuWO₄ is located at ca. 2.80 V *vs.* reversible hydrogen electrode (RHE) [5,10], which is much higher than the redox potential of water oxidation (1.23 V *vs.* RHE). Therefore, the photoinduced holes in the valence band of CuWO₄ have enough energy to oxidize water. Besides, the excellent stability in a relatively wide pH window makes it superior to WO₃ and Fe₂O₃ when acting as a photoanode for oxygen evolution reaction (OER) [11,12]. All the above properties make CuWO₄ a promising candidate as a photoanode material for PEC OER. Up to now, great effort has been made on the preparation of CuWO₄ using different synthesis techniques including electrodeposition [13], atomic layer stack deposition [14], sol-gel method [15], spray pyrolysis [16], and hydrothermal reaction [17]. However, the obtained CuWO₄ usually had a denselypacked film structure, which was unfavorable for improving its activity for PEC water oxidation. Therefore, controlled synthesis of CuWO₄ is still an important issue for the improvement of its activity in solar water splitting.

Recently, Hill and Choi reported the successful preparation of nanoporous CuWO₄ film by using a thermal solid-state reaction between nanoporous WO₃ and CuO [18]. Inspired by this work, Li's [12] and our groups [10] separately developed a sacrificial template synthesis strategy to fabricate CuWO₄ nanoflakes (NFs) photoanode, in which WO₃ NFs were used as templates. This method involved three main steps: (1) preparation of FTO-supported WO₃ NFs, (2) drop-casting of copper acetate or nitrate solution on the surface of WO₃ NFs, and (3) thermal solid-state reaction at 450-550 °C [10,12]. The merit of this method is that the resulting CuWO₄ resembles the morphology of the WO₃ templates. However, we also demonstrated that a high temperature during the thermal solid-state reaction could destroy the NF structure and resulted in the failure of morphology control [10]. Therefore, a question rises, that is under what conditions the sacrificial template synthesis is a successful approach to fabricating morphology-controlled CuWO₄, especially when WO₃ samples with different morphology and crystal structure are used as templates.

As reported previously, we have demonstrated that WO₃ with different morphology and structure could be prepared via nanoseed-assisted hydrothermal growth [19-22]. These WO₃ samples can be employed as templates to prepare CuWO₄. The purpose of this work is to reveal the effect of preparation conditions (such as the morphology and crystal structure of WO₃ templates, and the temperature of thermal solid-state reaction) on the morphology and photoactivity of the resulting CuWO₄. We found that the temperatures, which were applied to obtain well-crystallized and morphology-keeping CuWO₄, depended greatly on the average particles size of the WO₃ templates. Whereas, the crystal structure of the WO₃ templates had little influence on the resulting CuWO₄, because only triclinic CuWO₄ could be produced during thermal solid-state reaction. We also demonstrated that the activity for PEC OER relied significantly on the morphology of the CuWO₄. We believe this work sheds light on the improvement of photoactivity of CuWO₄ by morphology- and structure-controlled synthesis of CuWO₄.

2. EXPERIMENTAL

2.1 Chemicals and substrates

Tungsten powder, hydrogen peroxide (H₂O₂), isopropanol (C₃H₈O), ethanol (C₂H₆O), acetonitrile (C₂H₃N), 20wt% Pt/C, sodium tungstate dihydrate (Na₂WO₄·2H₂O), urea (H₂NCONH₂), oxalic acid (H₂C₂O₄), hydrochloric acid (HCl), tungstic acid (H₂WO₄), polyvinyl alcohol ((C₂H₄O)n) and acetic acid (C₂H₄O₂) were purchased from Beijing Chemical Works. Cupric nitrate trihydrate (Cu(NO₃)₂·3H₂O) was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were analytically pure grade and were used without further purification. Fluorine-doped tin oxide (FTO) substrates (F:SnO₂, 8 Ω ·sq⁻¹,transparency 80%) were purchased from Asahi Glass, Japan.

2.2 Preparation of different WO₃ templates

The WO₃ templates including nanoflakes (NFs), nanoneedles (NNs), and nanobricks (NBs) were prepared via hydrothermal reaction route [10,19-23]. The WO₃ NPs and WO₃ bulk film were synthesized through a modified electrodeposition method [24]. The detailed processes are as follows.

2.2.1 Preparation of WO₃ NFs and NNs template

FTO substrates (3 cm \times 1 cm) were firstly cleaned by ultrasonication in 0.1 M KOH aqueous solution, ethanol and deionized water successively and each for 10 min, and then dried in a stream of high purity N₂ at room temperature. FTO substrates were immersed in aqueous solution prepared by dissolving 0.125 g of polyvinyl alcohol and 0.313 g of H₂WO₄ in 10 mL H₂O. Then hydrothermal reaction was conducted at 250 °C for 2 h. The purpose of this step is to generate WO₃ nanoseeds. The WO₃-nanoseed-modified FTO substrates were employed to grow WO₃ NFs via a hydrothermal reaction in the solution containing 20 mg urea, 20 mg oxalic acid, 0.5 mL 6 M HCl, 12.5 mL acetonitrile and 3.0 mL of 0.05 M H₂WO₄. The hydrothermal reaction was conducted in the sealed autoclave at 180 °C for 2 h. While for the growth of WO₃ NNs, the hydrothermal solution contained 3.0 mL of 0.05 M H₂WO₄, 0.5 mL of 6 M HCl, 10 mL of acetonitrile and 2.5 mL deionized water, and the reaction was carried out at 180 °C for 6 h. The resulting samples of WO₃ NFs and NNs were washed with deionized water and then dried in a stream of No₃ high purity N₂ at room temperature.

2.2.2 Preparation of WO₃ NBs template

FTO substrates were cleaned according to the procedures described above. The WO₃ NBs were also prepared via a hydrothermal method in an aqueous solution containing 5 mL 0.1 M Na₂WO₄, 10 mL 0.1 M H₂C₂O₄, and 10 mL 1 M HCl. The hydrothermal reaction was carried out in a 100 mL Teflon-lined stainless steel autoclave at 180 °C for 2 h. The obtained WO₃ NBs were washed with deionized water and then dried in a stream of high purity N₂ at room temperature.

WO₃ NPs were prepared by an electrodeposition method. The solution for electrodeposition was prepared by dissolving 2 g tungsten powder in 10 mL of 30% hydrogen peroxide solution, and after the exothermic reaction ended, the resulting solution was diluted with 30 mL of isopropanol and 100 mL of deionized water. The electrodeposition was performed on a CHI 660E work station (CH Instruments Co) with a conventional three-electrode cell, where FTO, a coiled Pt wire and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. The deposition was carried out at -0.40 V *vs.* SCE for 60 s. While for the WO₃ film, the preparation conditions remained the same, except that the ethanol was used as solvent instead of isopropanol and the electrodeposition time was prolonged to 30 min. After deposition, the resulting WO₃ was washed with ethanol and water and then dried in a stream of high purity N₂ at room temperature.

2.3 Synthesis of CuWO₄ smaples

Nanostructured CuWO₄ samples were prepared via a sacrificial template synthesis method in which FTO-supported WO₃ was employed as template. In detail, copper precursor solution was prepared by dissolving Cu(NO₃)₂·3H₂O in acetic acid and the final concentration of Cu(NO₃)₂ was 0.1 M. The excessive amount of Cu(NO₃)₂ solution was drop-cast onto the surface of the WO₃ template. After the solution was evaporated in air, the samples were annealed in the muffle furnace at required temperature (450, 475, 500, 550, and 650 °C) for required time. After annealing, the excess copper oxide was removed by immersing the sample in 0.5 M HCl for 30 min and then the pure CuWO₄ samples with a yellow color were obtained.

2.4 Characterization

The crystal structure of the obtained CuWO₄ was characterized by X-ray diffraction (XRD) (Rigaku, rint2000 advance theta-2theta powder diffractometer) with Cu K α radiation. UV–vis diffuse reflection spectra were collected on a Shimadzu 3600 UV–vis–NIR spectrophotometer. The morphological characterization was performed on a Hitachi S-4800 field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 5 kV.

2.5 Electrochemical and photoelectrochemical measurements

All the electrochemical and PEC measurements were carried out with a CHI 660E work station (CH Instruments Co) in a conventional three-electrode cell, in which the FTO-supported CuWO₄, a coiled Pt wire and a saturated calomel electrode (SCE) served as the working, the counter and the reference electrodes, respectively. For PEC measurements, a 300 W xenon lamp was used as the light source. The photoelectrodes were illuminated from the front side with an area of 0.23 cm² exposed to

illumination. The incident light intensity on electrode was calibrated to 100 mW·cm⁻². All PEC measurements were performed in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7). All potentials in this work are reported with reference to SCE and RHE ($E_{RHE} = E_{SCE} + 0.0571*pH + 0.244$) [25].

3. RESULTS AND DISCUSSION

Figure 1a, b and c show the typical SEM images of the WO₃ samples composed of NFs, NNs, and NPs, respectively. The sample of WO₃ NFs had a network structure that was composed of crossintersected NFs, which were nearly perpendicularly oriented to the FTO substrates (Figure 1a). The WO₃ NFs had a very small thickness and were employed as 2-dimensional (2D) templates. As shown in Figure 1b, the WO₃ NNs sample was composed of densely grown NNs that protruded from the FTO substrate, and these WO₃ NNs were used as 1-dimensional (1D) templates. For the WO₃ film shown in Figure 1c, small NPs can be clearly identified, indicating that the film was made up of densely-packed NPs. These WO₃ NPs were used as quasi zero-dimensional (0D) templates. We performed statistical analysis for the size of 2D, 1D, and quasi 0D WO₃ templates by using large amount of high magnification SEM images, and the results are shown in Figure 2. The thickness of WO₃ NFs, the cross-section diameter of WO₃ NNs, and the particle size of quasi 0D NPs are 28 nm, 25 nm, and 45 nm, respectively. This means that, for all the NF, NN, and NP templates, there was at least one dimension size smaller than 50 nm. As was discussed previously, small dimensional size of the WO₃ templates ensured a shorter length for Cu^{2+} and O^{2-} ions to diffuse into WO_3 during thermal solid-state reaction, and then required a lower reaction temperature [10]. As the morphology of the WO₃ templates is easier to retain at a lower reaction temperature, the nanostructured WO₃ made it possible for the morphology-controlled synthesis of CuWO₄ via sacrificial template method.



Figure 1. Typical SEM images of (a) - (c) WO₃ templates and (a') - (c') CuWO₄ prepared from the corresponding WO₃ templates. (a) WO₃ nanoflakes (NFs) and (a') CuWO₄ NFs obtained at 550 °C, (b) WO₃ nanoneedles (NNs) and (b') CuWO₄ NNs obtained at 475 °C, (c) film of WO₃ nanoparticles (NPs) and (c') film of CuWO₄ NPs prepared at 550 °C.



Figure 2. Size distribution histograms of WO₃ templates. (a) thickness of WO₃ NFs, (b) cross-section diameter of WO₃ NNs, and (c) particle size of WO₃ NPs.

Figure 1a', b' and c' show typical SEM images of the CuWO₄ NFs, NNs, and NPs that were prepared from the corresponding 2D, 1D, and 0D WO₃ templates, respectively. It is clearly seen that the morphological features of the templates were retained in the resulting CuWO₄ samples, suggesting

that sacrificial template synthesis is successful to prepare morphology-controlled CuWO₄. This result is important for the controlled fabrication of CuWO₄ because previous work concerning the preparation of CuWO₄ showed that nearly all the obtained products were bulk films with no fine microstructures, no matter different preparation strategies were used, including electrodeposition, atomic layer deposition, sol-gel growth, spray pyrolysis, and hydrothermal synthesis [13-17]. Therefore, the convenient regulation of morphology is one of the main advantages for the sacrificial template method [10,12,18], as compared with other synthesis routes.



Figure 3. XRD patterns of (a) WO₃ templates and (b) the obtained products.

The crystal structure of WO₃ and CuWO₄ was characterized by XRD and the results are shown in Figure 3. The WO₃ NN template exhibited a XRD pattern of hexagonal WO₃ (PDF 33-1387), while the WO₃ NF and NP template possessed a monoclinic crystal structure (PDF 43-1035) (see Figure 3a). These results are consistent with the previous investigation [19-23]. After thermal solid-state reaction, the WO₃ NFs, NNs, and NPs were converted into triclinic CuWO₄, as can be clearly seen from the XRD peaks at 15.3 and 19.0 degree, which are uniquely characteristic of (010) and (100) diffractions of triclinic CuWO₄ (Figure 3b). In addition, other XRD peaks also match well with the standard card of CuWO₄ (PDF 73-1823) [10,12,26]. All these results suggest that well-crystallized CuWO₄ NFs, NNs, and NPs were obtained from the corresponding WO₃ templates. Figure 3 also demonstrates that, regardless of the original crystal structure of WO₃ templates, the obtained CuWO₄ invariably had a triclinic structure, implying that the crystal structure of the templates has no influence on the resulting CuWO₄.

It should be pointed out herein that the dimension size of the nanostructured WO₃ templates and the thermal reaction temperature are two crucial and correlated factors that dominate the success or failure of the sacrificial template synthesis. We found that, due to the difference of the WO₃ templates in morphology and size, the temperature to obtain CuWO₄ with good crystallinity while keeping the morphology of the templates was quite different. For example, single-crystalline CuWO₄ NNs could be obtained at a low temperature of 475 °C, whereas to obtain well-crystallized CuWO₄ NFs and NPs, the temperature should be 550 °C. Interestingly, if the WO₃ NNs were used as templates and the thermal solid-state reaction was carried out at 550 °C, well-crystallized CuWO₄ were obtained, however, the 1D structure of the template could not be preserved, as shown in Figure 4a and a'. We believe that the 1D structure and small cross-section diameter are the main causes for the failure of morphology control. This phenomenon is quite similar to the observation that the 2D structure of CuWO₄ NFs could not survive high temperature of 650 °C during thermal solid-state reaction [10].



Figure 4. SEM images of (a) - (c) WO₃ templates and (a') - (c') the corresponding products after thermal solid-state reaction at 550 °C. (a) WO₃ NNs and (a') the corresponding CuWO₄ obtained at 550 °C, (b) WO₃ nanobricks (NBs) and (b') the obtained product NBs, (c) WO₃ film and (c') the obtained film of product.

As demonstrated in Figure 1 and 2, the WO₃ templates, which were successfully transformed into CuWO₄ via thermal solid-state reaction, had at least one-dimensional size smaller than 50 nm. To further study the effect of dimensional size of WO₃ templates on the formation of CuWO₄, we employed large-sized templates: WO₃ nanobricks (NBs) and bulk film. Figure 4b and c show the SEM images of WO₃ NBs and bulk film, respectively. The average thickness of WO₃ NBs is ca. 350 nm, while the thickness of WO₃ bulk film is ca. 450 nm, both are much larger than 50 nm. When the

thermal solid-state reaction was performed at 550 °C, the morphological features of the template remained after reaction (see Figure 4b' and c'). However, as shown in Figure 3b, the unique diffraction peaks of CuWO₄ at 15.3 and 19.0 degree could not be observed in the XRD patterns, indicating that CuWO₄ was not produced during thermal solid-state reaction. In other words, well-crystallized triclinic CuWO₄ could not be produced at 550 °C when the smallest dimension size of the templates was larger than 350 nm.



Figure 5. UV-vis absorption spectra (a) and the Tauc plots (b) of the three obtained CuWO₄.

The optical absorption is a significant property to evaluate a semiconductor catalyst, especially when it is employed as a photoelectrode. Herein, we examined the UV-vis absorption spectra of the obtained CuWO₄ samples, and the corresponding results are shown in Figure 5a. Although the assynthesized CuWO₄ samples showed a quite different absorption intensity from each other, they all had a band edge absorption at ca. 525 nm, which is well consistent with the previous reports [5,10,12]. Based on the reflection and absorption spectra, Tauc plots of the three obtained CuWO₄ photoanodes were achieved on the assumption of indirect optical transition for CuWO₄ [27]. As we can see in Figure 5b, band gap energies for CuWO₄ NFs, NNs, and NPs are 2.39, 2.40 and 2.44 eV, respectively, which agree well with the values reported in recent years [13,14,16].



Figure 6. Mott–Schottky plots of the three obtained CuWO₄ (a) NFs (b) NN₅ (c) NPs acquired at frequency of 500 Hz and 1000 Hz in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7).

The small difference in band gap energy implies that the morphology and crystal structure of the WO₃ templates have little influence on the energy band structure of CuWO₄. As compared to the WO₃ with the band gap energy of ca. 2.8 eV [9,28,29], the reduction of ca. 0.4 eV in the band gap energy is attributed to the rise of the valence band position of CuWO₄ [30]. The relatively smaller band gap energy ensures that the CuWO₄ photoanode can absorb more visible light as compared to its binary counterpart WO₃. It is worth noticing that, among the three obtained CuWO₄ photoanodes, the CuWO₄ NFs exhibited the highest absorption intensity (see Figure 5a), implying that the network

structure of 2D NFs had a significantly higher light absorption efficiency. We believe that this is due to the fact that most of the NFs in network structure were perpendicularly oriented to the substrates, and this orientation greatly enhanced the probability of light absorption because NFs acted as walls to prevent light from escaping. This light absorption feature favors the improvement of the activity of CuWO₄ NFs for PEC OER.

The electrical conductivity is an important property for semiconductors especially when they are used as photoelectrode materials for water splitting. The conductivity of a semiconductor relies on its majority carrier density, which can be quantitatively estimated from Mott–Schottky plot [31]. To obtain the Mott-Schottky plots of CuWO₄ NFs, NNs, and NPs, EIS measurements were conducted at the frequency of 500 Hz and 1000 Hz in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7) in the dark. The resulting Mott-Schottky plots are demonstrated in Figure 6. All CuWO₄ samples showed a positive slope in Mott-Schottky plot, indicating that they are n-type semiconductors. This result is consistent with the previous reports [10,13,18]. The intercept of the Mott-Schottky plot with the potential axis stands for the flatband potential, which is 0.61, 0.61 and 0.79 V vs. RHE for CuWO₄ NFs, NNs, and NPs, respectively. The flatband potentials obtained here are within the value range reported for the polycrystalline CuWO₄ (0.45 V vs. RHE) [32] and the monocrystalline CuWO₄ (0.81 V vs. RHE) [33]. The difference in flatband potential among CuWO₄ samples may arise from the variation of the surface states and their densities, which were sensitive to the preparation conditions. The flatband potential of n-type semiconductor reflects the theoretical potential at which a photocurrent can be detected. However, the observed onset potential for photoanode is usually more positive than the flatband potential in the PEC water splitting. As shown in the Figure 7a, only when the applied potential exceeds 0.80 V vs. RHE, the photocurrent for the three samples can be clearly seen. This is due to the sluggish oxidation kinetics for OER.





Figure 7. (a) Current density *vs* potential curves of the three obtained CuWO₄ at a potential sweep rate of 10 mV⋅s⁻¹ in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7) under chopped illumination (100 mW⋅cm⁻²); (b) the current density values of the three obtained CuWO₄ at three selected potential 1.05, 1.23 and 1.45 V *vs*. RHE.

The majority carrier density can be calculated using the Mott–Schottky equation [34]:

$$\frac{1}{C_{scr}^2} = \frac{2}{N_d e \varepsilon \varepsilon_0} (E - E_{fb} - \frac{k_B T}{e})$$

where C_{scr} is the capacitance of the space charge region, N_{d} is the charge carrier density (namely electron density for n-type semiconductors such as CuWO₄), *e* is the electron charge, ε represents the dielectric constant of CuWO₄ (taken as 83 here) [27], ε_0 is the permittivity of vacuum, *E* is the applied potential, E_{fb} stands for the flatband potential, k_{B} is the Boltzmann's constant, and *T* is the absolute temperature. For the obtained CuWO₄ NFs, NNs, and NPs, the electron density were calculated to be $5.07 \times 10^{19} \text{ cm}^{-3}$, $1.83 \times 10^{19} \text{ cm}^{-3}$, and $4.70 \times 10^{19} \text{ cm}^{-3}$, respectively.



Figure 8. Current density-time responses of the three obtained CuWO₄ at the potential of 1.23 V vs. RHE in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7) under illumination (100 mW·cm⁻²).

These values are in the same order of magnitude as that reported for monocrystalline CuWO₄ [35] $(5.50 \times 10^{19} \text{ cm}^3)$, but lower than the value reported for polycrystalline CuWO₄ films [13] $(2.7 \times 10^{21} \text{ cm}^3)$. Even so, all of these values are much higher compared to that of intrinsic semiconductor (<10¹⁸ cm³). For n-type semiconductor, higher electron density will result in a faster carrier transfer rate, and usually leads to an enhanced PEC performance for solar water splitting [36].

The linear sweep voltammetry (LSV) was used to investigate the photoactivity of the obtained CuWO₄ NF, NN, and NP photoanodes. Figure 7a shows the detailed results of LSV measurement in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7) under chopped illumination (100 mW \cdot cm⁻²). As the CuWO₄ electrode is electrochemically inert for OER [14-16], no oxidation current can be perceived on three obtained CuWO₄ samples within the whole potential sweep range in the dark. While, once the light was projected onto the photoanodes, an oxidation photocurrent could be instantly observed for all three CuWO₄ samples at the potential range more positive than 0.80 V vs. RHE. Compared to the other two CuWO₄ photoanodes, the CuWO₄ NFs exhibited an enhanced photoactivity toward OER especially at the high potential region. The photocurrent densities at the thermodynamic potential of water oxidation (1.23 V vs. RHE) on the CuWO₄ NF, NN, and NP photoanodes were 0.36, 0.11, and 0.13 mA·cm⁻², respectively. In addition, the photocurrent densities obtained at 1.05 and 1.45 V vs. RHE are also presented in Figure 7b, in which we can see that the difference of photocurrent density between NFs and the other two samples is increasing with the increase of applied potential. We believe that the much higher activity of the CuWO₄ NFs toward PEC OER comes from the higher light absorption efficiency and larger electron density, as the former can lead to the generation of more holes in CuWO₄ and the latter can improve the conductivity. In fact, the photocurrent density obtained on CuWO₄ NFs for OER is among the highest reported in previous literature on bare CuWO₄ photoanodes under the same conditions [1,2,4-6,12-18,37-41]. As mentioned above, the 2D NF network not only guaranteed a large specific surface area but also provided numerous rooms with vertically aligned walls that could trap the scattered light, and then benefiting the improvement of light absorption efficiency. Besides, the NF network structure also provided a large-area CuWO₄/solution interface for PEC reaction. Moreover, the small thickness of NFs (ca. 28 nm, see Figure 2a) ensured a short transport distance for the photoinduced holes from where they were generated to the CuWO₄/solution interface where they oxidized water. This short transport distance of holes significantly reduced the possibility of electron-hole recombination. Accordingly, we believe that the perpendicularly aligned NF network structure of CuWO₄ photoanodes is the main reason for the high PEC activity for OER.

The stability is another important property to assess the performance of photoanode material during solar water splitting. Therefore, we estimated the stability of the CuWO₄ photoanodes during PEC OER by using chronoamperometry. The chronoamperometric measurements were conducted at 1.23 V *vs.* RHE in 0.1 M KH₂PO₄/K₂HPO₄ buffer solution (pH 7) under illumination (100 mW·cm⁻²), and the results are shown in Figure 8. It can be clearly seen that all the three CuWO₄ photoanodes showed good stability in neutral solution. Only slight delay on the photocurrent density was observed after one hour's reaction. The stable photocurrent values of ca. 0.35, 0.11, and 0.13 mA·cm⁻² were achieved on the NF, NN and NP photoanodes, respectively, which are consistent with the results of

LSV measurement. These results provided solid evidences that, though the morphology and size of the nanostructured CuWO₄ photoanodes greatly influenced their activity toward solar water oxidation, they had a trifling effect on the stability of CuWO₄ during PEC OER. The morphology- and size-independent stability is a desirable property for CuWO₄ as a promising photoanode material for solar water splitting.

4. CONCLUSIONS

In summary, we have successfully prepared 2D, 1D, and quasi 0D CuWO₄ photoanodes via a sacrificial template synthesis method that involved a drop-casting procedure and a thermal solid-state reaction. These CuWO₄ photoanodes were composed of perpendicularly oriented NFs, NNs, and randomly packed NPs, respectively. We found that the morphology and the dimension size of WO₃ templates had a significant effect on the thermal reaction temperature at which not only good crystallinity but also desired morphology could be obtained. The well-crystallized CuWO₄ NFs and NPs were obtained at 550 °C, however, the NNs could not maintain their 1D structure at this temperature. The 1D structure of NNs could only be retained at a much lower temperature of 475 °C. While using the "larger" WO₃ templates, whose smallest dimension size is larger than 300 nm, CuWO₄ could not even be obtained. All the resulting CuWO₄ samples exhibited activity and good stability for PEC OER. We found that the morphology and particle size of CuWO₄ photoanodes significantly influenced the photoactivity, however it has a trifling effect on the stability. Among the CuWO₄ samples, the 2D NFs exhibited the highest activity. The high activity was attributed to (1) the high light absorption efficiency obtained from the oriented 2D structure and (2) the large electron density. This work demonstrates that the sacrificial template method provides a feasible way to control the morphology of the CuWO₄ and then to modulate its photoactivity for OER.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of this work by National Natural Science Foundation of China (NSFC 51672017, 51872015, and 51604310), Beijing Natural Science Foundation (2142020 and 2151001), Open Foundation of State Key Laboratory of Environmental Protection for Iron and Steel Industry (2016YZC03).

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