Preparation of well-aligned WO₃ nanoflake arrays vertically grown on tungsten substrate as photoanode for photoelectrochemical water splitting

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1. Introduction

In recent years, visible-light responsive WO₃ photoanode, with thermodynamically stability against photocorrosion in aqueous solution, has attracted great interest for photoelectrochemical water splitting for solar energy recovery [1–7]. A lot of methods have been reported for preparing highly-effective WO₃ photoanode including solution-gel technique [3,4], electrochemical anodization [8,9], atomic layer deposition (ALD) method [5] and hydrothermal reaction [10–12], among which the hydrothermal reaction as a facile, efficient and inexpensive approach receives more and more attentions. Both the experimental conditions and crystal growth in the hydrothermal reaction can be easily controlled. This method also provides the technological feasibility for large-area synthesis for practical application [13,14]. The current reported WO₃ photoanodes [10–12] via the hydrothermal reaction with well-confined microstructure exhibited good photoelectrochemical properties. However, these studies mainly used conductive glass as the substrate, which needs to be initially coated a thin-layer of WO₃ film as seeded sites for crystal growth. The WO₃ photoanode growing on the homogeneous substrate with mechanical flexibility and stability was rather rare reported.

Herein, we present a typical hydrothermal process for fabricating well-aligned WO₃ nanoflake arrays (WNA) vertically growing on tungsten sheet as photoanode for photoelectrochemical water splitting.

Well-aligned WO₃ nanoflake arrays (WNA) as effective photoanode was vertically fabricated on tungsten sheet through a facile hydrothermal process. Before reaction, the tungsten sheet was pre-annealed to produce a thin-layer WO₃ on surface to serve as seeded sites for crystal growth in hydrothermal reaction, which also provided a strong connection between the growing WO₃ and substrate. Polyethylene glycol (PEG) was used as the structure-directing agent to confine the crystal growth. This preparation route obviously facilitated the charge transfer and reduced the recombination of photoexcited electron/hole. The saturated photocurrent density and IPCE value were found to be 2.35 mA cm⁻² at 1.5 V and 56% which were much higher than that prepared in the absence of pre-annealed WO₃ layer and PEG.

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2. Experimental section

2.1. Synthesis of WNA

Tungsten sheets (0.25 mm thick, 99.9% purity), cut into samples of size 1 cm × 2 cm, were degreased by sonicating in 1:1 acetone and ethanol, followed by rinsing with DI water and dried in a stream of air. After that, it was annealed in air at 450 °C for 30 min to oxidize its
surface. During a hydrothermal reaction, Na₂WO₄·2H₂O solution (0.03 M) containing 1/10 (v/v) PEG were used as the precursor along with HCl to adjust the solution pH to reach 2.0. The oxidized tungsten foil was then perpendicular placed into the growth solution and hydrothermal treated at 180 °C for 2 h. Finally, the obtained film was annealed at 550 °C for 3 h in air for dehydration with heating and cooling rates of 1 °C/min.

2.2. Characterization

The phase of products were identified by X-ray powder diffraction (XRD, Shimadzu), using Cu KR (λ = 0.15406 nm) radiation at 50 kV and 50 mA at a scanning rate of 8°/min in the 2θ range from 10 to 60° at room temperature. TEM images were collected by using a field emission scanning electron microscopy (FESEM FEI-Sirion200). UV-visible absorption spectra of the samples were recorded on a photospectrometer (TU-1901, Peneral, China).

The photoelectrochemical experiments were carried out using a three-electrode system with a saturated calomel electrode (SCE) as the reference, a platinum foil as the auxiliary electrode and as-prepared films as the working electrode. The working electrode potential and current were controlled by an electrochemical workstation (CHI 660c, CH Instruments Inc. USA). A 350 W Xe lamp (Shanghai Hualun Bulb Factory) with AM 1.5 filter was used for light illumination (light density: 100 mW cm⁻²). Incident-photon-to-charge conversion efficiency (IPCE) was measured by a Zahner Zennium electrochemical workstation (UATIL, Germany) using the three-electrode system at 1.0 V in 0.1 M Na₂SO₄ solution.

3. Results and discussion

3.1. The XRD characterization results

Fig. 1A shows X-ray diffraction (XRD) patterns of the pre-annealed tungsten foil (a), the WNA before (b) and after annealing (c). The directly oxidized tungsten foil corresponds to the cubic WO₃ (JCPDS 46–1096). All diffraction peaks of the unannealed WNA can be exclusively indexed by orthorhombic WO₃·0.33H₂O (JCPDS 54–1012) with the strongest reflection of (400) diffraction peak. The annealed WNA is monoclinic WO₃ (JCPDS 43–1035) according to the three characteristic diffraction peaks of (200), (020), and (002), and the (200) diffraction peak is the strongest reflection. Both of the products exhibit the high purity.

3.2. The SEM characterization results

Fig. 1B corresponds to the scanning electron microscope (SEM) image of WNA at low magnification. The smooth and uniform morphology indicates effective control of nanocrystal growth in the hydrothermal process. The compact arranged nanoflakes could be well viewed from the higher-magnification SEM image as shown in Fig. 1C. It should be noted that the single nanoflake is not flat but prickly on the surface with the
overall thickness less than 100 nm as seen from the insert. Such a prickly structure possesses mesoporous networks which provides efficient transport pathways to the interior voids [17]. More importantly, compared with the flat surface, another obviously advantage of the prickly structure is the effective absorbance of the incident photons due to light scattering [18]. Fig. 1D shows the SEM cross-sectional image of annealed WNA with the crystalline nanoflakes vertically deposited on the substrate. The height is calculated to be 3.91 μm.

The insert of Fig. 1B shows the digital photos of the real sample which is dark yellowish color and the bending test for flexibility and stability. In fact, the flexibility of the sample is controllable and depended on the tungsten substrate due to its adjustable thickness. In this paper, the tungsten foil of 0.25 mm in thickness is used as the substrate. The as-prepared sample not only retains the flexibility, but also exhibits good stability since the bending test does not lead to the flaking of the nanoflake arrays. The possible reason could attribute to the self-seeded layer on tungsten substrate resulting in strong adhesion to the growing nanoflake arrays. Therefore, it can be concluded that by using different thickness tungsten substrates, the well-aligned WNA with the anticipated flexibility are expected in order to meet diverse demands. For example, the thinner tungsten foil with more flexibility can be used for growing WNA and further for fabricating flexible solar cells.

In order to investigate the effect of the self-seeded layer and structure-directing agent of PEG on the WO3 nanocrystal growth, comparative experiments were done by employing the pure tungsten foil as substrate instead of the pre-annealed and the aqueous solution without PEG in the hydrothermal reaction, respectively (data not shown). The as-prepared WO3 films are noted as WF1 and WF2 which showed the aggregation of microflowers and compact aggregate WO3 rods, respectively. That is to say, the well-aligned WNA can not be formed without the self-seeded layer and PEG. The self-seeded layer provides the fixed pre-existing nuclei for the preferential WO3 nanocrystal growth in the hydrothermal process. At the same time, the crystal growth orientation is confined by PEG. PEG molecules possible are adsorbed on the growing crystallites and decreased its activity, thus lead to the anisotropic growth of the tungsten trioxide nanocrystal. The nanocrystal growth is confined in the certain direction and the crystal aggregation is suppressed. As a result, the isotropy growth of the tungsten trioxide colloid on the substrate is obviously inhibited, and the nanoflake arrays form instead.

3.3. The UV-vis absorption characterization results

Fig. 2A shows the spectra of annealed WNA, unannealed WNA, WF1 and WF2 with the corresponding band gap plots. The annealed WNA, WF1 and WF2 can effective absorb visible light at long wavelength, while the unannealed WNA only shows slight absorbance below the wavelength of 420 nm. The corresponding bandgap values are determined accordingly as shown in the insert [19,20]. After calculation, the
band gaps of the annealed WNA, WF1 and WF2 are all about 2.6 eV while that of the unannealed WNA is 3.0 eV. The spread photoreponse and lower band gap at higher crystallization could attribute to the crystalline transformation from orthorhombic WO$_3$-0.33H$_2$O to monoclinic WO$_3$.

3.4. Photoelectrochemical properties

Fig. 2B gives the chopped current-potential plots of the annealed WNA, unannealed WNA, WF1 and WF2 under AM 1.5 illumination (100 mW cm$^{-2}$), respectively. The highest photocurrent density is found to be 2.35 mA cm$^{-2}$ at 1.5 V at the annealed WNA, which is comparable with the recently reported WO$_3$ and WO$_3$/Mn photoanodes in references [5,21] and higher than the WO$_3$ photoanodes in [13,22].

This result indicates the advantages of the as-prepared WNA for photoelectrochemical water splitting. The slight photocurrent density at unannealed WNA attributes to its crystal phase and the weak light absorbance. The annealing process, which caused crystallization from orthorhombic WO$_3$-0.33H$_2$O to monoclinic WO$_3$ and enhanced photo-absorbance, results in the increase of photocurrent density [11,12].

The photocurrent of WF1 is very low (0.7 mA cm$^{-2}$). The small photocurrent could attribute to the unnatural connection between WO$_3$ film and the tungsten substrate, which can establish a depletion layer and enormously decrease the electron transfer rate. The self-seeded layer as a part of the tungsten substrate and the pre-existing nuclei for nanocrystal growth provides a natural channel facilitating the electron transfer to a large extent. The photocurrent of WF2 is also obviously smaller than that of the annealed WNA, which indicates the crucial important of PEG for enhancing photoelectrocatalytic property of WNA. Under the structure orientation, the vertically growing WNA leads to the larger surface area and increases the interface between WNA and electrolyte, facilitating incident photons absorbance and the charge transfer for the separation of photoexcited hole/electrons. Therefore, the well-aligned WNA as effective photoanode is resulted from the cooperation of the self-seeded layer and the structure-directing agent of PEG. The rate of hydrogen generation was given in Fig. 2C which was calculated to be 28 μmol h$^{-1}$ cm$^{-2}$ at the applied bias of 1.0 V.

The incident photon to current conversion efficiency (IPCE) experiment is used to measure the effectiveness in converting photons incident to photocurrent flowing (Fig. 2D). The initial photoresponse of the annealed WNA, WF1 and WF2 are found at the visible light illumination, while the unannealed WNA only exhibits slight photoreponse even below 400 nm. The IPCE value of 56% is found at annealed WNA at 367 nm, which is obviously higher than that of the WF1, WF2 and unannealed WNA, suggesting the advantages of the vertically well-aligned nanocrystalline structure and crystalline transformation for solar energy utilization. This result is in accordance with the absorption spectra and photocurrent density analysis.

4. Conclusion

In summary, we present a typical hydrothermal process for fabricating well-aligned WNA vertically grown on tungsten substrate. The tungsten substrate was self-seeded by pre-annealing to provide pre-existing nuclei for nanocrystal growth as well as the natural and strong connection between WNA and tungsten substrate. PEG was employed as the structure-directing agent to orientate the nanocrystal growth. Thus synthesized WNA exhibited superior photoelectrochemical properties indicated by UV–vis absorption spectra, chopped current-potential and IPCE analysis. The synthesis scheme shown here also provides a typical facile approach for constructing nanosteucture on the homogeneous substrate.

Acknowledgments

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