Epitaxial Growth of ZnWO$_4$ Hole-Storage Nanolayers on ZnO

Photoanodes for Efficient Solar Water Splitting

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Experimental Section

All reagents were used without any further purification.

**Preparation of ZnO nanorod arrays thin films:** The ZnO nanorod arrays were fabricated by the sol-gel spin coating and hydrothermal methods in our previous report\(^1\). Fluorine-doped tin oxide (FTO, 1.0×5.0 cm\(^2\))-coated glass substrate were ultrasonically cleaned for 20 min with acetone, isopropanol, ethanol and deionized water, respectively. In a typical experimental procedure, 0.05 M zinc acetate dehydrate \([\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}]\) was dissolved in ethylene glycol monomethyl ether (EM) and stirred at 60 °C for 30 min. Then, an equal amount of diethanolamine (DEA) was added to the mixture to stabilize the solution and stirred at 60 °C for 2 hours. After that, the as-prepared sol was sealed and put for 2 days. Next, the precursor sol (100 μL) was spin coated over an FTO substrate using a vacuum spin coater. The sample was dried in an oven at 150 °C for 15 min and repeated the process for three times. The thin film was annealed in a muffle furnace in air at 350 °C for 30 min to remove residual solvent and obtain the ZnO seed layer. Then, the ZnO seed layer was subjected to the hydrothermal process for the growth of ZnO nanorod arrays. The coated ZnO seed substrate was immersed into the solution mixture to grow ZnO nanorod arrays at 95 °C for 6 h, which contained 0.04 M aqueous solutions of zinc nitrate \([\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}]\) and 0.04 M hexamethylene tetraamine (HMT). Finally, the film was washed with deionized water and absolute ethyl alcohol for several times to remove excess HMT and unreacted or non-adherent particles, followed by a drying step in an oven at 60 °C. Then, the ZnO nanorod arrays thin film was annealed in a muffle furnace in air at 250 °C for 1 h with a heating rate of 2 °C min\(^{-1}\).

**Preparation of the umbrella array structure of ZnWO\(_4\)/ZnO:** The umbrella array structure of ZnWO\(_4\)/ZnO was fabricated by hydrothermal method. The as-prepared ZnO nanorod array was immersed into the solution mixture to grow umbrella structure of ZnWO\(_4\) at 160 °C for 1 h, which contained 0.25 mM aqueous solutions of zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O}]\) and 0.25 mM sodium tungstate dihydrate \((\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O})\). The films were then rinsed thoroughly with deionized water and dried at 60 °C in vacuum. The umbrella array structure of ZnWO\(_4\)/ZnO as prepared was further annealed in air at 400 °C for 1 h.

**Preparation of the umbrella array structure of NiOOH/ZnWO\(_4\)/ZnO:** The umbrella array structure of NiOOH/ZnWO\(_4\)/ZnO was prepared by solution impregnation. The ZnWO\(_4\)/ZnO thin
film was immersed in a mixed solution of 0.5 mM ethylenediamine tetraacetic acid disodium salt (EDTA) and 0.5 mM nickel sulfate hexahydrate (NiSO₄·6H₂O) for 30 min and then washed with deionized water and dried at room temperature.

**Preparation of the umbrella array structure of FeOOH/ZnWO₄/ZnO:** The umbrella array structure of FeOOH/ZnWO₄/ZnO was prepared by solution impregnation. The ZnWO₄/ZnO thin film was immersed in a mixed solution of 0.5 mM ethylenediamine tetraacetic acid disodium salt (EDTA) and 0.5 mM ferrous sulfate heptahydrate (FeSO₄·7H₂O) for 30 min and then washed with deionized water and dried at room temperature.

**Characterization:** The crystal structures of the films were determined by X-ray diffraction (PANalytical X’Pert PRO) using graphite monochromized Cu Kα radiation (40 kV). The morphology and elemental distributions of these as-prepared products were observed by using a field-emission scanning electron microscope (JSM-6701F, JEOL, 5kV) with an energy dispersive spectrometer (EDS). The element composition was carried out by using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) with X-ray monochromatisation as the excitation source. The UV-vis absorption spectra were recorded on a UV-2550 (Shimadzu) spectrophotometer by using BaSO₄ as the reference.

**Photoelectrochemical Measurements:** The photoelectrochemical measurement of the photoanodes were carried out in a three-electrode configuration (photoanode as working electrode, SCE as reference electrode and Pt as counter electrode) under an air mass 1.5 (AM 1.5G, 100 mW·cm⁻²) illumination provided by a solar simulator. An aqueous solution of 0.02 M KOH was used as the electrolyte and the data was recorded by an electrochemical workstation (CHI760E). The scan rate of linear sweep voltammograms (LSV) was 10 mV s⁻¹ and the scanned range was -0.7 V to +0.7 V (vs. SCE). The recorded potentials vs. SCE were converted to the reversible hydrogen electrode (RHE) scale according to the following equation 1:

\[ E_{RHE} = E_{SCE} + 0.059pH + E^0_{SCE} \]

where \( E_{SCE} \) was the experimentally measured potential and \( E^0_{SCE} = 0.24 \) V at room temperature. Stability measurements (current-time) were conducted at a bias voltage of 1.23 V (vs. RHE). Electrochemical impedance spectroscopy (EIS) measurements were performed by applying -0.1 V (vs. SCE) at a frequency range of \( 10^{-2} \) Hz to \( 10^5 \) Hz with small AC amplitude of 10 mV. The incident photon to current efficiency (IPCE) was measured with the aid of a monochromator (Oriel Cornerstone1301/8 m), and calculated using the following
Equation 2:

$$IPCE(\%) = \frac{1240 \times I(\text{mA/cm}^2)}{P_{\text{light}} \ (\text{mW/cm}^2) \times \lambda(\text{nm})} \times 100$$ (2)

where $I$ is the measured photocurrent density at a specific wavelength, $\lambda$ is the wavelength of incident light and $P_{\text{light}}$ is the measured light power density at that wavelength. Supposing 100% Faradaic efficiency, the maximum applied bias photon to current efficiency (ABPE) was calculated using the following Equation 3:

$$ABPE(\%) = \frac{I(\text{mA/cm}^2) \times (1.23 - V_{\text{bias}})(\text{V})}{P_{\text{light}} \ (\text{mW/cm}^2)} \times 100$$ (3)

where $I$ is the measured photocurrent density, $V_{\text{bias}}$ is the applied potential, $P_{\text{light}}$ is the incident illumination power density (100 mW·cm$^{-2}$). The $\eta_{\text{surf}}$ can be calculated by the Equation 4:

$$\eta_{\text{surf}} = \frac{J_{\text{H}_2}}{J_{\text{Na}_2\text{SO}_3}}$$ (4)

Where $J_{\text{H}_2}$ and $J_{\text{Na}_2\text{SO}_3}$ are the photocurrent density at 0.02 M KOH with/without Na$_2$SO$_3$ electrolyte.

Using Ar as a carrier gas, the evolved amounts of H$_2$ and O$_2$ from the PEC cell system were analyzed by an online gas analysis system (Labsolar 6A, Beijing Perfectlight Technology Co. Ltd.) and a gas chromatograph (GC 7890A, Agilent Technologies). Light source and electrolyte were the same as these used for above PEC measurements. The produce of H$_2$ and O$_2$ was performed in a three-electrode system at a constant bias of 1.23 V$_{\text{RHE}}$ under AM 1.5G illumination (100 mW cm$^{-2}$).
Additional Figures and Discussions

Fig. S1 (A, C) Top-view SEM images of pure ZnO nanorod arrays and umbrella array NiOOH/ZnWO₄/ZnO; (B, D) Top-view and cross-section SEM images of ZnWO₄/ZnO.

Fig. S2 XRD patterns of pure ZnO nanorod arrays, ZnWO₄/ZnO and NiOOH/ZnWO₄/ZnO photoanode.
Fig. S3 High-resolution XPS spectra of (A) Ni 2p, (B) O 1s, (C) W 4f and (D) Zn 2p of the NiOOH/ZnWO$_4$/ZnO photoanode.

**Additional discussions**

Fig. S3 shows the high-resolution Ni 2p, O 1s, W 4f and Zn 2p spectra of NiOOH/ZnWO$_4$/ZnO photoanode. The high resolution O 1s spectra (Fig. S3B) show three peaks at 531.9 eV, 530.6 eV and 530.1 eV, which could be assigned to the chemisorbed hydroxyl oxygen and lattice oxygen of ZnO and ZnWO$_4$, respectively$^{1,2}$. In Fig. S3C, the high resolution W 4f spectra show two peaks located at 37.8 eV and 35.6 eV, corresponding to W 4f$_{5/2}$ and W 4f$_{7/2}$, respectively$^3$. For the Zn 2p spectra (Fig. S3D), the two peaks of Zn 2p located at 1044.4 eV and 1021.4 eV could be indexed to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively, illustrating that the valence state of zinc species was in the form of Zn$^{2+}$ ions$^4$. 
Fig. S4 SEM images of pure ZnO (A), and ZnWO$_4$/ZnO hydrothermal time for 30 min (B), 40 min (C), 90 min (D) and 120 min (E) at 160 °C.

**Additional discussions**

To reveal the apparent growth process of ZnWO$_4$ nanoplates on the ZnO nanorod arrays, the hydrothermal reaction time for the ZnO nanorod arrays in Fig. S4 were controlled for 4 hours. The effect of hydrothermal time on the morphology of ZnWO$_4$ was investigated at 160 °C. When the reaction time is 30 min, the top regions of well-defined hexagonal ZnO nanorods have been slightly dissolved into conical structures. The small ZnWO$_4$ nanoplates are formed on ZnO nanorod arrays with the hydrothermal time increased up to 40 min. The umbrella array structure is completely formed with increasing time from 90 min to 120 min. However, when the hydrothermal time is too long, the umbrella array structure of ZnWO$_4$/ZnO is too tight and large in diameter. Therefore, the optimum hydrothermal time is 60 min in this study.
Additional discussions

The comparison experiments were designed to elucidate the effect of hydrothermal temperature on the morphology variety of as-prepared ZnWO₄/ZnO. As shown in Fig. S5B, C, and D, when the hydrothermal temperature increased from 100 °C to 180°C, the morphology of ZnWO₄ changes from particles to umbrella array structure. The umbrella array structure of ZnWO₄/ZnO synthesized at 140 °C is incomplete. However, the umbrella array structure of ZnWO₄/ZnO is too tight and large in diameter with the hydrothermal temperature further increased up to 180 °C, which is harmful for the absorption of light. Therefore, the optimum hydrothermal temperature is 160 °C in this study.
**Fig. S6** Amperometric i-t curves of different photoanodes at 1.23 $V_{\text{RHE}}$ in 0.02 M KOH (pH=12.3) under AM 1.5 G (100 mW cm$^{-2}$) illumination, (B) the enlarged view of i-t curve for NiOOH/ZnWO$_4$/ZnO.

**Additional discussions**

Transient photocurrent density versus time was recorded at a fixed potential of 1.23 $V_{\text{RHE}}$ under light on/off illumination cycles to investigate the photoresponse of different photoanodes. As shown in Fig. S6A, the rise and fall of the photocurrent corresponded well to the illumination being switched on and off. The ZnWO$_4$/ZnO photoelectrode exhibited higher photocurrent conversion efficiency than pristine ZnO photoanode, indicating that ZnWO$_4$ could enhance the electron-hole separation and transport for improving the photocurrent density of ZnO nanorod arrays. After the modification NiOOH cocatalyst on ZnWO$_4$/ZnO, the photocurrent density could be further enhanced, demonstrating that NiOOH accelerated the water oxidation and decreased the charge transfer resistance at the electrode-electrolyte interface. Additionally, Fig. S6B shows the enlarged i-t curve of NiOOH/ZnWO$_4$/ZnO photoanode, and a slightly transient photocurrent could be observed. However, owing to the rapid hole transfer between ZnWO$_4$/ZnO interfaces resulted from their well-matched lattices, the transient photocurrent of this photoanode is not obvious.
**Additional discussions**

The PEC performances under front-side illumination (ZnO side) and back-side illumination (glass side) have been compared in Fig. S7. It can be clearly observed that compared with front-side illumination, the photocurrent density under back-side illumination has been significantly decreased. Furthermore, owing to the limitations of light penetration-depth in photoelectrode layers, the front-side and back-side illumination would result in different charge transport modes. More specifically, the front-side illumination would induce the electron transport across the entire photoelectrode layers to the FTO fundus. In contrast, the back-side illumination would induce the hole transport across the photoelectrode layers to the electrode/electrolyte interfaces.\(^5,6\) Thereby, it was considered that the hole transport is much more sluggish than electron transport in the present photoanodes, which resulted in higher PEC activities under front-side illumination than that of back-side illumination.
Fig. S8 (A) $J$-$V$ curves and (B) i-t curves for NiOOH/ZnWO$_4$/ZnO photoanodes with different NiOOH impregnation times (from 10 min to 60 min) measured with 0.02 M KOH electrolyte in the dark and under AM 1.5G irradiation.
Fig. S9 (A) XRD patterns, (B) $J$-$V$ curves in the dark and under AM 1.5G irradiation, (C) ABPE, (D) i-t curves, (E) IPCE at 1.23 $V_{RHE}$ under monochromatic irradiation, (F) EIS, (G) $J$-$V$ curves with Na$_2$SO$_3$ in the electrolyte and (H) $\eta_{\text{surf}}$ for ZnO, ZnO-Annealed, ZnWO$_4$/ZnO, EDTA/ZnWO$_4$/ZnO and NiOOH/ZnWO$_4$/ZnO photoanodes. ZnO-Annealed refers to ZnO anneal at 400 °C.

**Additional discussions**

Since the synthesis of ZnWO$_4$ and NiOOH with an annealing process and adding into EDTA, respectively, we explored the performance of pure ZnO annealed at 400 °C for 1 h marked as ZnO-Annealed and the performance of EDTA/ZnWO$_4$/ZnO. The XRD patterns of ZnO-Annealed and EDTA/ZnWO$_4$/ZnO are explored shown in Fig. S9A. The results indicated that the crystalline structure of ZnO nanorod arrays and ZnWO$_4$ were not changed after annealed or added into EDTA. Furthermore, the PEC performance of different photoanodes are examined in 0.02 M KOH (pH=12.3) under AM 1.5G simulated sunlight (100 mW cm$^{-2}$) (Fig. S9). The photocurrent density of the ZnO-Annealed was slightly enhanced to 0.79 mA cm$^{-2}$ at 1.23 $V_{RHE}$ compared to the pristine ZnO nanorod arrays (0.53 mA cm$^{-2}$ at 1.23 $V_{RHE}$), which may result from the improved crystallinity of ZnO thin films. Additionally, the photocurrent density of EDTA/ZnWO$_4$/ZnO (1.22
mA cm$^{-2}$ at 1.23 $V_{RHE}$) is only a little improvement compared to ZnWO$_4$/ZnO (1.16 mA cm$^{-2}$ at 1.23 $V_{RHE}$) photoanode, which implied that the effect of EDTA on photocurrent is negligible. Transient photocurrent density versus time curves, ABPE curves, IPCE curves, EIS curves and the surface charge separation efficiencies ($\eta_{surf}$) present the similar results. Therefore, the effect of the annealing process and adding into EDTA on the PEC performances of ZnWO$_4$/ZnO and NiOOH/ZnWO$_4$/ZnO can be excluded.

![Graph showing J-V curves](image)

**Fig. S10** $J$-$V$ curves of pristine ZnWO$_4$ measured with 0.02 M KOH electrolyte in the dark and under AM 1.5G irradiation (100 mW cm$^{-2}$).

**Additional discussions**

As shown in Fig. S10, the photocurrent density of pure ZnWO$_4$ is $1.68 \times 10^{-4}$ mA cm$^{-2}$ at 1.23 $V_{RHE}$, which is almost negligible relative to ZnO (0.53 mA cm$^{-2}$ at 1.23 $V_{RHE}$).
Fig. S11 (A) UV-vis diffuse reflectance spectra and (B) the $(a h v)^2$ versus photon energy plots for pristine ZnO and ZnWO$_4$, respectively; (C, D) valence band XPS spectra of pristine ZnO and ZnWO$_4$; (E) schematic band structures of pristine ZnO and ZnWO$_4$.

Additional discussions

The UV-vis diffuse reflectance spectra (DRS) of pristine ZnO nanorod arrays and ZnWO$_4$ are shown in Fig. S11A. The pristine ZnO and ZnWO$_4$ exhibited a characteristic absorption peak near 390 nm and 320 nm, which agreed well with the band gap of 3.16 eV and 3.89 eV (Fig. S11B). The relative valence band (VB) XPS of pristine ZnO and ZnWO$_4$ are 2.33 eV and 1.65 eV (Fig. S11C and D). Therefore, the conduction band (CB) of pristine ZnO and ZnWO$_4$ would occur at -0.83 eV and -2.24 eV, respectively. Based on the above results, the schematic band structures of pristine ZnO and ZnWO$_4$ is shown in Fig. S11E. As a result of the wide bandgap ($E_g$=3.89 eV) of
ZnWO₄, it almost cannot be excited under AM 1.5G simulated sunlight (100 mW cm⁻²). Therefore, under illumination, plenty of the photogenerated electrons and holes are formed on the conduction band and valance band of ZnO, respectively. The position of VB for ZnO is more positive than that of ZnWO₄, thus the photogenerated holes could transfer easily from ZnO into the VB of ZnWO₄. However, the photogenerated electrons are blocked from the CB of ZnO to ZnWO₄, due to the position of CB for ZnWO₄ is more negative than that of ZnO. Furthermore, the valence band position of ZnWO₄ vs NHE could be calculated according to the following equation⁷:

\[ E_{\text{NHE}} = E_{\text{work function}} + E_{\text{Fermi level}} - 4.44 \]

The work function of ZnWO₄ is 4.8 eV,⁸,⁹ and the valence band position of ZnWO₄ (vs NHE) is equal to 2.01 eV, which is consistent with the previous reports.¹⁰,¹¹ Moreover, the work function of ZnO is 5.3 eV,¹² and the calculated valence band position of ZnO (vs NHE) is 3.19 eV. Therefore, relative to NHE reference, the valence band of ZnWO₄ is also matched to that of ZnO.

Fig. S12 (A) Top-view SEM images and (B) high-resolution XPS spectra of Fe 2p for FeOOH/ZnWO₄/ZnO; (C) \(J-V\) curves in the dark and under AM 1.5G irradiation and (D) \(i-t\) curves for ZnWO₄/ZnO and FeOOH/ZnWO₄/ZnO photoanodes.
Fig. S13 (A, C) Top-view and cross-sectional view SEM images and (B) high-resolution XPS spectra of Mn 2p for MnO₂/ZnWO₄/ZnO.

**Additional discussions**

In order to further illustrate the existence of hole on the surface of ZnWO₄, the oxidation cocatalyst MnO₂ was selectively deposited on ZnWO₄ by photo-deposition method¹³. As shown in Fig. S13A and C, it can be clearly observed that MnO₂ nanoparticles have been uniformly dispersed on the surface. Furthermore, the high resolution spectrum for Mn 2p peaks located at 653.5 eV and 641.7 eV clearly confirmed the formation of MnO₂ nanoparticles (Fig. S13B). This result indicates that ZnWO₄ could serve as a hole-storage layer for promote the hole transfer from ZnO nanowires arrays for selective oxidation of MnSO₄ into MnO₂ by the photo-deposition method.

**Notes and references**


