Materials

$(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$：Shanghai Aladdin Biochemical Technology Co., Ltd., AR; $Zn(NO_3)_2 \cdot 6H_2O$，$FeSO_4 \cdot 7H_2O$：Xilong Chemical Co., Ltd., AR; $Na_2WO_4 \cdot 2H_2O$, $(NH_4)_2C_2O_4 \cdot H_2O$: Shanghai Macklin Biochemical Technology Co., Ltd., AR; HCl: Sinopharm Chemical Reagent Co., Ltd., AR; FTO: 2.2 mm in thickness, 14 Ω in resistance, 90% in transmittance, 350 nm in conductive film thickness, Wuhan Jingge Solar Technology Co.; With all reagents being of analytical grade without further purification, the solution solvent was deionised water.

Characterizations

Scanning electron microscopy (SEM; Zeiss Supra 55) was taken at an accelerating voltage of 15 kV. High-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100) images were recorded at an accelerating voltage of 200 kV. X-ray diffraction analysis (XRD; Rigaku UItimaIII) was performed at a scanning speed of 10°/min in the range of 5-70° diffraction angle. UV-visible diffuse reflectance spectra were recorded on a UV-visible spectrophotometer (Shimadzu UV-2501PC). Raman spectra were collected using a 785 nm laser as an excitation source (LabRAM Aramis). X-ray photoelectron spectroscopy (XPS) spectra were performed with an Axis supra X-ray photoelectron spectroscopy.

Electrochemical measurements of photoanode

PEC water splitting performance tests were measured by an electrochemical workstation (Shanghai Chenhua CHI660E) in 0.5 M Na_2SO_4 electrolyte. The prepared $WO_3/ZnWO_4/ZnFe$ LDH photoanode (1×2 cm^2) was the working electrode, and the

reference and counter electrodes were Ag/AgCl and Pt wires. The illumination source was a 300 W xenon arc lamp (AM 1.5 G filter) with an output power of 100 mW·cm^{-2}. Photocurrents were measured by linear scanning voltammetry (LSV) at a scan rate of 20 mV·s^{-1}. Mott-Schottky plot measurements were performed in the dark at a frequency of 1 kHz. Electrochemical impedance spectroscopy (EIS) was measured at 10^5 to 0.1 Hz in the light.

The E$_{RHE}$ was calculated by:

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^0 + 0.059pH \tag{1}$$

Where $E_{Ag/AgCl}^0 = 0.197V$ at room temperature

The incident photon-to-current conversion efficiency (IPCE) can be calculated by the following Eq. (2):

$$IPCE = 1240 \times I/P_{light} \times \lambda \tag{2}$$

Where P_{light}, λ and I are light intensity (mW·cm^{-2}), wavelength (nm) and photocurrent density (mA·cm^2), respectively.

The applied bias photon-to-current efficiency (ABPE) of photoanodes can be estimated through Eq. (3):

$$ABPE = J(1.23 - E_{RHE})/P_{light} \tag{3}$$

Where J (mA·cm^{-2}) refers to the photocurrent density of the tested photoanode.

Mott-Schottky tests were performed at 1 kHz in the dark and the flat band potential (V$_{FB}$) and carrier density (N$_D$) of the photoanode were calculated based on the M-S curves and the following Eq. (4) and (5).

$$\frac{1}{c^2} = \frac{2}{\varepsilon\varepsilon_0 A^2 e N_D}\left(V - V_{FB} - \frac{k_B T}{e}\right)$$

(4)

$$N_D = \frac{2}{e\varepsilon\varepsilon_0}\left[\frac{d(1/c^2)}{dV}\right]^{-1}$$

(5)

Where A, ε, ε_0, e and V are the area of working electrode, the relative permittivity of a semiconductor electrode, the vacuum permittivity, the elementary charge and the applied potential, $k_B T/e$ is the temperature dependent term and can be neglected at room temperature.

The PEC water oxidation photocurrent density can be expressed as the following Eq. (6) and (7):

$$J_{H_2O} = J_{abs} \cdot \eta_{inj} \cdot \eta_{sep}$$

(6)

$$\eta_{inj} = \frac{J_{H_2O}}{J_{Na_2SO_3}} \times 100\%$$

(7)

where J_{H_2O} and $J_{Na_2SO_3}$ are photocurrent density measured without and with hole scavengers, respectively; J_{abs} is the maximum theoretical high current density, a constant derived from the region of overlap between the UV-Vis absorption spectrum and the AM 1.5G solar spectrum; η_{inj} is the electron injection efficiency; η_{sep} is the electron separation efficiency.

Eq. 6 reflects the energy loss in different reaction steps in PEC water splitting. In order to calculate the detailed efficiency of each step, a hole scavenger is added to the electrolyte to eliminate the energy loss from surface water oxidation, which assumes that $\eta_{inj} = 1$. Thus, it results that $J_{Na_2SO_3} = J_{abs} \cdot \eta_{sep}$, and η_{sep} can be derived quite simply

by measuring the photocurrent density with the addition of the hole scavenger. By combining the equation $J_{Na_2SO_4} = J_{abs} \cdot \eta_{sep}$ and Eq. 6, η_{sep} can be calculated (Eq. 7).

Supplementary Figures
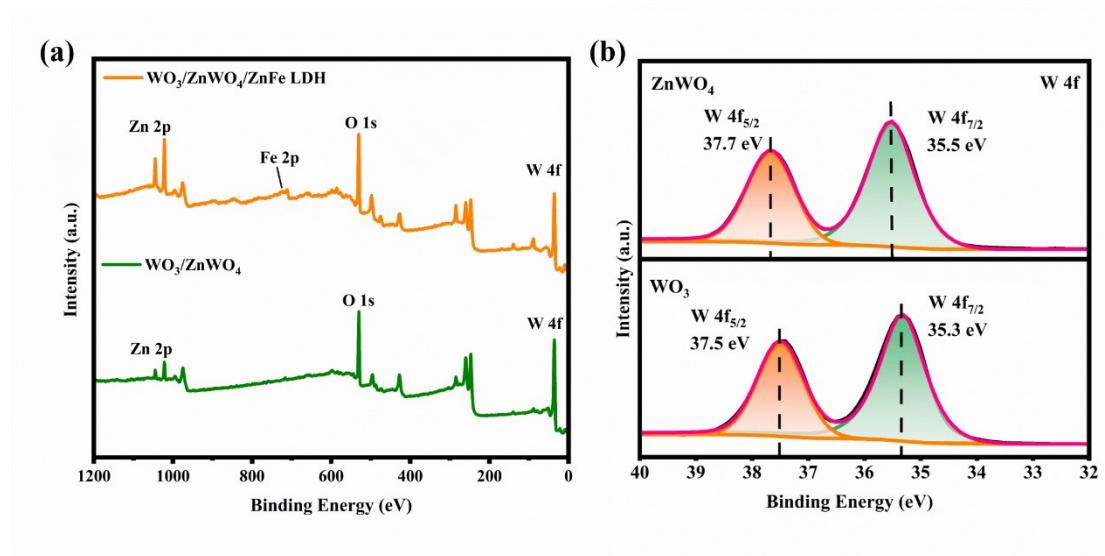

Fig. S1 (a) XPS survey scan spectra of different photoanodes; (b) XPS spectra of W 4f for WO_3 and $ZnWO_4$
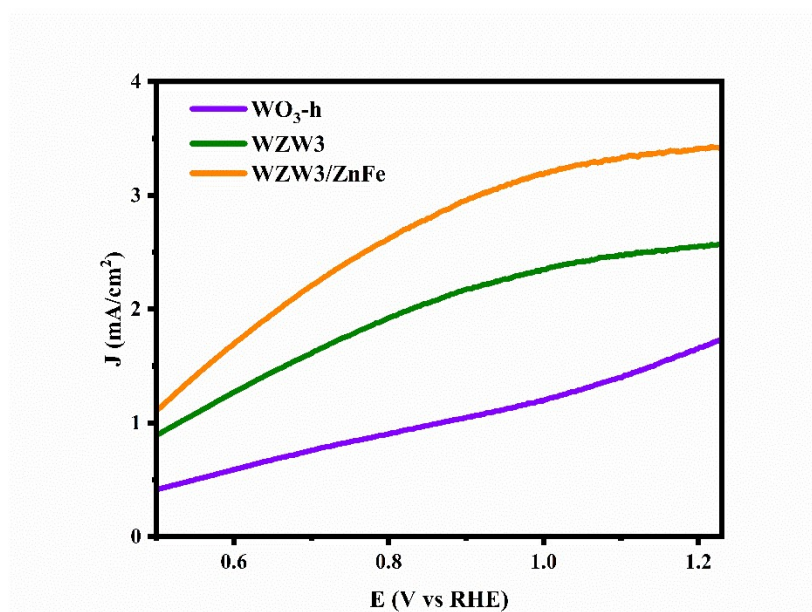
Fig. S2 Photocurrent-potential curves with hole scavengers

The fitted straight line represents the rate of hydrogen (or oxygen) evolution as shown in Fig. S3. The rates of oxygen and hydrogen evolution for WO_3/$ZnWO_4$/ZnFe LDH were 0.1913 μmol·min^{-1} and 0.3852 μmol·min^{-1}, respectively.
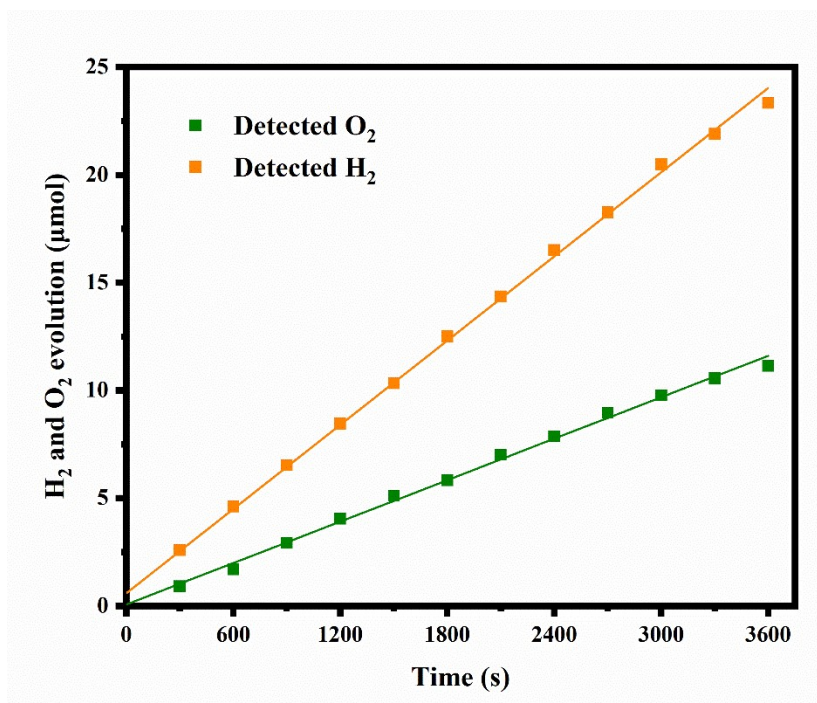
Fig. S3 Hydrogen and oxygen evolution curves of WO_3/$ZnWO_4$/ZnFe LDH