

Hierarchical zeolites containing embedded $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ as a photocatalyst for hydrogen production from seawater

Yue Yuan^{†a}, Feng-Juan Wu^{†a}, Shi-Tian Xiao^{†a}, Yi-Tian Wang^{†a}, Zhi-Wen Yin^{†a}, Gustaaf Van Tendeloo^{ab}, Gang-Gang Chang^a, Ge Tian^a, Zhi-Yi Hu^{*a}, Si-Ming Wu^{*a}, Xiao-Yu Yang^{*a}

Author contributions

Y.Y., F.J.W., S.T.X., Y.T.W., Z.W.Y. contributed equally to this work. Y.Y., F.J.W. carried out the experiments of synthesis, photocatalytic performance and photoelectrochemical performance. X.Y.Y. conceived the project, provided the idea, and designed the experiments. Z.W.Y and Z.Y.H. performed the measurements of TEM and corresponding analysis. Y.T.W., S.T.X, S.M.W. guided the experiments, helped with photocatalysis, corresponding mechanism and helped with the pictures drawing. G.T. conceived the project and revised the paper. G.G.C., Z.Y.H. and G.V.T revised the paper. Y.Y., Y.T.W., S.T.X., S.M.W. and X.Y.Y. wrote and revised the paper. All the authors discussed results and analyzed the data and have given approval to the final version of the manuscript.

EXPERIMENTAL SECTION

Chemicals

Ethanol, *N, N*-Dimethylformamide (DMF), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), ethylene glycol (EG), sodium sulfite (Na_2SO_3) and sodium chloride (NaCl) were provided by Sinopharm Chemical Reagent Co., Ltd. Hexadecyl trimethyl ammonium Bromide (CTAB), tetraethyl orthosilicate (TEOS), tetrapropylammonium hydroxide (TPAOH), cadmium acetate dihydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) and zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) were provided by Shanghai Aladdin Biochemical Technology Co, Ltd. Sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was provided by Shanghai Macklin Biochemical Technology Co., Ltd. 1-octyl-3-methylimidazolium tetrafluoroborate ($[\text{OMIM}]\text{BF}_4$) was provided by Lanzhou Greenchem ILs. Deionized water was used in the whole experiment.

Synthesis

The 100 nm mesoporous silica (100 nm MS) was synthesized by sol-gel method. Under magnetic stirring, 57 g deionized water, 57 g DMF, 2.4 g CTAB and 3 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ were added into the beaker. After full and uniformly mixing, 6 mL TEOS was added and stirred for 3 h. When the reaction was completed, the suspension was centrifuged, washed and dried to obtain white powder. The white powder was calcined in Muffle furnace at 550 °C for 6 h so that 100 nm MS was obtained.

The lamellar closed pore hierarchal zeolite Silicalite-1 (S-1) was synthesized by solid phase method. In a typical experiment, 0.2 g 100 nm MS was added into the mortar and been fully grinded, then 200 μL [OMIM] BF_4 , 500 μL deionized water and 200 μL TPAOH were added to grind in order. After grinding evenly, the gel was added into a 25 mL sealed Teflon-lined stainless steel autoclave, and reacted at 180 $^\circ\text{C}$ for 18 h. The sample after reaction was centrifuged, washed and dried to obtain white powder. The white powder was calcined in Muffle furnace at 550 $^\circ\text{C}$ for 6 h so that S-1 was obtained.

The $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}@S-1$ (CZS@S-1) composites were obtained by a one-step solvothermal method.¹ 0.013 g $\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 0.044 g $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ and 30 mL EG were added into 100 mL Teflon lining and stirred for 30 min to form a uniform solution. At the same time, an appropriate amount of as-prepared S-1 was dispersed in 10 mL EG for 30 min by sonication. The obtained S-1 solution was slowly added into the above mixed salt solution and stirred for 1 h. Then 10 mL 0.03 M Na_2S aqueous solution was added dropwise under continuous stirring. After stirring for 2 h, the samples were put into a stainless steel autoclave and maintained at 160 $^\circ\text{C}$ for 4 h. The samples after reaction were filtered, washed and dried to obtain CZS@S-1 composites. The as-synthesized samples containing 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt% CZS are labeled 10% CZS@S-1, 15% CZS@S-1, 20% CZS@S-1, 25% CZS@S-1 and 30% CZS@S-1, respectively. For comparison, the pure CZS sample was also prepared using the similar solvothermal method in the absence of S-1.

Characterization

The sample morphology was characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800), transmission electron microscope (TEM), High-Resolution High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HR-HAADF-STEM) and integrated differential phase contrast scanning transmission electron microscopy (iDPC-STEM) (Thermo Fisher Talos F200S, Titan Themis G2 60-300, Helios Nanolab G3 UC). The crystal structure was characterized by the X-ray diffraction diffractometer (XRD, Bruker AXS D8 ADVANCE X-ray diffractometer, Cu K α radiation, $\lambda = 0.15406$ nm). The porous structure was investigated by N₂ adsorption/desorption at 77 K (TriStar TM II 3020, Micromeritics) and the samples were degassed at 100 °C for 12 h before the measurements. Ultraviolet-visible spectroscopy diffuse reflectance spectra (UV-vis DRS) were obtained by a UV-vis spectrophotometer (Lambda 750 S). X-ray photoelectron spectra (XPS) of the samples were recorded using a monochromatic Al-K α X-ray source, all binding energies were calibrated to the C1s peak at 284.8 eV (ESCALAB250Xi). The chemical composition of the samples were characterized by Fourier transform infrared spectra (FT-IR, Nicolet Avatar 360 FT-IR infrared spectrometer).

Photocatalytic activity Evaluation

Photocatalytic H₂ production was performed in a closed circulation system using a MC-PF300C lamp (Beijing merry change technology co., ltd) with UV-vis spectroscopy. The lamp was set 10 cm higher than the reaction solution liquid level. 20 mg of sample was suspended

in 80 mL sodium chloride solution or MgCl_2 solution of 0.1M $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$ (NaCl solution concentration is 0 wt%, 3.5 wt% or 10 wt%, MgCl_2 solution concentration is 5.2 g/L). The mixture was sealed in a quartz vessel and vacuumed for 15 min to remove the dissolved oxygen, a continuous magnetic stirrer and cooling water were applied during the experiment. The produced H_2 was analyzed by gas chromatograph (GC, Agilent 7890 A) with a thermal conductivity detector (TCD).

Photoelectrochemical Measurements.

An electrochemical workstation (Autolab PGSTAT302N) was used to carry out the photoelectrochemical measurements, including the photocurrent tests, electrochemical impedance spectra (EIS) and Mott–Schottky curves measurements. Photocurrent tests were carried out in a conventional three-electrode with a Pt foil as the counter electrode and a Ag/AgCl Electrode reference electrode under a PLS-SXE-300C lamp. The working electrodes were prepared by dispersing catalysts (5 mg) and Nafion solution (10 μL , 5 wt%) in water/ethanol mixed solvent (500 μL , 1:1 v/v) at least 10 min of sonication to form a homogeneous ink. The working electrode was synthesized by drop-casting the above ink (25 μL) onto FTO glass with an area of 1 cm^2 . EIS were obtained with a frequency range of 100 kHz to 0.1 Hz. Mott–Schottky curves were recorded at frequencies of 3.0 and 5.0 kHz, respectively.

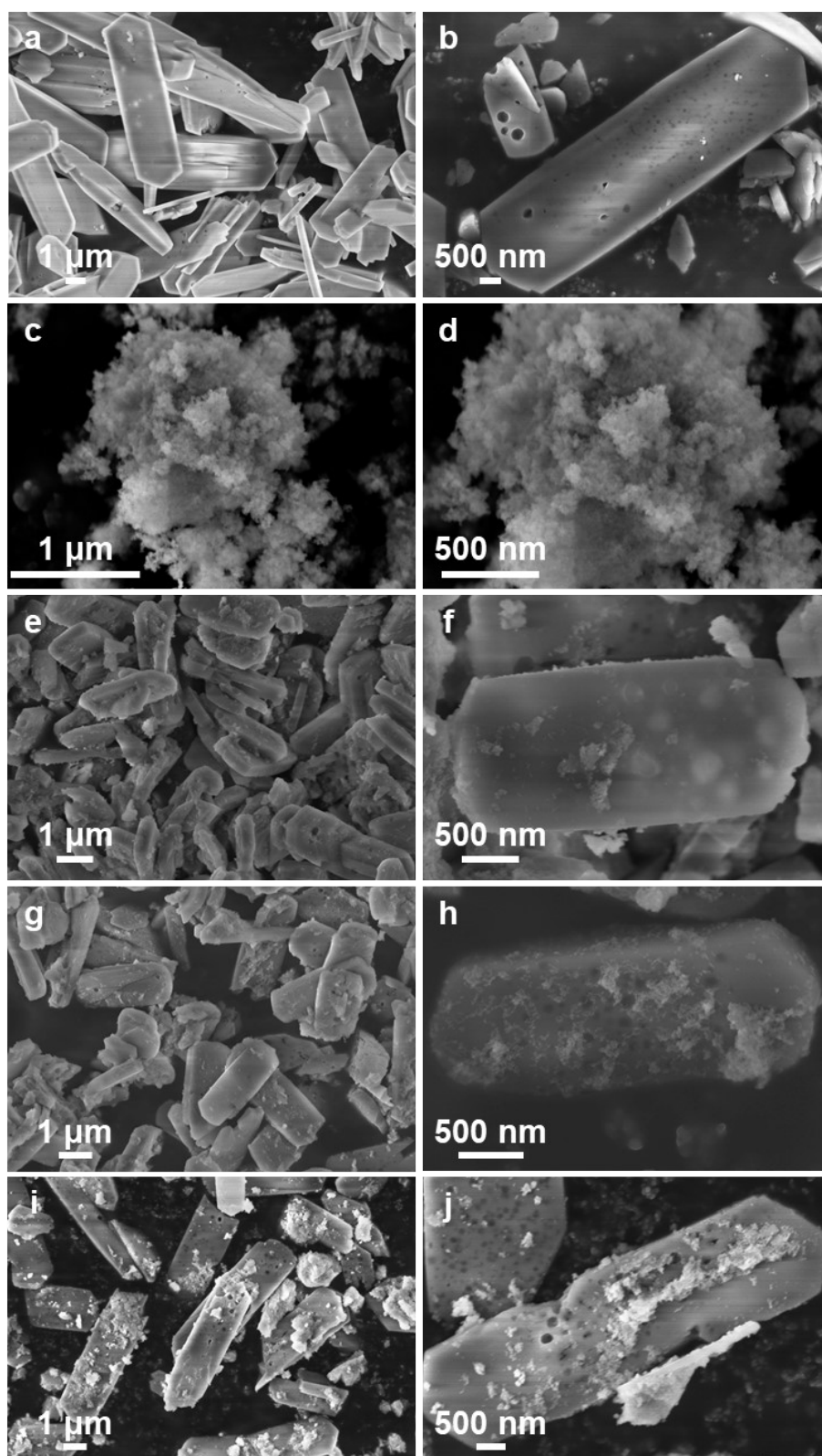


Fig. S1 SEM images of (a-b) S-1, (c-d) CZS, (e-f) 10% CZS@S-1, (g-h) 20% CZS@S-1 and (i-j) 30% CZS@S-1.

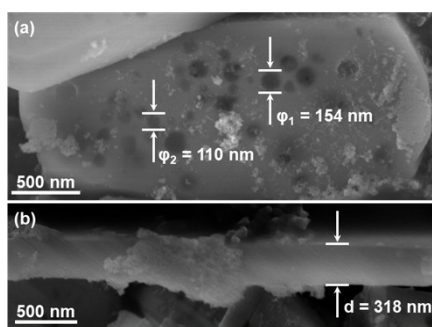


Fig. S2 SEM images of 20% CZS@S-1.

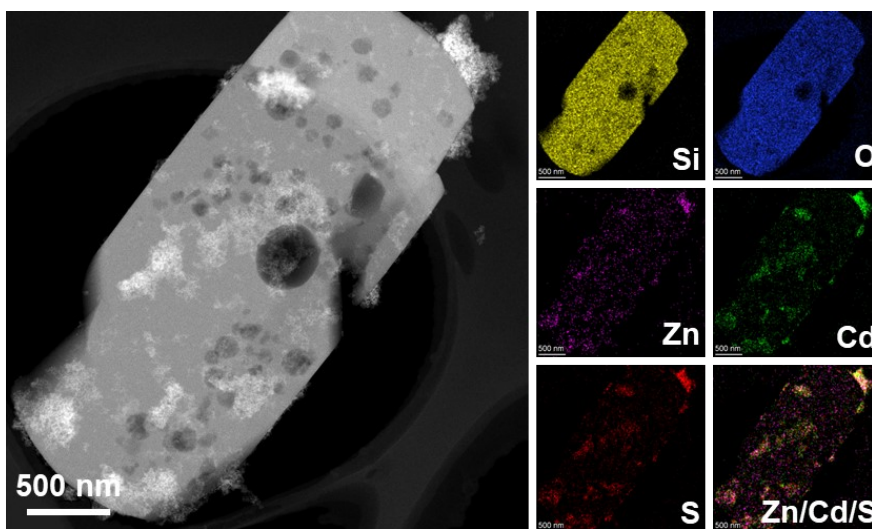


Fig. S3 HAADF-STEM image and EDX elemental maps of 20% CZS@S-1: Si (yellow), O (blue), Zn (pink), Cd (green) and S (red).

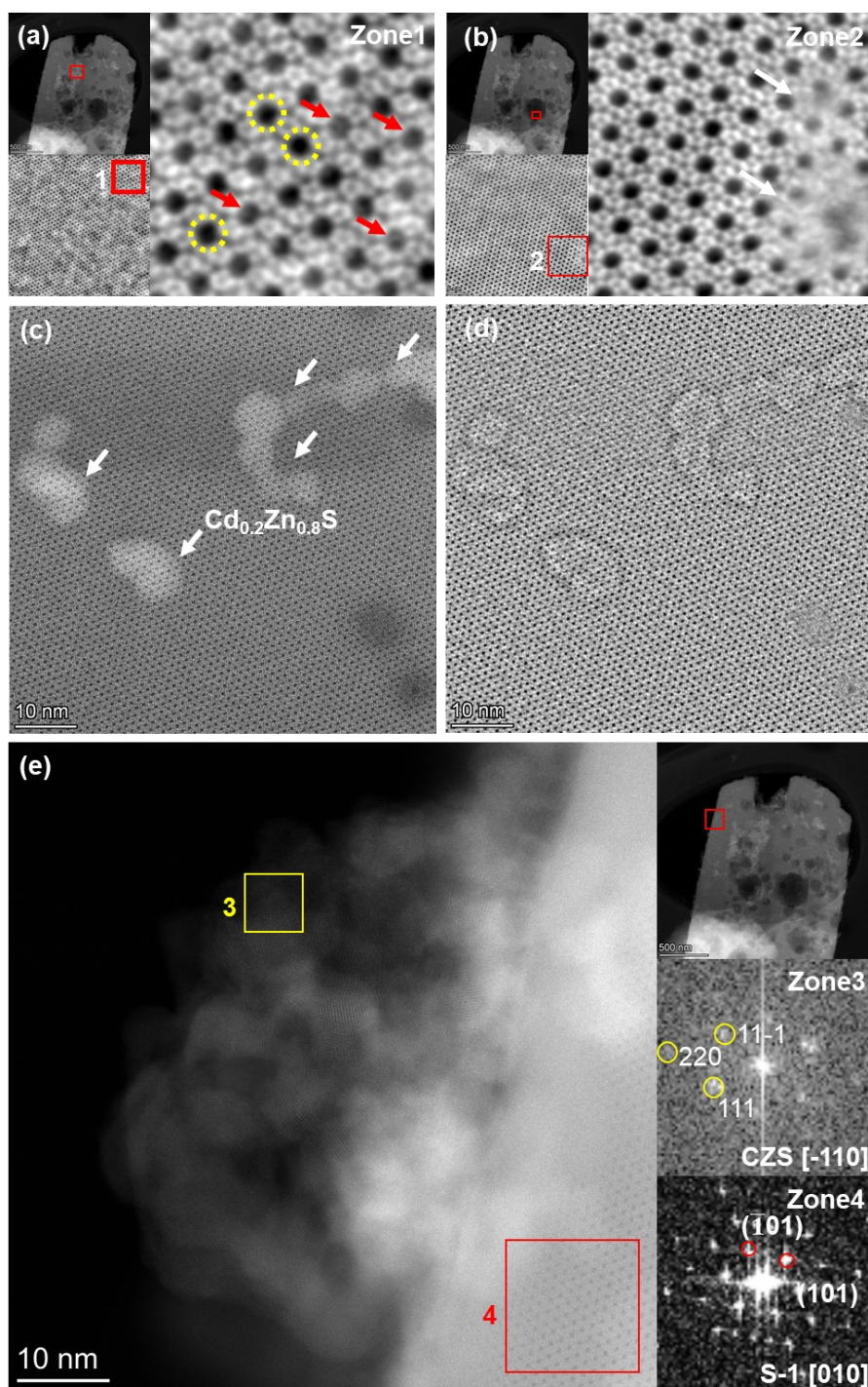


Fig. S4 (a-b) HAADF-STEM image and corresponding iDPC-STEM image, (c) Low dose HAADF-STEM raw image, (d) Low dose HAADF-STEM image with filter, and (e) HR-STEM image, HAADF-STEM image and corresponding FFT of the zone3 and zone4 of 20% CZS@S-1.

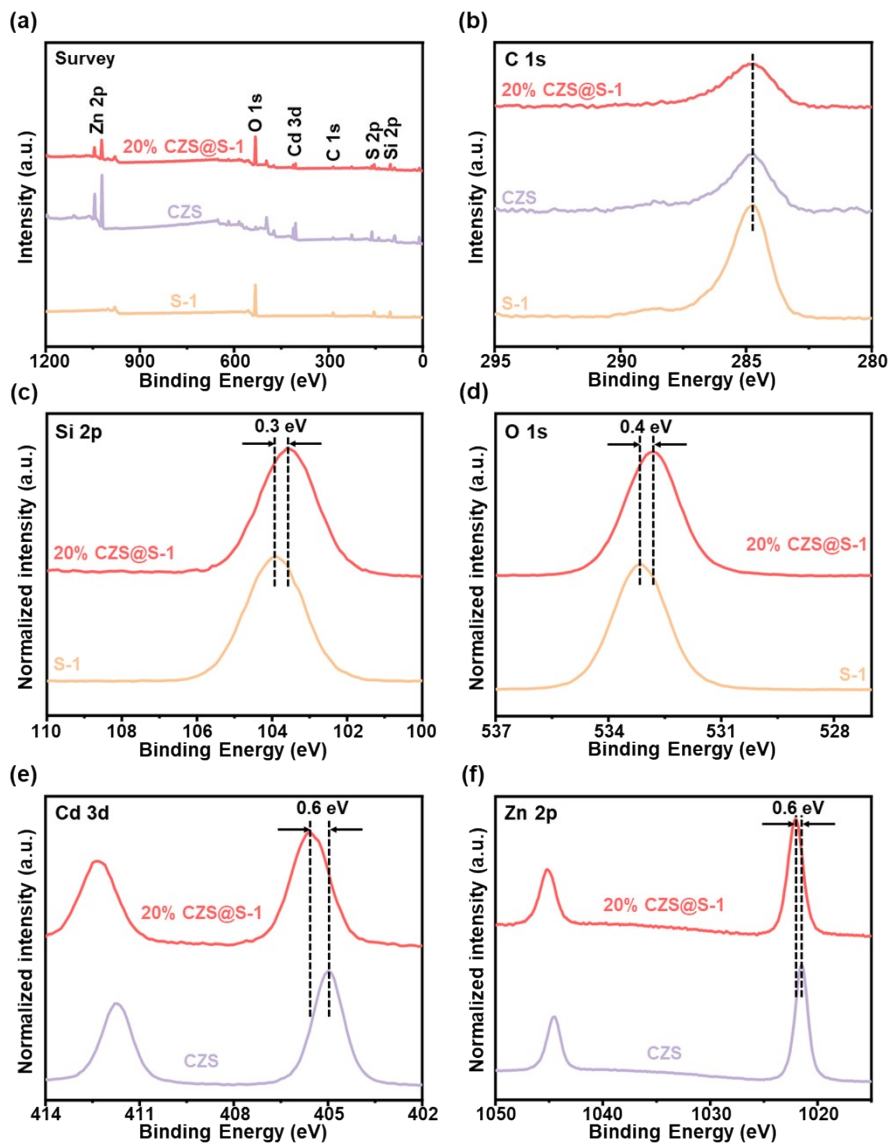


Fig. S5 XPS spectra of (a) survey spectra and (b) C 1s of S-1, 20% CZS@S-1 and CZS, (c) Si 2p and (d) O 1s of S-1 and 20% CZS@S-1, (e) Cd 3d and (f) Zn 2p of 20% CZS@S-1 and

CZS.

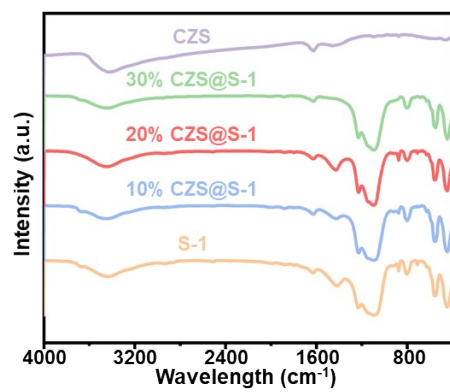


Fig. S6 FT-IR spectra of S-1, 10% CZS@S-1, 20% CZS@S-1, 30% CZS@S-1 and CZS.

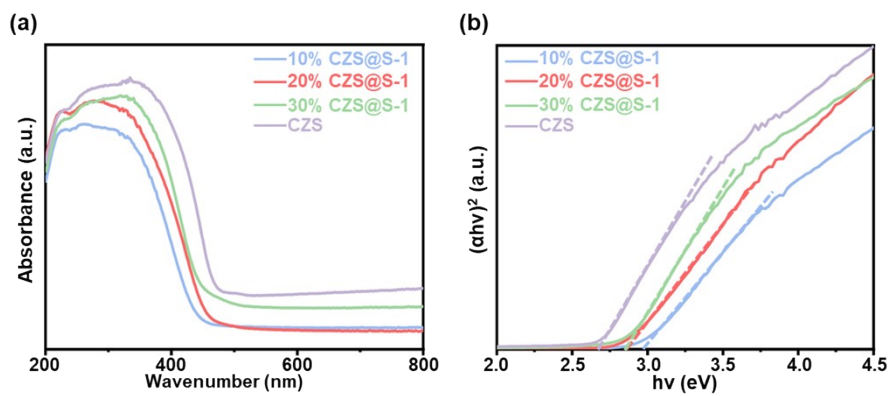


Fig. S7 (a) UV-vis diffuse reflectance spectrum of 10% CZS@S-1, 20% CZS@S-1, 30% CZS@S-1 and CZS, (b) Plots of the Kubelka-Munk function (vertical axis) against the photon energy.

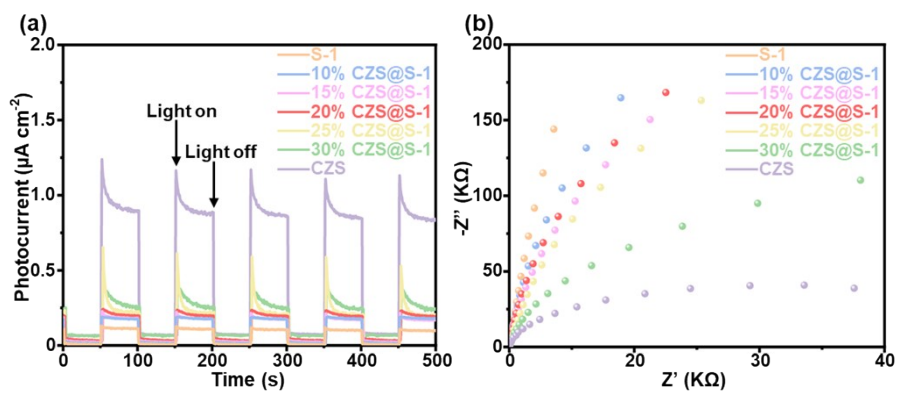


Fig. S8 (a) Transient photocurrent response curves, (b) EIS Nyquist plots of S-1, 10% CZS@S-1, 15% CZS@S-1, 20% CZS@S-1, 25% CZS@S-1, 30% CZS@S-1 and CZS.

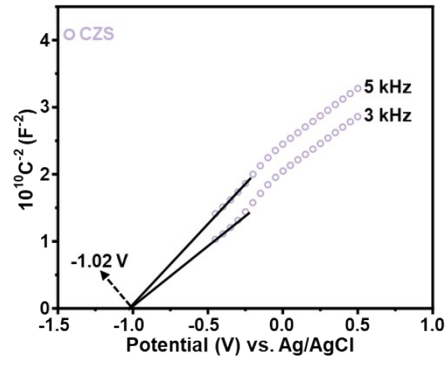


Fig. S9 Mott-Schottky curves of CZS.

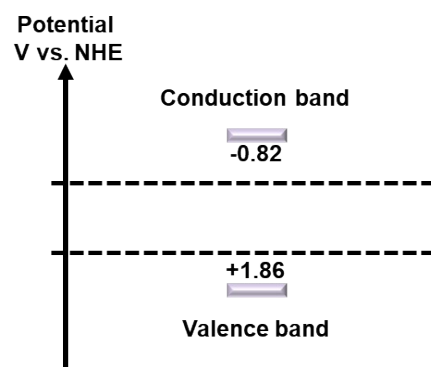


Fig. S10 Schematic representation of the conduction and valence band positions of CZS.

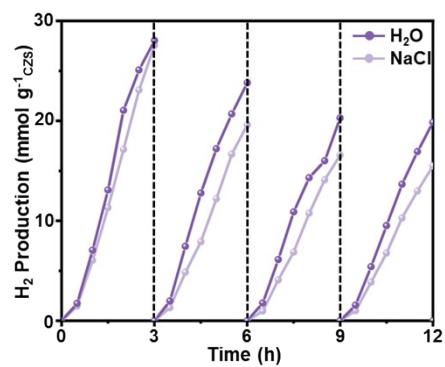


Fig. S11 Photocatalytic H₂ production promoted by CZS in H₂O and simulated seawater during different time cycles, a certain amount of sacrificial agent is added during each cycle.

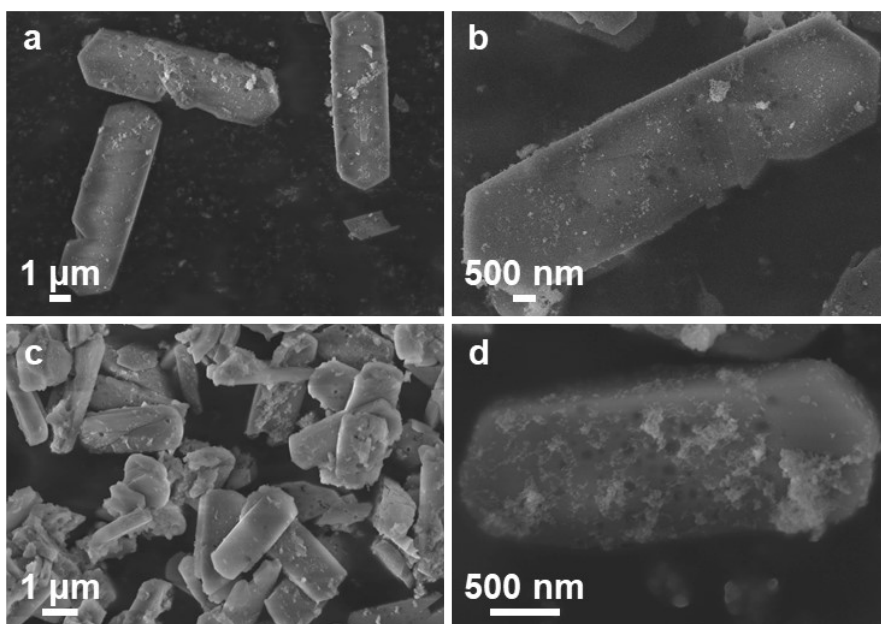


Fig. S12 SEM images of (a-b) 20% CZS@S-1 after being illuminated for 12 h in simulated seawater and (c-d) 20% CZS@S-1.

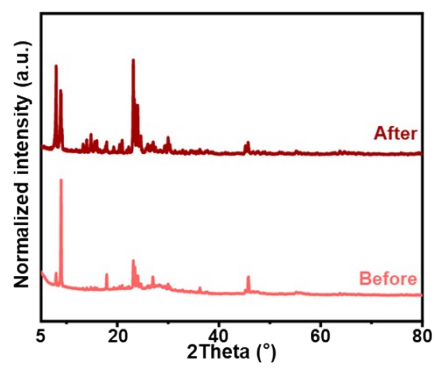


Fig. S13 XRD patterns of 20% CZS@S-1 after being illuminated for 12 h in simulated seawater and 20% CZS@S-1.

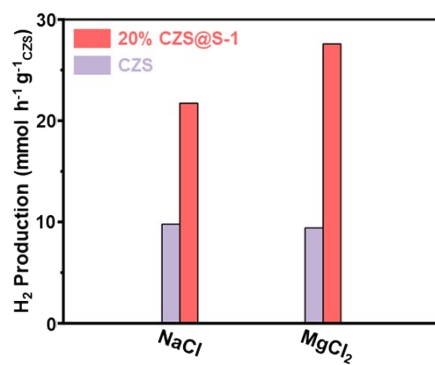


Fig. S14 Photocatalytic H₂ production activities of 20% CZS@S-1 and CZS in 3.5 wt% NaCl and 5.2 g/L MgCl₂.

Table S1 The BET surface areas and pore distributions of S-1, 10% CZS@S-1, 20% CZS@S-1, 30% CZS@S-1 and CZS.

Samples	S _{bet} (m ² /g)	Pore diameter (nm)
S-1	325	2
10% CZS@S-1	231	11
20% CZS@S-1	218	11
30% CZS@S-1	220	10
CZS	123	25

Table S2 The elemental and CZS contents in the CZS@S-1 composites

Sample	Atomic ratio (Zn : Cd)	CZS (wt%)
10% CZS@S-1	3.7±0.4 : 1	8.9±0.4
15% CZS@S-1	4.0±0.4: 1	12.2±0.6
20% CZS@S-1	4.5±0.5: 1	19.4±1.0
25% CZS@S-1	5.0±0.5: 1	22.7±1.1
30% CZS@S-1	5.0±0.5: 1	27.5±1.4
CZS	4.2±0.4: 1	100

REFERENCE

1. Y. Su, Z. Zhang, H. Liu and Y. Wang, *Appl. Catal. B.-Environ.*, 2017, **200**, 448-457.