

Electronic Supporting Information for

Regulated TiO₂@NC@ZCS Photocatalyst for Efficient Hydrogen Evolution: Insights into the Role of Carbon Layer Positioning

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Chemicals

2-Aminoterephthalic acid ($C_8H_7NO_4$, 98%, Energy Chemical), Titanium(IV) isopropoxide ($C_{12}H_{28}O_4Ti$, 99%, Energy Chemical), N,N-Dimethylformamide (DMF, 99.5%, Sinopharm Group), Methanol (CH_3OH , 99.5%, Sinopharm Group), Cadmium acetate dihydrate ($C_4H_{10}CdO_6$, 98%, Energy Chemical), Zinc acetate dihydrate ($C_4H_{10}O_6Zn$, 99%, Energy Chemical), Thiourea (CH_4N_2S , 98%, Energy Chemical). All the above reagents were used without further purification.

Catalyst preparation

(1) Synthesis of Ti-NH₂-MIL-125 hexahedron: Titanium isopropoxide (TIPT) was used as the titanium source, and 2-aminoterephthalic acid as the organic linker. A simple hydrothermal method was employed, reacting at 150°C for 24 h. After the autoclave was naturally cooled to room temperature, the sample was collected by centrifugation, thoroughly washed 3-4 times with ethanol, and dried at 60°C. Finally, a monodisperse Ti-NH₂-MIL-125 template with a hexahedral structure was obtained.

(2) Synthesis of TiO₂@NC: Ti-NH₂-MIL-125 was used as the precursor. It was calcined at 500°C under a nitrogen atmosphere at a heating rate of 5°C·min⁻¹ for 2 h to obtain TiO₂@NC.

(3) Synthesis of TiO₂@NC@Zn_{0.2}Cd_{0.8}S: 20 mg of TiO₂@NC, 6.7 mg of cadmium acetate dihydrate, 22 mg of zinc acetate dihydrate, and 13.5 mg of thiourea were dispersed in 15 mL of N,N-dimethylformamide to prepare a suspension. The suspension was then transferred to a round-bottom flask and heated at 120°C for 4 h. After the flask was cooled, the sample was collected by centrifugation, washed 3-4 times with ethanol, and dried at 60°C to obtain TiO₂@NC@Zn_{0.2}Cd_{0.8}S(TiO₂@NC@ZCS).

(4) Synthesis of Zn_{0.2}Cd_{0.8}S (ZCS): 2.5 mmol of cadmium acetate, 2.5 mmol of zinc acetate, and 5 mmol of thiourea were dissolved in 80 mL of ethylene glycol. The solution was placed in a 100 mL autoclave and heated at 140°C for 4 h. The cooled product was repeatedly washed with ethanol and dried in an oven at 60°C.

(5) Synthesis of TiO₂@Zn_{0.2}Cd_{0.8}S@NC: 20 mg of Ti-NH₂-MIL-125, 6.7 mg of cadmium acetate dihydrate, 22 mg of zinc acetate dihydrate, and 13.5 mg of thiourea were added to 15 mL of N,N-dimethylformamide. The suspension was then transferred to a round-bottom flask and heated at 120°C for 4 hours. After cooling, the sample was collected by centrifugation, washed 3-4 times with ethanol,

and dried at 60°C to obtain NH₂-MIL-125@Zn_{0.2}Cd_{0.8}S. Finally, the product was calcined at 500°C under a nitrogen atmosphere at a heating rate of 5°C·min⁻¹ for 2 h to obtain TiO₂@Zn_{0.2}Cd_{0.8}S@NC (TiO₂@ZCS@NC).

(6) Synthesis of pristine TiO₂: 100 mg of TiO₂@NC was used as the precursor. It was calcined at 500°C in air for 2 h to obtain TiO₂.

(7) Synthesis of TiO₂@Zn_{0.2}Cd_{0.8}S: The synthesis of TiO₂@ZCS was similar to that of TiO₂@NC@Zn_{0.2}Cd_{0.8}S, except for changing TiO₂@NC to TiO₂.

Photocatalytic hydrogen production test

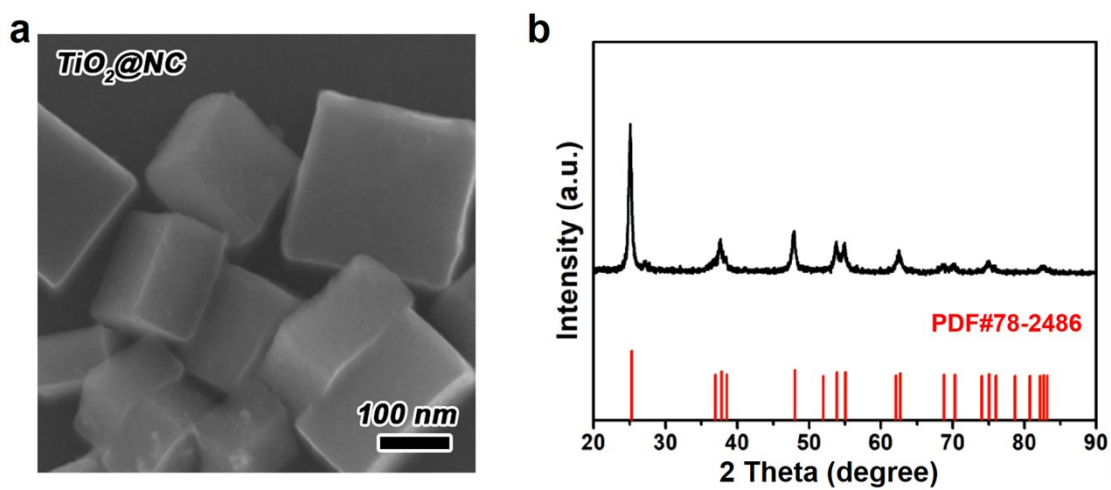
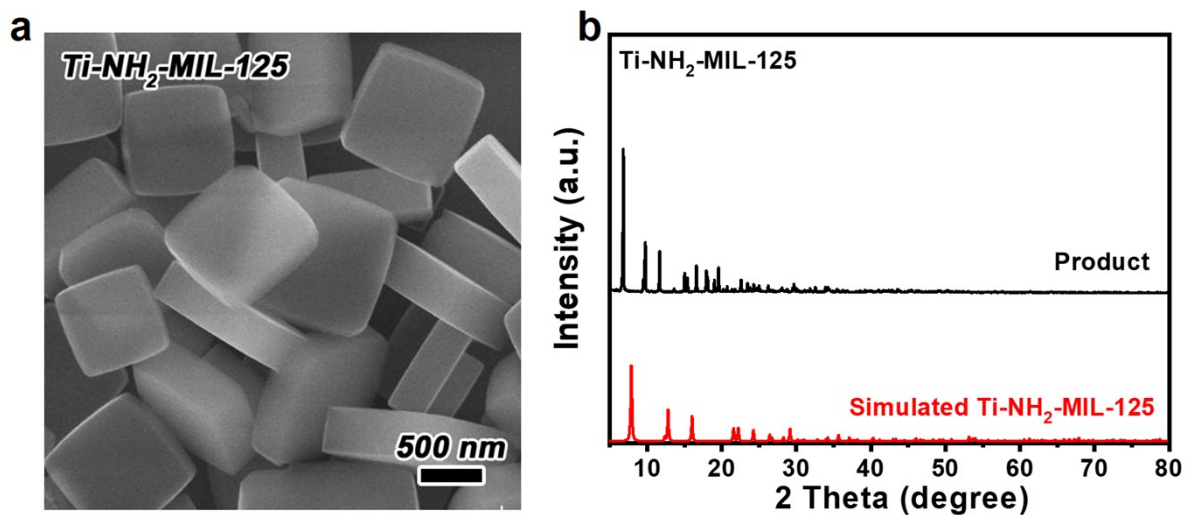
The photocatalytic reaction was carried out in a gas-closed system with a reactor made of quartz. A 300 W xenon lamp was used as a light source. The distance between the lamp and the reactor is 3 cm. In a typical experiment, the photocatalyst (5 mg) was added into the aqueous solution (8 mL) containing triethanolamine (TEOA) (8 vol%). The mixture was sonicated for 5 min to form a homogeneous suspension. Then, N₂ was bubbled in the suspension for 30 min. After the gas-closed system was vacuumed, the suspension was irradiated. The amounts of hydrogen produced were measured with a gas chromatograph (GC-7900, China, molecular sieve 5 Å, TCD) using N₂ as a carrier gas.

Characterization

The micromorphology of the sample was observed by field emission scanning electron microscopy (FE-SEM, SU-8010II) under the acceleration voltage of 15.0 kV. High-resolution TEM (HRTEM) images and elemental mapping were captured on a Tecnai G2 F30 S-TWIN at an acceleration voltage of 300 kV. The crystal phase was performed by X-ray diffraction (XRD) on a Bruker D8 Advanced X-ray Diffractometer (Cu-Kα radiation: λ = 0.15406 nm). X-ray photoelectron spectra (XPS) were carried out on a Physical Electronics PHI Quantum 2000. The specific surface areas of these samples were measured by the Brunauer-EmmettTeller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. The light absorption capacity was tested by Cary 5000 UV-visible-near-infrared absorption spectrometer.

Photo-electrochemical test

Photoelectrochemical measurements were performed using a PAR VMP3 multichannel potentiostat in a custom-made three-electrode quartz cell. A Pt plate was used as the counter electrode, and a Hg/HgCl₂ electrode served as the reference electrode. The working electrode was prepared on fluorine-doped tin oxide (FTO) glass, which was ultrasonically cleaned in a mixture of ethanol and acetone for 10 minutes and dried at 60°C. Typically, 5 mg of sample powder was ultrasonically dispersed in 0.2 mL of ethanol to obtain a slurry. The slurry was then applied onto the FTO glass, with its edges protected by transparent adhesive tape. After air drying, the adhesive tape was removed. The working electrode was further dried at 150°C for 2 h to enhance adhesion. The exposed area of the working electrode was 2.5 cm². Electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI-760E workstation under open-circuit potential conditions, using 0.025 M KH₂PO₄ and 0.025 M Na₂HPO₄ standard buffer solutions (25°C, pH = 6.864) as the electrolyte in the three-electrode cell, without any added additives. The visible light irradiation source was a 300 W xenon arc lamp system. Cathodic polarization curves were obtained using linear sweep voltammetry (LSV) with a scan rate of 100 mV s⁻¹. The photocurrent density of the sample was measured at 0.2 V vs. Hg/Hg₂Cl₂ under both dark (non-illuminated) and illuminated (light) conditions.



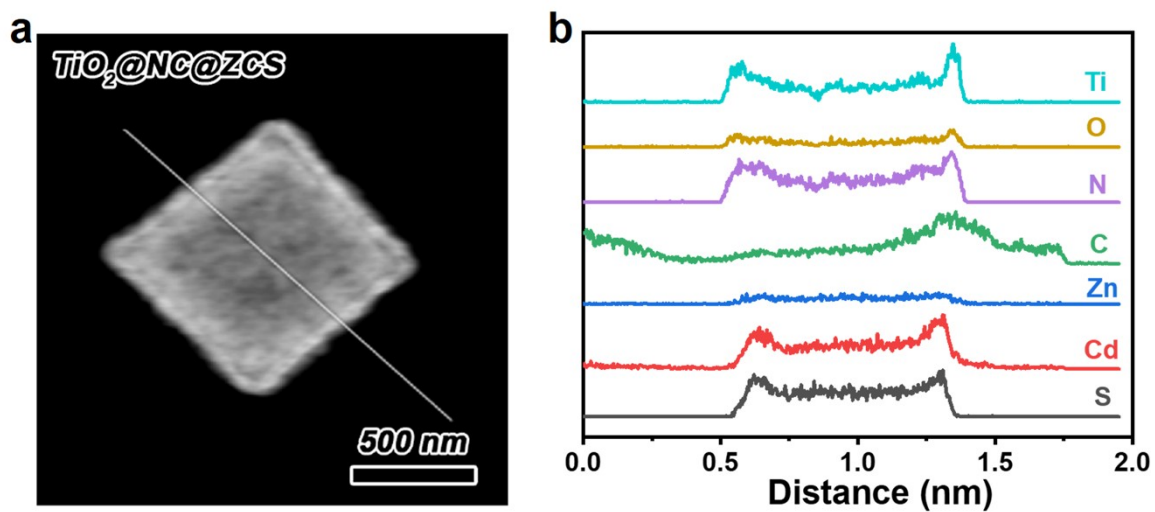


Figure S3. STEM Elemental line-scan analysis

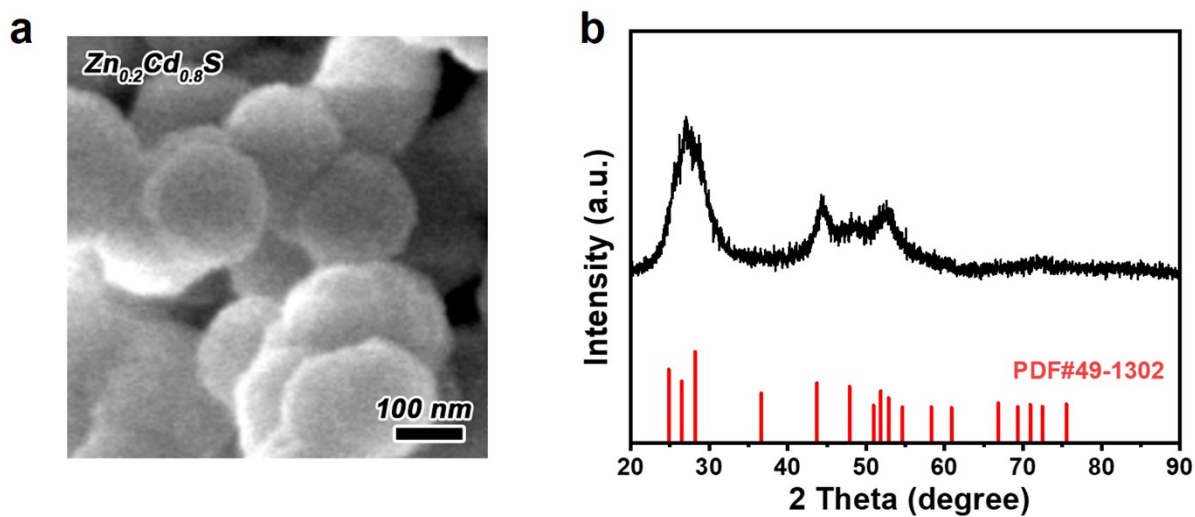


Figure S4. (a) SEM image and (b) XRD pattern of ZCS.

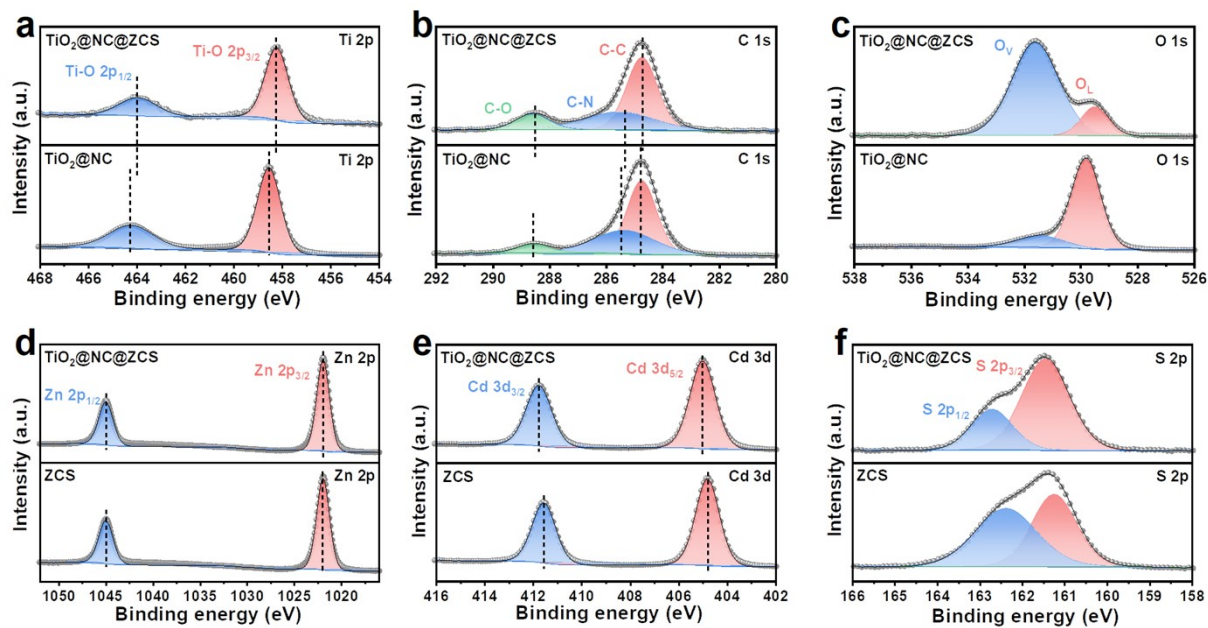


Figure S5. High-resolution XPS spectra of the prepared catalysts: (a) Ti 2p. (b) C 1s. (c) O 1s. (d) Zn 2p. (e) Cd 3d. (f) S 2p.

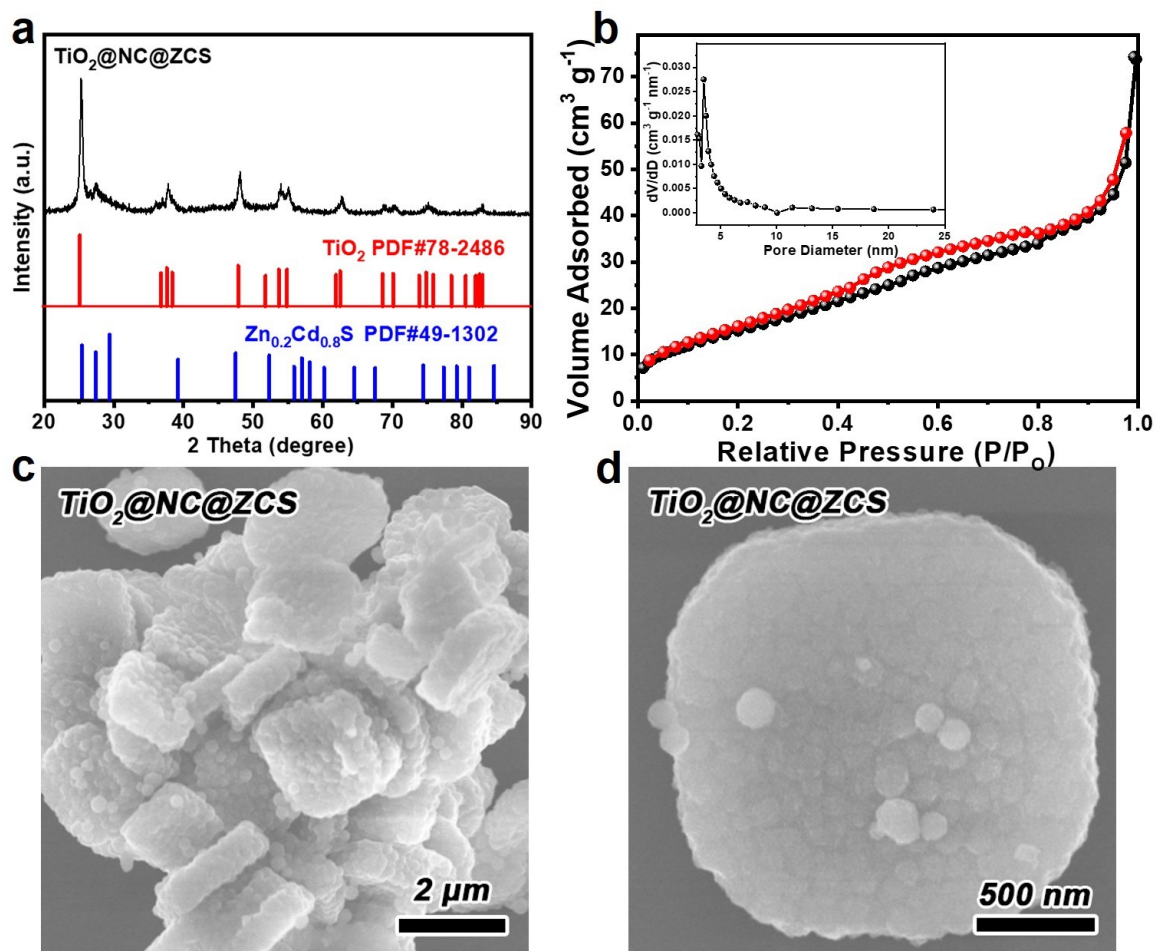


Figure S6. (a) XRD, (b) N_2 adsorption/desorption isotherms and (c, d) SEM images of $\text{TiO}_2@NC@ZCS$.

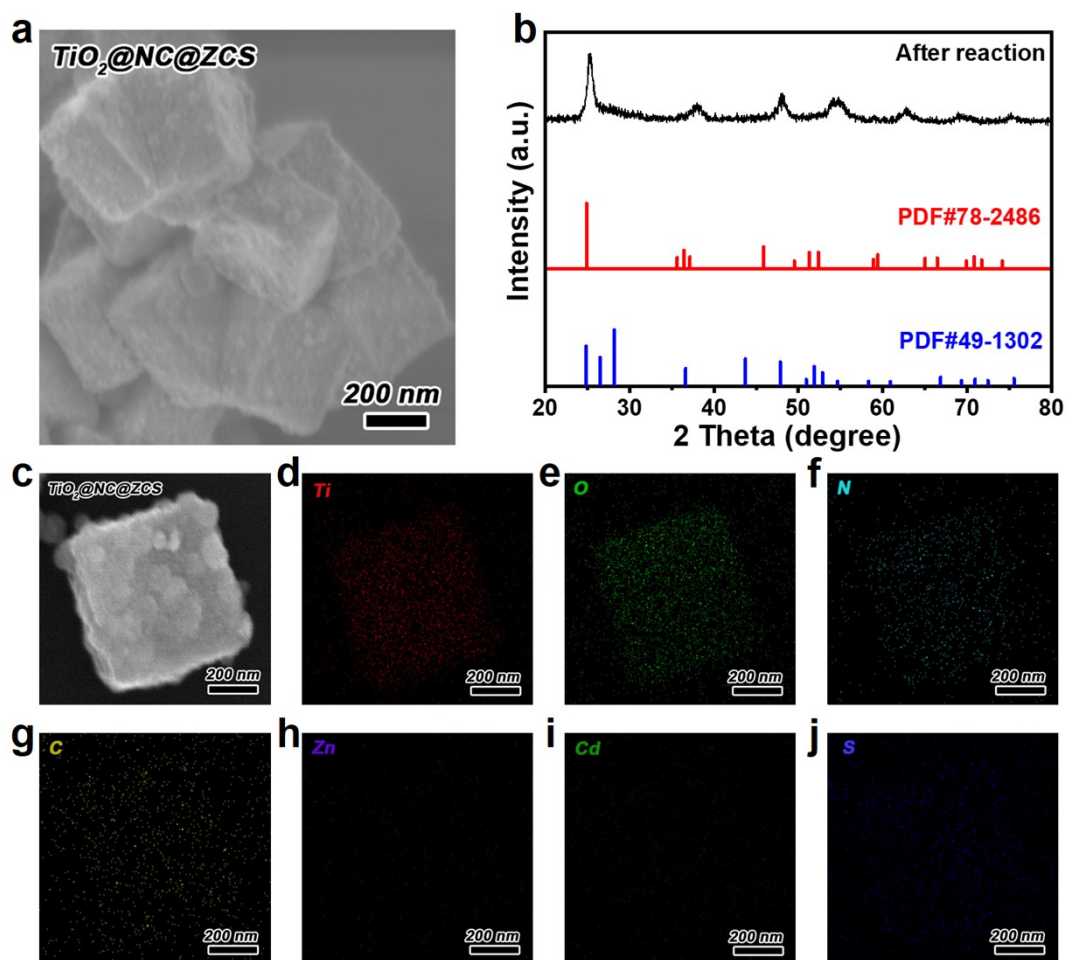


Figure S7. Material characterization of used $\text{TiO}_2@\text{NC}@\text{ZCS}$ after photocatalytic reaction. (a) SEM image. (b) XRD patterns. (c-j) SEM and corresponding elemental mapping.

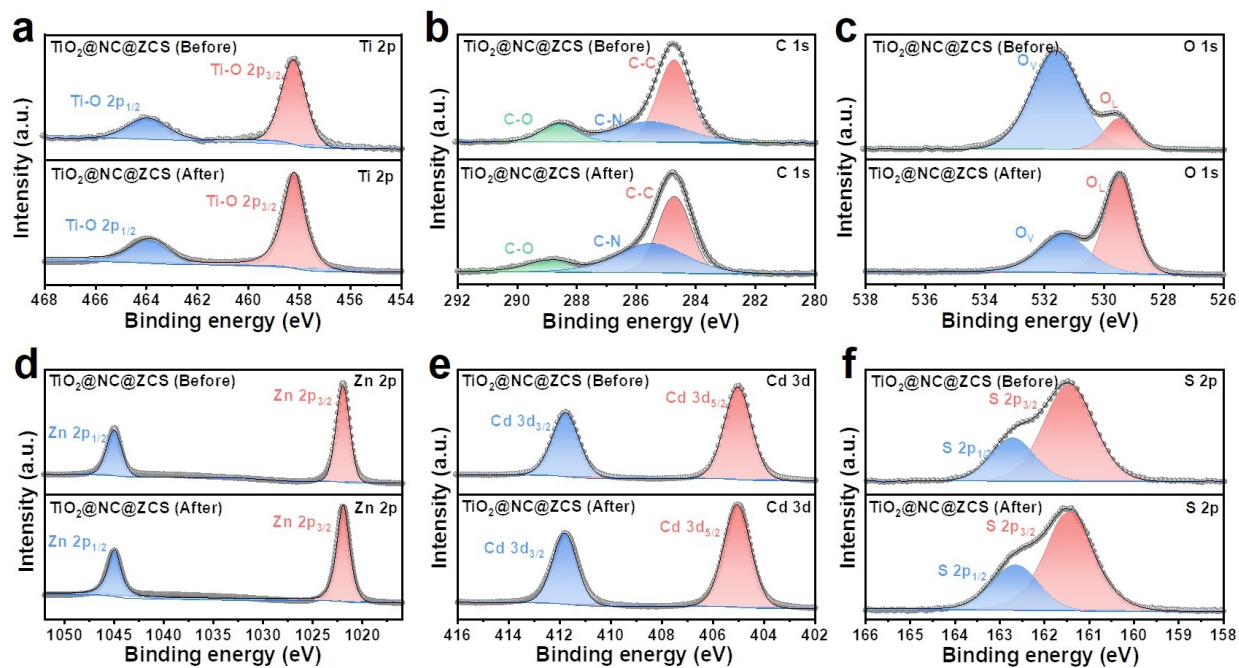


Figure S8. XPS spectra of used $\text{TiO}_2@\text{NC}@\text{ZCS}$ after photocatalytic reaction.

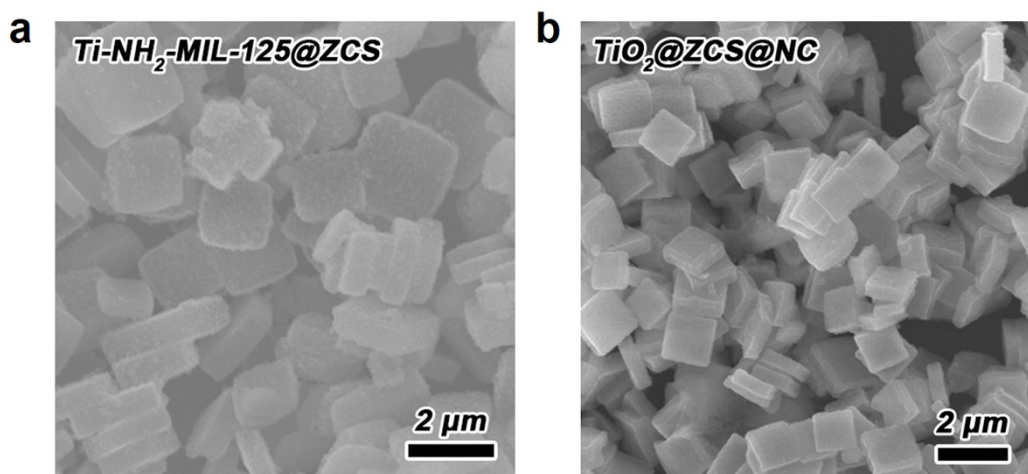


Figure S9. SEM image of (a) $\text{Ti-NH}_2\text{-MIL-125}$ and (b) $\text{TiO}_2\text{@ZCS@NC}$.

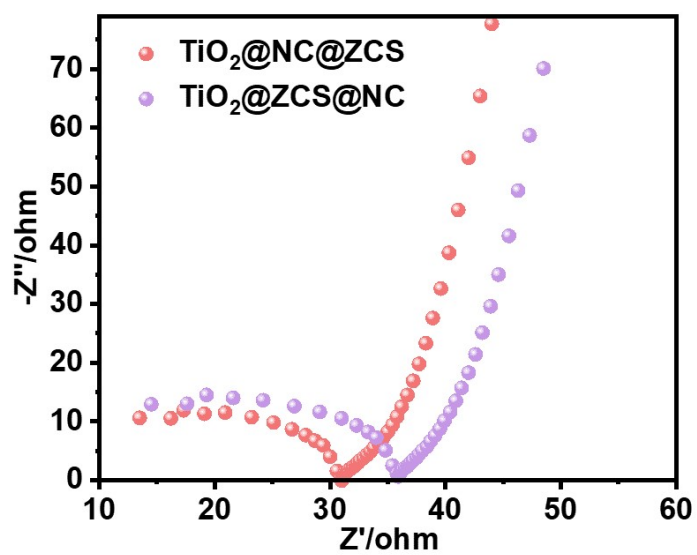


Figure S10. EIS Nyquist curves of the samples.

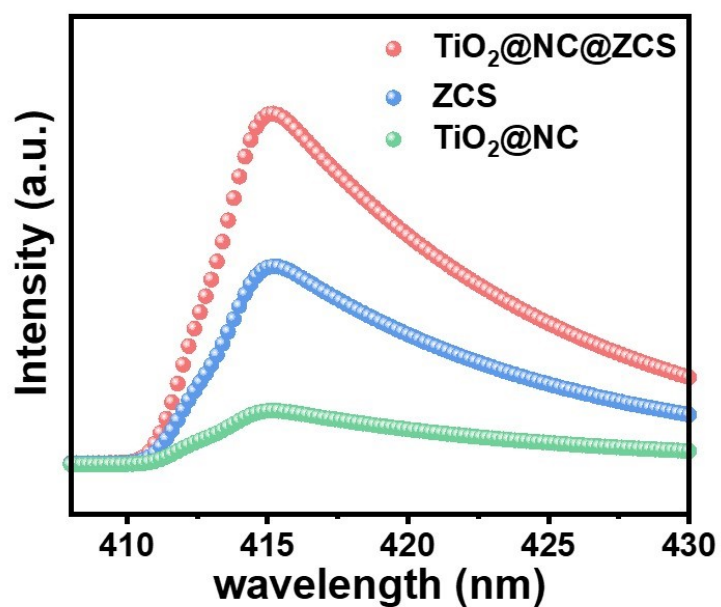


Figure S11. Steady state photoluminescence spectra of the samples.

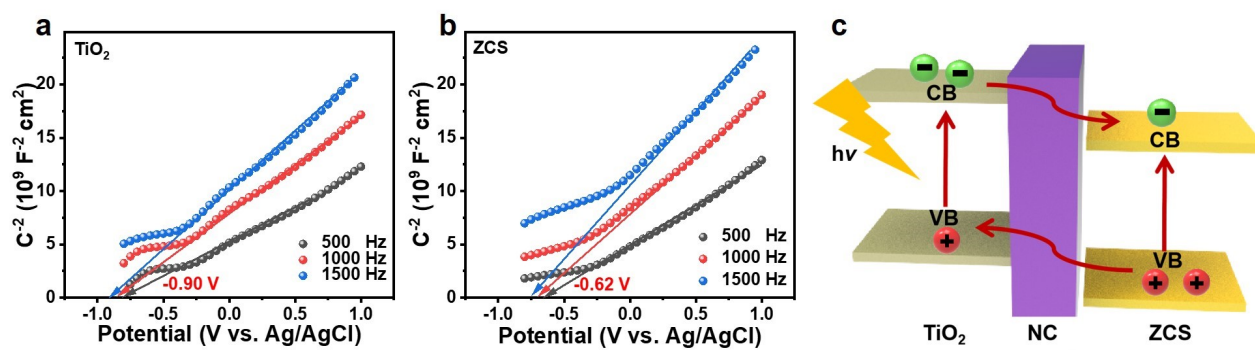


Figure S12. Mot-schottky plots of (a) TiO₂ and (b) ZCS. (c) Schematic illustration of the charge migration behavior in TiO₂@NC@ZCS.

Table S1. Photocatalytic hydrogen evolution rate comparison in different catalytic systems.

Catalysts	Light Source	Reaction Conditions	HER Rate (mmol/g/h)	Ref.
TiO ₂ @NC@ZCS	300 W Xe lamp	TEOA and H ₂ O	10.24	This work
ZnCdS nanoflowers	5W LED ($\lambda > 420$ nm)	Na ₂ S and Na ₂ SO ₃	11.47	1
Hollow Zn _{0.5} Cd _{0.5} S nanocages	300 W Xe arc lamp with a 420 nm cutoff filter	TEOA and H ₂ O	3.6	2
ZnCdS	300 W Xe lamp with a light intensity of 100 mW cm ⁻²	Na ₂ S and Na ₂ SO ₃	0.51	3
CdS nanospheres	300 W Xe lamp with a UV-light cutoff filter ($\lambda > 420$ nm)	10% lactic acid	2.70	4
CdS nanoroads	300 W Xe lamp with a UV-cutoff filter ($\lambda > 400$ nm)	10% lactic acid	3.60	5
M-ZnS	300 W Xe lamp with a UV-cutoff filter ($\lambda > 400$ nm)	Na ₂ S and Na ₂ SO ₃	6.59	6
ZnS nanoframe	300 W Xe arc lamp equipped with AM 1.5 G filter	Na ₂ S and Na ₂ SO ₃	0.71	7
CdS/Ni@NC	300 W Xe lamp with a UV-light cutoff filter ($\lambda > 420$ nm)	Aqueous solution and Benzy alcohol	1.88	8
CoWO ₄ /Zn _{0.3} Cd _{0.7} S	300 W Xe lamp with a UV-cutoff filter ($\lambda > 400$ nm)	Cl-PhCH ₂ OH and DMF	15.58	9
Zn _{0.5} CdS/GDY/NiO	5 W white light	15% lactic acid	24.44	10
ZnCdS/Co-MoS _x	300 W Xe lamp with a UV-light cutoff filter ($\lambda > 420$ nm)	10% lactic acid	0.40	11

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