Electronic Supplementary Information

Synergistic effect of oxygen vacancy and Ni particles over $ZnWO_4$/CdS heterostructure for enhancing photocatalytic reduction and oxidation activities

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Materials and Characterizations

All chemicals commercially obtained were used directly. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was obtained from Xiya Chemical Technology (Shandong) Co., Ltd. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), Zinc chloride ($ZnCl_2$, AR), Thiourea ($CS(NH_2)_2$, AR) and Cadmium acetate dihydrate ($Cd(Ac)_2 \cdot 2H_2O$) were provided from Sinopharm Chemical Reagent Co., Ltd.

X-ray diffraction (XRD) of the as-obtained products were carried out on the RigakuUltima IV X-ray diffractometer using Cu-Kα (λ=1.5418 nm) radiation. The accelerating voltage and the applied current were at 40 kV and 40 mA, respectively. Scanning electron microscope (SEM, JEOL JSM 7500F), transmission electron microscope (TEM, Tecnai G2 F20 S TWIN) equipped with an energy dispersive spectrometer (EDS) and high-resolution transmission electron microscopy (HRTEM) images were used to observe or determine the morphology and microstructure. X-ray photoelectron spectroscopy (XPS) measurement was taken with the Escalab 250 Xi multifunctional photoelectron spectrometer produced by Thermo Fisher Scientific. The Brunauer–Emmett–Teller (BET) specific surface was determined by nitrogen adsorption in a Belsorp max physical adsorption instrument (Bayer, Japan). The desorption isotherm was used to analysis the pore size distribution by Barrett-Joyner-Halenda (BJH) method. The UV-2550 ultraviolet-visible spectrophotometer produced by Shimadzu Corporation was used to obtain the light absorption performance (Diffuse reflection spectrum, DRS) of the sample at a wavelength range of 200–800 nm. Photo-luminescence (PL) analysis and Time-resolved photoluminescence (TRPL) was recorded with a LS55 fluorescence spectrometer (Perkin-Elmer, USA). The analysis of free radicals was recorded with the electron spin resonance (ESR, JES FA200 spectrometer, Japan) by mixing the photocatalysts in a 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) solution tank (methanol dispersion for DMPO-·OOH/O_2·- and aqueous dispersion for DMPO-·OH). And the generation of vacancies was determined by electron paramagnetic resonance (EPR, Bruker, USA). Electrochemical and photoelectrochemical tests were implemented on the CHI 660E electrochemical system in a standard three-electrode quartz cell with the as-prepared samples as the working electrode, a platinum wire (Pt) as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode, respectively.

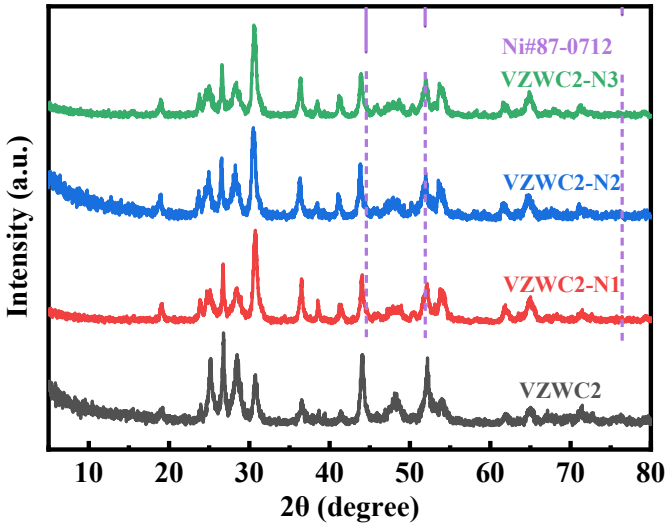

Fig. S1 XRD patterns of VZWC2, VZWC2-N1, VZWC2-N2, and VZWC2-N3

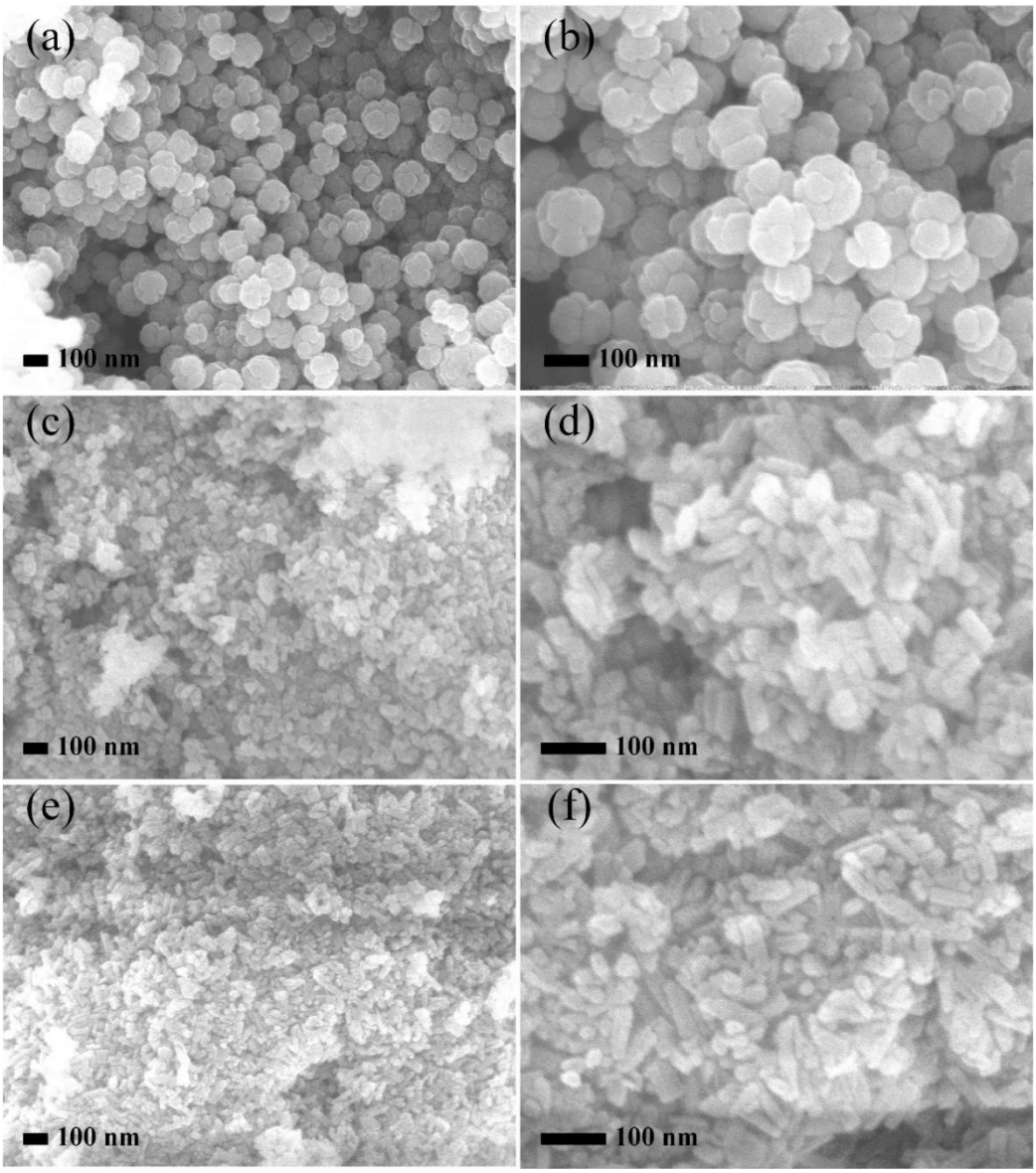

Fig. S2 FESEM images of (a-b) CdS, (c-d) Vo-$ZnWO_4$,(e-f) $ZnWO_4$

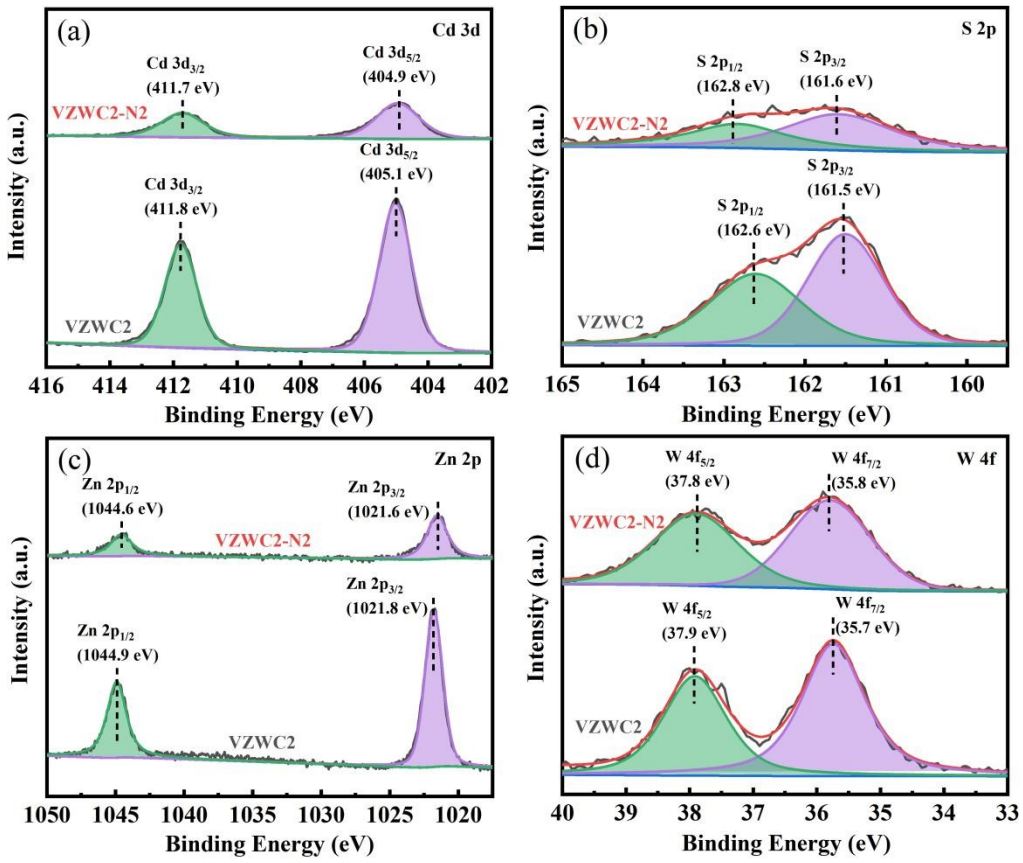

Fig. S3 High-resolution XPS spectra of (a) Cd 3d, (b) S 2p, (c) Zn 2p, (d) W 4f for ZWC2-N2.

Fig. S3a-d shows the XPS spectra of Cd 3d and S 2p, Zn 2p, W4f. In VZWC2, the high-resolution Cd spectrum indicated the existence of Cd 3d 5/2 and 3d 3/2 peaks centered at 411.7 eV and 404.9 eV, respectively. The binding energies of the S 2p 1/2 and 2p 3/2 peaks are located at 162.6 eV and 161.5 eV. The peaks located at 1021.6eV and 1044.6eV in the XPS spectrum of Zn 2p could be ascribed to the characteristic peaks of Zn $2p_{3/2}$ and Zn $2p_{1/2}$ spin-orbit components of Zn^{2+}. The W4f XPS spectra of the Vo-$ZnWO_4$ surface are simple spin dipoles with BE of 37.8 and 35.8 eV corresponding to W $4f_{5/2}$ and W $4f_{7/2}$, respectively, indicating the presence of the W^{6+} state in Vo-$ZnWO_4$.

Table S1 Summary of material properties

Sample	Specific surface area	Mean pore diameter
Vo-$ZnWO_4$	28.820	27.075
CdS	12.696	13.769
VZWC2	22.964	29.039
VZWC2-N2	17.713	35.959

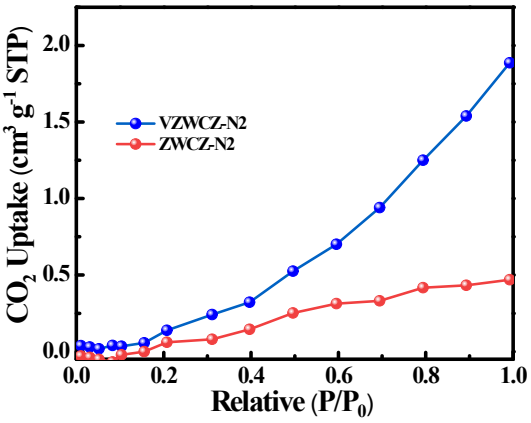

Fig. S4 CO_2 adsorption curves measured at 298 K of VZWC2-N2 and ZWC2-N2.

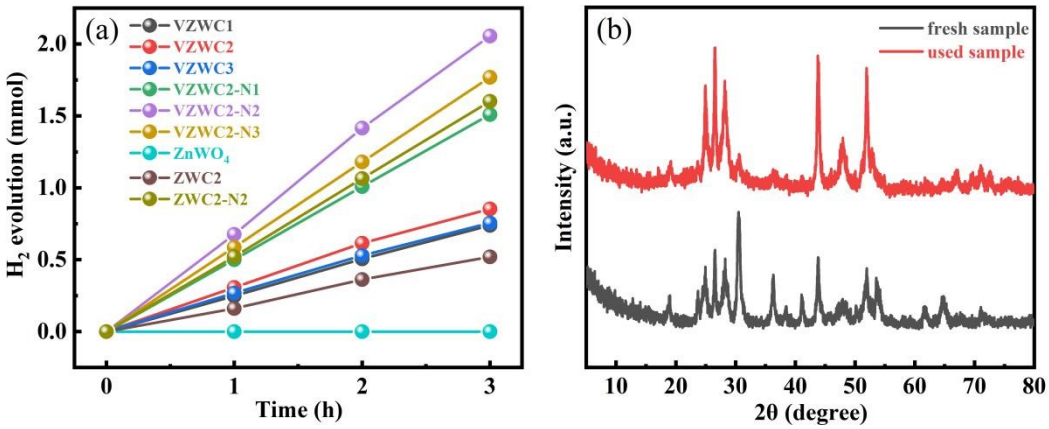

Fig. S5 (a) The comparison of photocatalytic H_2 production activities of different photocatalystsunder visible light irradiation.(b) XRD patterns of ZWC2-N2 before and after test.

Table S2 The radiative fluorescence lifetimes and relative percentages of the photoinduced charge carriers in the samples

Sample	τ1 (ns)	Rel. (%)	τ2 (ns)	Rel. (%)	τ (ns)
Vo-$ZnWO_4$	0.1253	86.24	1.0024	13.76	0.617105
CdS	0.5421	68.21	2.5678	31.79	1.936273
VZWC2	1.9256	48.35	5.2637	8.3649	4.412167
VZWC2-N2	2.1188	58.01	8.3649	41.99	6.745767

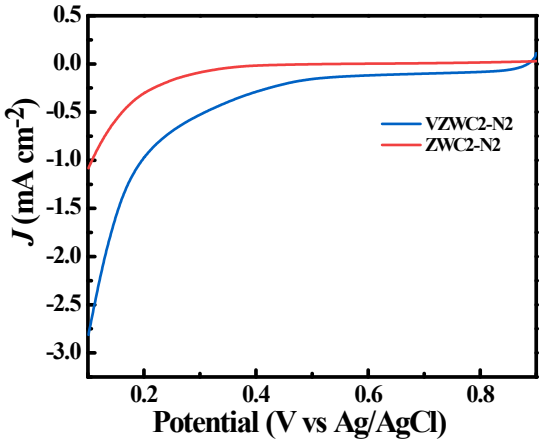

Fig. S6 Linear sweep voltammograms of VZWC2-N2 and ZWC2-N2 in 0.5 M H_2SO_4 aqueous solution.