

Electronic Supplementary Information

Tuning the Interfacial Electronic Structure via Au Clusters for Boosting Photocatalytic H₂ Evolution

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Experimental Section

Materials: Melamine ($C_3N_6H_6$, CP, >99.0%), ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, AR, >99.0%), gold(III) chloride trihydrateurea ($HAuCl_4\cdot 3H_2O$, AR, 99.9%), hydrochloric acid (HCl, AR, 36.0~38.0%), ethanol (C_2H_5OH , AR, >99.7%), methanol (CH_3OH , AR, >99.5%), sodium hydroxide (NaOH, AR, >96.0%), Lactic acid ($C_3H_6O_3$, AR), zinc acetate dihydrate ($C_4H_6O_4Zn\cdot 2H_2O$, AR, >99.0%), cadmium acetate dihydrate ($C_4H_6CdO_4\cdot 2H_2O$, AR, >98.5%) and sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$, AR, >98.0%) and sodium sulfate (Na_2SO_4 , AR, >99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All materials were used as received without further purification. Deionized (DI) water is obtained from local sources.

Synthesis of Mo_2C/Au and Mo_2C : Typically, 2.0 g melamine was dispersed in 100 mL absolute methanol under ultrasonication, and keep stirring for 1h, obtaining uniformly dispersed melamine suspension. Meanwhile, 0.4650 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was added in 75 mL ethanol solution (20 vol%), and a certain volume of 1M HCl is added to accelerate the dissolution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, forming a homogeneous solution with the pH of 2. The obtained $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution was dropwise added into the prepared melamine suspension under vigorous stirring. Then, a certain volume of $HAuCl_4$ solution was added and the pH value of the resulting suspension was adjusted to 6 using 1 M HCl solution. The resulting suspension was stirred in 80 °C water bath to vaporize all solvent completely, and the solid product was collected and ground well. Subsequently, the as-obtained powder was put in a porcelain boat with a cover, and calcined at 500 °C for 2h with a heating rate of 5 °C·min⁻¹, further heated to 700 °C for another 2 h and then allowed to cool down to the room temperature naturally. The whole pyrolysis process is under N₂ flow. The resulted black product was Mo_2C/Au , in which the theoretical mass ratio of Au is 1%. In contrast, Mo_2C was synthesized through a similar process, without the addition of $HAuCl_4$ solution.

Synthesis of $(Mo_2C/Au)@ZCS$, $Mo_2C@ZCS$ and ZCS : $(Mo_2C/Au)@ZCS$, $Mo_2C@ZCS$ and ZCS were prepared by the co-precipitation method. For $(Mo_2C/Au)@ZCS$, a certain amount of previously prepared Mo_2C/Au or Mo_2C was ultrasonically dispersed in 100 mL DI water to obtain homogeneous Mo_2C/Au or Mo_2C suspension. Then, 0.7996 g cadmium acetate and 0.6585 g zinc acetate were added to Mo_2C/Au or Mo_2C suspension. The pH value of the resulting suspension was adjusted using 0.2 M NaOH solution to be 7.0. After stirring for half an hour, add 12 mL Na_2S solution (0.5 M) drop by drop. Continue stirring for 18 hours, the resulting product was filtered and washed with DI water and absolute ethanol several times. Finally, the product was dried at 60 °C in vacuum overnight, obtaining $(Mo_2C/Au)@ZCS$ or

Mo₂C@ZCS composite, in which the theoretical mass ratio of Mo₂C/Au or Mo₂C was 4% . Besides, ZCS was prepared via the same procedure without the introduction of Mo₂C/Au or Mo₂C.

Synthesis of Au/ZCS and Mo₂C@ZCS/Au: Au/ZCS and Mo₂C@ZCS/Au samples were prepared via photocatalytic reduction method. In brief, 100 mg as-prepared ZCS or Mo₂C@ZCS was dispersed into 50 mL 5 vol% methanol solution. Then a certain volume of HAuCl₄ solution was added, and the weight ratio of Au and ZCS or Mo₂C@ZCS was 0.04%. The suspension was irradiated by full-solar light for 0.5 h under vacuum. Then, the resulting product was filtered and washed with DI water and absolute ethanol several times. Finally, the product was dried at 60 °C in a vacuum overnight.

Characterization: XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer, which operated at 40 kV and 40 mA with Cu K α radiation. The scan rate was 0.5 (2 θ •s⁻¹). SEM images were obtained using a HITACHI SU8000 field-emission scanning electron microscope. (HR)TEM images and HAADF-STEM mapping images were taken on a with a transmission electron microscopy (FEI TecnaiG2F20) with an accelerating voltage of 200 kV. XPS analysis on a multifunctional imaging electron spectrometer (Thermo Scientific ESCALab 250XI) equipped with a monochromatic Al K α as the X-ray source, sample stage with multi-axial adjustability and hemispherical analyzer. UV-vis DRS was measured by a UV-vis spectrophotometer (UV-2600, Shimadzu). PL spectra were obtained using a fluorescence spectrophotometer (Horiba FluoroMax Plus). SPV response was recorded on a surface photovoltage spectrometer (PL-SPS/IPCE1000). Aberration-corrected cross-sectional HAADF-STEM was performed on a FEI Theims Z. The Fourier transformed infrared spectroscopy (FT-IR) was performed on a Nicolet Nexus 670 FT-IR spectrophotometer at a resolution of 4 cm⁻¹.

Electrochemical measurements: The electrochemical measurements were carried out on a CHI760E electrochemical workstation with a typical three-electrode system. In which platinum plate, Ag/AgCl electrode and samples prepared on ITO were used as the counter electrode, reference electrode and working electrode respectively, while 0.2 M Na₂SO₄ solution was served as the electrolyte. The detailed prepare process for the working electrode is as follow: 10 mg of the as-prepared sample was dispersed in 0.5 mL N,N-dimethyl formamide (DMF) solution by sonication, and the slurry (20 μ L) was pipetted on indium tin oxide (ITO) conductor glass substrate with an area of 5 \times 5 mm². After dry naturally, the uncovered parts on ITO were painted by insulating epoxy resin then air-dried.

Photocatalytic H₂ evolution reactions: Typically, 30 mg as-prepared samples were dispersed into 100 mL lactic acid solutions (10 vol%). Then, the suspension was poured into a quartz reactor, and vacuumed using a vacuum pump for 2 h to drive away from the residual air. The photocatalytic water splitting to produce H₂ was carried out by vertically irradiating the suspension with a 300W xenon lamp equipped with a cut-off filter ($\lambda > 420$ nm). The temperature of the reaction solution was kept at 4 °C. The gas product was analyzed every 1 h by a Techcomp 7900 chromatograph (GC) with TCD detector and Ar as the carrier gas.

Computational methods and models: The calculation was performed using Vienna *ab initio* simulation package (VASP). Exchange and correlation effects were accounted by means of the generalized gradient approximation (GGA) using PBE (Purdew-Burke-Ernzerhof) functional. A cutoff energy of 400 eV for the grid integration was utilized and the convergence threshold for force and energy was set 0.02 Å and 10⁻⁵ eV, respectively. Ion cores are described by projector augmented wave PAW potentials. For hydrogen adsorption, we used (1 × 1) surface cells and (5 × 5 × 1) Monkhorst-Pack grids. For geometry optimization, all atoms were allowed to relax. The free energies of the intermediate were calculated by the formula $\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$, where H* represents the H atom adsorbed on the surface, ΔE_{H^*} , ΔZPE and ΔS represent the binding energy, zero point energy and entropy change between adsorption H and gas phase, respectively.

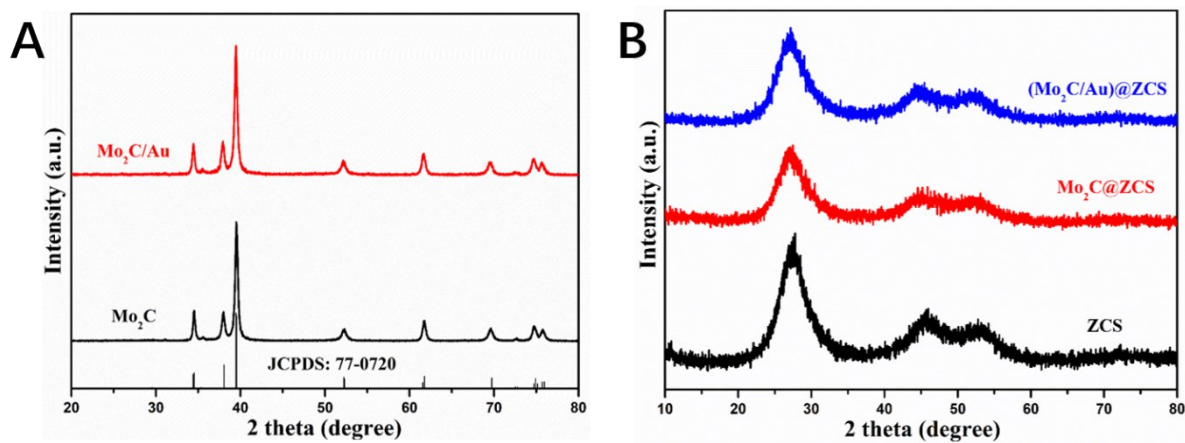


Fig. S1 (A) XRD patterns of Mo_2C and $\text{Mo}_2\text{C}/\text{Au}$. (B) XRD patterns of ZCS, $\text{Mo}_2\text{C}@ZCS$ and $(\text{Mo}_2\text{C}/\text{Au})@ZCS$.

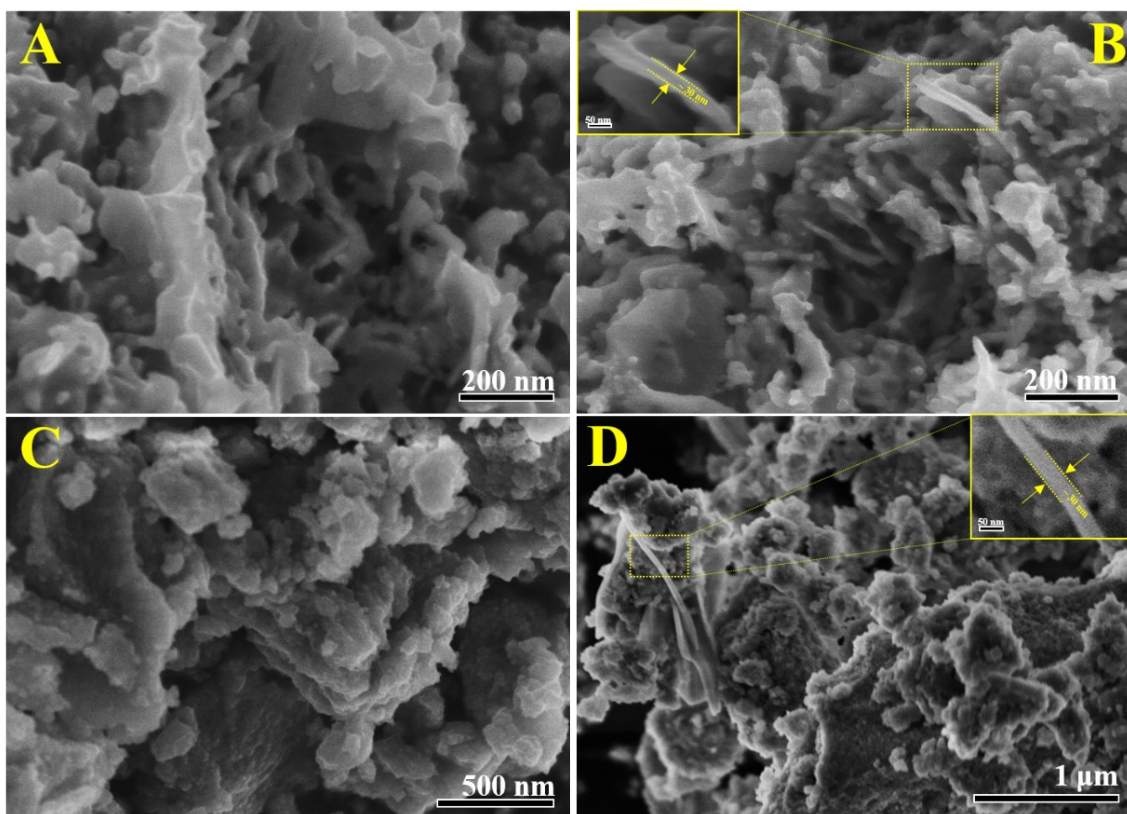


Fig. S2 SEM images of (A) Mo_2C , (B) $\text{Mo}_2\text{C}/\text{Au}$, (C) $\text{Mo}_2\text{C}@ZCS$ and (D) $(\text{Mo}_2\text{C}/\text{Au})@ZCS$.

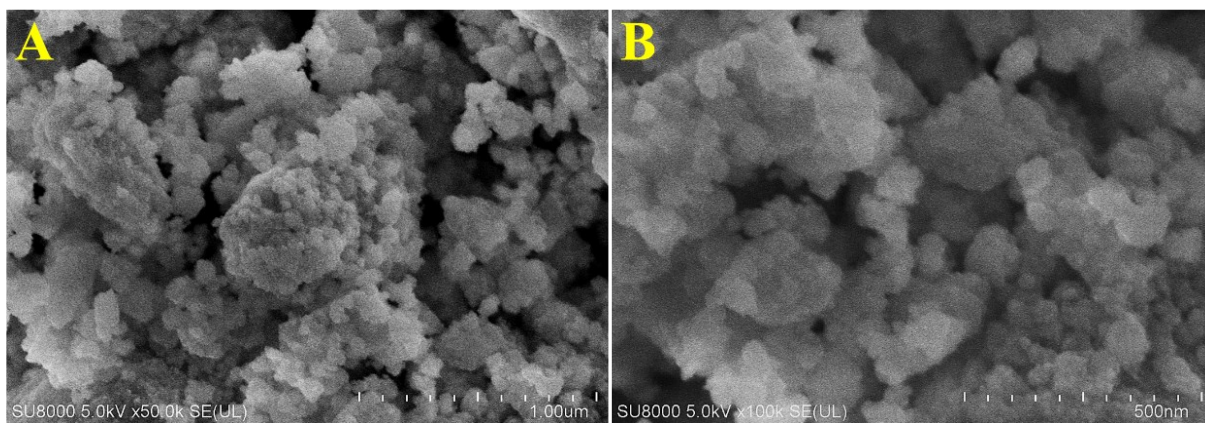


Fig. S3 SEM images of ZCS.

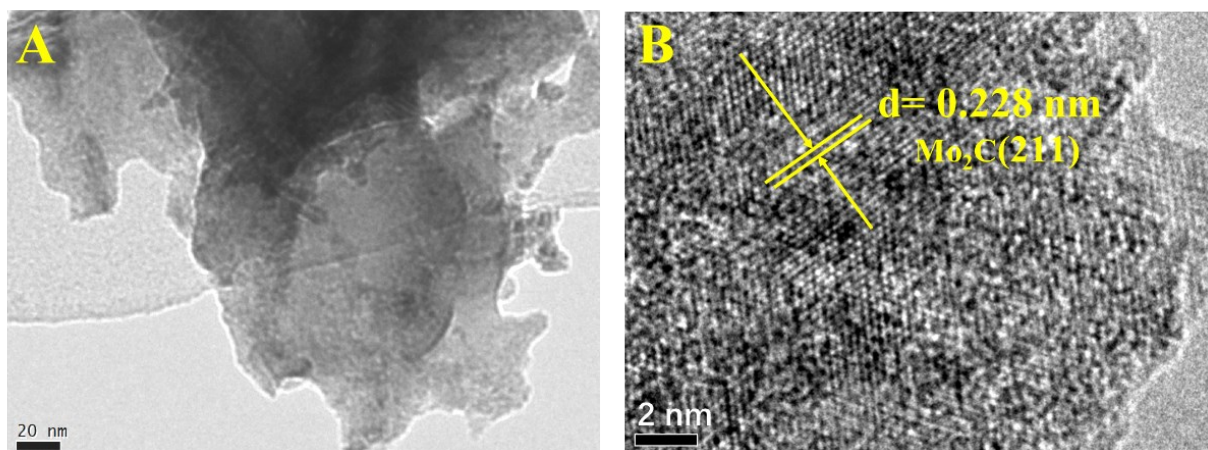


Fig. S4 (A) TEM and (B) HRTEM image of Mo_2C .

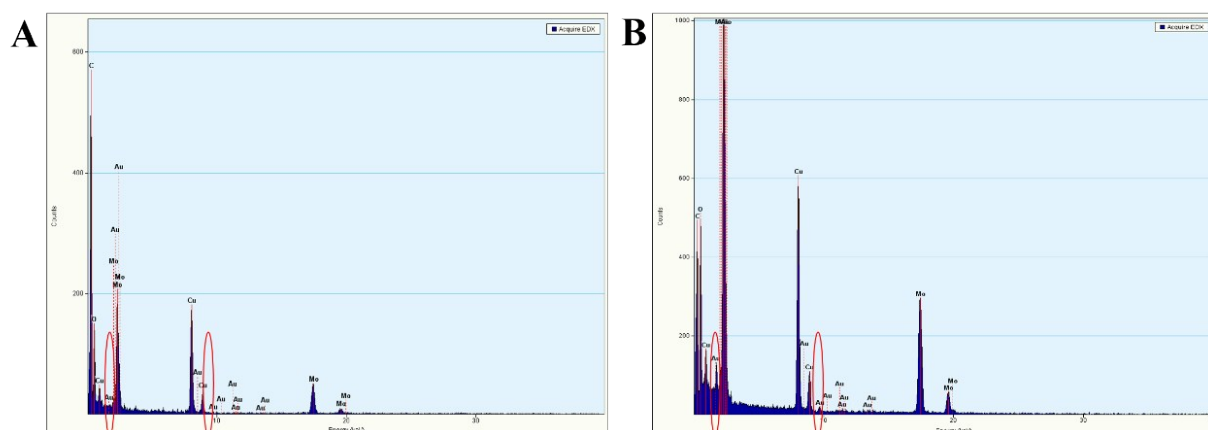


Fig. S5 EDS spectra of (A) Mo_2C and (B) $\text{Mo}_2\text{C}/\text{Au}$.

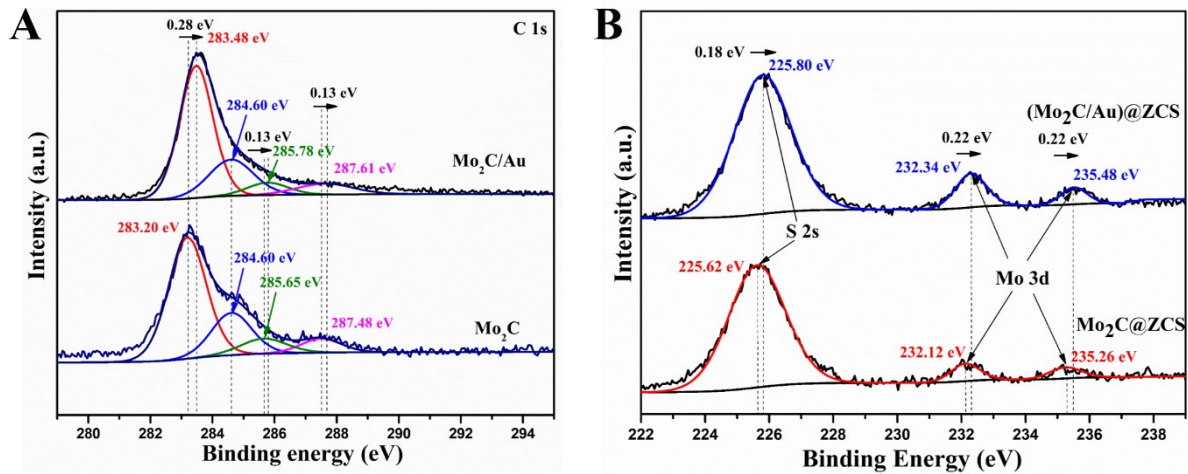


Fig. S6 (A) XPS C 1s spectra of Mo₂C and Mo₂C/Au. (B) XPS S 2s and Mo 3d spectra of Mo₂C@ZCS and (Mo₂C/Au)@ZCS.

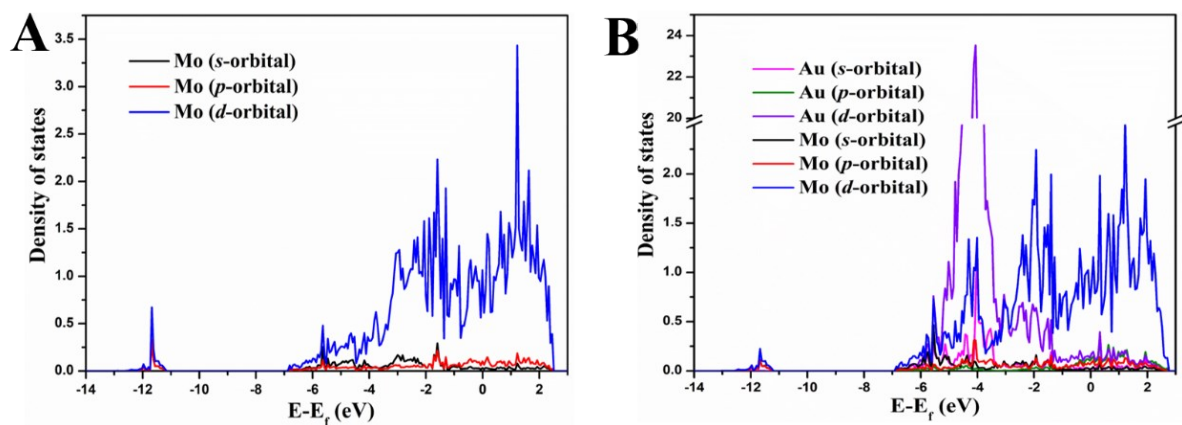


Fig. S7 (A) DOS of *s*, *p*, *d*-states of surface Mo atom for Mo₂C model. (B) DOS of *s*, *p*, *d*-states of surface Au and Mo atom for Mo₂C/Au model.

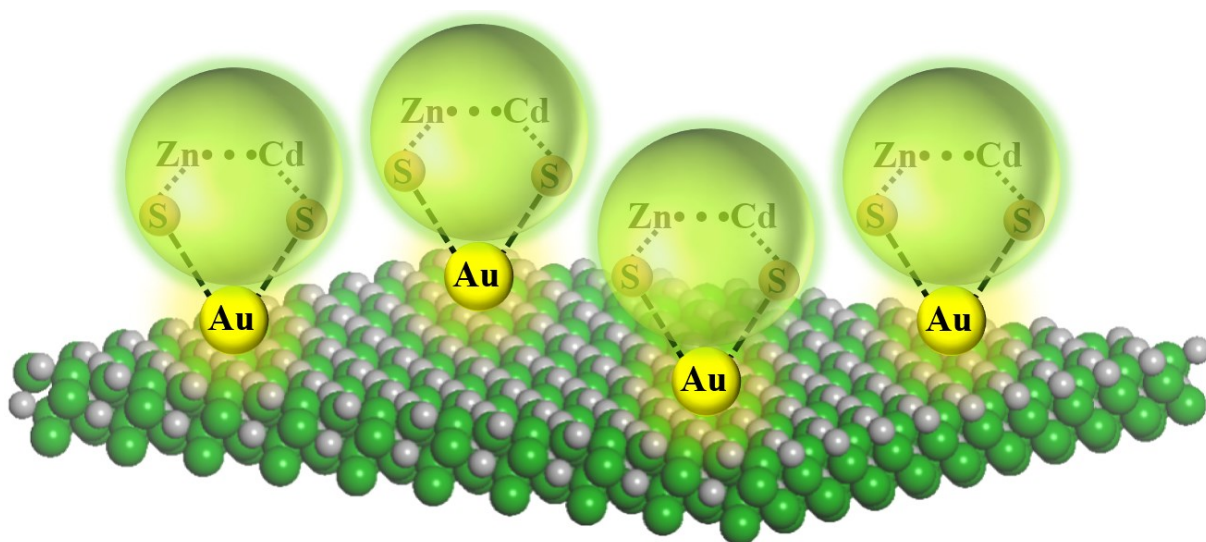


Fig. S8 Schematic illustration of Au-S-Zn and Au-S-Cd bonds in the $(\text{Mo}_2\text{C}/\text{Au})@\text{ZCS}$ sample.

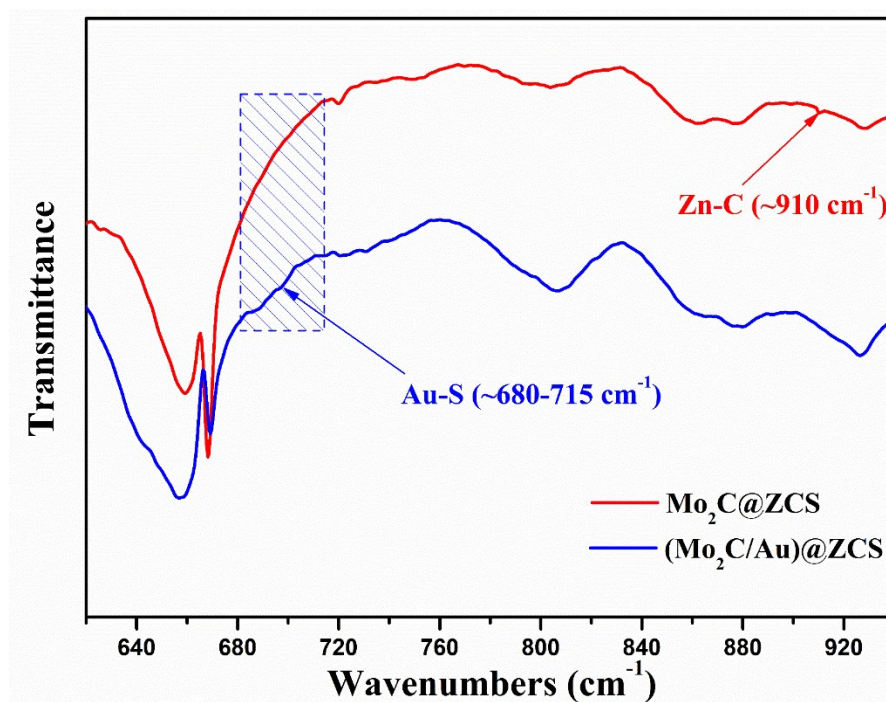


Fig. S9 FTIR spectra of the $\text{Mo}_2\text{C}@\text{ZCS}$ and $(\text{Mo}_2\text{C}/\text{Au})@\text{ZCS}$ samples

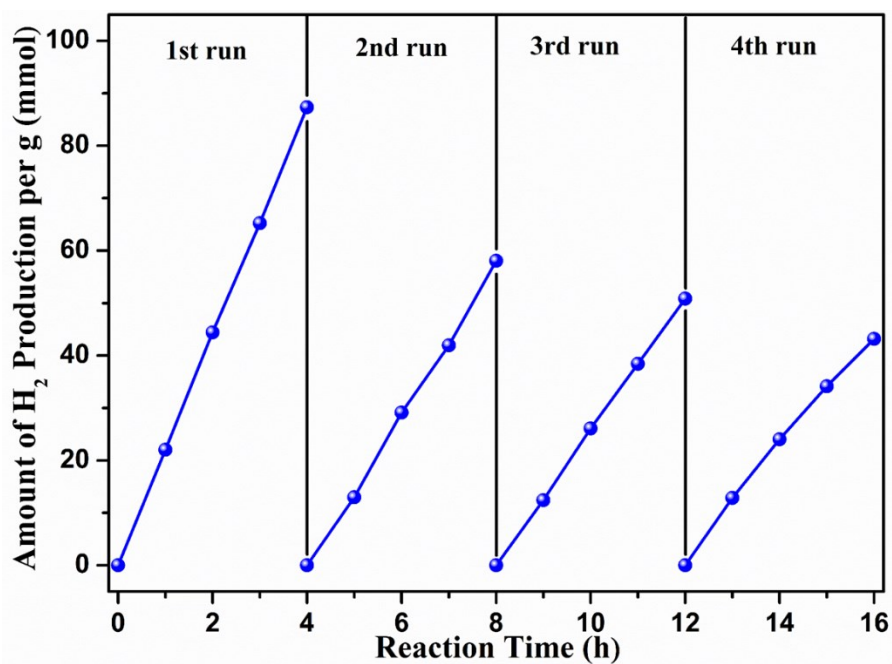


Fig. S10 Recycling photocatalytic H₂ evolution over the (Mo₂C/Au)@ZCS composite

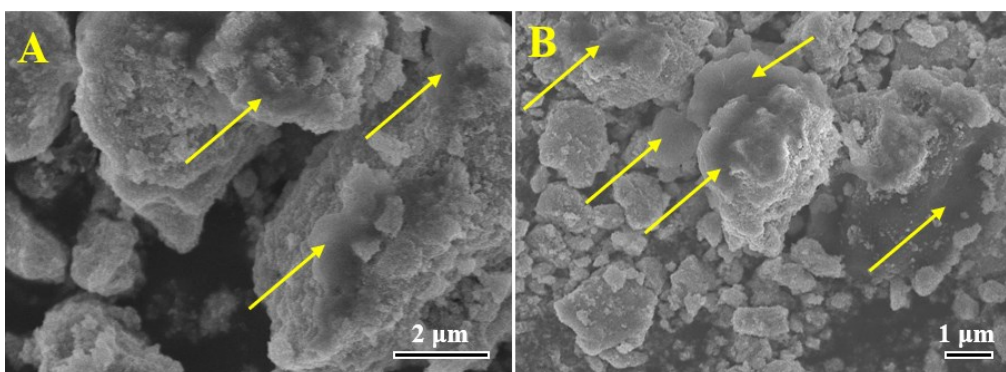


Fig. S11 SEM images of fresh (A) and used (B) (Mo₂C/Au)@ZCS composite

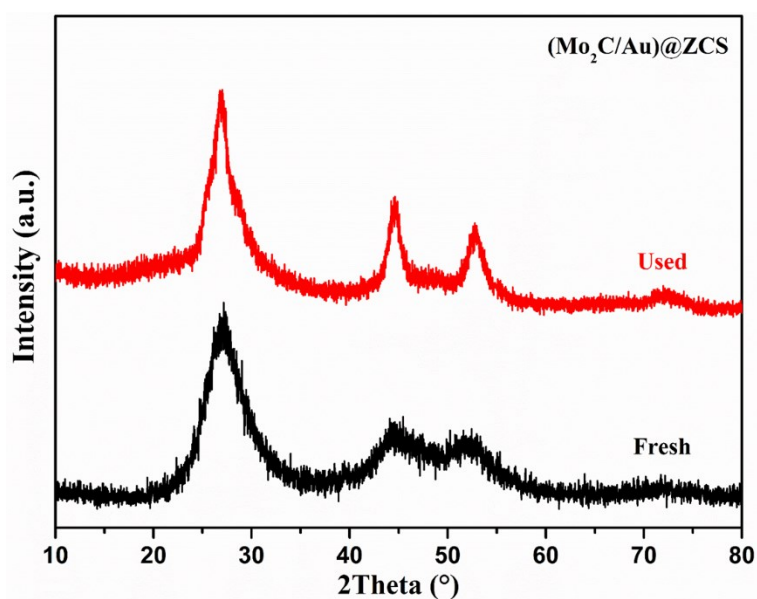


Fig. S12 XRD patterns of fresh and used (Mo₂C/Au)@ZCS composite

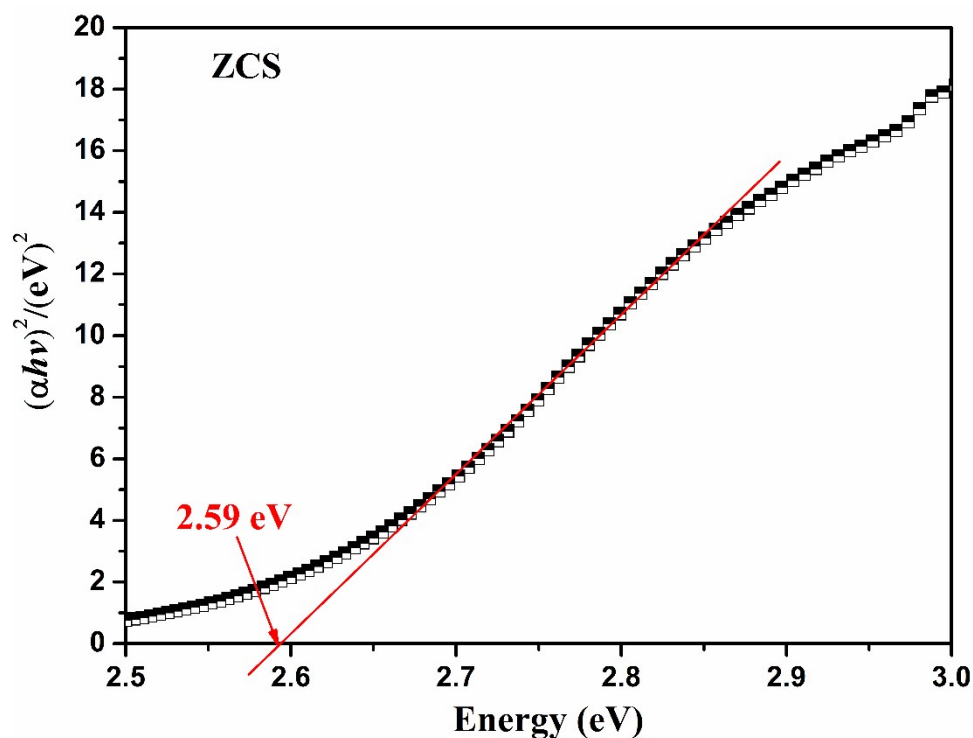


Fig. S13 The calculated band gap of ZCS

The bandgap energy value (E_g) is estimated by Kubelka-Munk (K-M) method. As shown in **Fig. S13**, the bandgap energy value (E_g) approximates to the intercept obtained by extrapolating the linear plots of the K-M function $(\alpha h\nu)^2$ vs. exciting light energy ($h\nu$) to horizontal axis. As depicted, E_g of ZCS is *ca.* 2.59 eV. Subsequently, the conduction band potential (E_{CB}) and valance band potential (E_{VB}) of ZCS can be calculated according to the following formulas:

$$E_{CB} = \chi - Ee - 0.5Eg$$

$$E_{VB} = Eg - E_{CB}$$

Where χ is absolute electronegativity of the semiconductor, which is determined to be 5.22 eV, i.e. the geometric mean of the electronegativity of Zn, Cd and S atom. Ee is the energy of free electrons on the hydrogen scale (4.5 eV). Through calculation, E_{CB} is -0.57 V vs. NHE, while E_{VB} is +2.02 V vs. NHE.