Efficient Visible-Light Driven Photocatalytic Hydrogen Production by Z-Scheme $ZnWO_4/Mn_{0.5}Cd_{0.5}S$ Nanocomposite without Precious Metal Cocatalyst

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1. Characterization

X-ray powder diffraction (XRD) patterns were obtained on a SmartLab diffractometer. Scanning electron microscopy (SEM) images were captured on a Hitachi S-8100 microscope. Energy dispersive spectroscopy (EDS) and elemental mapping images were obtained on an attachment to the SEM. Transmission electron microscopy (TEM) images were captured on a FEI Tecnai G^2-20 microscope. X-ray photoelectron spectra (XPS) were taken on an ESCALab MKII X-ray photoelectron spectrometer. The powder samples were pressed into tablets for XPS analysis. UV-vis diffuse reflectance spectroscopy (DRS) was tested by a Shimadzu UV-2450 spectrometer with MgO powder as the reference. N_2 adsorption–desorption isotherms were tested on a Micromeritics ASAP 2460 volumetric adsorption equipment at 77 K using Barrett-Emmett-Teller (BET) calculations for surface area. The active radical was measured by electron spin resonance (EPR, Bruker F-67166, Wissembourg) spectra. Electrochemical responses were tests by a Chenhua CHI760E electrochemical analyzer. The electrolyte solution was 1.0 M Na_2SO_4. The working electrode was prepared by mixing 10 mg catalyst with 10 μL 5% Nafion and 0.1 mL ethyl alcohol to form a slurry, and then coating the slurry onto a 1.0 cm^2 ITO conductive glass. The photocatalytic activity for H_2 evolution test was performed on a gas chromatograph (GC-126N, INESA, China)

2. Equations

The valence bands (E_{VB}) and conduction bands (E_{CB}) of $Mn_{0.5}Cd_{0.5}S$ and $ZnWO_4$ are obtained by the following Equations (S1)–(S3):

$$\alpha(hv) = A(hv - Eg)^{1/2} \quad \text{(S1)}$$

$$E_{VB} = X - E^e + 0.5E_g \quad \text{(S2)}$$

$$E_{CB} = E_{VB} - E_g \quad \text{(S3)}$$

Here, α represents for absorption coefficient, h represents for Planck coefficient, V represents for frequency, and A represents for constant. The X values of $Mn_{0.5}Cd_{0.5}S$ and $ZnWO_4$ are 5.01 and 6.03, respectively. E^e is a constant with a value of 4.5 eV.

3. Computational detail

Computational detail: We use density functional theory (DFT) to describe plane wave expansion of wave function, pseudopotential description of electron-nucleus interaction and first-principle pseudopotential of electron-electron interaction. We used CASTEP (Cambridge Serial Total Energy Package) in materials studio to calculate. The generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) is used to deal with forward variations and related interactions. The convergence accuracy is set to Fine. A vacuum layer of 20 Å was constructed to eliminate interactions between periodic structures of surface models. Other parameters use default values.

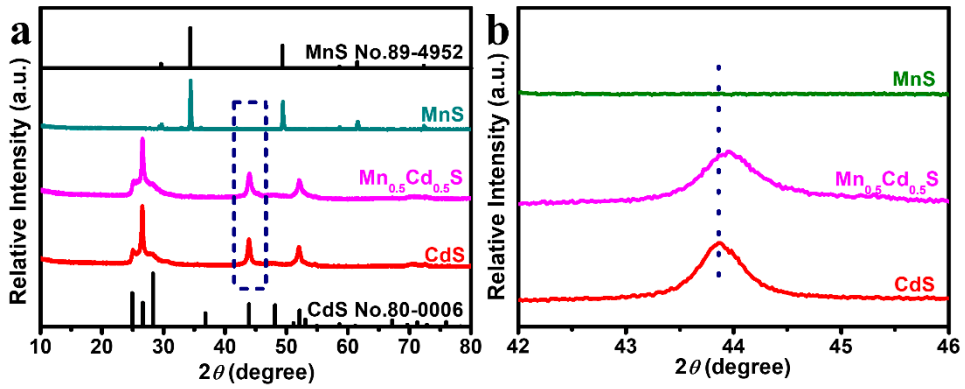

Figure S1. (**a**) XRD patterns of as-prepared CdS, MnS and $Mn_{0.5}Cd_{0.5}S$ (**S1.** (**b**) is an enlarged view of the dotted box area.).

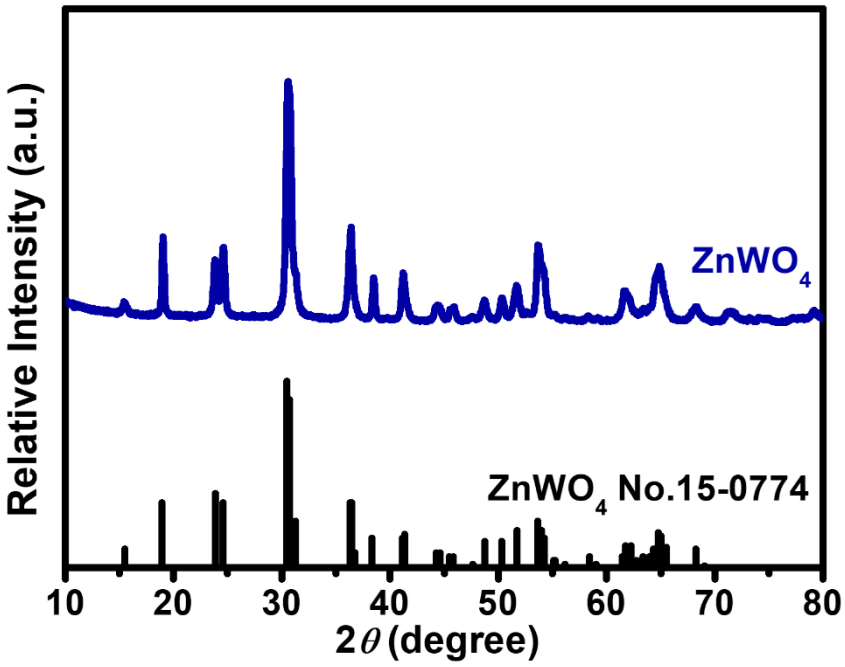

Figure S2. XRD patterns of as-prepared $ZnWO_4$.

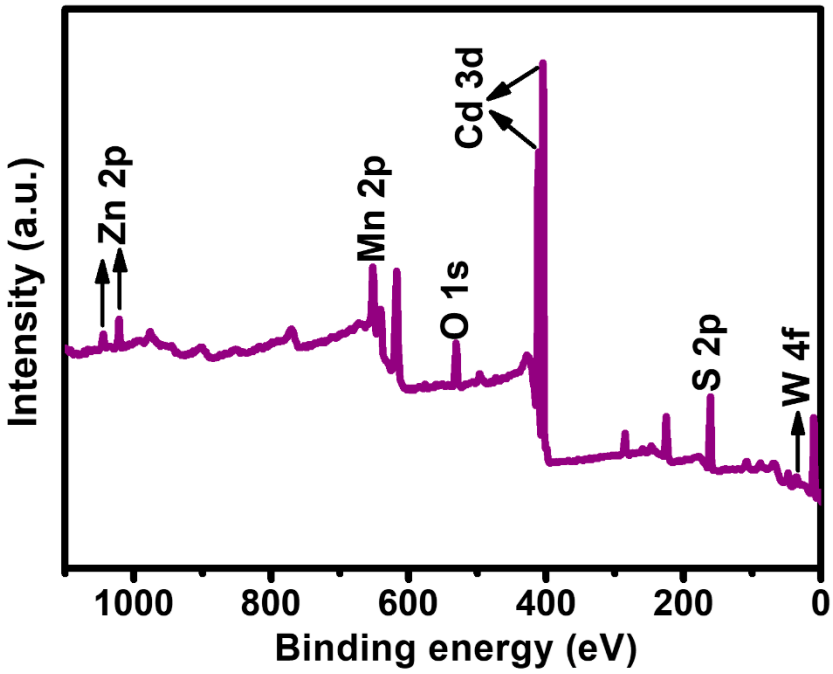

Figure S3. XPS survey spectra of ZWMCS-2 nanocomposite.

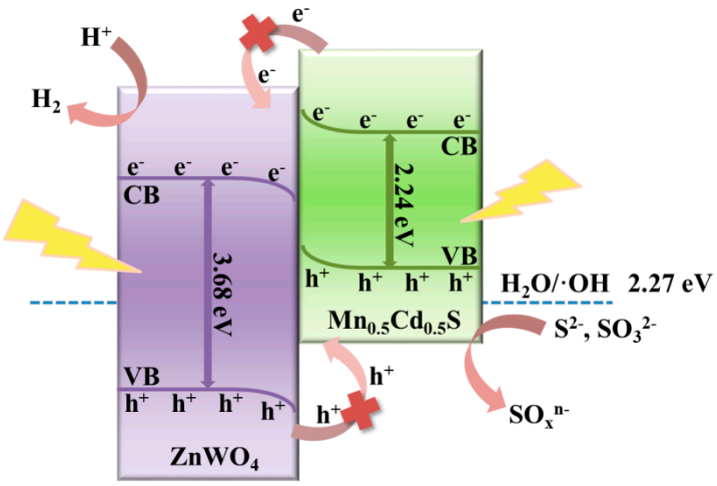

Figure S4. The schematic diagrams of charge transfer in supposed Type-II heterojunction.