Supplementary Material

Constructing an S-scheme Heterojunction between Defect Modified MnCdS-Vs/Se and H-GDY for Enhanced Photocatalytic Hydrogen Evolution

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1. Synthesis of Se-doped MnCdS nanoparticles with sulfur vacancies (MCSe)

First, the 5 mmol of $Mn(Ac)_2 \cdot 2\ H_2O$, 5 mmol of $Cd(Ac)_2 \cdot 2\ H_2O$ and the certain amount (x mmol) of thioacetamide (TAA) were dissolved in 43 mL of deionized water to obtain a uniformly mixed solution. (12-x) mmol of Se powder was added, with the molar ratio of Se to S limited to 12 mmol, and the mass ratios of Se to (Se+TAA) set at 0%, 1%, 3%, 5%, and 7%. Under a water bath at 80°C, 7 mL of hydrazine hydrate was added to the above mixed solution and stirred for 30 minutes. After achieving a homogeneous mixture, the solution was transferred to a 100 mL stainless steel autoclave lined with polytetrafluoroethylene and reacted in an oven at 180 °C for 12 h. The resulting sulfur vacancy-doped selenium sulfide manganese chromate nanomaterials were collected by centrifugation, washed several times with deionized water and ethanol, and then vacuum-dried at 60 °C for 8 h. They were designated as MCSe-x (x=0, 1, 3, 5, 7) respectively.

Using the same preparation method as for MCSe, MnCdS nanoparticles with sulfur vacancies were synthesized without the addition of Se and they were designated as MCSV.

2. Synthesis of H-substituted graphdiyne (H-GDY)

The H-substituted graphdiyne was synthesized based on previous work. First, 9 mL trimethylsilyne was dissolved in 35 mL tetrahydrofuran, and then 24 mL n-butyl lithium tetrahydrofuran solution was slowly added under nitrogen protection, and then the reaction mixture was stirred at -78 °C for 30 min. Afterwards, 50 mL of anhydrous zinc chloride tetrahydrofuran solution (1 mol/L) was slowly added to the reaction mixture, and then the resulting mixture was stirred at -78 °C for 30 min. The mixture was

then heated to room temperature and 3.14 g of tribromophenyl, 600 mg of $Pd(PPh_3)_4$ and 60 mL of toluene were added. The reaction was stirred in an oil bath at 80 °C for 72 h, and nitrogen was used as a protective gas. After the reaction was completed, 50 mL dilute hydrochloric acid (1 mol/L) was added to the reaction solution. The organic liquid phase layer was extracted with ethyl acetate, and then the ethyl acetate extract was obtained by washing with saturated saline. Next, an anhydrous sodium sulfate is used to dry the organic layer to remove any residual water. Finally, the organic compounds were purified by column chromatography (dichloromethane:n-hexane =17:3) to obtain a yellowish-brown substance Tris[(trimethylsilyl)ethynyl]benzene. Then, the pyridine solution of 1,3,5-tris[(trimethylsilyl)ethynyl]benzene(TEB-TMS) was obtained by dissolving 30 mL pyridine. In a ball mill, 3 mL DMF, 3 mL TEB-TMS pyridine solution, 300 mg CuCl and 50 g stainless steel balls were added. Then seal the ball mill. The sealed ball mill was placed in a planetary ball mill and ground at 600 r/min for 6 h. The black turbid liquid obtained after ball milling was washed with DMF, dichloromethane and methanol in turn, and then the product was washed with dilute ammonia water. Finally, dried in vacuum at 60 °C to obtain brown H-GDY powder.

3. Synthesis of MCSe/H-GDY

Start by filling a beaker with 100 mg of MCSe and x mg of H-GDY (where x=20, 25, 30, 35). After that, adding 20 ml of pure ethanol to the beaker and sonicating the mixture for 10 min in an ultrasonic bath. The catalyst should be fully dissolved in the pure alcohol after 6 h of stirring. Lastly, let the solution-filled beaker evaporate in a water bath set at 85°C to produce MCSe/H-GDY-x (where x=20, 25, 30, 35).

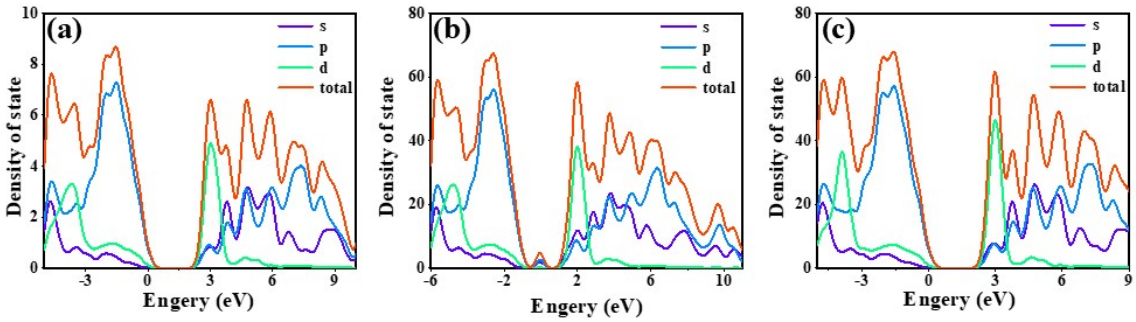

Fig. S1. The crystalline configuration of (a) MCS, (b) MCSV and (c) MCSe

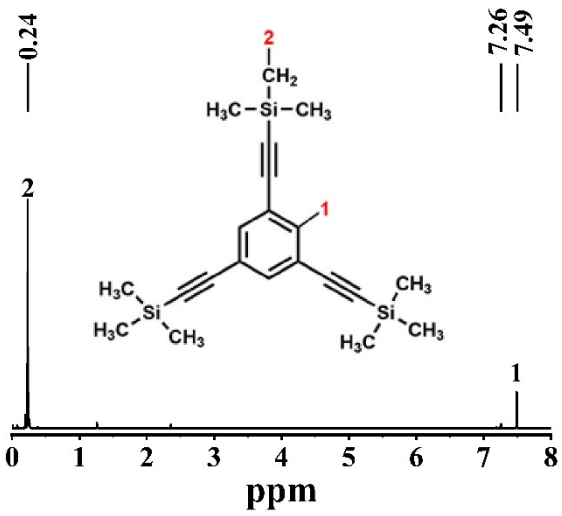

Fig. S2. ^{1}H NMR of compound TEB-TMS in $CDCl_3$.

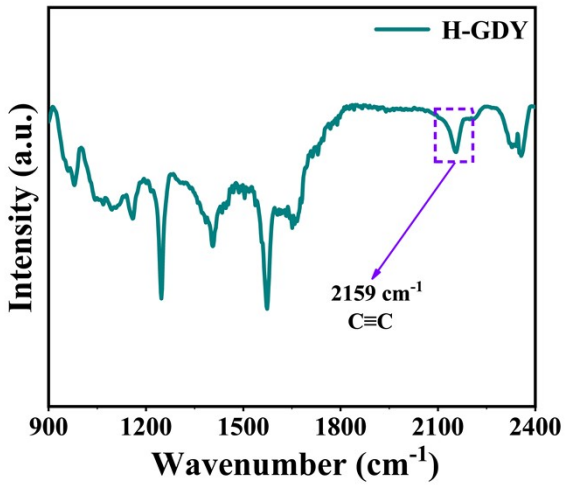

Fig. S3. FTIR analysis of H-GDY spectrum

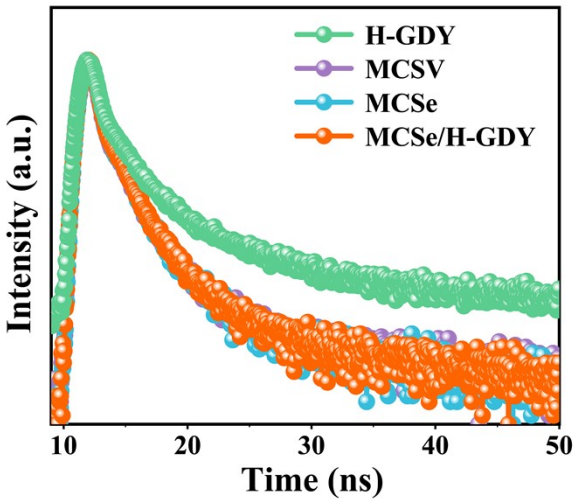

Fig. S4. TRPL spectra of H-GDY, MCSV, MCSe and MCSe/H-GDY.

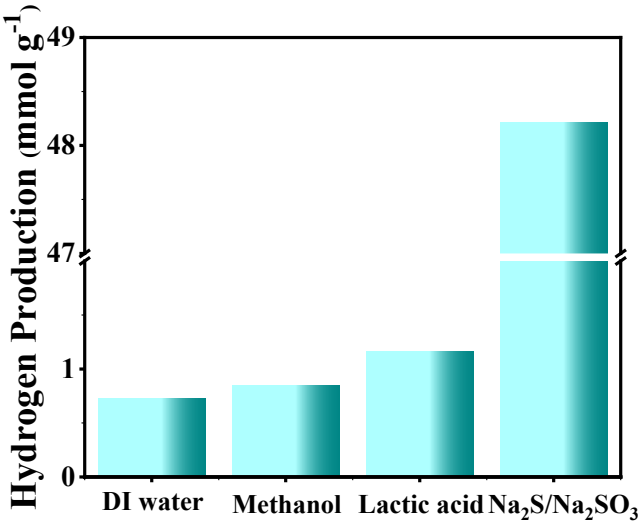

Fig. S5. Comparison of hydrogen generation from MCSe/H-GDY in different system

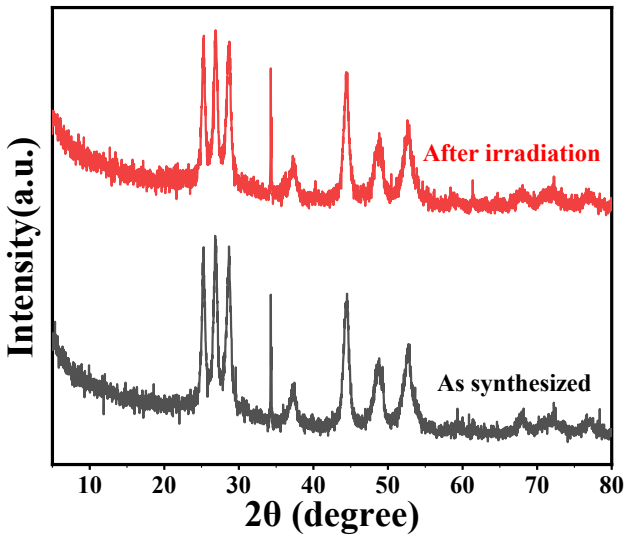

Fig. S6. Before and after hydrogen development in XRD patterns.

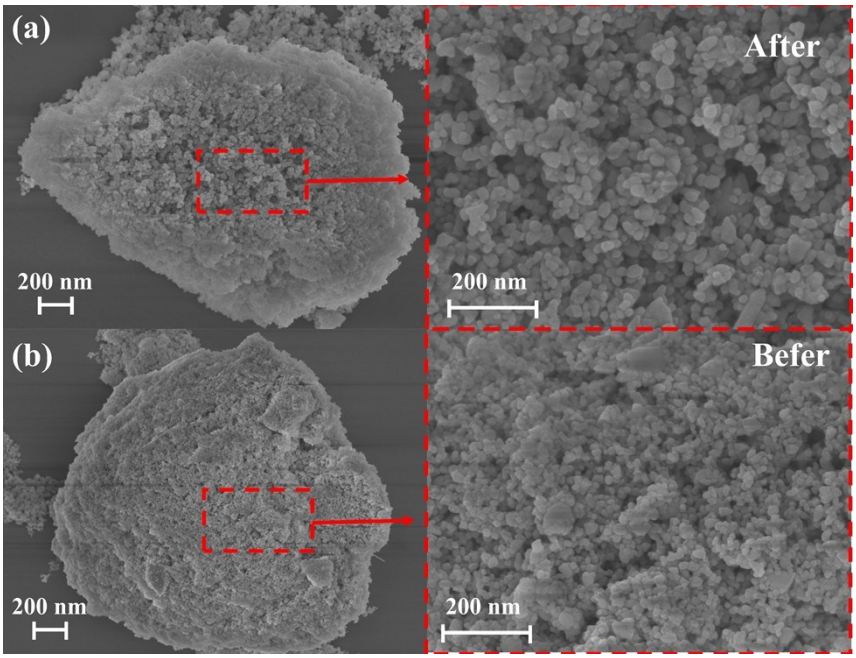

Fig. S7. After(a) and before(b) hydrogen development in Sem patterns.

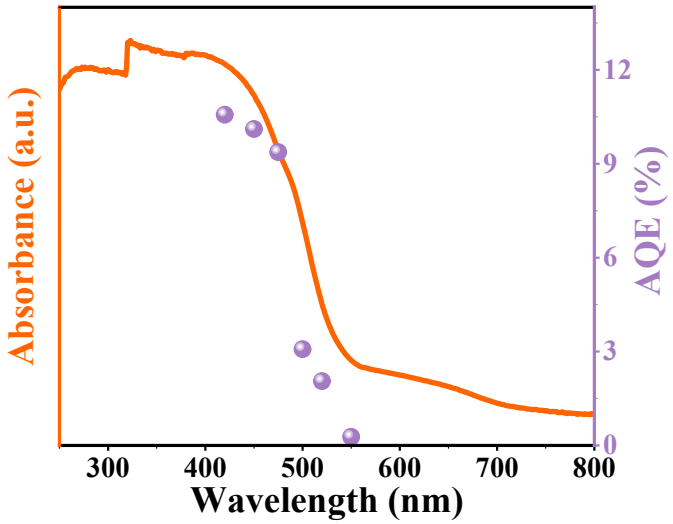

Fig. S8. The AQE of MCSe/H-GDY.

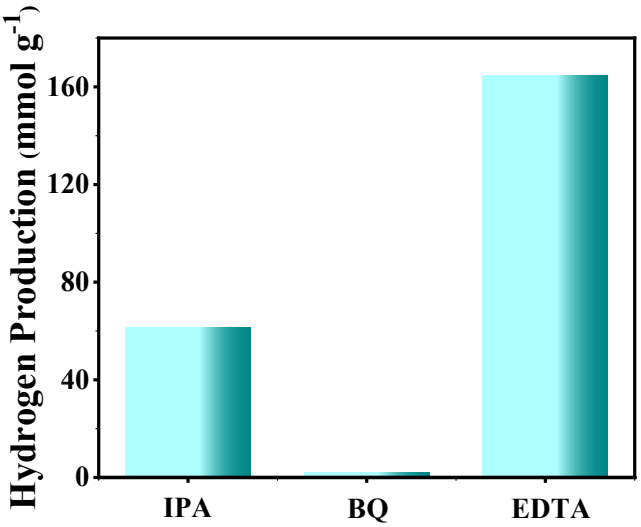

Fig. S9. The scavenger experiments of MCSe/H-GDY.

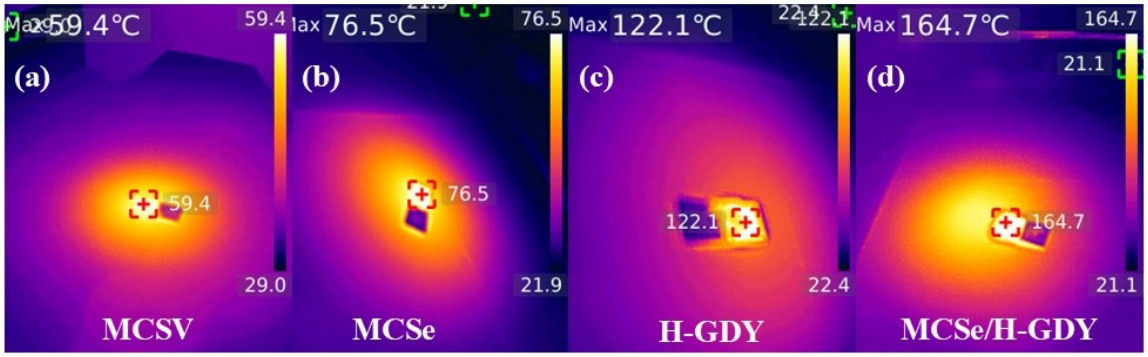

Fig. S10. Infrared radiation thermal image of (a) MCS, (b) MCSV, (c) MCSe and (d) MCSe/H-GDY

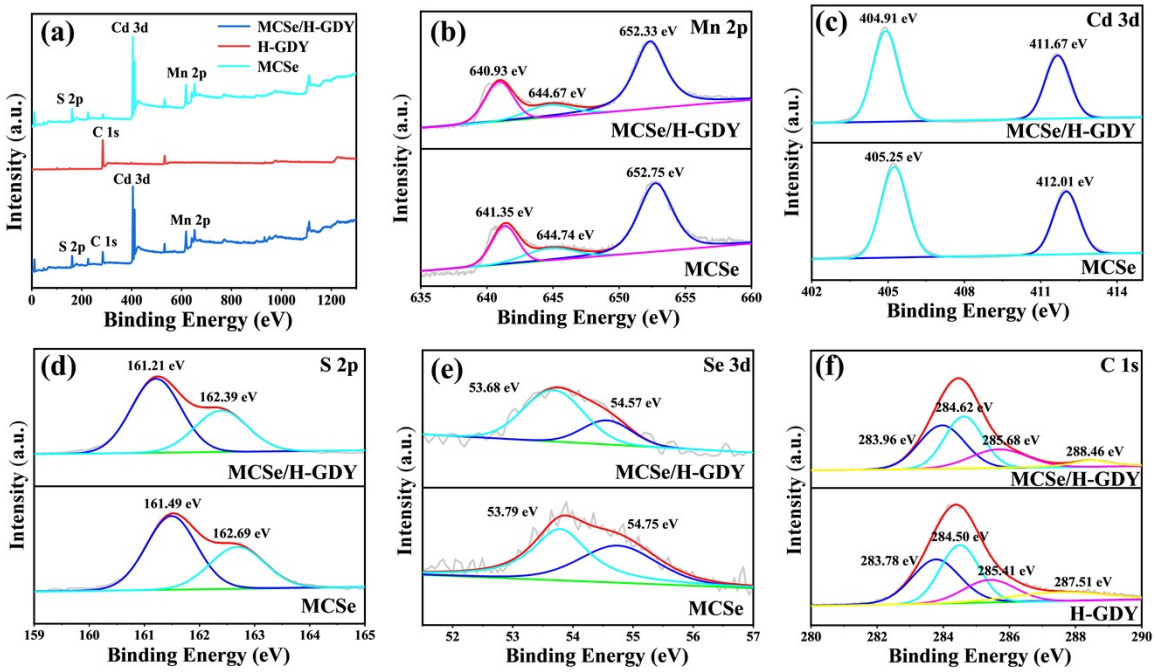

Fig. S11. (a) Full spectrum analysis of MCSe, H-GDY and MCSe/H-GDY, the XPS of H-GDY, MCSe and MCSe/H-GDY: (b) Mn 2p, (c) Cd 3d, (d) S 2p, (e) Se 3d and (f) C 1s.

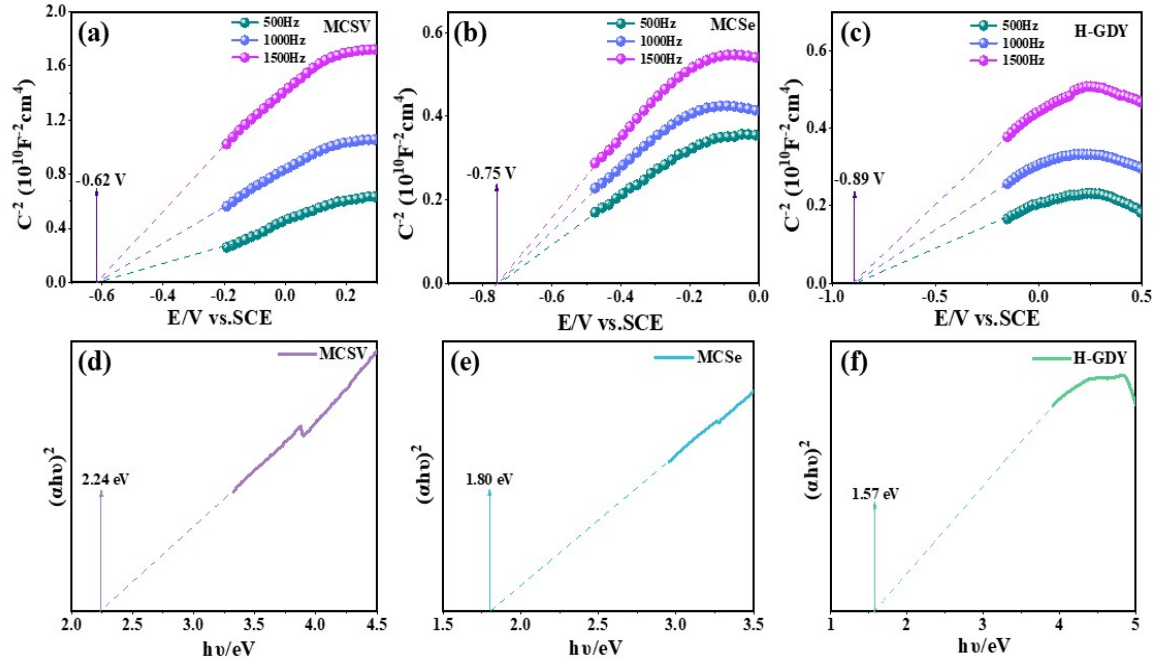

Fig. S12. (a) Mott-Schottky plots of MCSV, (b) Mott-Schottky plots of MCSe, (c) Mott-Schottky plots of H-GDY, (d) Bandgap calculation of MCSV, (e) Bandgap calculation of MCSe, (f) Bandgap calculation of MCSe/H-GDY.

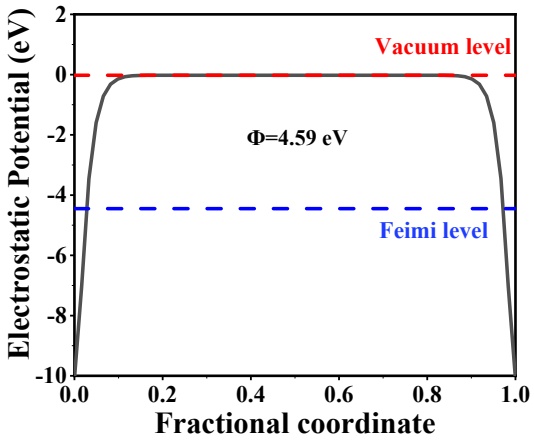

Fig. S13. Work function of H-GDY