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Supplementary Information

Triazinyl graphdiyne induces electron directional migration to drive charge separation of CdS for photocatalytic hydrogen evolution

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1. Experimental section

1.1 Characterization

Used Rigaku RINT-2000 to measure the X-ray diffraction (XRD) patterns of all samples. The operating parameters are copper Kα radiation, ranging from 5 to 80 (2θ), the current is 30 mA and the operating voltage is 40 kV. Next, we used scanning electron microscope (SEM, JSM-6701FJEOL) and transmission electron microscope (TEM, JEM1200EXJOOL) to further studied micro-morphology characteristics of the samples. Then, we use X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi) to study the surface chemical structure. Next, we employed a UV-250 (Shimadzu) spectrometer to analyze the diffuse reflectance spectra (DRS) of the catalysts we prepared. To ensure accuracy, we conducted baseline calibration using BaSO4 powder. We utilized the Horiba LabRAM HR Evolution Raman Spectrometer from Japan to investigate the Raman spectra. Next, we conducted photoluminescence (PL) testing on the sample using the steady-state spectrometer (FluorOMAx-4, HORIBA) and the single photon counting controller (floor hub, floor center). Finally, we carried out electrochemical experiments on the electrochemical workstation (VersaSTAT4-400, AMETEK), using Na_2SO_4(0.2 M, pH=7) as electrolyte. In DFT calculations, the generalized gradient approximation by Perdew-Burke-Ernzerhof (PBE) was employed to describe the exchange-correlation functional. A plane wave basis with a cut-off energy of 500 eV is used in the structure optimisation process. A vacuum layer of 15.0 was added to avoid interactions between neighbouring layers.

1.2 Photocatalytic Experiments

In order to determine the best hydrogen production environment of CS/TA-10, we used a nine-channel reactor (PCX50A Discover system) and 300W (Full-arc) xenon lamp for photocatalytic reaction. The reactor uses a 5 W LED light source (λ>420nm), a current of 0.90 A, a stirring speed of 322 n, and a switching time of 34 s. First, 10 mg catalyst was added to a 60 mL quartz bottle, and then 30 mL 10% lactic acid solution was added, which was uniformly dispersed by ultrasonic vibration. We used a gas chromatograph (TianmiGC00, TCD/13X column, N_2 gas chromatography as carrier gas) to measure the amount of hydrogen produced in 0.5 mL of gas extracted from the quartz bottle per hour. In order to test the stability, four hydrogen production experiments were carried out within 20 hours. Starting from the second cycle, the hydrogen in the quartz bottle needs to be discharged with N_2 before each cycle. Through such experimental design and steps, we can systematically evaluate the hydrogen production performance of CS/TA-10 and determine the optimal hydrogen production conditions.

1.3 Synthesis

1.3.1 Synthesis of 2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-triazine.

First, 12.9 mL trimethylsilyne was dissolved in 35 mL tetrahydrofuran, and then 30 mL n-butyl lithium tetrahydrofuran solution was slowly added under nitrogen protection, and then the reaction mixture was stirred at -78 °C for 30 minutes. Afterwards, the anhydrous zinc chloride solution in 50 mL tetrahydrofuran was slowly added to the reaction mixture, and then the resulting mixture was stirred at -78 °C for 30 minutes. The mixture was then heated to room temperature, and 2.76 g of cyanuric chloride, 600 mg of $Pb(PPh_3)_4$ and 80 mL of toluene were added. The reaction was stirred in an oil bath at 30 °C for 1 day, and nitrogen was used as a protective gas. After the reaction was completed, 50 mL 1 mol/L dilute hydrochloric acid 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 (eluent n-hexane : ethyl acetate =10 : 1) to obtain a yellowish-brown substance 2,4,6-Tris [(trimethylsilyl)ethynyl]-1,3,5-triazine(TETA-TMS). Then, the pyridine solution of TETA-TMS was obtained by dissolving 30 mL pyridine.

1.3.2 Synthesis of TA-GDY.

In a ball mill, 3 mL DFM, 3 mL TETA-TMS pyridine solution, 60 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 600r/min(rpm) for 6 hours. The black turbid liquid obtained after ball milling was washed with DMF, dichloromethane and methanol in turn, and dried in vacuum at 60 °C to obtain brown-black TA-GDY powder.

1.3.3 Synthesis of GDY

he synthesis of graphyne adopts a similar method. First, 12.9 mL of trimethylsilylacetylene is dissolved in 35 mL of tetrahydrofuran (THF). Then, a slow addition of 36 mL of n-butyllithium in THF solution is carried out, dropwise, into the trimethylsilylacetylene solution at -78 °C. The reaction mixture is stirred for 30 minutes at -78 °C. Next, a slow dropwise addition of a solution containing 60 mL of THF and anhydrous zinc chloride is performed, maintaining the reaction mixture at -78 °C for an additional 30 minutes. After raising the temperature to room temperature, 5.52 g of hexabromobenzene, 700 mg of $Pd(PPh_3)_4$, and 80 mL of toluene are added to the reaction mixture under a nitrogen atmosphere. The reaction was carried out at 80 °C in an oil bath pot for 3 days. After completion of the reaction, 50 mL of 1 M hydrochloric acid is added to the reaction mixture. The organic layer is extracted with ethyl acetate, and the combined organic extracts are washed with saturated brine solution. Drying with anhydrous sodium sulfate is performed, followed by purification through column chromatography to obtain hexakis-[(trimethylsilyl)ethynyl] benzene (HEB-TMS). This compound is then dissolved in 30 mL of pyridine for further use.

3mL HEB-TMS pyridine solution, 3mL DFM, 60mg CuCl and 50g stainless steel balls were added to the ball mill tank and sealed. The ball mill tank was placed in a planetary ball mill for 6h at a speed of 600r/min. The black solution obtained after ball milling was washed in turn with DMF, dichloromethane and methanol, and dried in vacuum at 60 °C to obtain black GDY powder.

1.3.4 Synthesis of g-C_3N_4

In a 50 mL porcelain crucible, 20 grams of urea were added and placed in a muffle furnace. The urea was calcined at a rate of 5 °C per minute up to a temperature of 550 °C and maintained at this temperature for 4 hours. After cooling to room temperature, the resulting light-yellow solid was ground into a powder and designated as g-C_3N_4, which can be used for further research purposes.

1.3.5 Synthesis of CdS nanorods

In a typical method, 1.92 g $Cd(NO_3)_2 \cdot 4H_2O$ and 1.42 g thiourea (NH_2CSNH_2) were slowly added into 50 mL ethylenediamine solution, which was dissolved by ultrasonic and magnetically stirred for 1 h to obtain a uniform solution. After the reaction solution was transferred to a 100 mL PTFE autoclave, it was reacted at 180°C for 24 hours. Then the autoclave was naturally cooled to room temperature, and the yellow precipitate was washed with deionized water and anhydrous ethanol for three times, and dried at 60 °C for 12 h to obtain yellow CdS nanorods.

1.3.6 Synthesis of CdS/TA-GDY

The preparation method of CdS/TA-GDY is a classic physical mixing method. 0.1 g CdS and a specific amount of TA-GDY were dissolved in 20 mL ethanol solution. Ultrasonic homogenize the mixed solution, then stirred overnight, then stir in a water bath at 80℃ to completely evaporate the ethanol, and collect and grind samples. The collected product is named as the collected products and marked as CS/TA-x (x = 5, 10, 15, 20), where X is the mass ratio of TA-GDY. For example, in CS/TA-10, '10 "means that the content of TA-GDY is 10%.

1.3.7 Synthesis of CdS/g-C_3N_4 and CdS/GDY

The synthesis of CdS/g-C_3N_4 and CdS/GDY composites is consistent with the above methods.

2. Supporting Figs. and Tables

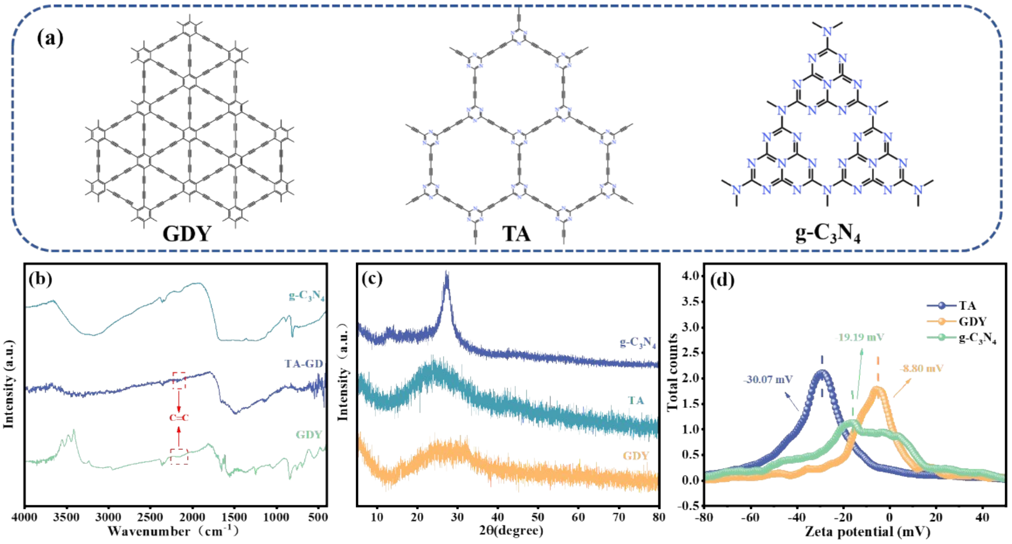

Fig. S1. (a) Structural diagram of TA-GDY, g-C_3N_4 and GDY; (b) The FT-IR spectra of TA-GDY, g-C_3N_4, GDY; (c) The XRD spectra of TA-GDY, g-C_3N_4, GDY; (d) The zeta potential of TA-GDY, g-C_3N_4, GDY.

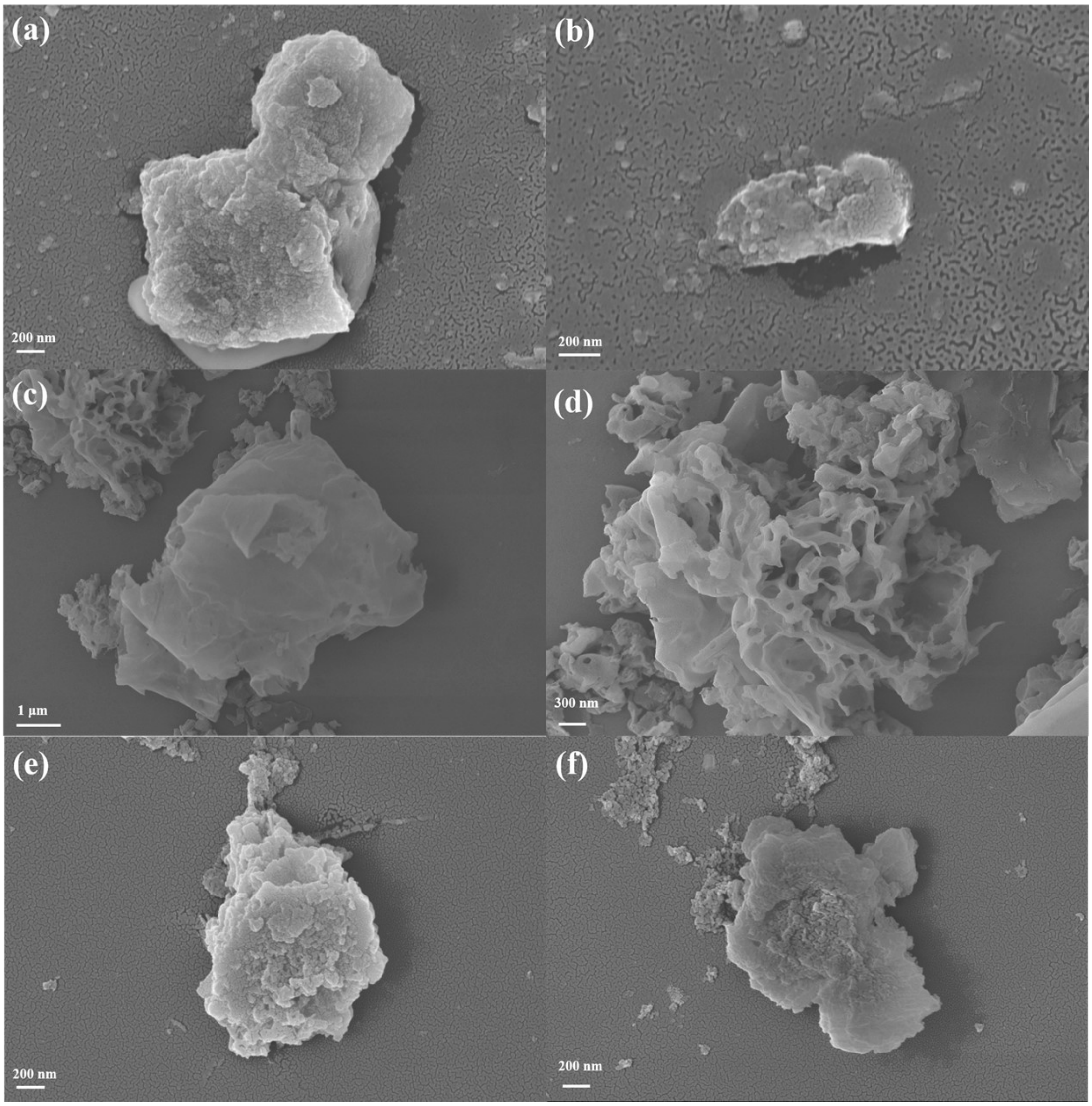

Fig. S2. SEM image of (a-b) TA-GDY, (b-c) g-C3N4 and (e-f) GDY prepared.

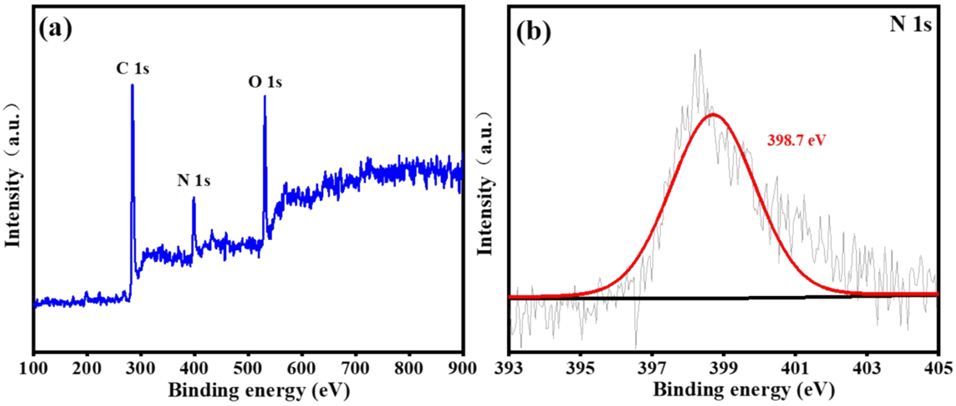

Fig. S3. (a) XPS spectra of TA-GDY (d) full-scan spectra of N 1s orbit of TA-GDY.

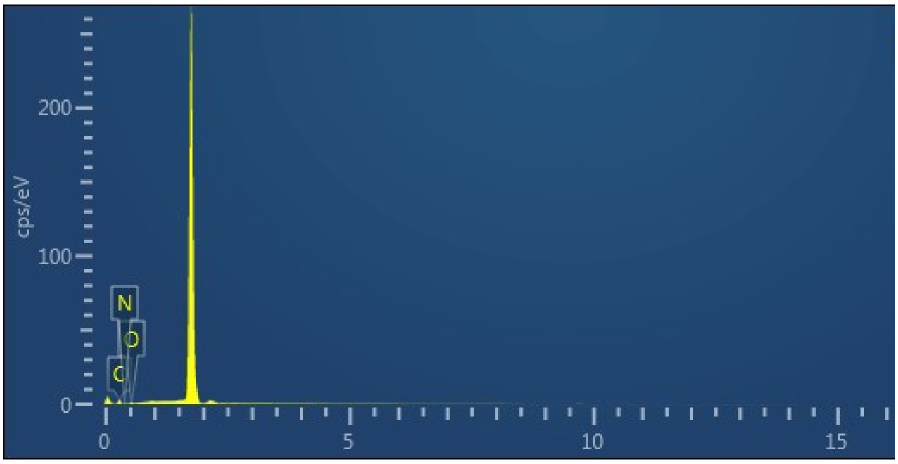

Fig. S4. EDX image of TA-GDY.

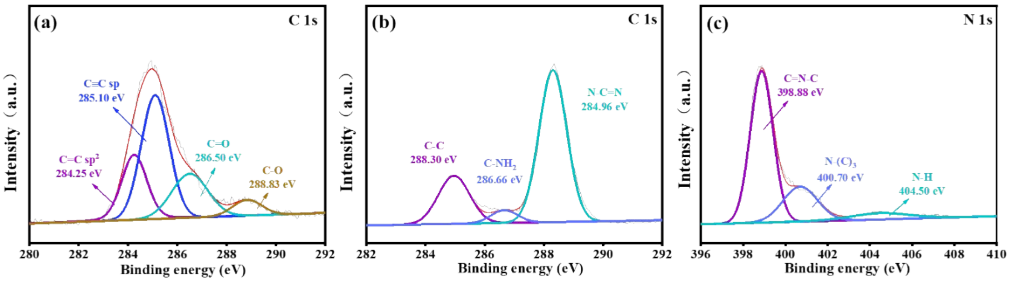

Fig. S5. (a) full-scan spectra of C 1sorbit of GDY; (b) full-scan spectra of C 1sorbit of g-C_3N_4; (c) full-scan spectra of N 1sorbit of g-C_3N_4.

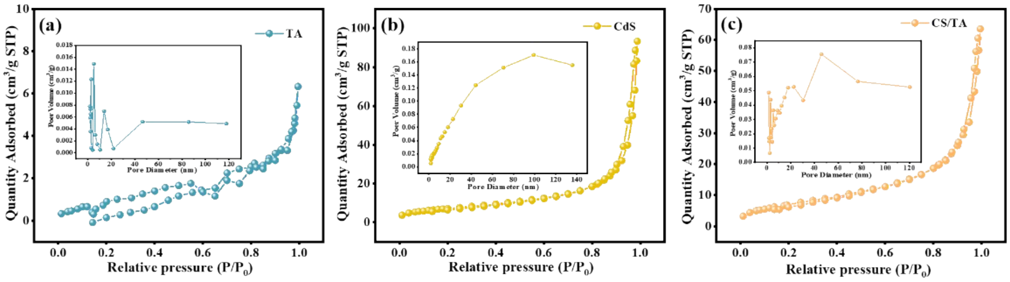

Fig. S6. N_2 adsorption analysis isotherm and pore size distribution of (a) TA-GDY, (b) CdS and (c) CS/TA-10.

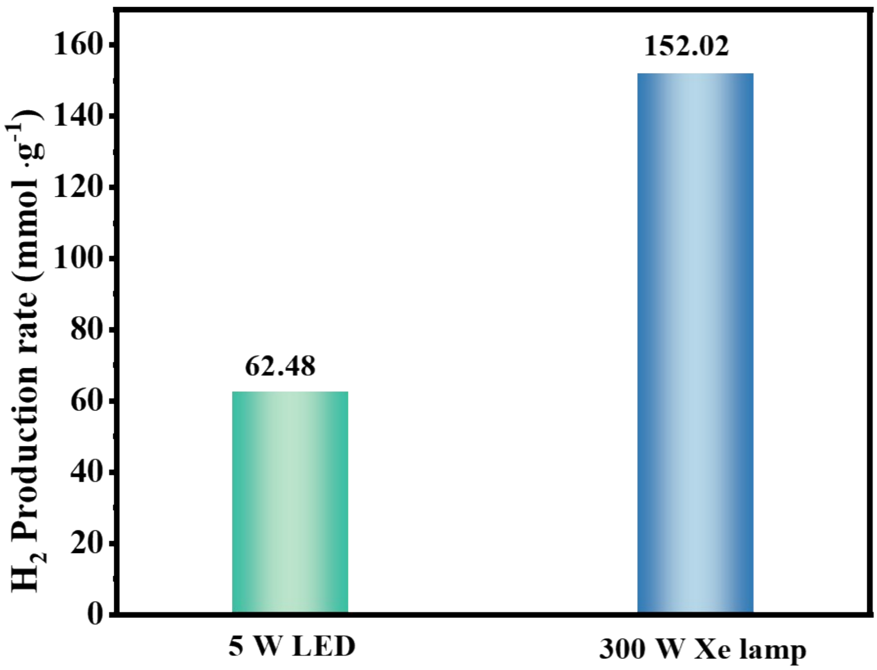

Fig. S7. H_2 evolution of CS/TA-10 5 W LED and 300 W xenon lamp

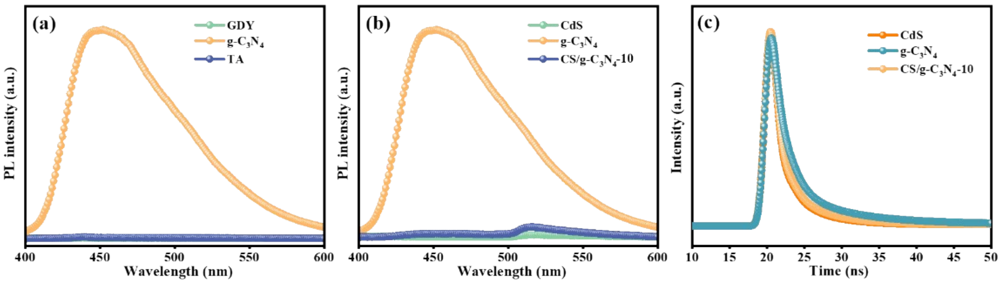

Fig. S8. (a) PL spectra of GDY, g-C_3N_4 and TA-GDY; (b) PL spectra of CdS, g-C_3N_4 and CS/g-C_3N_4-10; (c) TRPL spectra of CdS, g-C_3N_4 and CS/g-C_3N_4-10.

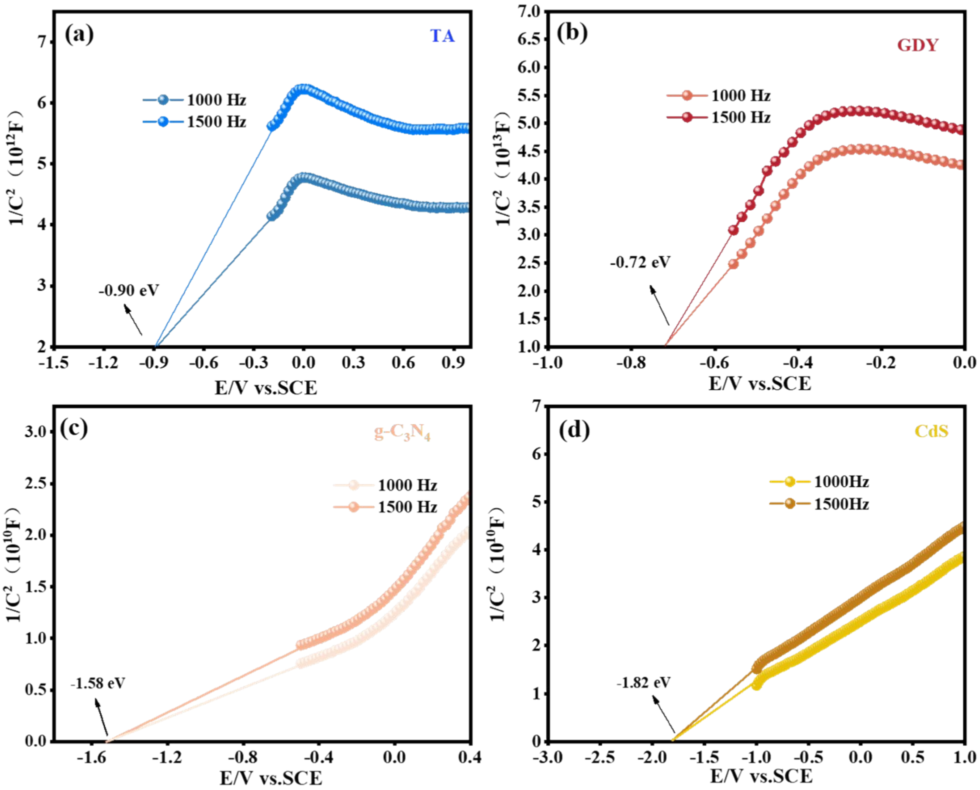

Fig. S9. Mott-Schottky plots of (a)TA-GDY, (b) GDY, (c) g-C_3N_4 and (d) CdS.

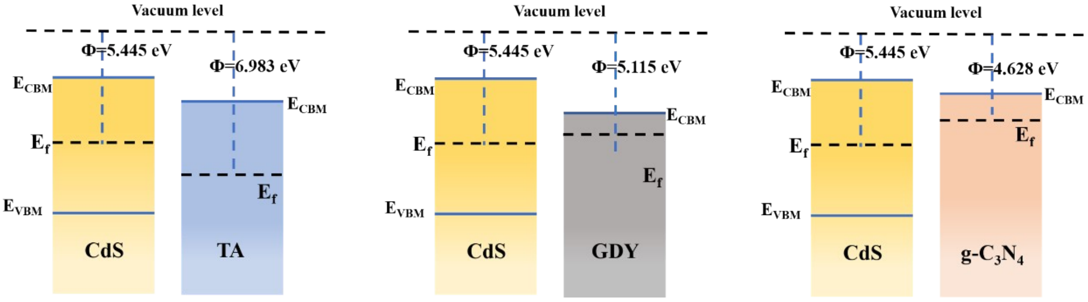

Fig. S10. Correspondence of work function of CdS with TA-GDY, GDY, g-C_3N_4.

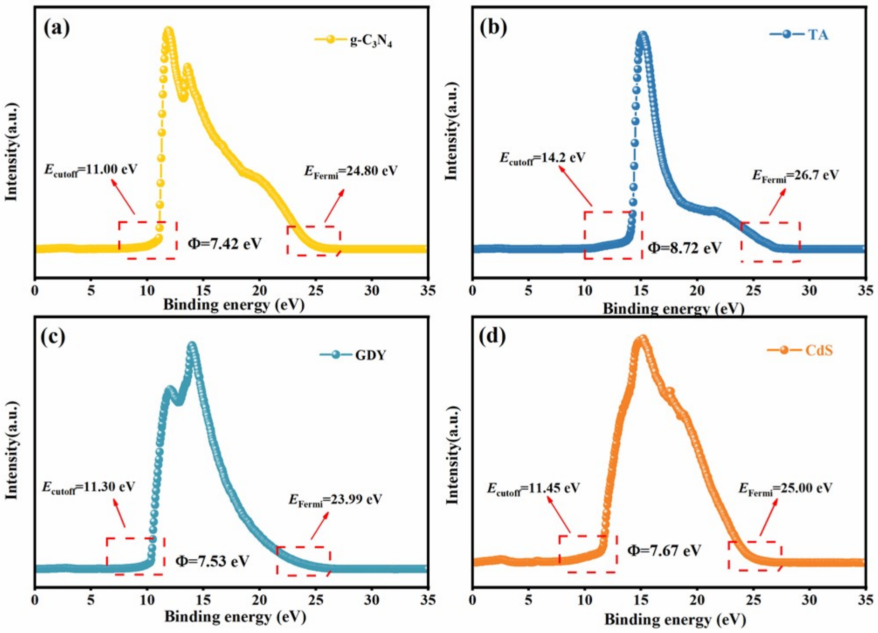

Fig. S11. UPS spectra of (a) g-C_3N_4; (b) TA-GDY; (c) GDY and (d) CdS.

Table S1 The N/C ratios of TA-GDY.

Methods	C (wt. %)	N (wt. %)	N/C (%)
EDX analysis	55.32	18.02	32.57
Elemental analyzer	46.13	14.98	30.79

Table S2. Attenuation parameters of g-C_3N_4, CdS, CS/g-C_3N_4-10, CS/GDY-10, CG-15, and CS/TA-10.

Samples	**Pre-exponential factors A**	**Lifetime, <τ> (n-9s)**	**Average lifetime, <τ> (ns)**	**χ^2**
g-C_3N_4	A_1= 33.69	τ_1=7.19	2.51	1.75
	A_2= 21.50	τ_2=77.57		
	A_3= 44.81	τ_3=1.28		
CdS	A_1= 28.03	τ_1=4.14	1.40	1.57
	A_2= 24.38	τ_2=136.90		
	A_3= 47.59	τ_3=0.74		
CS/g-C_3N_4-10	A_1= 29.00	τ_1=4.82	1.63	1.63
	A_2= 24.30	τ_2=115.41		
	A_3= 46.69	τ_3=0.84		
CS/GDY-10	A_1= 27.52	τ_1=4.18	1.43	1.48
	A_2= 25.28	τ_2=144.57		
	A_3= 47.20	τ_3=0.74		
CS/TA-10	A_3= 47.22	τ_3=0.75	1.44	1.53
	A_3= 26.87	τ_3=4.24		
	A_3= 25.91	τ_3=143.09		