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**Defective $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ Twin Crystal/ Ag_3PO_4 Z-Scheme
Heterojunctions Toward Optimized Visible-Light-Driven
Photocatalytic Hydrogen Evolution**

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Experimental section

Material preparation

The chemical reagents used were cadmium acetate dihydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Bide Pharmaceuticals), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Guangfu Group), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$ Aladdin Reagent Co.), and ethylenediamine, silver nitrate (AgNO_3 Aladdin Reagent Co.), Sodium phosphate tribasic (Na_3PO_4 Kaitong Chemical Reagent Co.), and they were all analytical grade and used without further purification.

$\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ was synthesized via ethylenediamine as an auxiliary pathway via a hydrothermal reaction. 6 mmol $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 14 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added into 50 mL deionized water under constant stirring. 25 mmol thioacetamide and 10 mL ethylenediamine were then added to the above aqueous solution, and the mixture was stirred for 1 h. Then, the above solution was transferred to a 100 mL polyethylene lined stainless steel autoclave and kept at 180 °C for 12 h. After the reaction was completed, the mixture was cooled to room temperature. After centrifugation and

washing three times with deionized water and ethanol, the product was dried in a vacuum oven at 60 °C for 12 h to obtain $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$.

A simple ion exchange method was applied to synthesize Ag_3PO_4 . In a typical synthesis, 0.255 g AgNO_3 , 1.14 g Na_3PO_4 were dispersed into 30 mL of deionized water and stirred for about 30 min. Then the Na_3PO_4 solution was added dropwise to the AgNO_3 solution step by step and kept stirring for about 30 min. After the reaction was completed, the precipitate in the mixture was cooled to room temperature and collected by centrifugation, and washed three times with water and ethanol, respectively. Finally, the sample was dried in an oven at 60 °C for 12 h to obtain Ag_3PO_4 .

$\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/\text{Ag}_3\text{PO}_4$ was synthesized by a simple in situ precipitation method. In a typical synthesis, the prepared $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$ was dispersed in 50 mL of deionized water and then sonicated for 3 hr. Under stirring for 1 h, Ag_3PO_4 was added to the above dispersion solution and stirred for 24 h under light-proof conditions. After the final reaction was completed the precipitate in the mixture was cooled to room temperature and collected by centrifugation and rinsed three times with water and ethanol, respectively. After that, the samples were ground for 4 h. Finally, the samples were dried in an oven at 60 °C for 12 h to obtain $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/\text{Ag}_3\text{PO}_4$. Different composites were synthesized according to different molar ratios of Ag_3PO_4 addition, which were noted as $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/1\%\text{Ag}_3\text{PO}_4$, $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/6\%\text{Ag}_3\text{PO}_4$.

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Characterizations

X-ray diffraction (XRD) patterns were obtained by a Bruker D8 diffractometer using Cu K α radiation. The microstructures were identified by scanning electron microscopy (SEM, FEI Sirion 200) and a transmission electron microscopy (FEI Talos F200S). Nitrogen adsorption-desorption isotherms, specific surface areas, and pore size distributions were collected on an ASAP 2460 aperture analyzer. Optical absorption and diffuse reflectance spectrometry (UV-DRS) were performed using the UV-Vis spectrophotometer (Lambda 950). X-band electron paramagnetic resonance (EPR) spectra were recorded using a BRUKER N500 EPR spectrometer. The photoluminescence (PL) were detected on a fluorescence spectrometer (PerkinElmer FL 6500) with an excitation wavelength of 243 nm. X-ray photoelectron spectroscopy (XPS) was used to understand the elemental chemical composition of different samples by ESCALab 250 systems. Raman spectroscopy is used to analyze lattice vibration of the samples by the HORIBA HR 800 spectrometer.

Photocatalyst test

The photocatalytic hydrogen production experiments were performed in a photocatalytic hydrogen production system (Labsolar-6A, Beijing Perfect Light Technology Co., Ltd.). A cut-off filter ($\lambda > 400$ nm) was used to remove the UV light to produce visible light, and a 300 W Xe-lamp was used as the light source. In a typical photocatalytic test, 50 mg of photocatalyst was dispersed in 100 mL of an aqueous solution containing 10 mL of lactic acid and 90 mL of water as the sacrificial reagent, and the solution was stirred continuously during the test. Before visible light irradiation, the opening was sealed with a quartz cap with a silicone rubber gasket, and the test apparatus was evacuated for 30 min to remove O₂ from the reaction system. Finally, the mixture was exposed under radiation and the gas product was analyzed using a gas chromatograph (Techcomp 7900, TCD, Ar carrier) to determine hydrogen production.

Photoelectrochemical measurements

The samples were tested on a Princeton Versa STAT 2 electrochemical workstation with a standard three-electrode system

(Ag/AgCl electrode reference electrode and Pt counter electrode) and the electrolyte was a 0.2 M Na₂SO₄ solution. First, 50 mg sample was dispersed into ethanol with ultrasonic treatment for 4 h. Then, the dispersion was uniformly sprayed onto the FTO glass. Finally, the FTO glass was placed in a tube furnace and calcined at 350 °C under a N₂ gas atmosphere with a heating rate of 5 °C/min for 2 h. The electrolyte was degassed by purging the solution with N₂ gas for 30 min before the photoelectrochemical test, which was performed using a 300 W Xe-lamp with a pass filter (AM 1.5) as the light source. It is worth noting that Mott-Schottky curves were tested under visible light irradiation with 0.2M Na₂SO₄ as the electrolyte. During the test, three different frequencies were used to make the test results more accurate. After obtaining the flat-band potential, the conduction band potential of the photocatalyst can be determined according to the quantitative relationship between the flat-band potential and the conduction band potential via $E(\text{NHE})=E(\text{Ag}/\text{AgCl})+0.197$. After the CB position was determined, the electrochemical driving force for hydrogen evolution was then obtained. To determine the carrier densities of the photoelectrons the following equation was applied,

$$N_d = \frac{2}{q\epsilon\epsilon_0} [d(1/c^2)/dv]^{-1} \quad (1)$$

where q , ϵ , ϵ_0 , and c are the charge of an electron (1.60×10^{-19} C), the dielectric constant of a semiconductor, the vacuum permittivity (8.854×10^{-12} F·cm⁻¹), and the capacitance of the depletion region, while V and $d(1/c^2)/dv$ are the applied voltage and the slope of a Mott-Schottky plot. All the tests were performed at pH=7. Moreover, during the test, a standard three-electrode system was used, with the photocatalyst as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. The conversion between the reversible hydrogen electrode (RHE), standard hydrogen electrode (SHE) and normal hydrogen electrode (NHE) is based on the following equations.

$$E(\text{RHE})=E(\text{NHE})+0.0591 \times \text{PH} \quad (2)$$

$$E(\text{RHE})=E(\text{SHE})+0.0591 \times \text{PH}+0.2415 \quad (3)$$

$$E(\text{NHE})=E(\text{Ag}/\text{AgCl})+0.197 \quad (4)$$

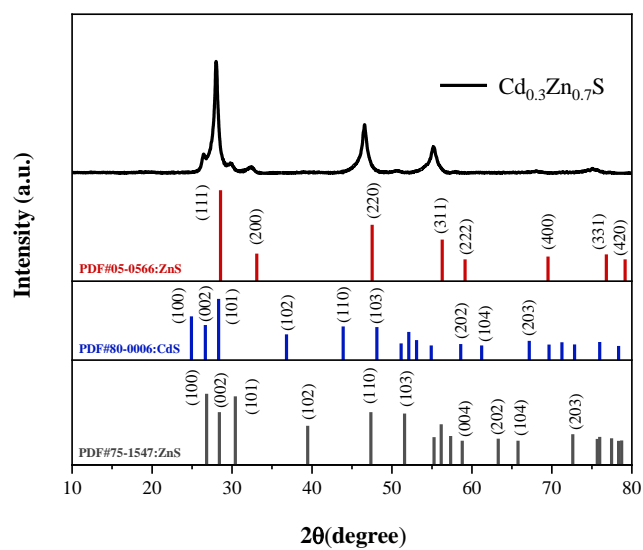


Figure S1 XRD patterns of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$.

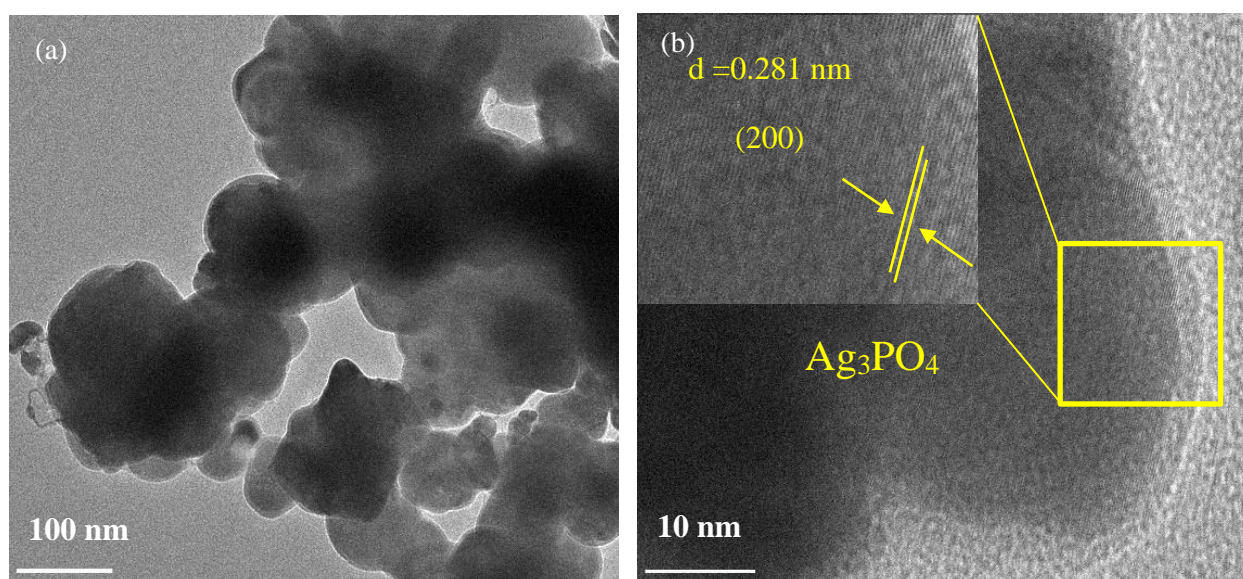


Figure S2 (a) TEM and (b) HRTEM images of Ag_3PO_4

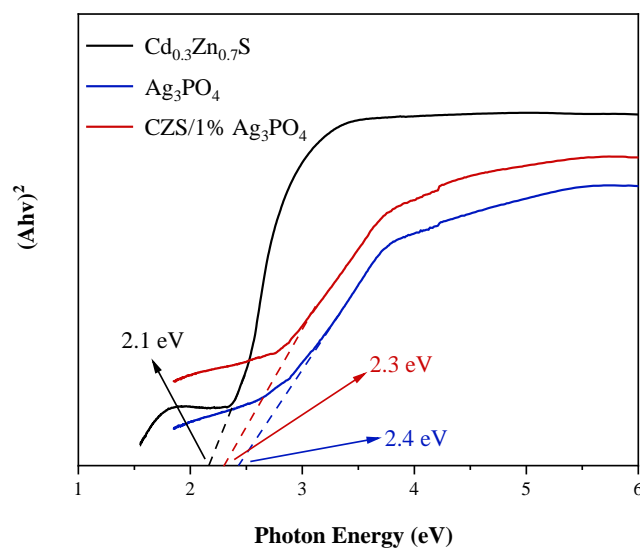


Figure S3 Optical band gaps of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$, Ag_3PO_4 , and $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/1\% \text{Ag}_3\text{PO}_4$.

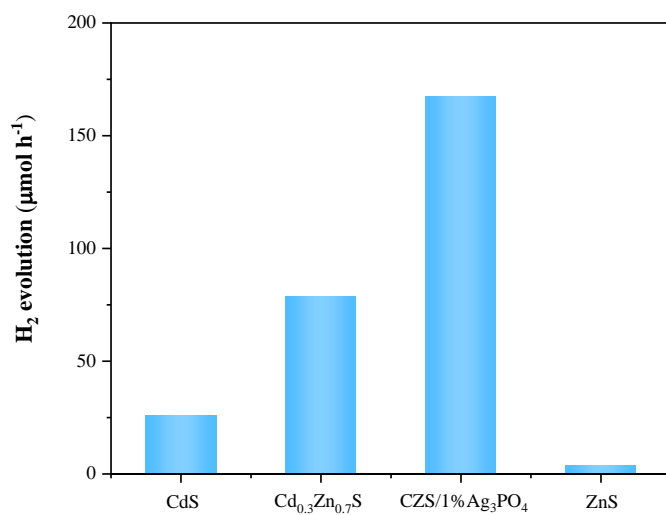


Figure S4 hydrogen production rate of CdS, $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$, $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/1\% \text{Ag}_3\text{PO}_4$ and ZnS.

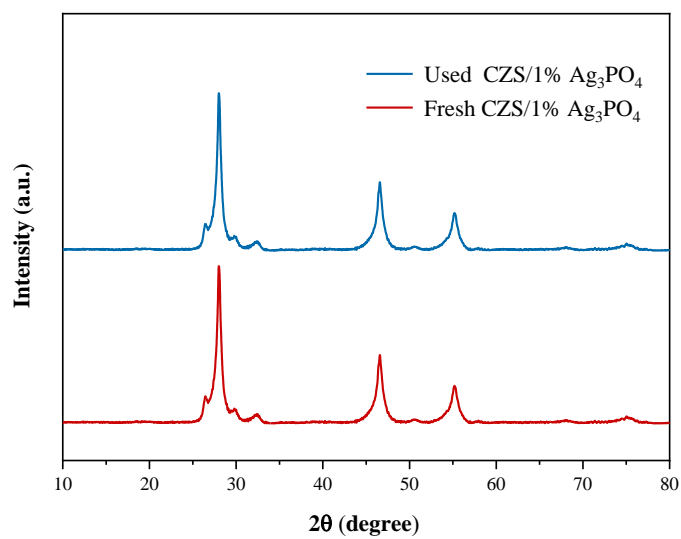


Figure S5 XRD patterns for fresh and used Cd_{0.3}Zn_{0.7}S/1% Ag₃PO₄.

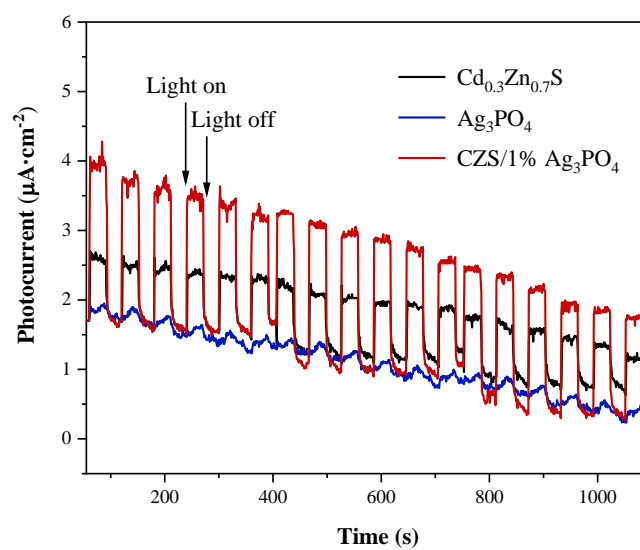


Figure S6 TPC plots of Cd_{0.3}Zn_{0.7}S, Ag₃PO₄, and Cd_{0.3}Zn_{0.7}S/1%Ag₃PO₄.

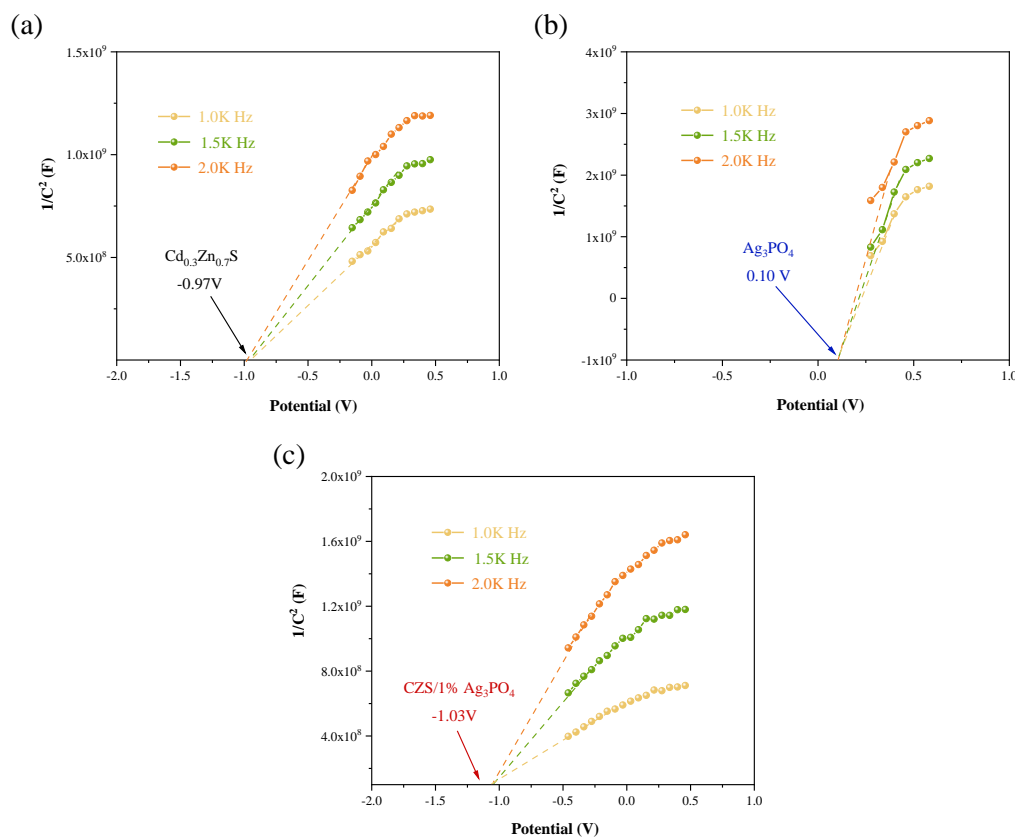


Figure S7 Mott-Schottky plots of (a) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$, (b) Ag_3PO_4 , and (c) $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/1\%\text{Ag}_3\text{PO}_4$.

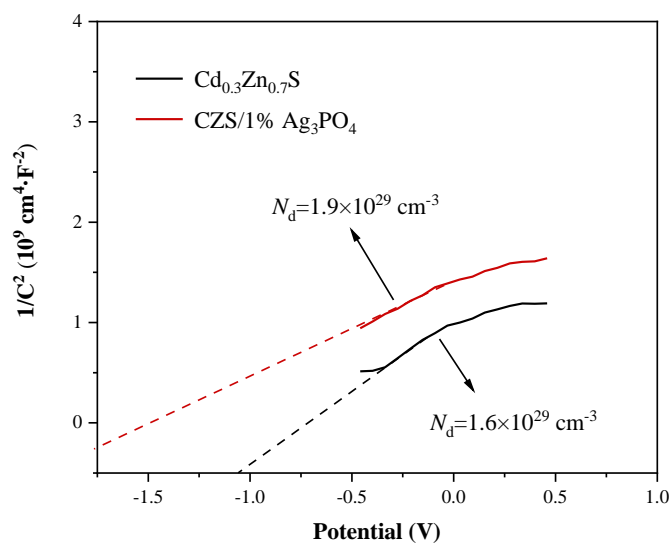


Figure S8 carrier density plots of $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}$, and $\text{Cd}_{0.3}\text{Zn}_{0.7}\text{S}/1\%\text{Ag}_3\text{PO}_4$.

Table S1 BET specific surface area, pore volume and pore size of different samples. ^a

Samples	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
Cd _{0.3} Zn _{0.7} S	35.032	0.302	32.945
Ag ₃ PO ₄	5.322	0.038	32.918
Cd _{0.3} Zn _{0.7} S/1%Ag ₃ PO ₄	30.930	0.349	41.201

^aThe error bar in all measurement errors within ± 0.002 .

Table S2 Experimental band gaps of CdS, ZnS and Cd_{1-x}Zn_xS.

Samples	CdS	Cd _{0.3} Zn _{0.7} S	ZnS	Cd _{0.5} Zn _{0.5} S ¹	Cd _{0.5} Zn _{0.5} S ²	Cd _{0.6} Zn _{0.4} S ³	CdS ⁴
Band Gap(eV)	2.20	2.10	3.30	2.52	2.22	2.47	2.13

Table S3 Comparison of photocatalytic H₂ evolution rate of the metal sulfide photocatalysts with previous reported photocatalysts.

Photocatalyst	Sacrificial agent	Light source	H ₂ evolution rate (μmol h ⁻¹ g ⁻¹)	Ref.
CdS/graphene	Lactic acid	350 W Xe (λ > 420 nm)	1120	5
3D NiO-CdS	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	500 W lamp	745	6
CdS nanosheets	0.25 M Na ₂ S/Na ₂ SO ₃	300 W Xe (λ > 420 nm)	3334	7
NiS ₂				
Cd _{0.5} Zn _{0.5} S	0.35 M Na ₂ S/0.6 M Na ₂ SO ₃	300 W Xe (λ > 420 nm)	284.7	8
CZS@Bi ₂ Fe ₄ O ₉	0.35 M Na ₂ S/0.6 M Na ₂ SO ₃	300 W Xe (λ > 420 nm)	811.5	8
CdZnS	Lactic acid	LDE lamp	449.4	9
rGO/Cd _x Zn _{1-x} S	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	150 W Xe arc lamp	1060	10
Cd _{0.5} Zn _{0.5} S	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	300 W Xe (λ > 400 nm)	1023	11

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In ₂ O ₃ /Cd _{0.5} Zn _{0.5} S	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	300 W Xe (λ > 420 nm)	1110	12	
ZnS /g-C ₃ N ₄	menthanol	UV-LDE lamp	194	13	
ZnS	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	300 W Xe (λ > 420 nm)	83.77	14	
W-ZnS	0.35 M Na ₂ S/0.25 M Na ₂ SO ₃	300 W Xe (λ > 400 nm)	63.68	15	
Cd_{0.3}Zn_{0.7}S/1% Ag₃PO₄	Lactic acid	300 W Xe (λ > 400 nm)	3345.79 (167.29 μmol h ⁻¹)	This work	

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