Supporting Information

Improving Photocatalytic Hydrogen Production through Switching Charge Kinetics from Type-I to Z-scheme via Defective Engineering

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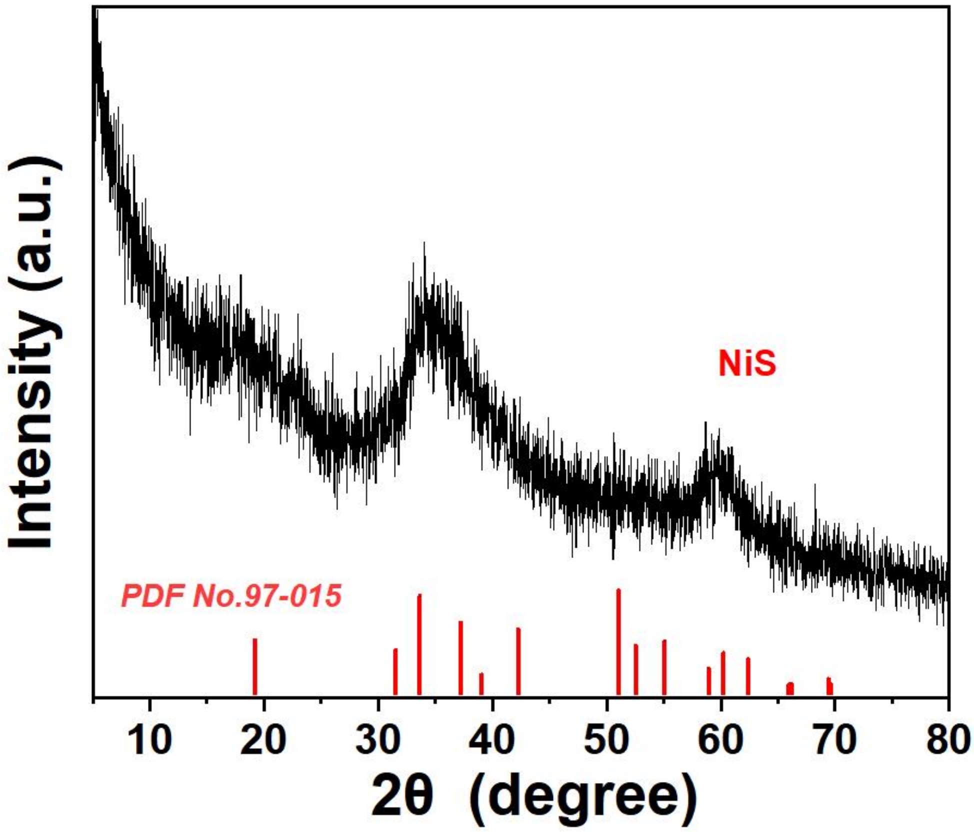

Figure S1. The XRD patterns of **NiS**.

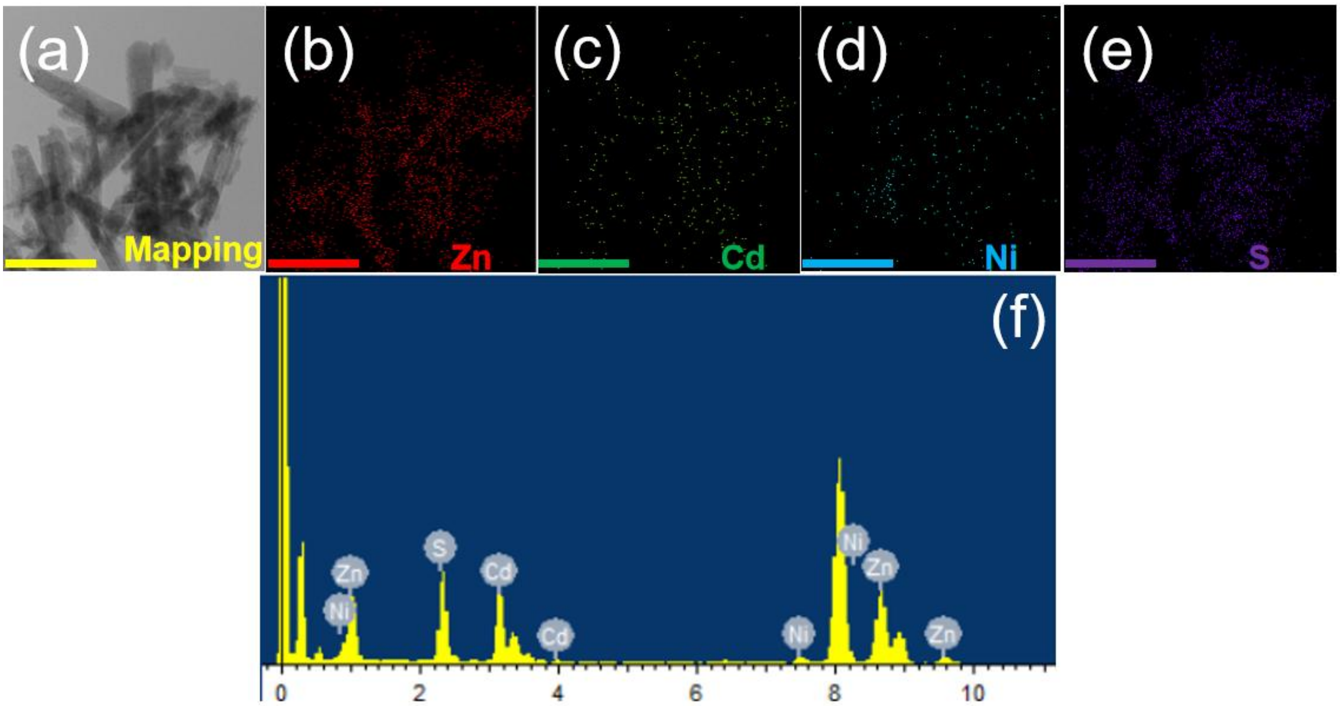

Figure S2. The elemental mapping images EDX (a-f) of **CZNS 6**.

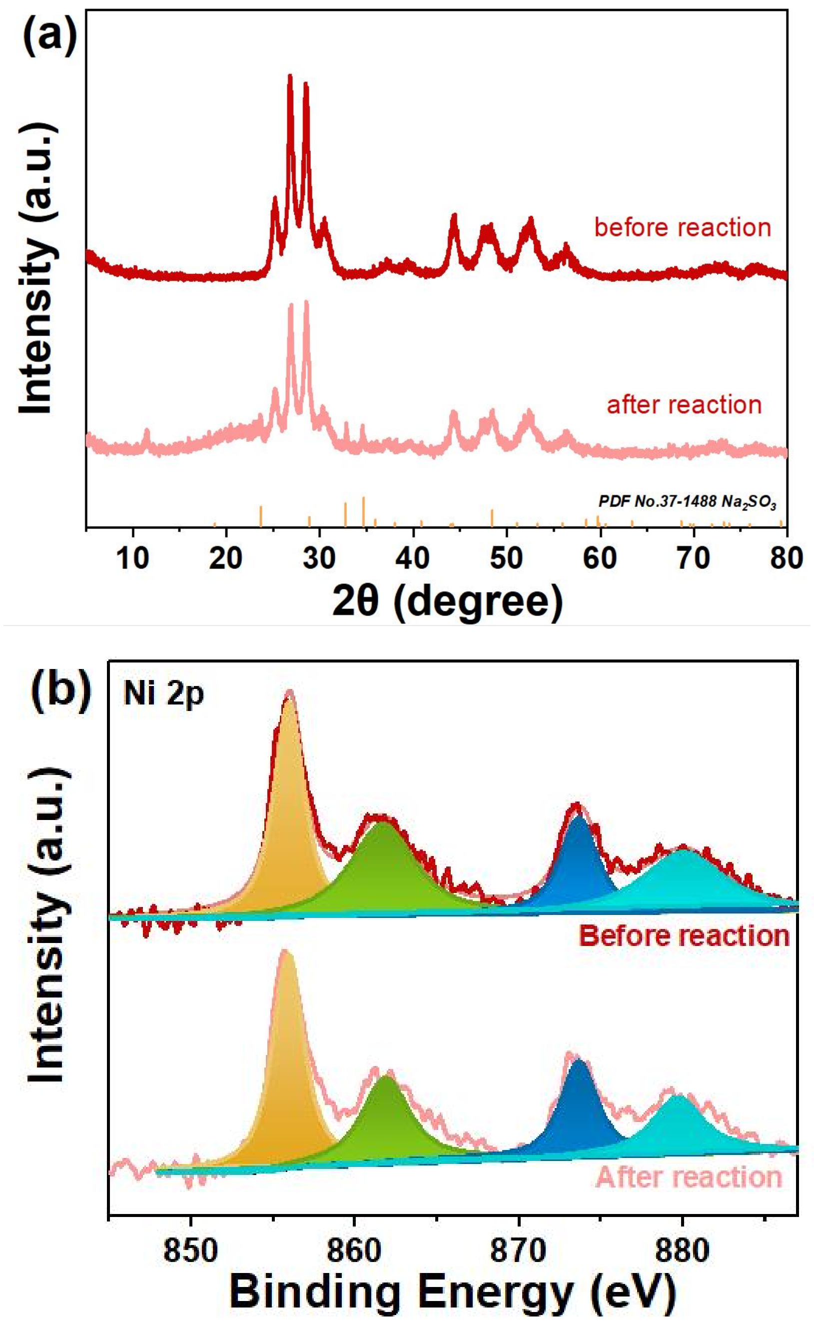

Figure S3. XRD patterns(a) and high-resolution XPS spectra (b) of Ni 2p for CZNS 6 before and after the photocatalytic hydrogen evolution reaction.

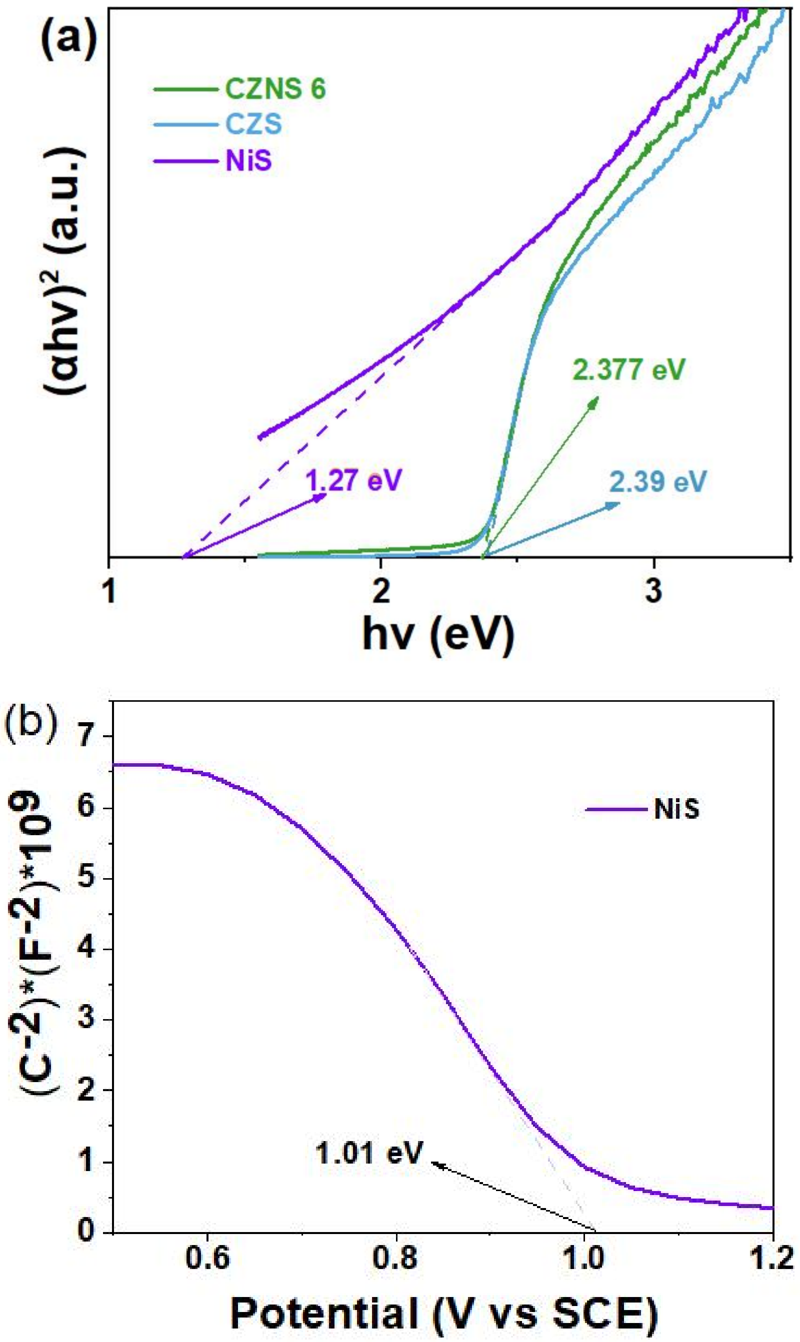

Figure S4. The Tauc plots of of NiS, CZS and CZNS 6(a); the Mott−Schottky plots of NiS (b).

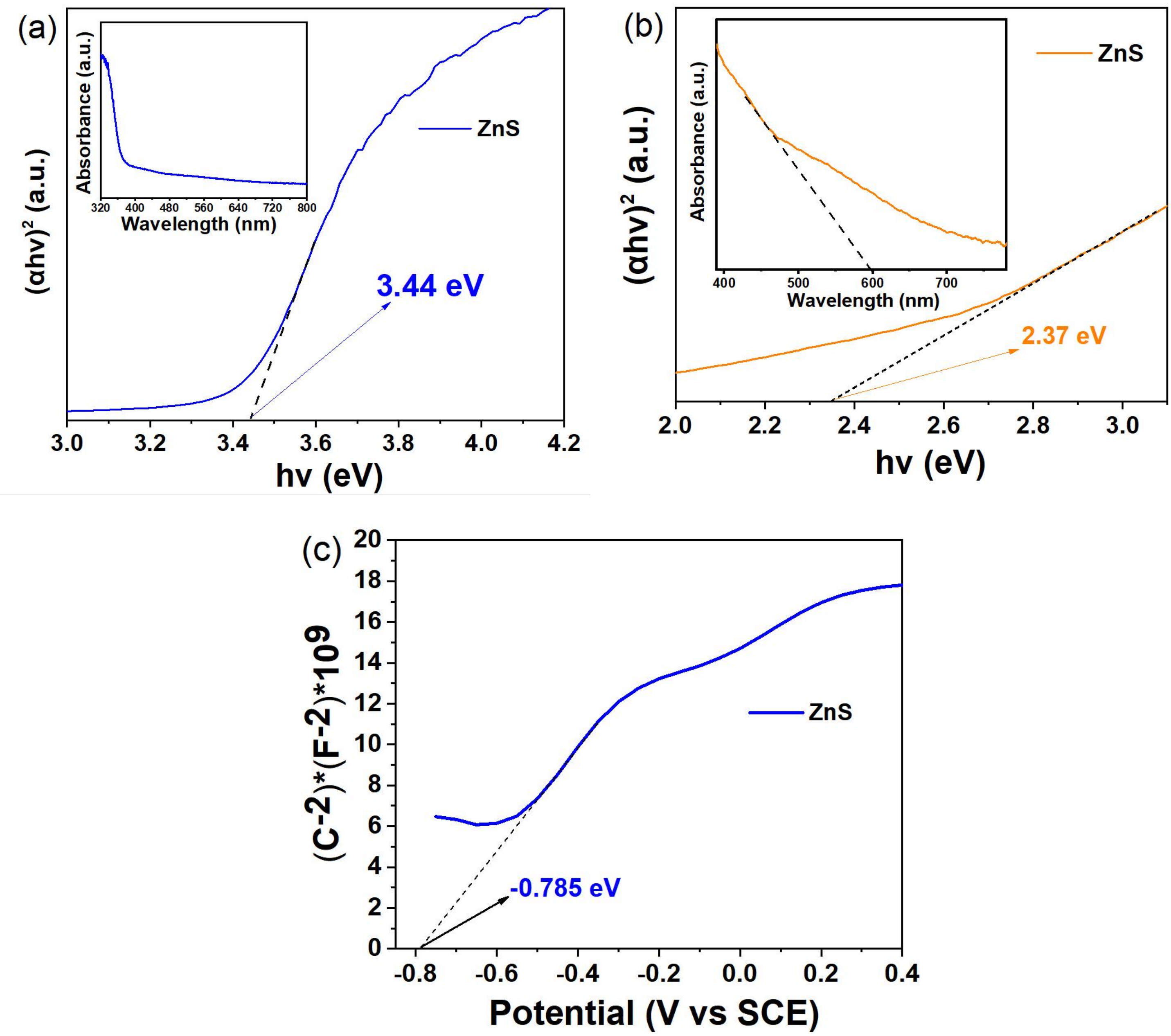

Figure S5. The Tauc plots of $(\alpha h\nu)^2$ versus $(h\nu)$ of ZnS (a) and enlarged view for ZnS at visible region local (b); the Mott−Schottky plots of ZnS (c).

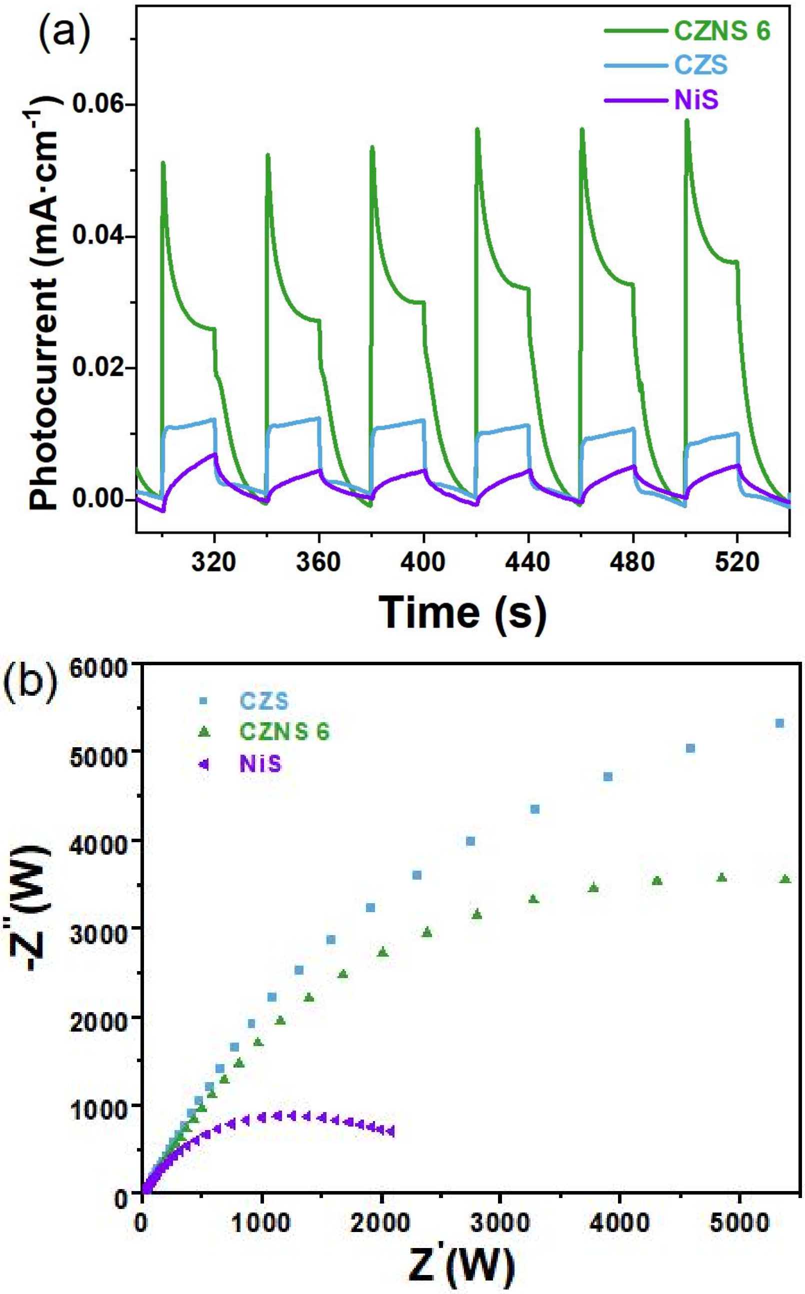

Figure S6. The photo-current curves (a) and Electrochemical Impedence Spectroscopy (EIS) (b) of CZS, NiS, and CZNS 6.

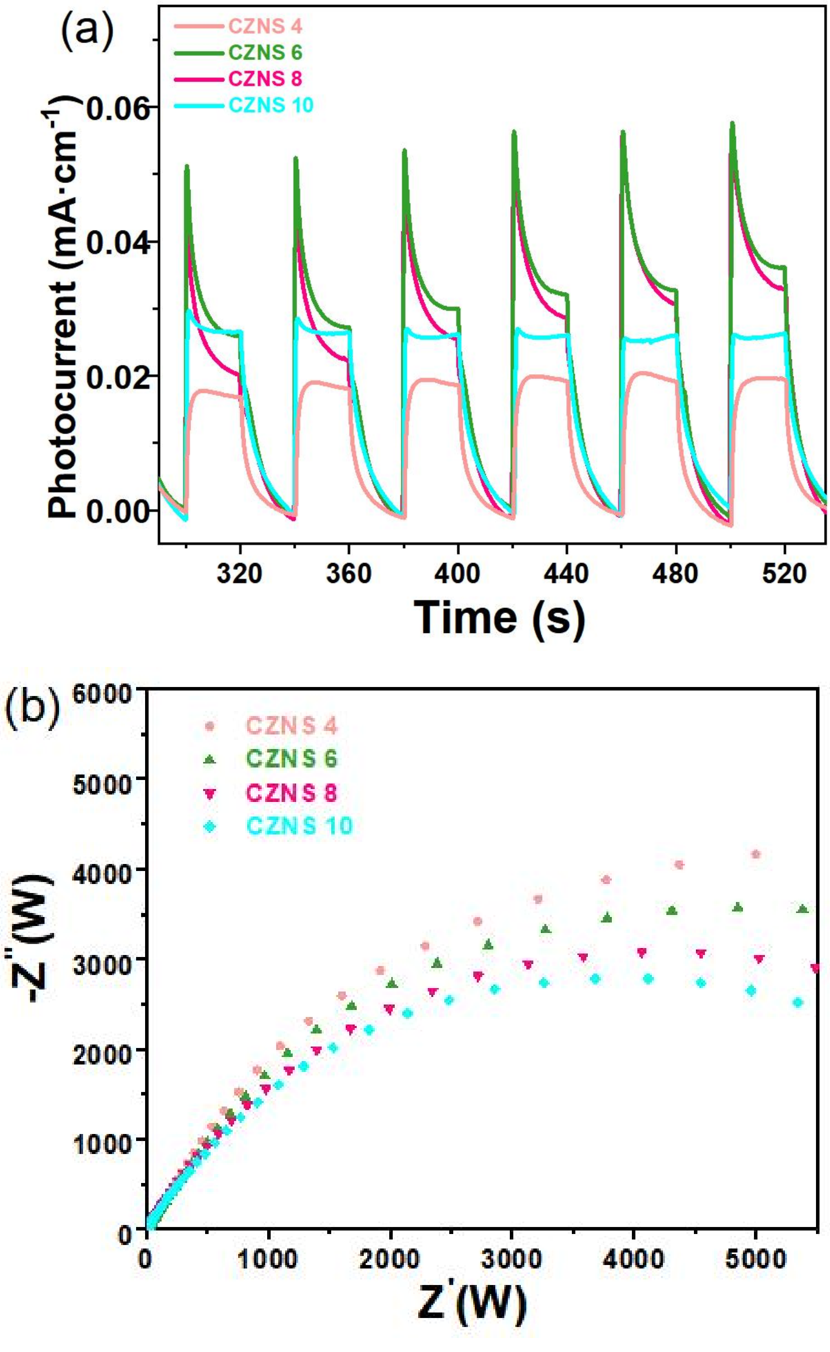

Figure S7. The photo-current curves(a) and Electrochemical Impedence Spectroscopy (EIS) (b) of samples with different NiS additions.

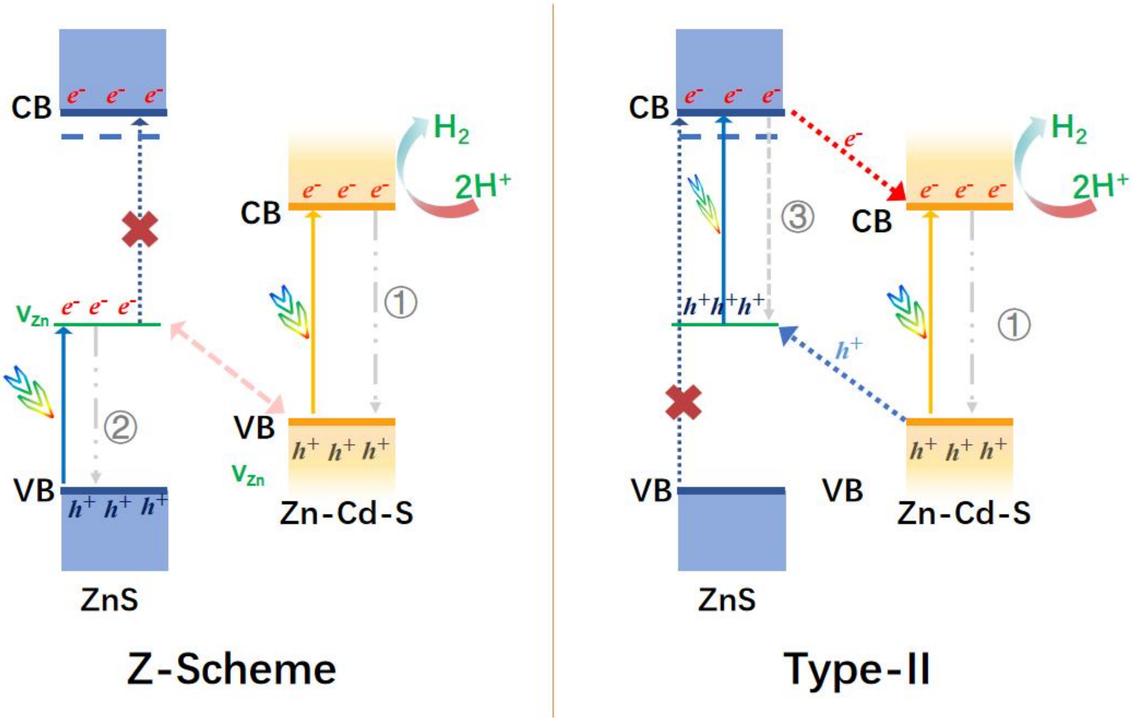

Figure S8. The band structure and charge transfer mechanism of sample CZS under visble light (> 420 nm): (a) Z-Scheme; (b) type-II.

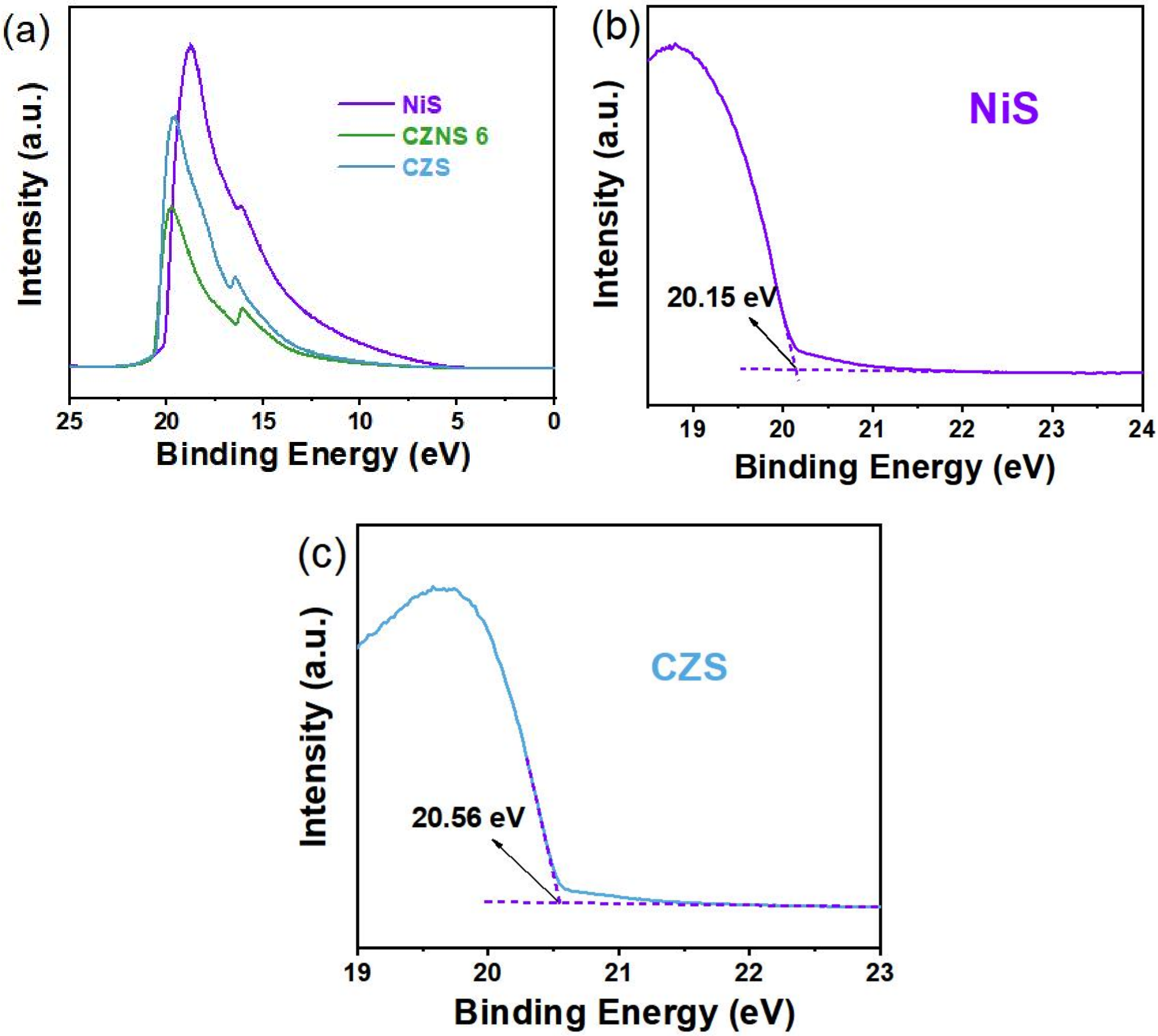

Figure S9. The UPS sepctra of NiS, CZS and CZNS 6 (a), and the corresponding photoemission cutoff spectra of NiS (b) and CZS (c) .

Table S1. The time-resolved photoluminescence of sample CZN and CZNS 6.

Samples	**CZS**	**CZNS 6**
A_1	**1.35**	**1.75**
$\tau_1{}^a$ (ns)	**2.45**	**0.38**
A_2	**1.28**	**0.38**
$\tau_2{}^b$ (ns)	**9.46**	**49.05**
A_3	**0.31**	
$\tau_3{}^c$ (ns)	**85.66**	
Ave τ (ns)	**57.1**	**47.4**

Table S2. Recent heterojunction photocatalytic systems for H_2 evolution based on the Zn-Cd-S nanomaterials.

Catalyst	Weight (mg)	Sacrificial agent	Light source	H_2 evolution ($mmol \cdot g^{-1} \cdot h^{-1}$)	Reference
$Cd_{0.5}Zn_{0.5}S$ nanorod	100	Na_2S and Na_2SO_3	300 W Xe lamp	2.58	1
ZnCdS/ZnCdS/ZnS	20	Na_2S and Na_2SO_3	300 W Xe lamp	0.2339	2
Pt-modified ZnCdS	25	Na_2S and Na_2SO_3	300 W Xe lamp	1.045	3
NiO/ZnCdS	40	Na_2S and Na_2SO_3	300 W Xe lamp	5.042	4
Pt-modified ZnCdS	10	Na_2S and Na_2SO_3	300 W Xe lamp	8.87	5
$Zn_{(1-x)}Cd_xS$	20	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	7.71	6
$ZnS/g\text{-}C_3N_4$	50	Na_2S and Na_2SO_3	300 W Xe lamp	0.713	7
ZnCdS QDs	50	Na_2S and Na_2SO_3	300 W Xe lamp	11.32	8
ZnO/CdS	30	Na_2S and Na_2SO_3	300 W Xe lamp	7.669	9
$Zn_{1-x}Cd_xS$/CdS	10	Na_2S and Na_2SO_3	300 W Xe lamp	2.7	10
$ZnS/g\text{-}C_3N_4$	30	Na_2S and Na_2SO_3	300 W Xe lamp	0.654	11
This work	30	Na_2S and Na_2SO_3	300 W Xe lamp (>420 nm)	16.68	/

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