Electronic Supplementary Information for:

An efficient hydrogen evolution catalyst composed of palladium phosphorous sulphide ($PdP_{\sim0.33}S_{\sim1.67}$) and twin nanocrystal $Zn_{0.5}Cd_{0.5}S$ solid solution with both homo- and hetero-junctions

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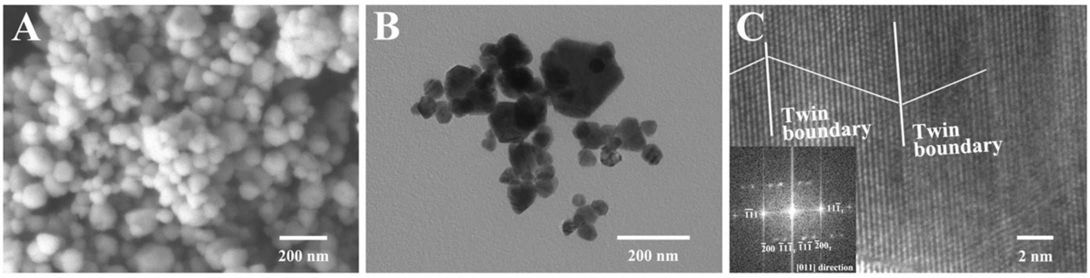

Fig. S1 SEM (A), TEM (B), HRTEM (C) and SAED (inset of fig. S1 C) images of twinned $Zn_{0.5}Cd_{0.5}S$ solid solution.

Table S1. The experimental data of inductively coupled plasma atomic emission spectrometry (ICP-AES) of twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$.

Sample	Weight percentage (wt %)				Atomic percentage (at %)			
	Zn	Cd	S	Pd	Zn	Cd	S	Pd
$Zn_{0.5}Cd_{0.5}S$	27.25	46.71	26.04		25.31	25.25	49.44	
$Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$	26.45	45.38	26.32	1.68	24.48	24.44	49.79	0.99

Table S2. The experimental data of electron dispersive spectrum (EDS) of twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$.

Sample	Weight percentage (wt %)					Atomic percentage (at %)				
	Zn	Cd	S	Pd	P	Zn	Cd	S	Pd	P
$Zn_{0.5}Cd_{0.5}S$	27.39	46.52	26.09			25.41	25.11	49.47		
$Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$	26.60	45.20	26.39	1.65	0.16	24.59	24.31	49.86	0.94	0.31

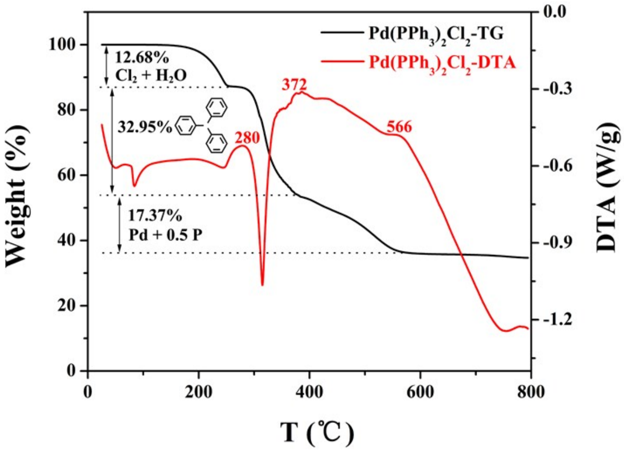

Fig. S2 TG and DTA curves of bis(triphenylphosphine) palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) in argon.

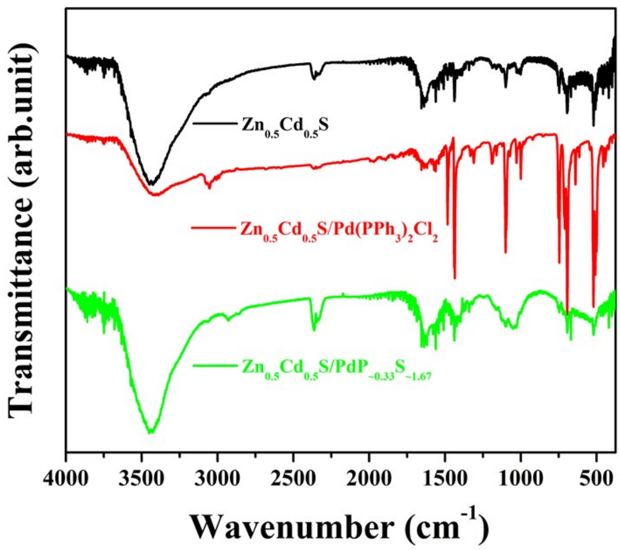

Fig. S3 IR spectra of $Zn_{0.5}Cd_{0.5}S$ (black), $Zn_{0.5}Cd_{0.5}S/Pd(PPh_3)_2Cl_2$ (red), $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$ (green).

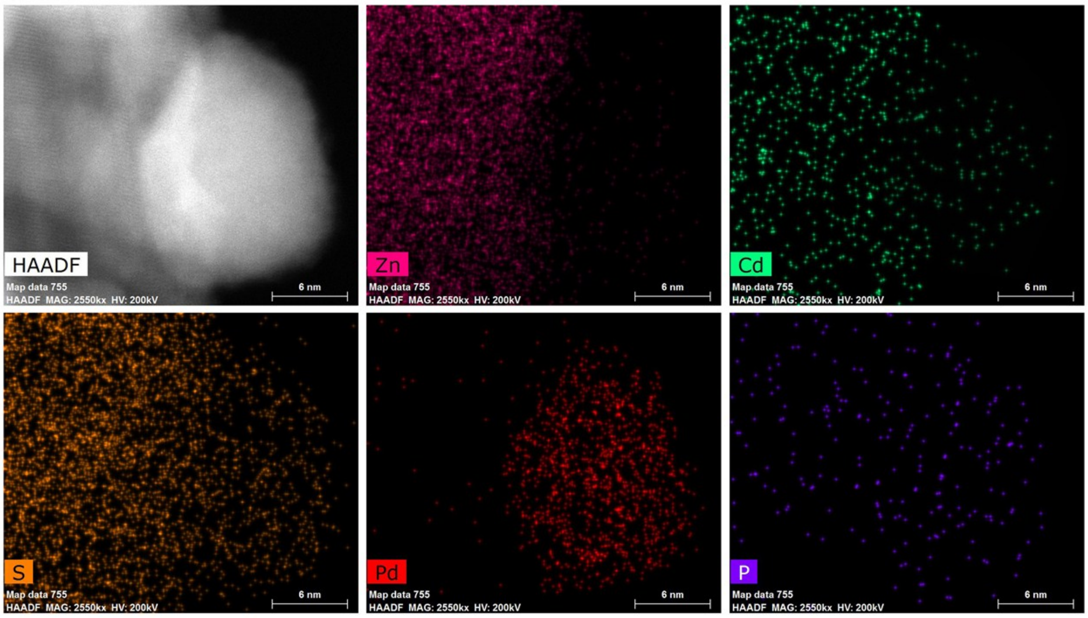

Fig. S4 STEM images of $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$.

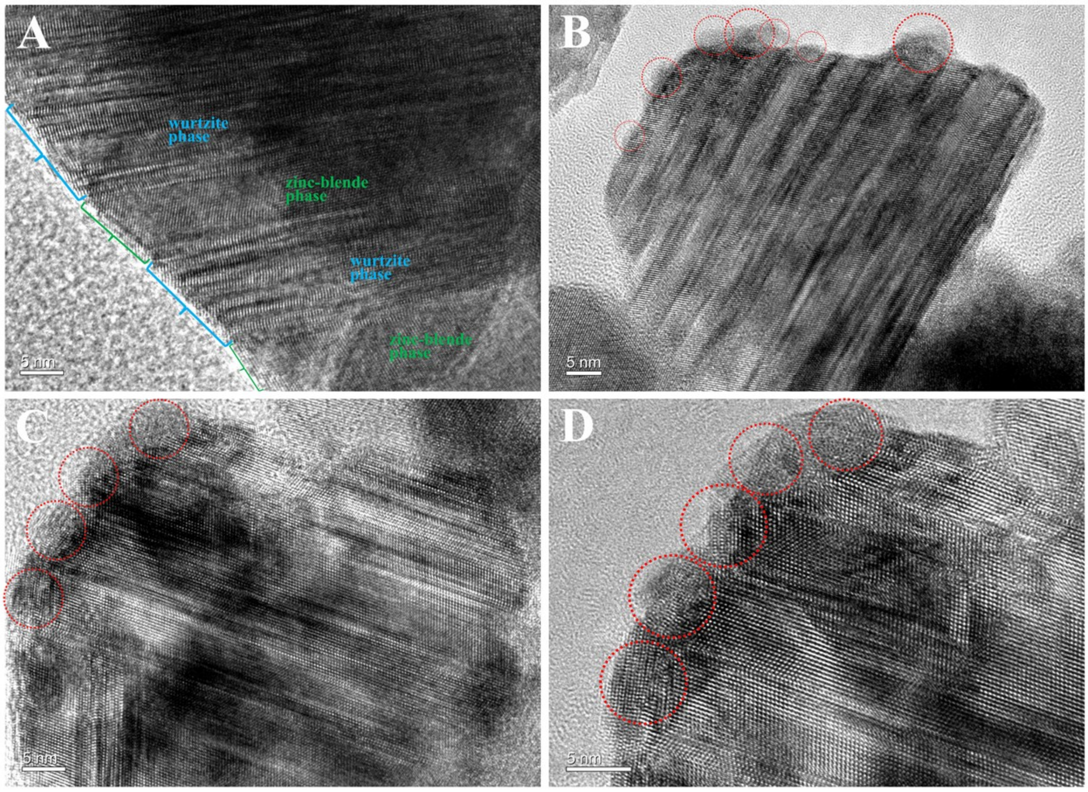

Fig. S5 HRTEM images of twinned $Zn_{0.5}Cd_{0.5}S$ (A) and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$ (B, C, D) photocatalysts. The $PdP_{\sim0.33}S_{\sim1.67}$ particles on the surface of twinned $Zn_{0.5}Cd_{0.5}S$ solid solution have been marked by red rings on B, C, and D.

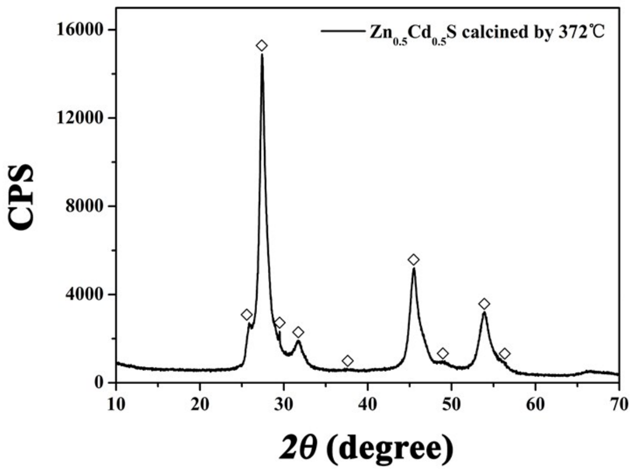

Fig. S6 The X-ray diffraction patterns of twinned $Zn_{0.5}Cd_{0.5}S$ calcined by 372 °C.

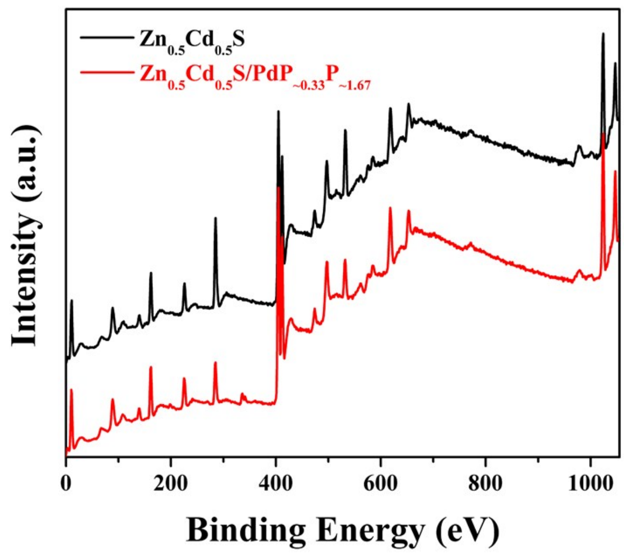

Fig. S7 The overall survey XPS spectrum of twinned $Zn_{0.5}Cd_{0.5}S$ (black) and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ (red) photocatalysts.

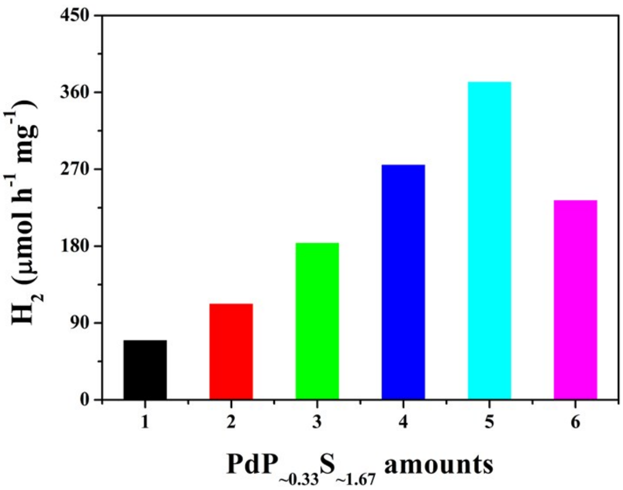

Fig. S8 The rate of H_2 evolution of $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ samples (1~6) loaded with various amounts of $PdP_{\sim 0.33}S_{\sim 1.67}$ cocatalyst.

Table S3. The rate of H_2 evolution (μmol h^{-1} mg^{-1}) under visible light ($\lambda > 420$ nm) irradiation after 3 hours using 1 mg photocatalyst for twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ in different sacrificial reagents.

	Lactic acid	Ascorbic acid	TEOA	Na_2S/Na_2SO_3
$Zn_{0.5}Cd_{0.5}S$	8.05	5.55	4.34	46.60
$Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$	197.93	372.12	91.81	246.04

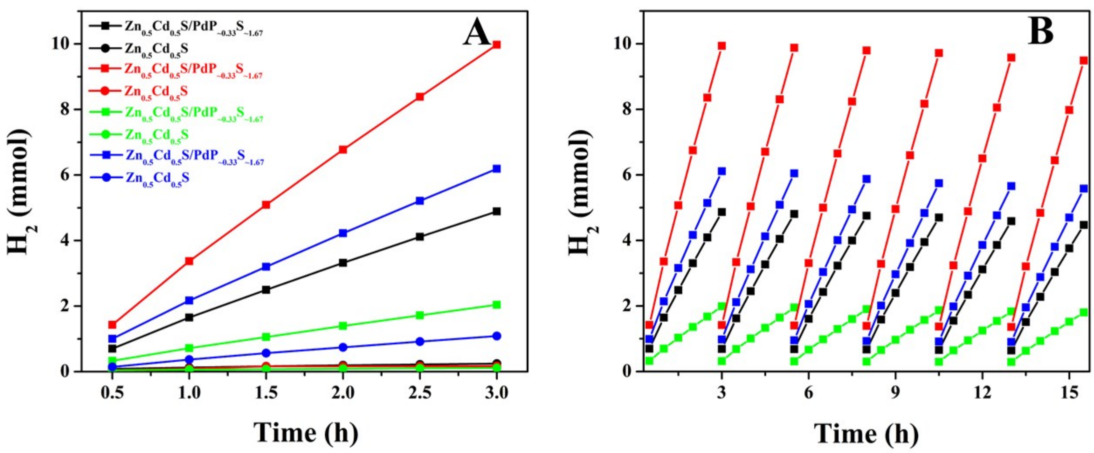

Fig. S9 The rate of H_2 evolution (A) and stability (B) test of twinned $Zn_{0.5}Cd_{0.5}S$ (solid circle) and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ (solid square) photocatalysts under visible light ($\lambda > 420$ nm) irradiation after 3 hours using **10 mg** photocatalyst in 20% lactic acid (pH = 1.64) (black), 0.75M ascorbic acid (pH = 2.39) (red), 20% TEOA (pH = 12.59) (green), 0.7M Na_2S and 0.5M Na_2SO_3 (pH = 13.86) (blue) sacrificial reagents aqueous solution.

Table S4. The rate of H_2 evolution (μmol h^{-1} mg^{-1}) for twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$ under visible light (λ > 420 nm) irradiation after 3 hours using **10 mg** photocatalyst in different sacrificial reagents.

	Lactic acid	Ascorbic acid	TEOA	Na_2S/Na_2SO_3
$Zn_{0.5}Cd_{0.5}S$	6.44	4.81	3.01	37.29
$Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$	166.59	339.80	68.05	206.26

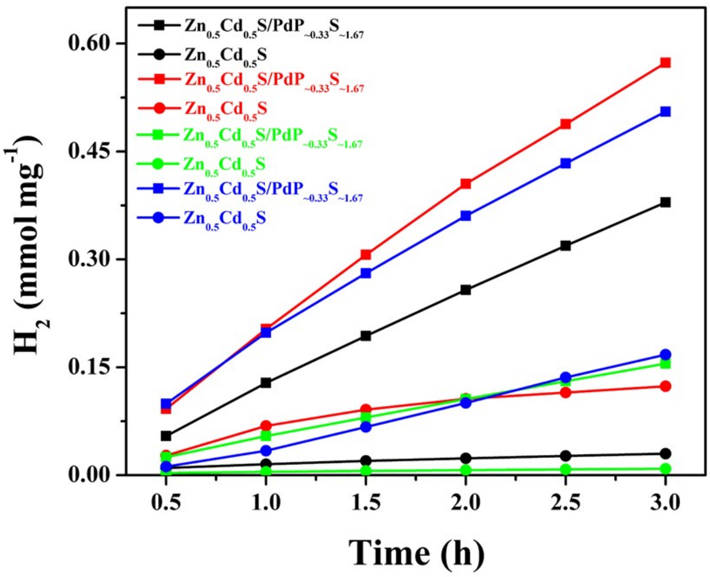

Fig. S10 Time courses of H_2 evolution of twinned $Zn_{0.5}Cd_{0.5}S$ (solid circle) and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim0.33}S_{\sim1.67}$ (solid square) photocatalysts under monochromatic 420 nm light irradiation after 3 hours using 1.0 mg photocatalyst in 20% lactic acid (pH = 1.64) (black), 0.75M ascorbic acid (pH = 2.39) (red), 20% TEOA (pH = 12.59) (green), 0.7M Na_2S and 0.5M Na_2SO_3 (pH = 13.86) (blue) sacrificial reagents aqueous solution.

Table S5. The apparent quantum yields (QEs) under monochromatic 420 nm light irradiation after 3 hours using 1 mg photocatalyst for twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ in different sacrificial reagents.

	Lactic acid	Ascorbic acid	TEOA	Na_2S/Na_2SO_3
$Zn_{0.5}Cd_{0.5}S$	0.80 %	3.73 %	0.24 %	6.56 %
$Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$	13.26 %	19.70 %	5.31 %	16.52 %

Table S6. The turnover number (TON) and turnover frequency (TOF) for $PdS_{\sim 1.67}P_{\sim 0.33}$ in different sacrificial reagents.

	Lactic acid	Ascorbic acid	TEOA	Na_2S/Na_2SO_3
TON	62025	114557	25399	73418
TOF	1241	2291	508	1468

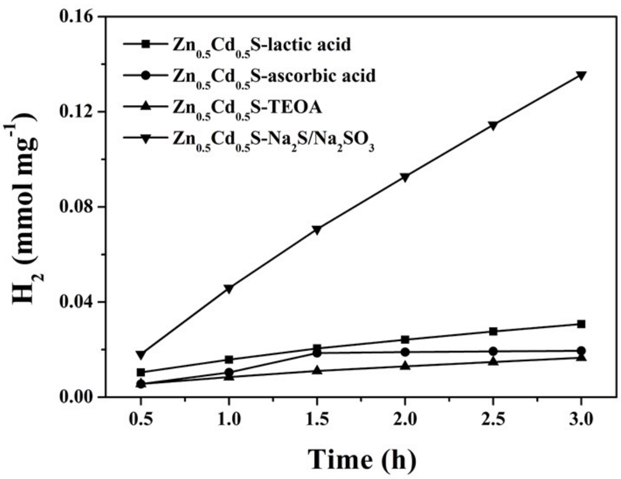

Fig. S11 The rate of H_2 evolution of twinned $Zn_{0.5}Cd_{0.5}S$ photocatalysts in the 20% lactic acid (pH = 1.64) (solid square), 0.75M ascorbic acid (pH = 2.39) (solid circle), 20% TEOA (pH = 12.59) (solid up triangle), 0.7M Na_2S and 0.5M Na_2SO_3 (pH = 13.86) (solid down triangle) sacrificial reagents aqueous solution.

Table S7. The experimental data of Brunauer-Emmett-Teller (BET) and Pole diameter of twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$.

	$Zn_{0.5}Cd_{0.5}S$	$Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$
BET (m^2 g^{-1})	20.74	16.52
Pole diameter (nm)	233.89	233.89

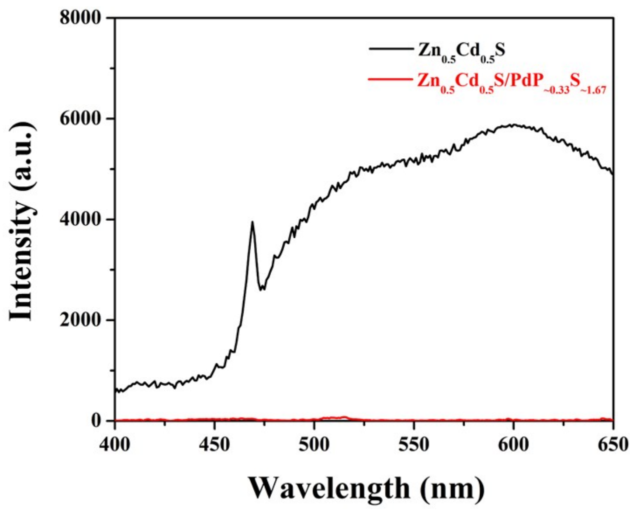

Fig. S12. Photoluminescence spectra of twinned $Zn_{0.5}Cd_{0.5}S$ (black) and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$ (red) under 350 nm excitation wavelength.

Table S8. The fluorescence quantum yield (Φ_f) of twinned $Zn_{0.5}Cd_{0.5}S$ and $Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$.

	$Zn_{0.5}Cd_{0.5}S$	$Zn_{0.5}Cd_{0.5}S/PdP_{\sim 0.33}S_{\sim 1.67}$
Φ_f (%)	5.7	0