Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Twins in $Cd_{1-x}Zn_xS$ Solid Solution: Highly Efficient Photocatalyst for Hydrogen Generation from Water

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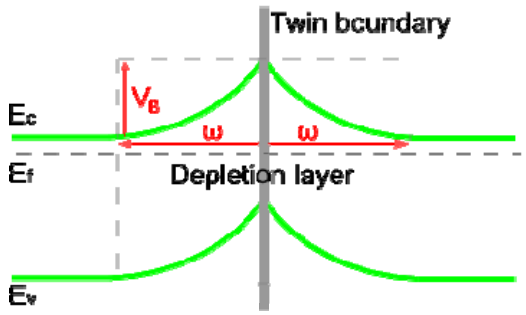
Estimation of depletion layer width of twin boundary in $Cd_{0.5}Zn_{0.5}S$-PH photocatalysts

Scheme S1. Twin boundary potential and depletion layer in photocatalysts.

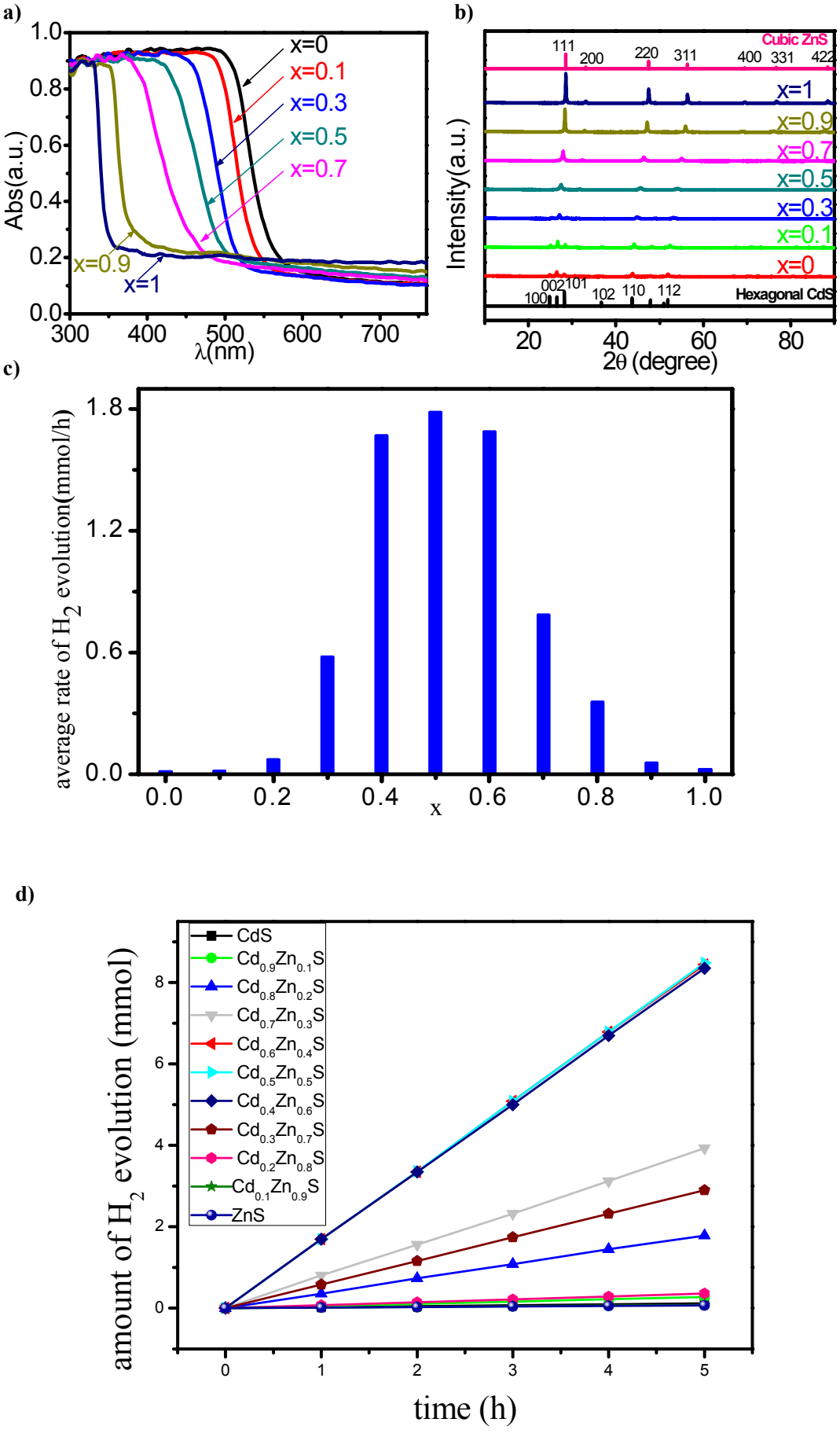


$$\frac{d^2V}{dx^2} = -\frac{N_d e}{\varepsilon\varepsilon_0} \quad \text{for } 0 \le x \le \omega \qquad (3)$$

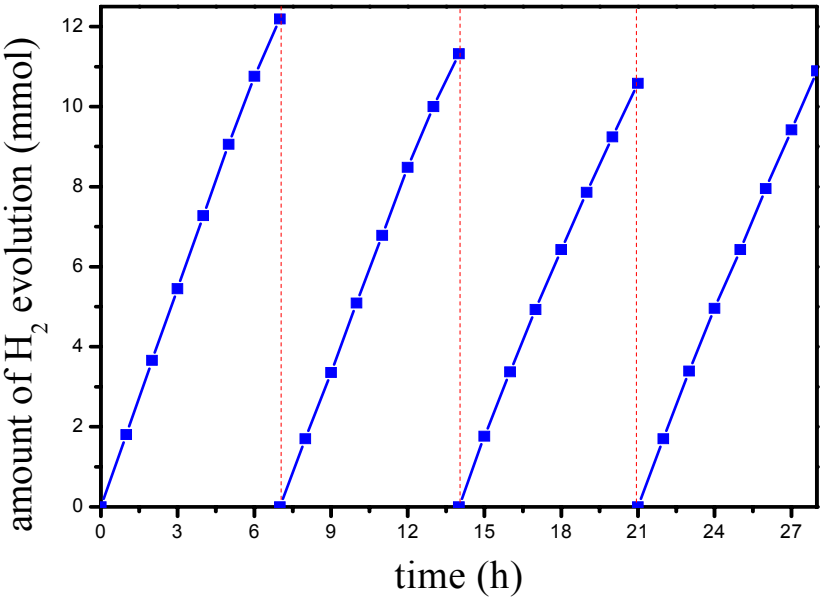
$$\omega = \sqrt{\frac{2\varepsilon\varepsilon_0 V_B}{eN_d}} \qquad (4)$$

The estimation the depletion layer width (2ω) is based on solving One Dimensional Poisson Equation (formulation (3)), where ε is the dielectric constant of the semiconductor and ε_0 is the permittivity of free space. N_d, is the excess charge desity at the depletion layer in the crystal. V_B is the potential at the boundry (x = 0), and at the edge of the depletion layer (x = w), the potential V = 0. Formulation (4) is the result [1]. The distribution of the boundary potential is schematically shown in Scheme S1.

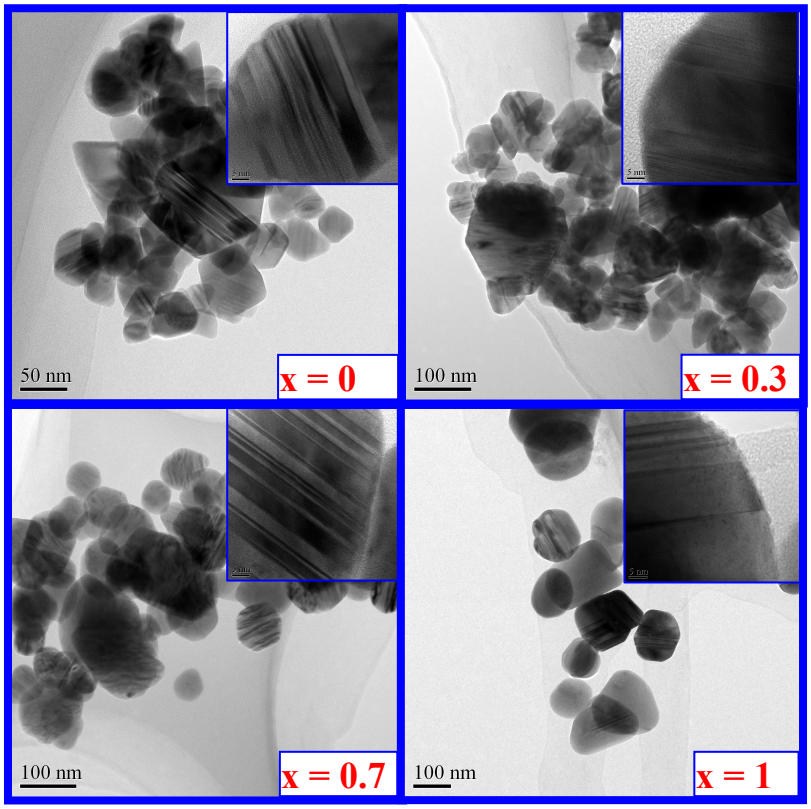
Considering the crystal size of $Cd_{0.5}Zn_{0.5}S$-PH photocatalysts (assumed the volum of crystal of 100 nm × 100 nm × 100 nm), the average number of twin boundary in this crystal (about 10 ~ 20, here denoted as 10), and the captured charge density in (111) twin boundary (in the order of magnitude of 10^{15} m^{-2}) [2] , we estimated the $N_d \approx 10^{23}$ m^{-3}. With $V_B \approx 0.05$ V for (111) twin boundary determined by other researchers [2, 3], ε ≈ 8.6 (ε (CdS) = 8.9, ε (ZnS) = 8.3), $\varepsilon_0 = 8.85 \times 10^{-12}$ F m^{-1}, $e = 1.6 \times 10^{-19}$ C, we obtain ω ≈ 22 nm. Therefore, the half width of depletion layer is a little larger than the distance of the coherent twin boundaries, resulting in the complete separation of photogenerated electrons and holes.


a)
Abs(a.u.)
λ(nm)
x=0
x=0.1
x=0.3
x=0.5
x=0.7
x=0.9
x=1
b)
Intensity(a.u.)
2θ (degree)
Cubic ZnS
111
200
220
311
400
331
422
x=1
x=0.9
x=0.7
x=0.5
x=0.3
x=0.1
x=0
100
002
101
102
110
112
Hexagonal CdS
c)
average rate of H2 evolution(mmol/h)
x
d)
amount of H2 evolution (mmol)
time (h)
CdS
Cd0.9Zn0.1S
Cd0.8Zn0.2S
Cd0.7Zn0.3S
Cd0.6Zn0.4S
Cd0.5Zn0.5S
Cd0.4Zn0.6S
Cd0.3Zn0.7S
Cd0.2Zn0.8S
Cd0.1Zn0.9S
ZnS

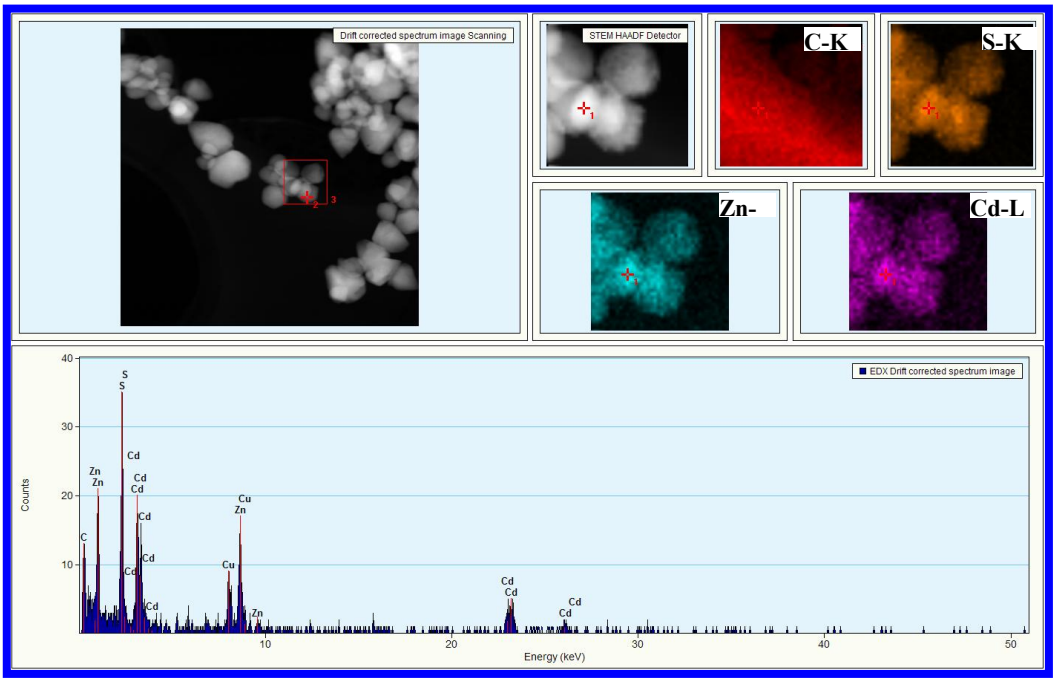
e)



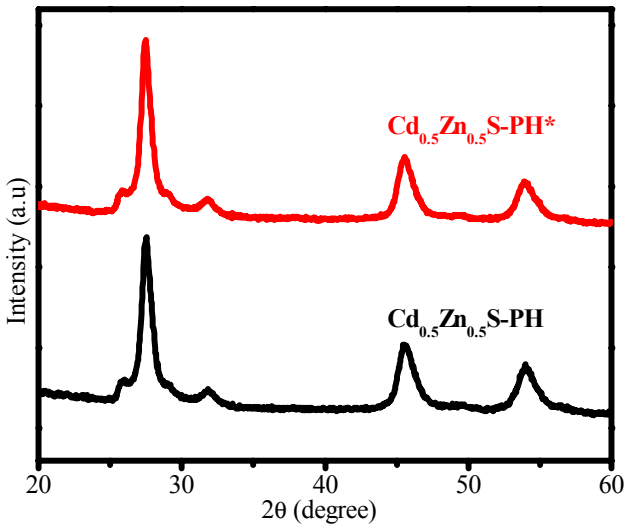
f)



g)


Drift corrected spectrum image Scanning
STEM HAADF Detector
C-K
S-K
Zn-
Cd-L
EDX Drift corrected spectrum image
Counts
Energy (keV)

h)


Cd0.5Zn0.5S-PH*
Cd0.5Zn0.5S-PH
Intensity (a.u)
2θ (degree)

i)

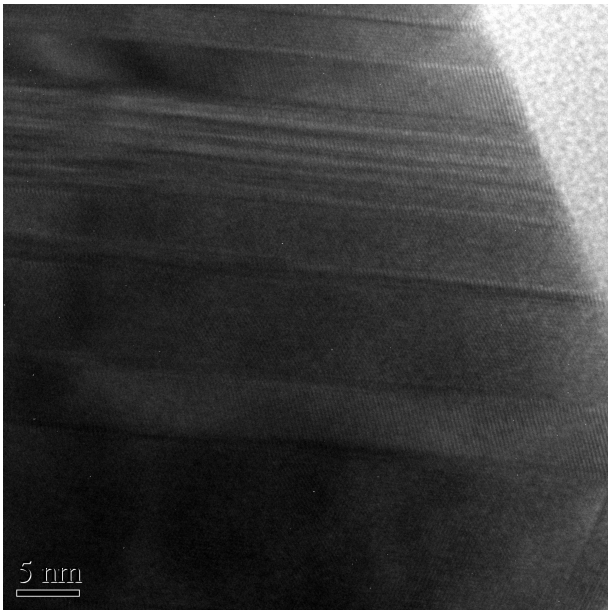


Figure S1 Characterizations of $Cd_{1-x}Zn_xS$-PH solid solutions. a, UV-Vis absorption spectra $Cd_{1-x}Zn_xS$-PH solid solutions which indicated the formation of the solid solutions of CdS and ZnS. **b,** XRD patterns of $Cd_{1-x}Zn_xS$-PH solid solution shows a transformed from hexagonal CdS to cubic ZnS. **c,** the rate of H_2 evolution over $Cd_{1-x}Zn_xS$ solid solution [a], showing that $Cd_{0.5}Zn_{0.5}S$-PH has the highest photocatalytic activity, which is a result of the balance of light absorption and high conduction band level. **d** and **e**, Time course Photocatalytic hydrogen production from an aqueous Na_2S (0.35 M) and Na_2SO_3 (0.25 M) solution under visible light from a PLS-SXE300/300UV Xe lamp with a 430 nm cutoff filter over $Cd_{1-x}Zn_xS$ solid solutions prepared by precipitation-hydrothermal method. 5 hours tests to get a primary photocatalytic activity of these solid solutions. More than 20 hours test over $Cd_{0.5}Zn_{0.5}S$-PH photocatalyst to investigate its photocatalytic stability. As shown here, the photocatalyst is still active enough for hydrogen production over 20 hours. We choose to add the Na_2S sacrificial electron donors every 7 hours due to the great consumption of sacrificial reagents. The amount of Na_2S added to the initially reacting solution was equal to the molar amount of H_2 evolution according to the photochemical reaction equations which were firstly and systematically investigated by Reber [4, 5, 6]. **f,** TEM images of $Cd_{1-x}Zn_xS$-PH solid solution show the nano-twin-modified $Cd_{1-x}Zn_xS$ solid solution. As we discussed in the article, coherent twin boundaries greatly decrease the recombination probability of free carries inside the crystal, however, the separation of them on the surface is still duo the high conduction band levels (without loading noble metal), which provide free election with more activity. Thus, the photocatalytic activity of CdS-PH and $Cd_{0.9}Zn_{0.1}S$-PH is not very high. The absorption of photons from visible light is another important factor. Therefore, the photocatalytic activity of $Cd_{0.2}Zn_{0.8}S$-PH, $Cd_{0.1}Zn_{0.9}S$-PH and ZnS is not high, too. The detailed discussion was given by Domen [7]. **g,** elemental mapping of C, S, Zn and Cd for ($Cd_{0.5}Zn_{0.5}S$-PH) by the energy-dispersive X-ray spectrometer (EDX) reveals that the distribution of all the ions is homogeneous. **h** and **i,** XRD patterns of $Cd_{1-x}Zn_xS$-PH solid solution before and after photocatalytic reaction, and HRTEM of $Cd_{1-x}Zn_xS$-PH after a 20 h photocatalytic reaction, confirms the structural stability of the nano twins.

[a] Catalyst: 0.1 g, 180 mL aqueous solution containing 0.35 M Na_2S and 0.25M Na_2SO_3, side irradiation Pyrex cell, PLS-SXE300 /300UV Xe lamp.

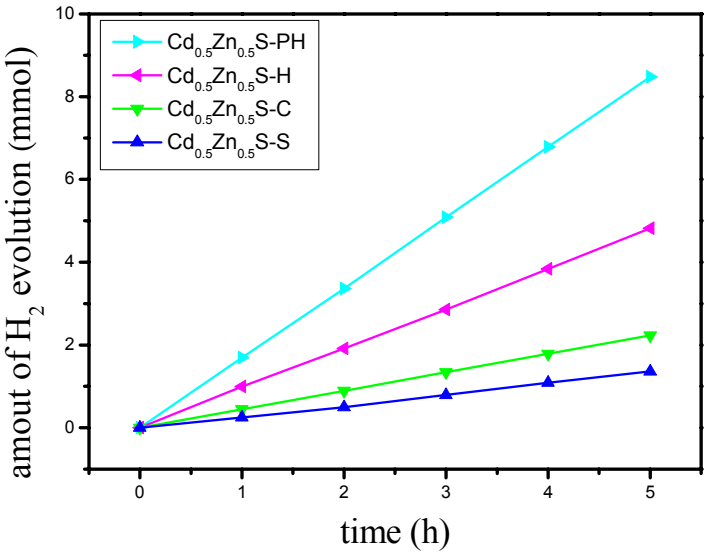
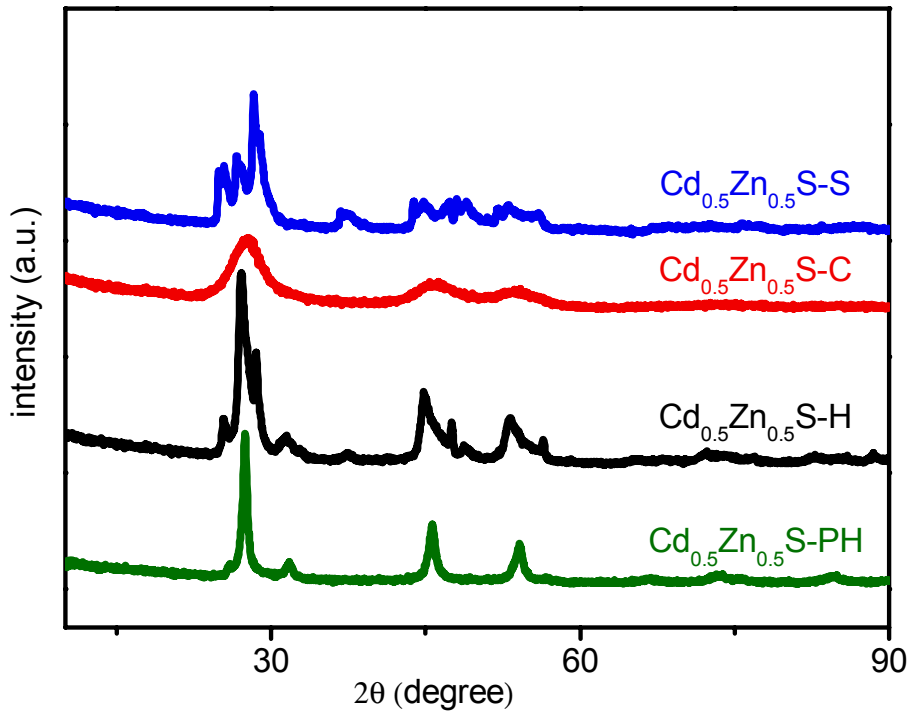


Figure S2. Photocatalytic hydrogen production from an aqueous Na_2S (0.35 M) and Na_2SO_3 (0.25 M) solution under visible light from a PLS-SXE300/300UV Xe lamp with a 430 nm over $Cd_{0.5}Zn_{0.5}S$ photocatalysts prepared by various methods.

a)



b)

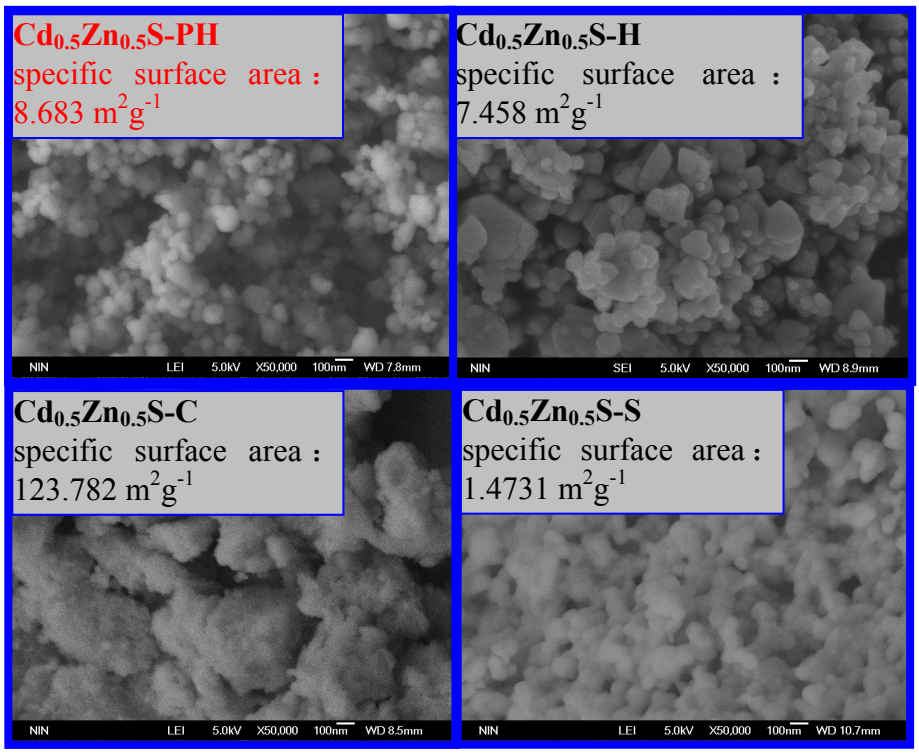
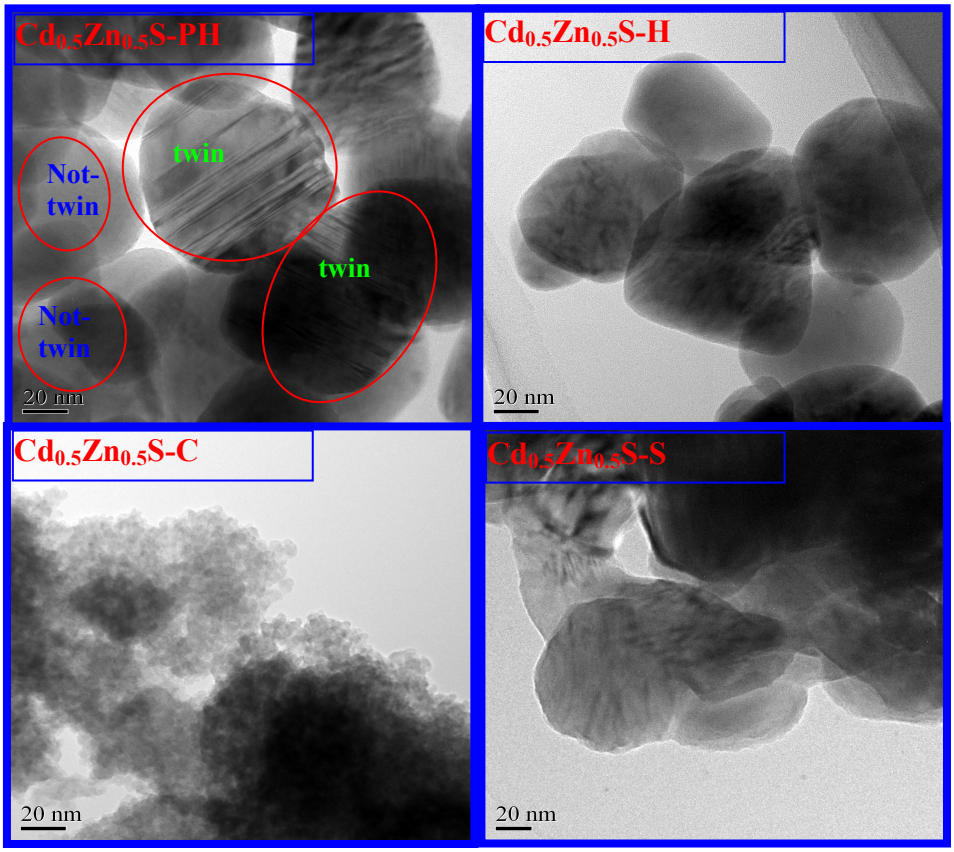


Figure S3 Characterizations of variouse $Cd_{0.5}Zn_{0.5}S$ photocatalysts. **a,** the XRD patterns of the various $Cd_{0.5}Zn_{0.5}S$ photocatalysts shows both hexagonal phase and cubic phase can be obtained by different preparing methods, and also indicate that crystal phase was not the key factor for the extremely high photocatalytic activity of $Cd_{0.5}Zn_{0.5}S$-PH. **b,** SEM images with the BET specific surface areas inset. The crystals are all in nano sizes, but none of them were perfect, even some of them have a good crystallinity. As can be concluded from the pictures, the surface area was not an important factor for water splitting on the present photocatalytic system as usual.

a)



b)

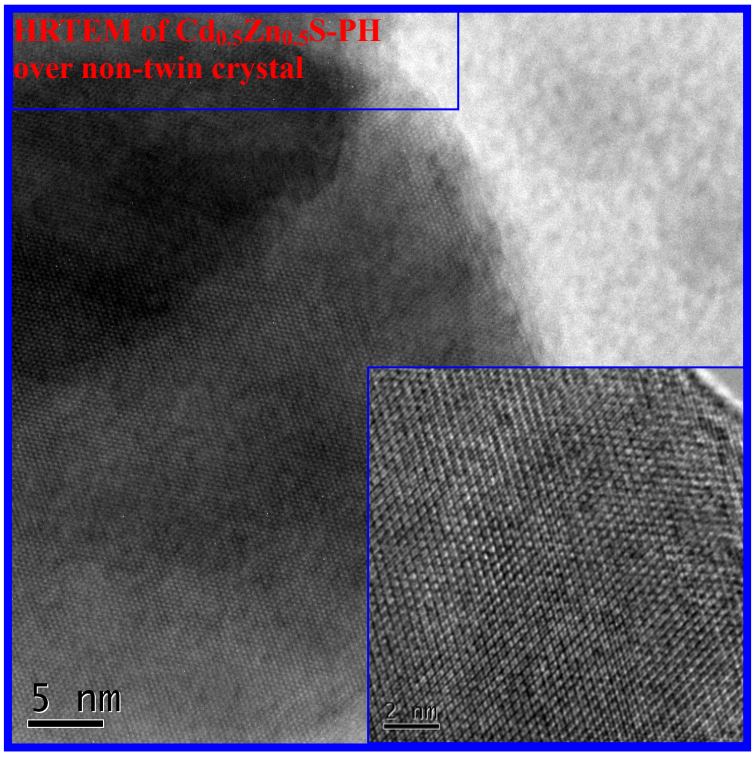


Figure S4 TEM images of the various $Cd_{0.5}Zn_{0.5}S$ photocatalysts. a, the special nano-strips are only found in the $Cd_{0.5}Zn_{0.5}S$-PH photocatalysts. But not all of the crystals (denoted as non-twin crystals) in $Cd_{0.5}Zn_{0.5}S$-PH have this special nano-structure. These nano-strips are proved to be coherent twin boundaries. **b,** HRTEM of $Cd_{0.5}Zn_{0.5}S$-PH over non-twin crystal**.**

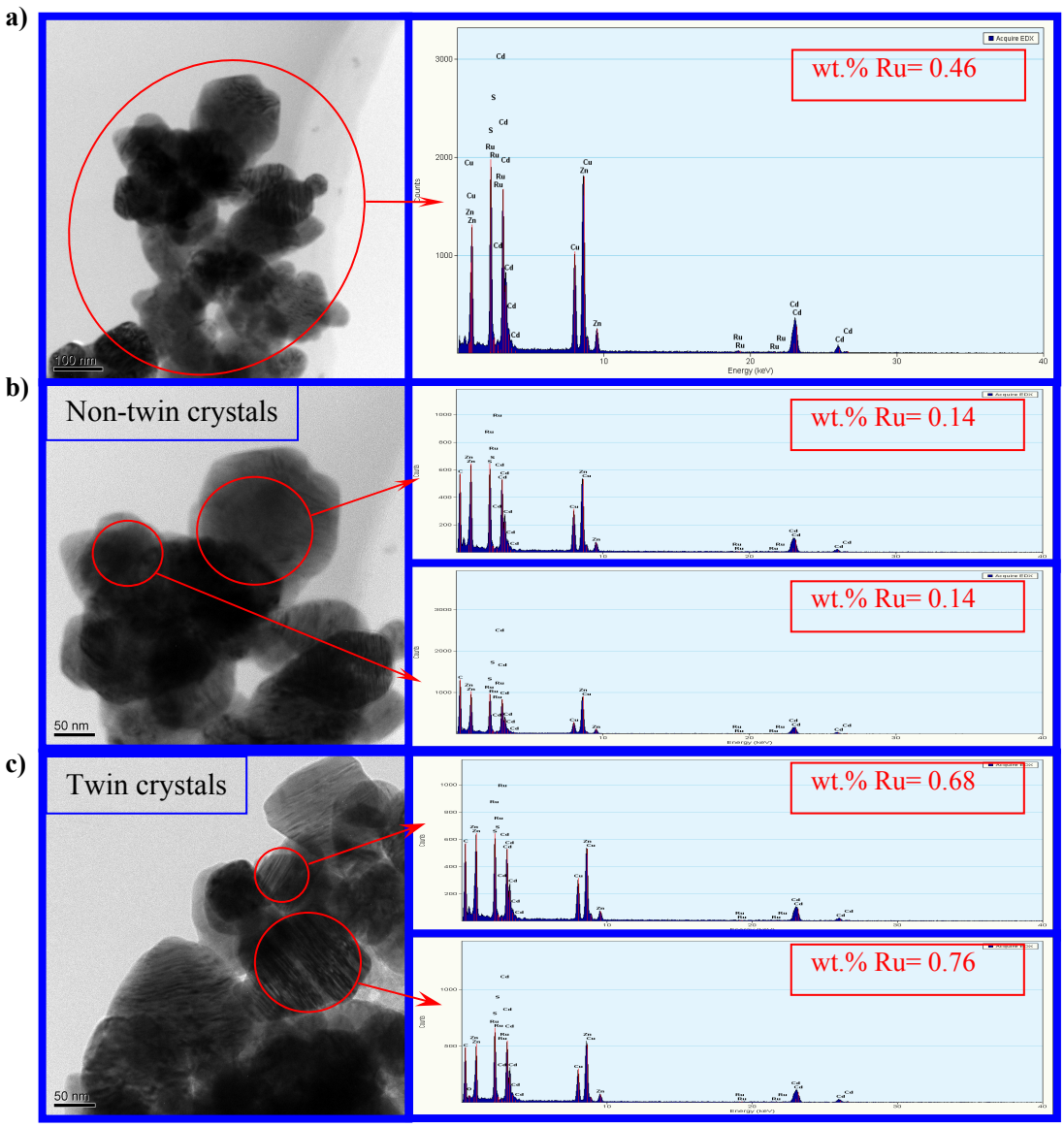


Figure S5 TEM images of Ru (wt. 0.44% in bulk)/$Cd_{0.5}Zn_{0.5}S$-PH and EDX spectra of it at different crystals (twin and non-twin crystals). a, Ru content in a big area was determined to be wt. 0.46%, which was very close to the Ru content in bulk (wt. 0.44%) determined by X-ray fluorescence spectrum (XRF). **b,** Ru contents on non-twin crystals were determined to be about wt. 0.14% and 0.14%. **c,** Ru contents on twin crystals were determined to be about wt. 0.68% and 0.76%. It was considered that Ru would like to be photodeposited at place where more free electrons were generated. Thus, it was concluded that more free electrons were photogenerated from the twin crystals. The contents' difference indicated that photocatalytic activity of twin crystal was about 5 times of that non-twin crystal.

References

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