Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Self-Template Synthesis of CdS/NiS$_x$ Heterostructured Nanohybrids for Efficient Photocatalytic Hydrogen Evolution

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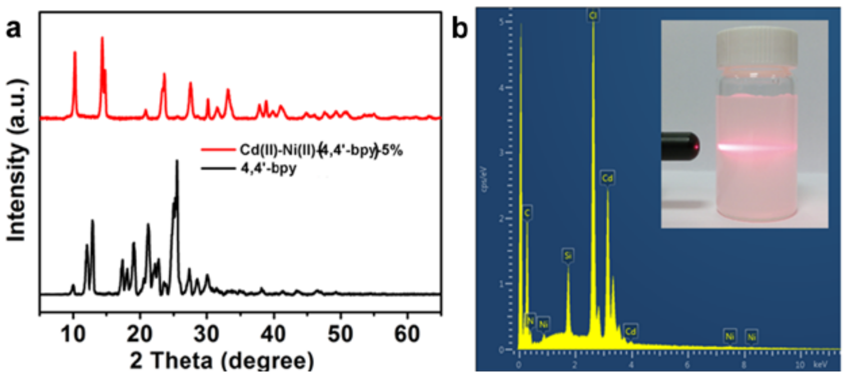

Fig. S1 (a) XRD patterns of 4,4'-bpy and the Cd(II)-Ni(II)-(4,4'-bpy)-5% coordination polymer. (b) EDX spectrum of the Cd(II)-Ni(II)-(4,4'-bpy)-5% coordination polymer. The inset of (b) is the photograph of the dispersion containing Cd(II)-Ni(II)-(4,4'-bpy)-5% coordination polymer. The light beam is incident from the side to demonstrate the Tyndall effect.

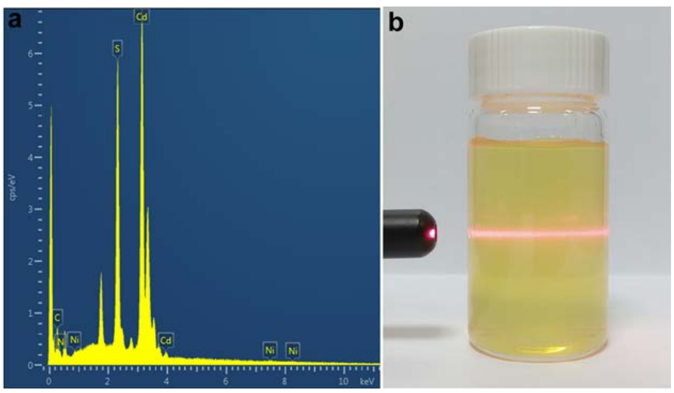

Fig. S2 (a) EDX spectrum of the CdS/NiS$_x$-5% nanohybrid. (b) The photograph of the dispersion containing CdS/NiS$_x$-5% nanohybrid. The light beam is incident from the side to demonstrate the Tyndall effect.

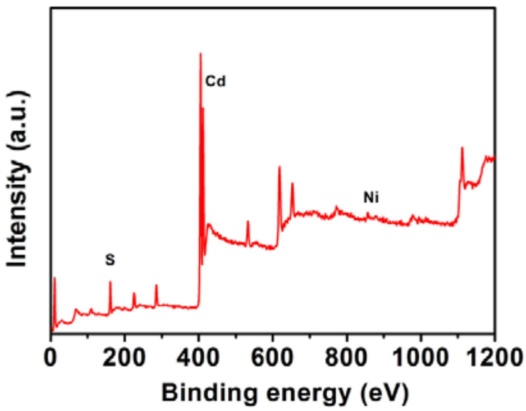

Fig. S3 XPS survey spectrum of the CdS/NiS_x-5% nanohybrid.

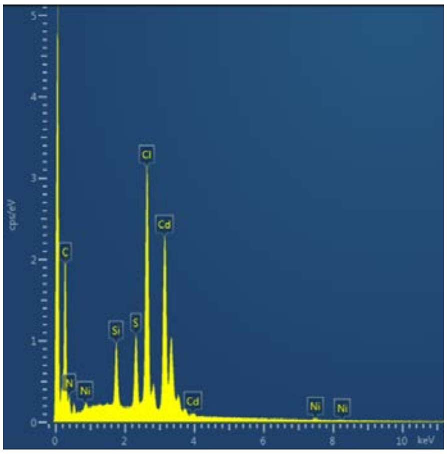

Fig. S4 EDX spectrum of the intermediate collected after 3 min reaction with S^{2-} anions.

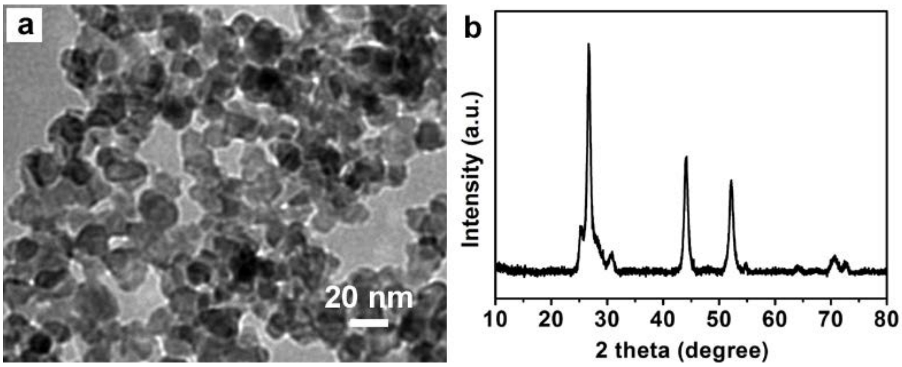

Fig. S5 (a) TEM image and (b) XRD pattern of CdS/NiS_x-5% sample obtained at 160 ºC under hydrothermal condition.

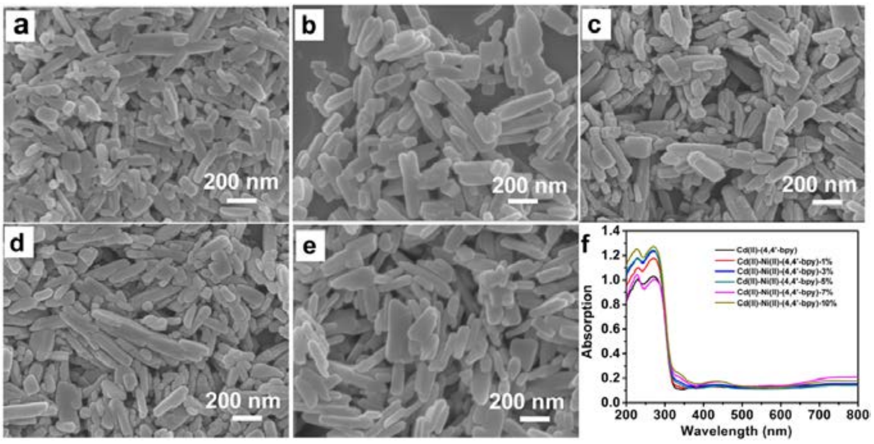

Fig. S6 (a-e) Cd(II)-(4,4'-bpy) and Cd(II)-Ni(II)-(4,4'-bpy) coordination polymers with different Cd/Ni mole ratios: (a) Cd(II)-(4,4'-bpy), (b) Cd(II)-Ni(II)-(4,4'-bpy)-1%, (c) Cd(II)-Ni(II)-(4,4'-bpy)-3%, (d) Cd(II)-Ni(II)-(4,4'-bpy)-7%, (e) Cd(II)-Ni(II)-(4,4'-bpy)-10%. (f) UV-visible absorption spectra of various Cd(II)-Ni(II)-(4,4'-bpy) coordination polymers.

Table S1 Ni content in various Cd(II)-Ni(II)-(4,4'-bpy)coordination polymers.

Samples	Ni content in metal precursors (mol%)	Ni content in coordination polymers (mol%)[a]
Cd(II)-Ni(II)-(4,4'-bpy)-1%	1	0.95
Cd(II)-Ni(II)-(4,4'-bpy)-3%	3	2.64
Cd(II)-Ni(II)-(4,4'-bpy)-5%	5	4.83
Cd(II)-Ni(II)-(4,4'-bpy)-7%	7	6.43
Cd(II)-Ni(II)-(4,4'-bpy)-10%	10	9.35

a The Ni content was obtained by ICP-AES test.

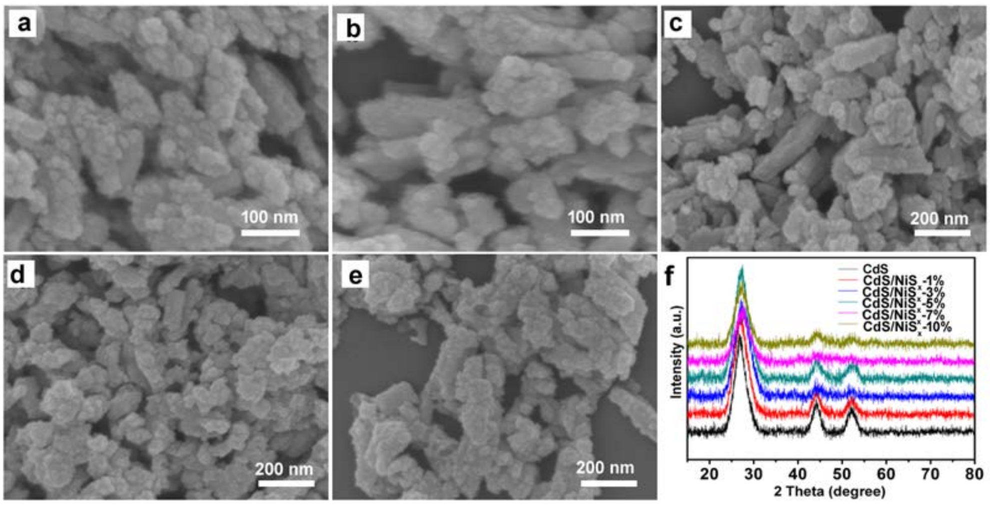

Fig. S7 (a-e) CdS and CdS/NiS_xnanohybrids with different Cd/Ni mole ratios: (a) CdS (b) CdS/NiS_x-1%, (c) CdS/NiS_x-3%, (d) CdS/NiS_x-7%, (e) CdS/NiS_x-10%. (f) XRD patterns of various CdS/NiS_x nanohybrids.

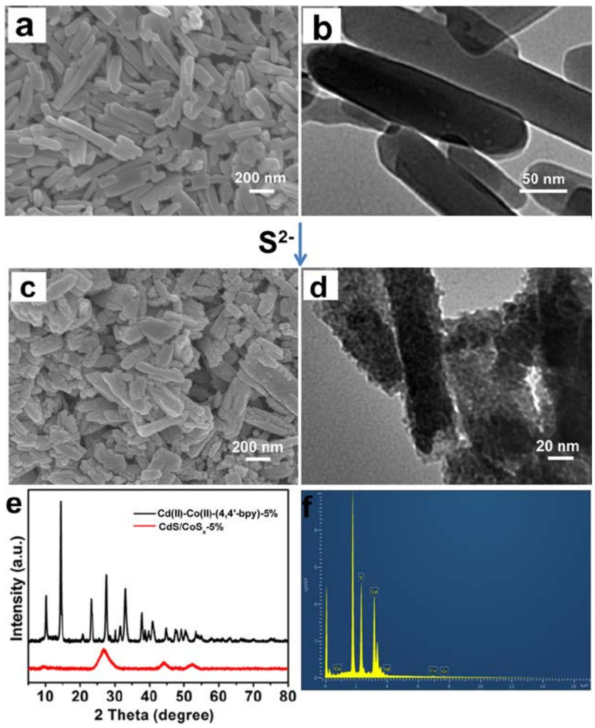

Fig. S8 (a) SEM image and (b) TEM image of the Cd(II)-Co(II)-(4,4'-bpy)-5% coordination polymer. (c) SEM image, (d) TEM image, (e) XRD pattern and (f) EDX spectrum of the CdS/CoS_x-5% nanohybrids.

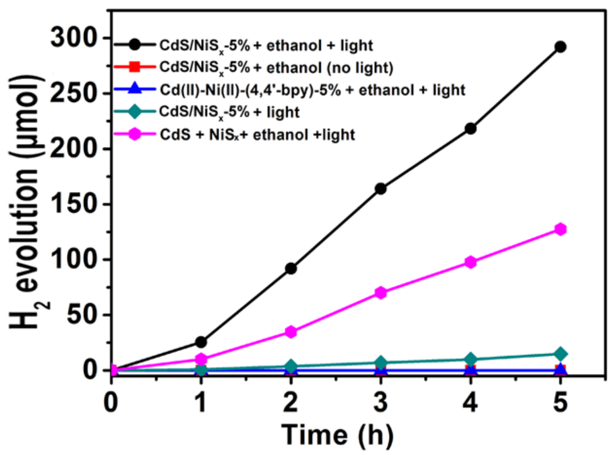

Fig. S9 Time course of photocatalytic H_2 evolution over various photocatalytic reaction conditions. It was found that a small amount of H_2 was detected when no ethanol was added due to the excess Na_2S in the suspension can also act as sacrificial reagent for photocatalytic H_2 evolution. These control experiments indicate that light, the photocatalyst (CdS/NiS_x-5% sample), and the sacrificial agent (ethanol) in this system are all essential for efficient H_2 evolution. The H_2 evolution activity over CdS/NiS_x-5% photocatalyst is also higher than that of mechanically mixed sample containing CdS and NiS_x with a similar mole ratio, which was obtained by adding an appropriate portion of $NiCl_2$ aqueous solution into the Cd(II)-(4,4'-bpy) suspension before adding Na_2S aqueous solution.

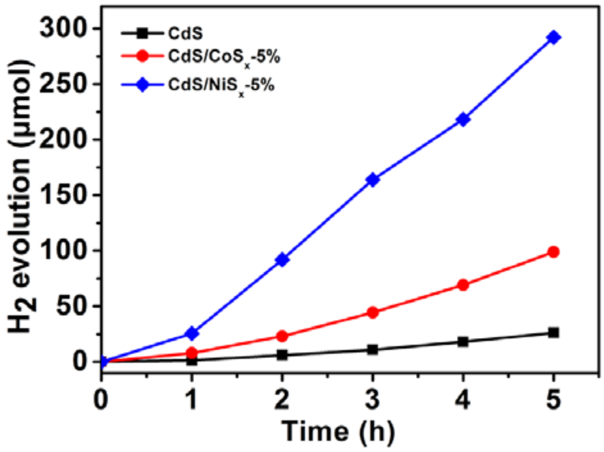

Fig. S10 Time course of photocatalytic H_2 evolution over various photocatalytic reaction conditions. It was found that the photocatalytic activity of CdS/CoS$_x$-5% is higher than that of CdS while lower than that of CdS/NiS$_x$-5% photocatalyst.

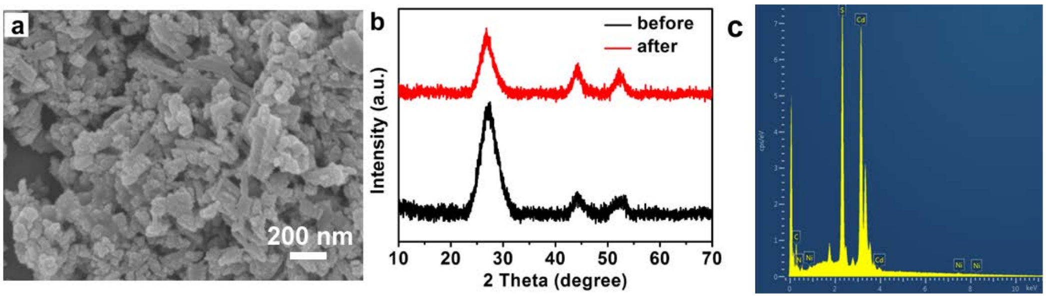

Fig. S11 (a) SEM image, (b) XRD pattern and (c) EDX spectrum of the CdS/NiS$_x$-5% nanohybrid photocatalyst after photocatalytic reaction test.

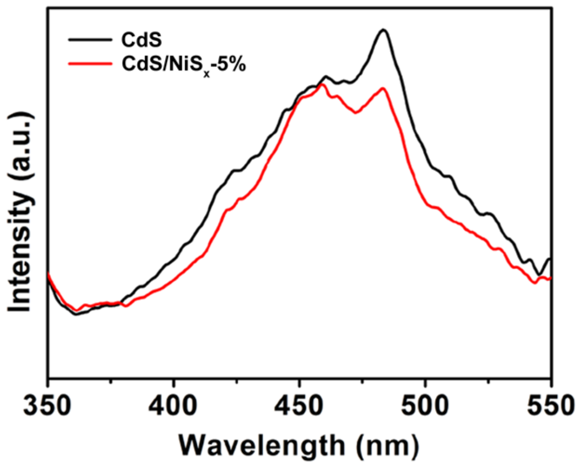

Fig. S12 Photoluminescence spectra of the CdS and CdS/NiS$_x$-5% nanohybrid(excitation wavelength: 330 nm).