Electronic Supplementary Material (ESI) for RSC Advances.
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Supporting Information

1. Materials and measurements

Elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer. Powder X-ray diffraction (XRD) measurements were recorded ranging from 10 to 80° at room temperature on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation. The X-ray photoelectron spectra (XPS) were recorded on a USWHA150 photoelectron spectroscope using monochromatic Al Kα (1486.6 eV) radiation. The ultraviolet-visible diffuse reflectance spectra were obtained using a CARY 500 scan UV-vis-NIR spectrophotometer. Morphology and composition analyses were carried out on a FEI quanta 250 field emission scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDS) analysis accessory. Transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscope with an accelerating voltage of 200 kV. The photoluminescent (PL) properties were measured on an FLSP920 Edinburgh Fluorescence Spectrometer at room temperature. Surface photovoltage spectroscopy (SPS) were carried out on a Lock-in based surface photovoltage measurement system which was constituted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a sample cell and a computer. The hydrogen evolved was analyzed with a gas chromatograph (Agilent 6890GC, thermal conductivity detector, Ar carrier).

2. Synthesis of $Cd_{0.65}Zn_{0.35}S$ nanocrystals

All the reagents were of analytical grade and used without further purification. $Cd_{0.65}Zn_{0.35}S$ was synthesized by the following procedure : 4.567g $CdCl_2 \cdot 2H_2O$ and 1.363g $ZnCl_2$ were dissolved in 100 mL deionized water. $Cd_{0.65}Zn_{0.35}S$ was co-precipitated by slowly adding excess aqueous solution of Na_2S (7.2g) to the mixture of $CdCl_2$ and $ZnCl_2$ aqueous solution. The yellow mixture was stirred for 1 h at room temperature. After centrifugation, the precipitate was washed and dried at 333K overnight. After drying, the solid was annealed at 723 K for 1 h. The x value in $Cd_{1-x}Zn_xS$ was measured by an inductively coupled plasma (ICP) atomic emission

spectrometric analysis, which is ca. 0.35.

3. Synthesis of NiS/$Cd_{0.65}Zn_{0.35}S$ and Pt/$Cd_{0.65}Zn_{0.35}S$ photocatalyst

The as-prepared $Cd_{0.65}Zn_{0.35}S$ photocatalyst (0.2 g) was dispersed in 200 ml aqueous solution containing Na_2S (0.1 M) and Na_2SO_3 (0.1 M). The NiS co-catalyst was loaded onto the surface of $Cd_{0.65}Zn_{0.35}S$ by the direct precipitation method. The specific process was as follows: certain amounts of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in deaired distilled water (3 mL). The solution of $Ni(NO_3)_2$ was dispersed into the above mentioned mixture solution containing $Cd_{0.65}Zn_{0.35}S$ photocatalyst, Na_2S and Na_2SO_3. Then the suspension was stirred under visible light for 1 h. After reaction, the product was separated by centrifugation, washed with deionized water several times, and dried at 333K for 6 h in a vacuum oven. The content of NiS in NiS/$Cd_{0.65}Zn_{0.35}S$ was investigated by inductively coupled plasma atomic emission spectroscopy.

The process of the synthesis of Pt/$Cd_{0.65}Zn_{0.35}S$ is similar to the synthesis of NiS/$Cd_{0.65}Zn_{0.35}S$ except using H_2PtCl_6 instead of $Ni(NO_3)_2$.

4. Synthesis of Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ composites

NiS(1wt%)/$Cd_{0.65}Zn_{0.35}S$ photocatalyst (0.2 g), and different amount of $K_7HNb_6O_{19} \cdot 10H_2O$[1] (0, 0.5, 1, 2 and 3 wt%) were dispersed in 200 mL of aqueous solution containing Na_2S (0.1 M) and Na_2SO_3 (0.1 M). The mixture was stirred for 1 h at room temperature. After centrifugation, the precipitate was washed and dried at 333K for 6 h.

5. Photocatalytic activity measurements

The photocatalysts were dispersed by a magnetic stirrer in an aqueous containing Na_2S and Na_2SO_3 as the sacrificial reagents. The suspension was then thoroughly degassed and irradiated by a 300 W Xe lamp which is equipped with an optical filter (λ > 400 nm) to cut off the light in the ultraviolet region. The temperature of the reaction solution was maintained at 21 ºC by a flow of cooling water.

The apparent quantum yield (QY) was measured under the same reaction conditions except a band-pass interference filter (420 nm). The following equation was used to calculate the QY.

$$\text{QY (\%)} = \frac{\text{The number of evolved hydrogen molecules} \times 2}{\text{The number of incident photons}} \times 100$$

Reference:

1. M. Nyman, T. M. Alam, F. Bonhomme, M. A. Rodriguez, C. S. Frazer and M. E. Welk, *J. Cluster Sci.*, 2006, **17**, 197.

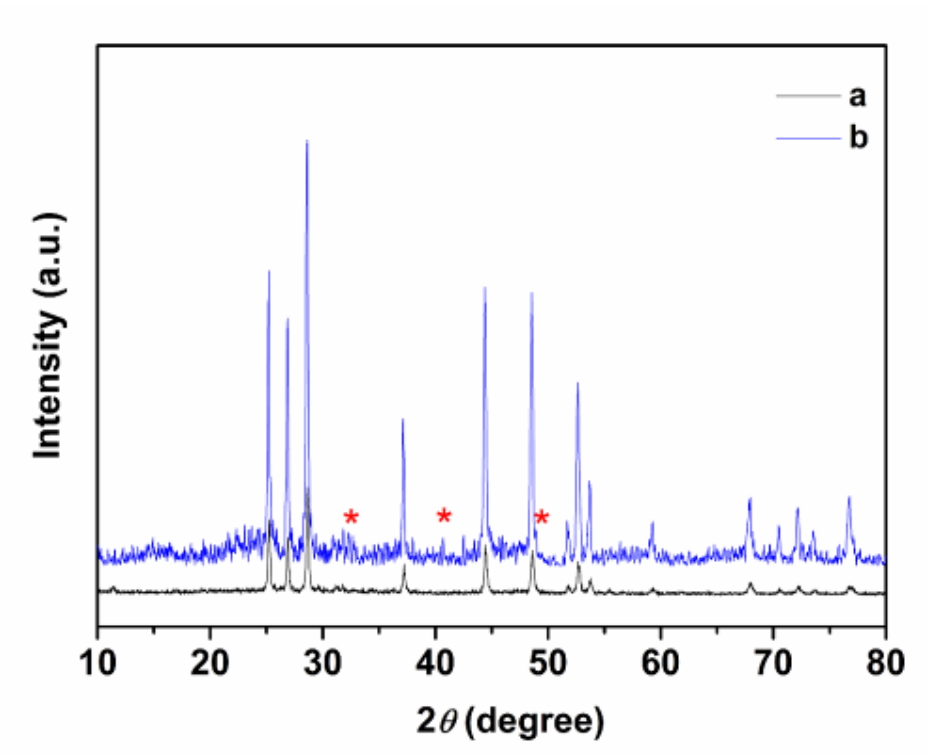


Fig. S1 The XRD patterns of $Cd_{0.65}Zn_{0.35}S$ (a) and Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ (b).

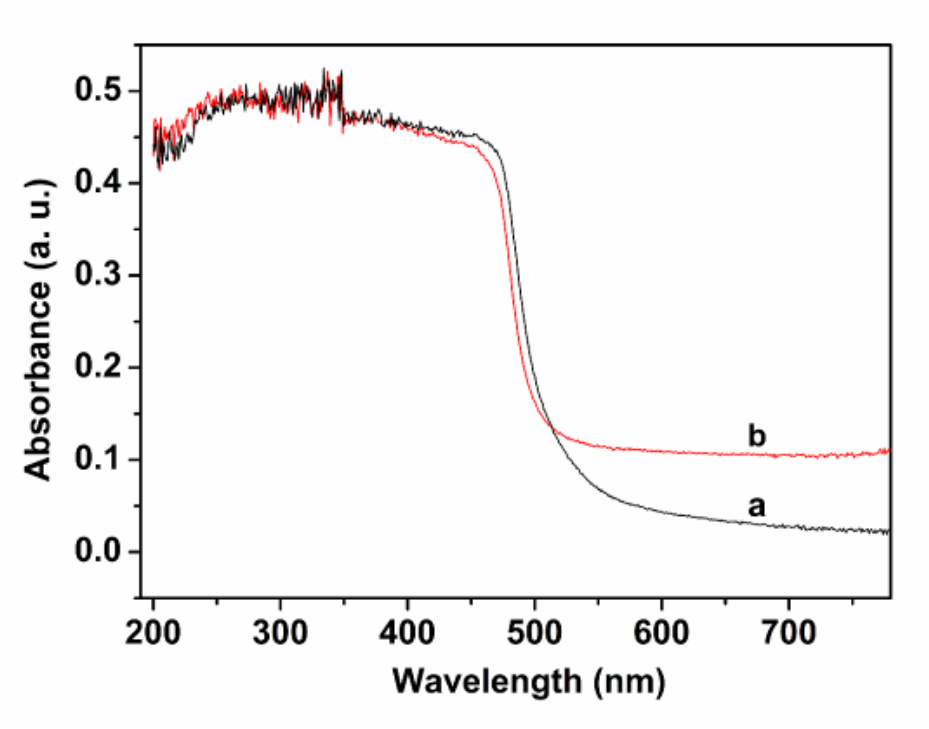
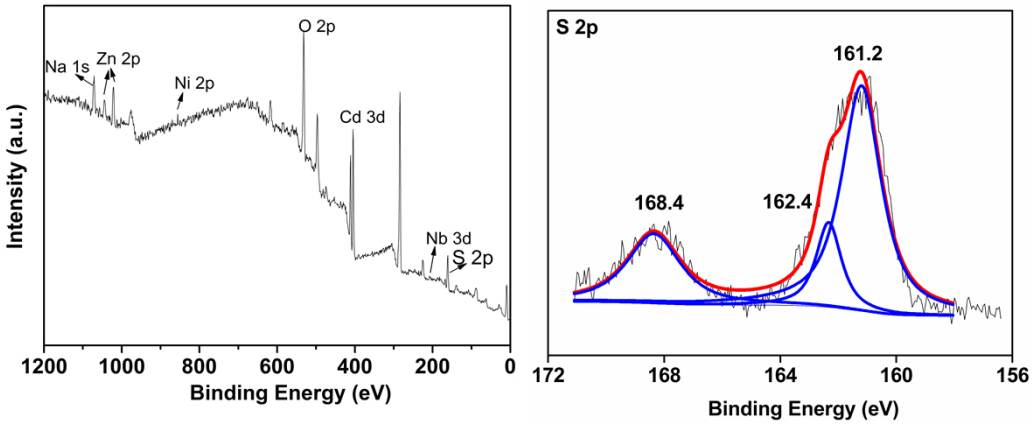
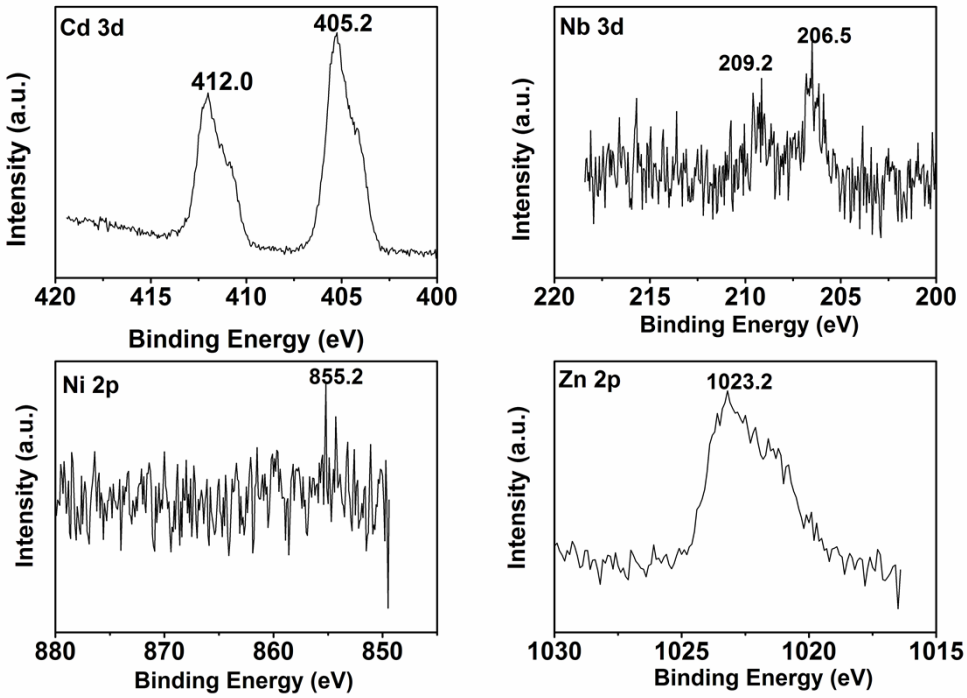


Fig. S2 UV-vis diffuse reflectance spectra of $Cd_{0.65}Zn_{0.35}S$ (a) and Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ (b).



(a)



(b)

Fig. S3 (a) XPS survey spectrum of Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ (left) and XPS spectrum of S 2p (right). (b) The XPS spectra of Cd 3d, Nb 3d, Ni 2p and Zn 2p in Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$.

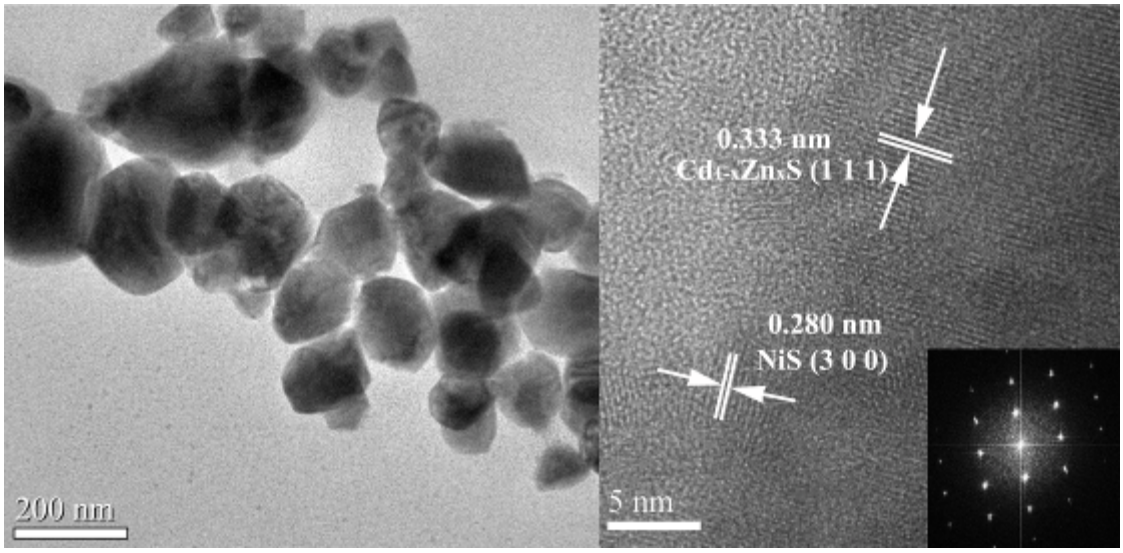


Fig. S4 TEM and HRTEM images of Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$.

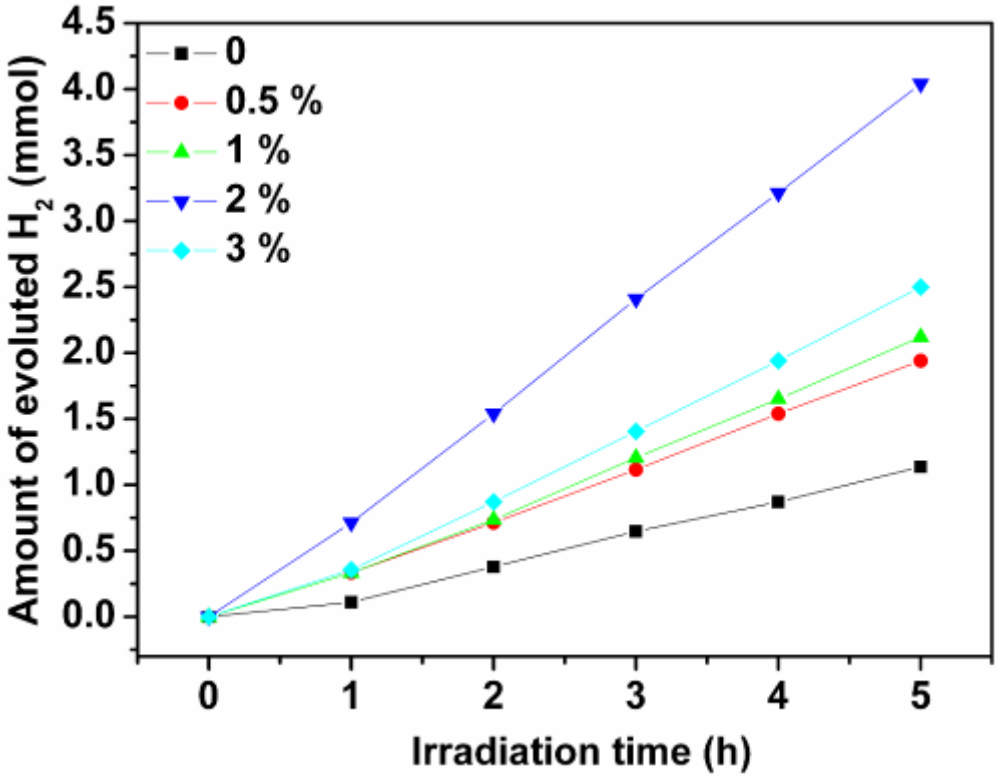


Fig. S5 H_2 evolution on Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ photocatalysts with different amount of Nb_6. Reaction condition: 0.2 g $Cd_{0.65}Zn_{0.35}S$ catalyst; 1 wt% NiS loaded; 200 ml aqueous solution containing 0.1 M Na_2S and 0.1 M Na_2SO_3; light source: 300 W Xe lamp ($\lambda > 400$ nm).

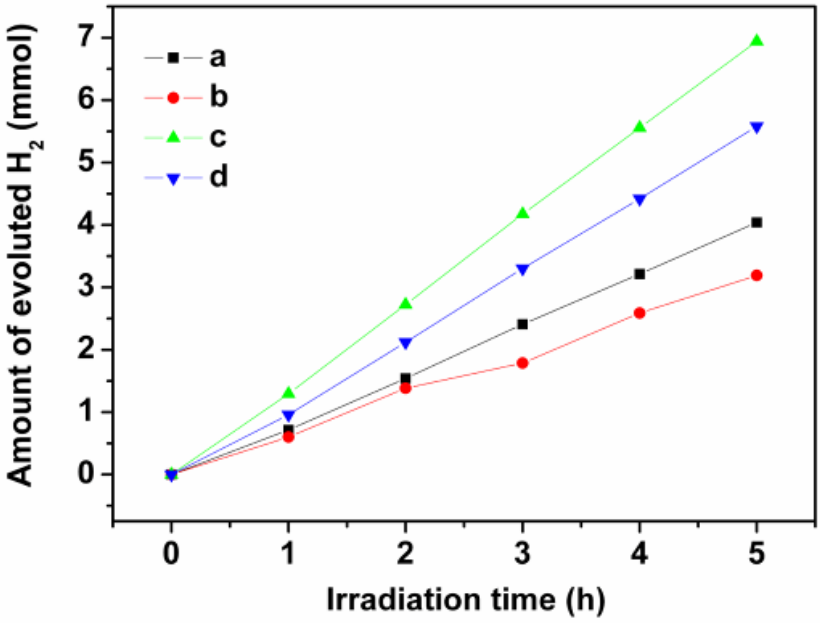


Fig. S6 H_2 evolution on Nb_6(2 wt%)-NiS/$Cd_{0.65}Zn_{0.35}S$ photocatalysts with different Na_2S/Na_2SO_3 concentration: (a) 0.1 M Na_2S/0.1 M Na_2SO_3; (b) 0.35 M Na_2S/0.25 M Na_2SO_3; (c) 0.25 M Na_2S/0.35 M Na_2SO_3; (d) 0.5 M Na_2S/0.5 M Na_2SO_3.

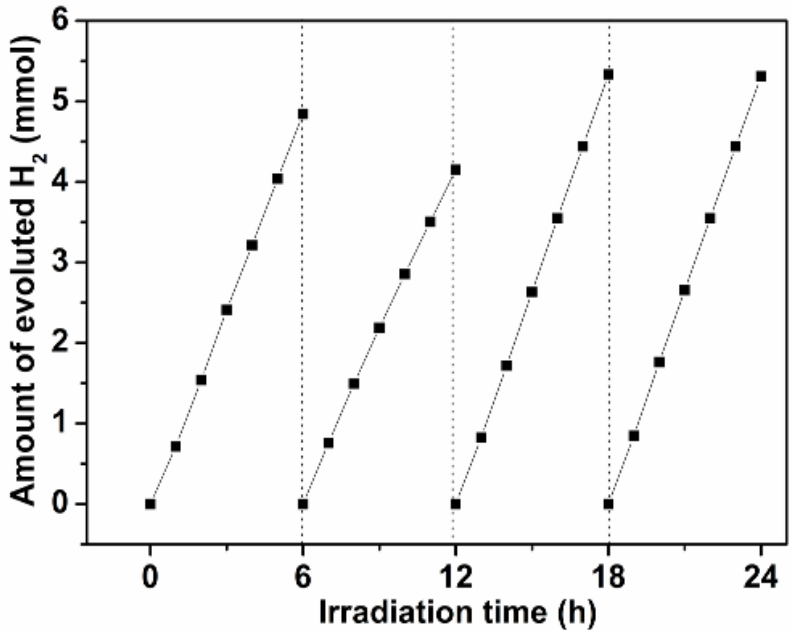


Fig. S7 Long-time stability test of Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ for hydrogen evolution. Reaction condition: 0.2 g catalyst; 200 ml aqueous solution containing 0.1 M Na_2S and 0.1 M Na_2SO_3; light source: 300 W Xe lamp (λ > 400 nm). The reaction solution was replaced by a new one after 12 h of the reaction.

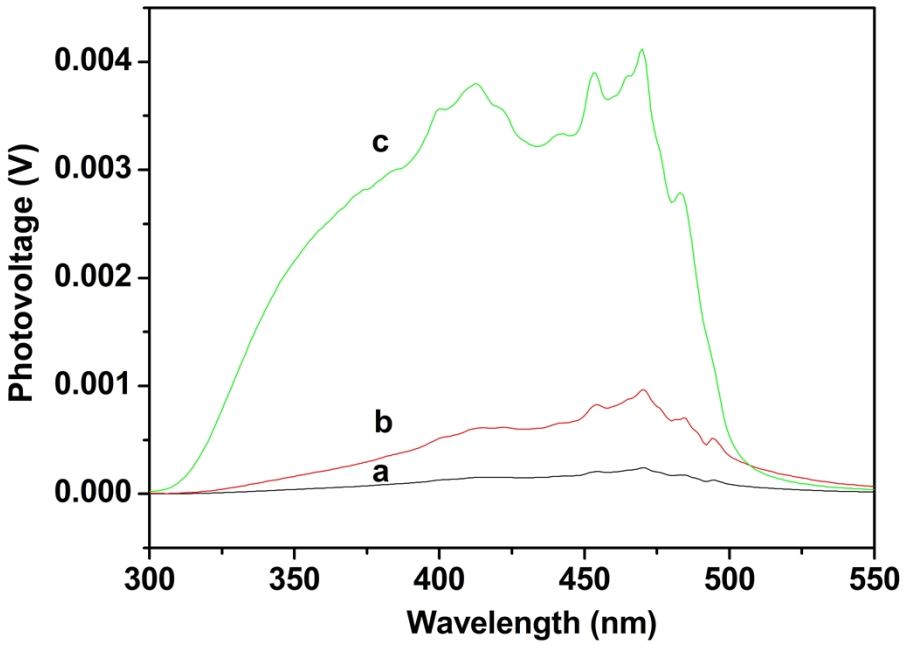


Fig. S8 The surface photovoltage spectroscopy (SPS) spectra of $Cd_{0.65}Zn_{0.35}S$ (a), $NiS/Cd_{0.65}Zn_{0.35}S$ (b) and Nb_6-$NiS/Cd_{0.65}Zn_{0.35}S$ (c).

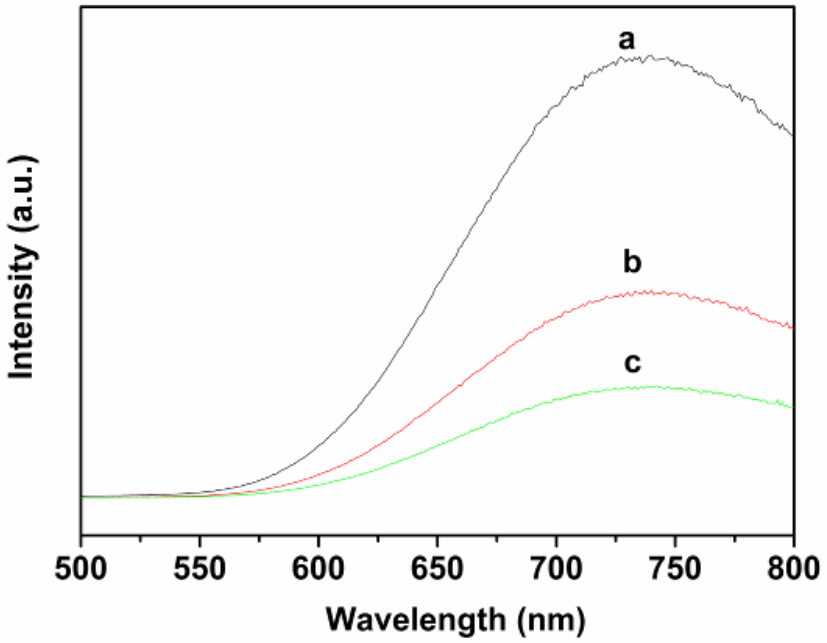


Fig. S9 The photoluminescent emission spectra of $Cd_{0.65}Zn_{0.35}S$ (a), $NiS/Cd_{0.65}Zn_{0.35}S$ (b) and Nb_6-$NiS/Cd_{0.65}Zn_{0.35}S$ (c) in solid state at room temperature.

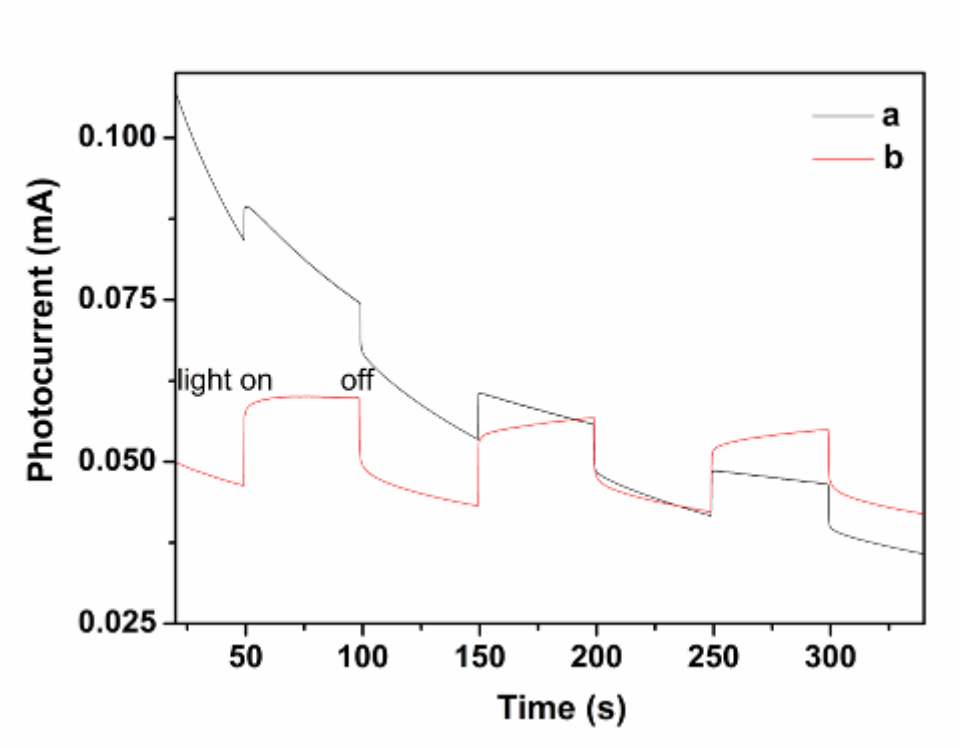


Fig. S10 Transient photocurrent responses of the films of NiS/$Cd_{0.65}Zn_{0.35}S$ (a) and Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ (b).

A three-electrode system was employed in a quartz cell with a Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum foil as the counter electrode, the film assembled ITO glass as the working electrode and 0.1 M Na_2S / 0.02 M Na_2SO_3 electrolyte.The comparison of the transient photocurrent responses proves a higher and much stable photocurrent in the Nb_6/NiS-$Cd_{0.65}Zn_{0.35}S$ sample, which further confirms that the introduction of Nb_6 can facilitate the separation and transfer of charge carriers between $Cd_{0.65}Zn_{0.35}S$ and NiS.

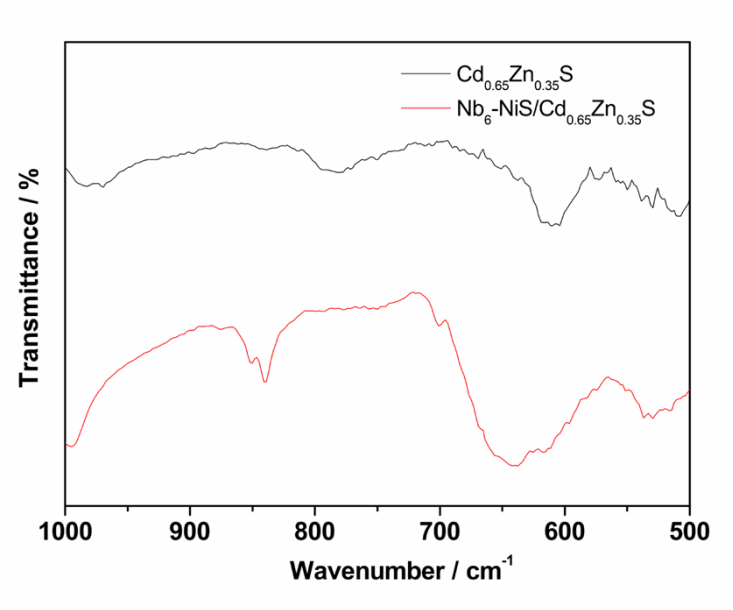


Fig. S11 IR spectra of $Cd_{0.65}Zn_{0.35}S$ and Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$. The characteristic peaks at 850, 640 and 530 cm^{-1} are attributed to the vibration of Nb—O and Nb—O—Nb bonds, which proves the existence of Nb_6 in the composite photocatalyst.

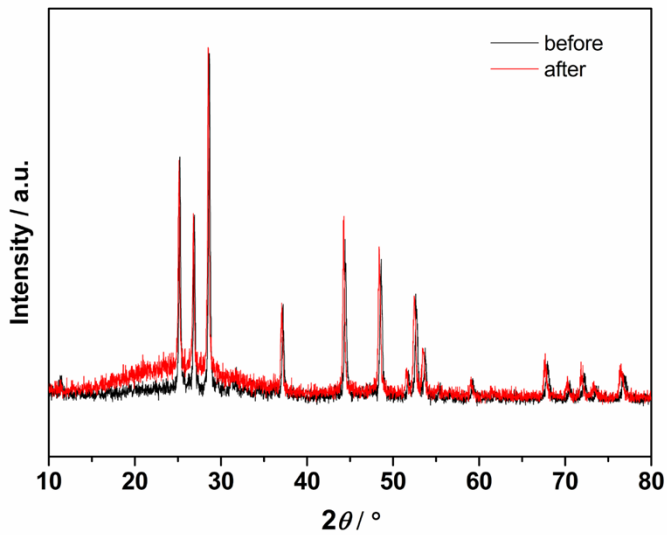


Fig. S12 The XRD patterns of Nb_6-NiS/$Cd_{0.65}Zn_{0.35}S$ before and after 12 h of photocatalytic reaction.