Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

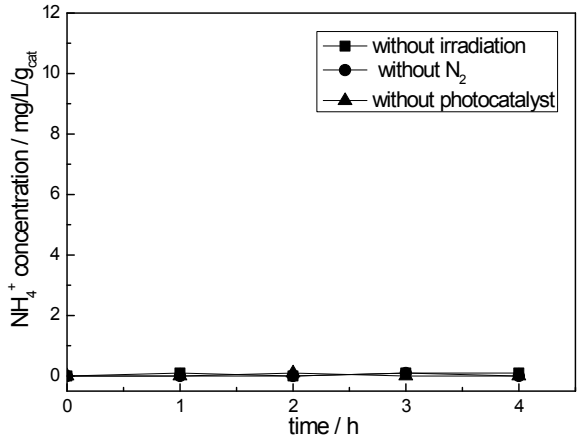

Figure S1. The N_2 photofixation ability over $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ in the absence of irradiation, N_2 or photocatalyst.

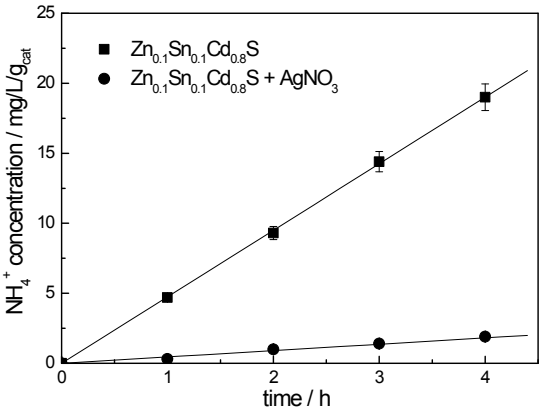

Figure S2. The N_2 photofixation ability over $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ using $AgNO_3$ as the electron scavenger.

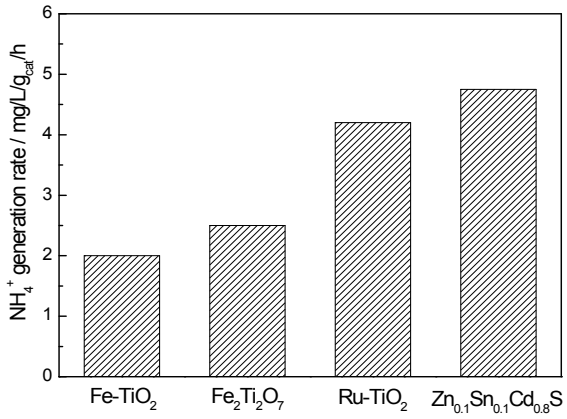

Figure S3. The comparison of nitrogen photofixation ability of Fe-TiO_2, $Fe_2Ti_2O_7$, Ru-TiO_2 and $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ under visible light.

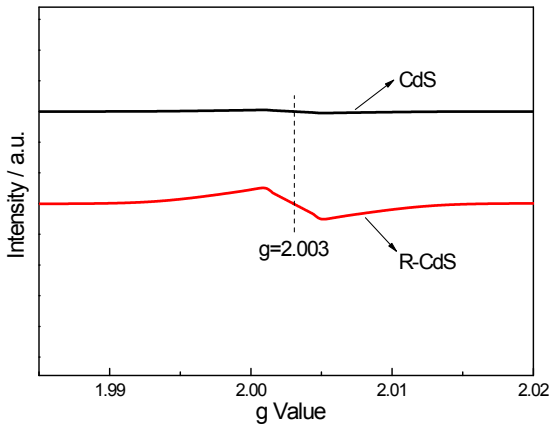

Figure S4. EPR of CdS and R-CdS.

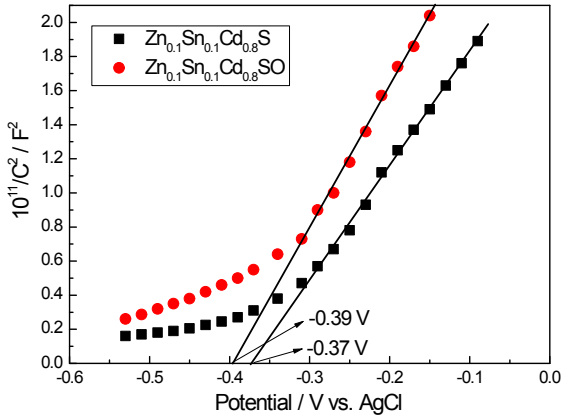

Figure S5. Mott-Schottky plot of $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ and $Zn_{0.1}Sn_{0.1}Cd_{0.8}SO$ in 0.2 M Na_2SO_4 aqueous solution.

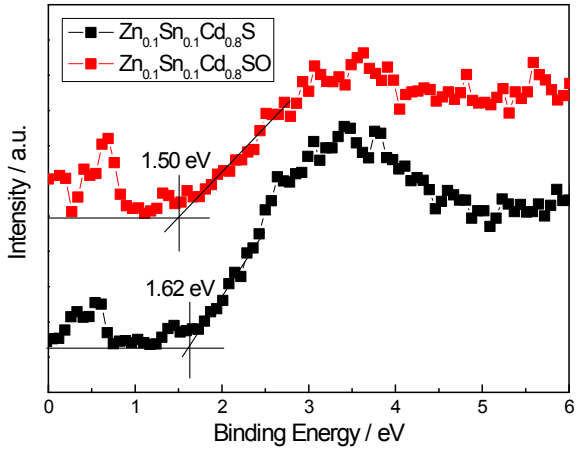

Figure S6. The VB XPS of $Zn_{0.1}Sn_{0.1}Cd_{0.8}S$ and $Zn_{0.1}Sn_{0.1}Cd_{0.8}SO$.

Table S1. The H_2 production ability of as-prepared ternary metal sulfide photocatalyst

Catalyst	$Zn_{0.05}Sn_{0.05}Cd_{0.9}S$	$Zn_{0.1}Sn_{0.1}Cd_{0.8}S$	$Zn_{0.2}Sn_{0.2}Cd_{0.6}S$	$Zn_{0.3}Sn_{0.3}Cd_{0.4}S$	$Zn_{0.1}Sn_{0.1}Cd_{0.8}SO$
H_2 production ($\mu mol \cdot h^{-1}$)	0.22	0.27	0.30	0.42	0.28

The photocatalytic H_2 production were performed in an outer-irradiation and air-tight Pyrex glass reactor, connected to a water-cooling system. In a typical run, 0.2 g photocatalyst was suspended in 100 ml deionized water with methanol (10 vol.%, used as the hole scavenger) under stirring. Prior to the photocatalytic reaction, the suspension was purged with Ar gas for 20 min to get rid of O_2. A 250 W high-pressure sodium lamp with UV cutoff filter ($\lambda > 420$ nm) were used as light source. A continuous magnetic stirrer was applied at the bottom of the reactor in order to keep the photocatalyst particles in suspension status during the whole experiment. The reaction products were analyzed on-line by thermal conductivity detectors on a micro-gas chromatography (Model Agilent P200 Series) equipped with a thermal conductivity detector (TCD) and a stainless steel column (2 m) packed with molecular sieves (5A) at 323 K. Ar was used as the carrier gas at a flow rate of 20 $cm^3 \cdot min^{-1}$. All runs were conducted at ambient pressure and 30 °C.