Electronic Supplementary Information

Materials characterization

X-ray diffraction (XRD) patterns were carried out to analyze the crystal phases of the samples on a Bruker D8 Advance X-ray instrument (Cu K$_\alpha$ radiations, $\lambda=1.5406$ Å) with a voltage of 40 kV and a current of 40 mA. The Fourier transform infrared (FTIR) spectrum was collected on Nicolet IS50 FTIR spectrometer (Thermo SCIENTIFIC). Field-emission scanning electron microscope (FESEM; Helios G4 CX) and transmission electron microscope (TEM; JEOL, JEM-2010) were used to analyze the morphology and structure of the samples. The composition of the samples was determined by energy-dispersive X-ray spectroscopy (EDX) attached to scanning electron microscope (SEM; Quanta 250). X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were carried out on a PHI Quantum 2000 XPS system with C 1s binding energy (284.6 eV) as the reference and He I excitation energy (21.22 eV) as the monochromatic light source. N$_2$ adsorption–desorption isotherms characterizations were conducted on a Micromeritics ASAP2020 under liquid nitrogen temperature (77 K). UV-vis diffuse reflectance spectra (DRS) were obtained using a Varian Cary 500 UV-vis spectrometer using BaSO$_4$ as a reference. The photoluminescence (PL) characterizations were carried out on Hitachi F-7000 spectrophotometer at room temperature. The fluorescence lifetime was determined by recording the time-resolved fluorescence emission spectra in a Deltaprobe Fluorescence Lifetime System. In situ electron spin resonance (ESR) measurement was carried out on a Bruker A300 and a 300 W xenon (Xe) lamp ($\lambda\geq420$ nm) was used as the light
source.

**Photoelectrochemical measurement**

The electrochemical measurement was carried out on Metrohm Autolab Electrochemical System, using a conventional three electrodes cell with Pt electrode and Ag/AgCl electrode as the counter electrode and reference electrode, respectively. Typically, 5 mg of the sample was dispersed in N, N-dimethylformamide (1 mL) by sonication to obtain a mixture. Then, the mixture was spread on the FTO glass with an area of ca. 0.25 cm$^2$ and dried at room temperature in the air. The transient photocurrent response spectra were conducted in Na$_2$SO$_4$ aqueous solution (0.2 M) with a 300 W xenon lamp ($\lambda \geq 420$ nm) as the light source. Electrochemical impedance spectroscopy (EIS) measurement was conducted at the open circuit potential and 1 mM K$_3$[Fe(CN)$_6$], 1 mM K$_4$[Fe(CN)$_6$] and 0.1 M KCl mixed solution was used as the electrolyte solution.

**Photocatalytic H$_2$ evolution**

The photocatalytic H$_2$ evolution reaction was carried out in closed quartz vessel equipped with Labsolar-6A all-glass automatic online trace gas analysis system (Perfectlight, Beijing). Typically, 40 mg photocatalyst was dispersed in 0.55 M Na$_2$S and 0.15 M Na$_2$SO$_3$ mixed solution (100 mL). Then, the system was stirred and under vacuum for 20 min. The temperature of the reaction was maintained at 10 $^\circ$C using a circulating condensing unit. The light source was a 300 W Xe lamp with a 420 nm long-pass cutoff filter. Lastly, the amount of H$_2$ was determined by Agilent 7820A gas chromatography (GC) equipped with a thermal conductive detector (TCD) and a 5 Å
molecular sieve column, using the Ar as carrier gas. Other reaction conditions were the same as those of the typical reaction. Besides, other typical sacrificial agents (e.g., lactic acid, trolamine and methanol) were also used to evaluate the photocatalytic performance of the NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S photocatalyst under otherwise identical conditions.

The apparent quantum yield (AQY) test was also performed under the conditions mentioned above, except that the filter was used a band-pass filter (i.e., 400, 420, 450, and 500 nm). The AQY was calculated as follow:

\[
\text{AQE} = \frac{2 \times \text{the number of generated } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%
\]

\[
\frac{2 \times n \times N_A \times h \times c}{I \times S \times t \times \lambda} \times 100\% \quad \text{(Eq1)}
\]

n is the amount of H$_2$ molecular, $N_A$ is Avogadro constant, h is the Planck constant, c is the speed of light, I is the intensity of light source, S is the illumination area, t is the photoreaction time, and $\lambda$ is the wavelength of the monochromatic light.
DFT calculation methods

The density function theory (DFT) calculation was performed using Vienna Ab-initio Simulation Package (VASP) code\textsuperscript{2,3}. According to the experiment fact, two 8-layer atoms Cd\textsubscript{0.5}Zn\textsubscript{0.5}S and NiTiO\textsubscript{3} models were established and the (100) and (104) crystal planes were exposed respectively, in which the top 4 layers of atoms were relaxed during the calculation and the other atoms were fixed to simulate the bulk phase. In addition, a 20 Å–thick vacuum layer was introduced to prevent the interaction between two adjacent slabs. The exchange-correlation function was utilized by generalized gradient approximation–Perdew–Burke–Ernzerhof (GGA-PBE) method\textsuperscript{4}. The interaction between core and electron was described by the Projector Augmented Wave (PAW) method\textsuperscript{5,6}, and the cutoff energy was set to 450 eV. The Brillouin-zone integration was performed on 4\times5\times1 and 1\times5\times1 k-points of gamma center for Cd\textsubscript{0.5}Zn\textsubscript{0.5}S and NiTiO\textsubscript{3} models, respectively. It can be considered that the accuracy of geometry optimization was reached when force of each atom was less than 0.02 eV/Å.
**Fig. S1** XRD patterns of Cd$_{0.5}$Zn$_{0.5}$S-p and NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S-p.

**Fig. S2** (a) XRD pattern and (b) FTIR spectrum of Ni-Ti-EG polymer.
**Fig. S3** The pore size distribution plots of Cd$_{0.5}$Zn$_{0.5}$S and NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S.

**Fig. S4** FESEM images of (a) Ni-Ti-EG polymer, (b) Cd$_{0.5}$Zn$_{0.5}$S-p and (c and d) NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S-p.
Fig. S5 UPS spectra of (a) NiTiO$_3$ and (b) Cd$_{0.5}$Zn$_{0.5}$S. The inset plots show the $E_{\text{edge}}$ values.

We use UPS to determine the valence band maximum and the minimum of the conduction band.$^{7-9}$ $E_{\text{cutoff}}$ and $E_{\text{edge}}$ are obtained by applying linear intersection method. According to Eq2 and Eq3, the $E_{\text{VB}}$ of NiTiO$_3$ and Cd$_{0.5}$Zn$_{0.5}$S are calculated to be -7.28 and -6.75 V ($\text{vs. vacuum}$), respectively, by subtracting the width of the He I UPS spectrum from the excitation energy (21.22 eV). Simultaneously, the work functions ($\Phi$) of NiTiO$_3$ and Cd$_{0.5}$Zn$_{0.5}$S are calculated to be 4.14 and 3.99 eV ($\text{vs. vacuum}$), respectively. The relationship between the vacuum energy ($E_{\text{Vac}}$) and the reversible hydrogen electrode potential ($E_{\text{RHE}}$) follows the formula $E_{\text{RHE}} = -E_{\text{Vac}} - 4.44$. The value of $E_{\text{RHE}}$ is consistent with the normal hydrogen electrode potential ($E_{\text{NHE}}$) at pH = 0.

Eventually, the $E_{\text{VB}}$ of the NiTiO$_3$ and Cd$_{0.5}$Zn$_{0.5}$S are calculated to be 2.43 and 1.89 V ($\text{vs. NHE, pH=7}$), respectively. On the basis of Eq4, the $E_{\text{CB}}$ of NiTiO$_3$ and Cd$_{0.5}$Zn$_{0.5}$S are located at 0.21 and -0.52 V ($\text{vs. NHE, pH=7}$), respectively.

\[ h\nu = E_{\text{cutoff}} + \Phi \quad \text{(Eq2)} \]
\[ E_{\text{VB}} = E_{\text{edge}} + \Phi \quad \text{(Eq3)} \]
\[ E_{\text{CB}} = E_{\text{VB}} - E_g \quad \text{(Eq4)} \]
Fig. S6 Optimized crystal structures of the (a) NiTiO$_3$ (104) surface and (b) Cd$_{0.5}$Zn$_{0.5}$S (100) surface. The purple, green, black, red, blue and white balls represent Ti, Ni, O, Cd, Zn and S atom, respectively.

Fig. S7 Stability tests of pure Cd$_{0.5}$Zn$_{0.5}$S.
Fig. S8 (a) XPS spectra of NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S before and after reaction. (b) SEM image of NiTiO$_3$/Cd$_{0.5}$Zn$_{0.5}$S after reaction.
<table>
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<th>Catalyst</th>
<th>Sacrificial agent</th>
<th>Cocatalyst</th>
<th>$\text{H}_2$ evolution rate (mmol h$^{-1}$ g$^{-1}$)</th>
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**Supplementary References**


