Noble-Metal-Free CdS Decorated Porous Ni\textsubscript{x}Co\textsubscript{1-x}O Skeleton Derived from Metal–Organic Framework for Efficient Visible-Light H\textsubscript{2} Production

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ABSTRACT: Noble-metal-free CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O photocatalyst was synthesized for the first time using a metal–organic framework (MOF) to serve as the template for efficient visible-light photocatalytic H\textsubscript{2} production. The entire preparation process mainly involved the calcination of NiCo-MOF and subsequent decoration of CdS nanoparticles (NPs) via hydrothermal treatment. The photoelectrical properties of pristine Ni\textsubscript{x}Co\textsubscript{1-x}O are optimized. With the introduction of CdS NPs, the H\textsubscript{2} production of CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O under visible light irradiation (λ > 420 nm) increased significantly from 0 to 2795.6 μmol g\textsuperscript{-1} h\textsuperscript{-1}, thereby indicating an excellent synergistic effect between CdS and the Ni\textsubscript{x}Co\textsubscript{1-x}O skeleton. The band gap of CdS in the CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O samples can be narrowed to ca. 1.54 eV. Compared with Ni\textsubscript{x}Co\textsubscript{1-x}O, CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O presents an enhanced electron paramagnetic resonance (EPR) peak and low photoluminescence (PL) spectrum, directly proving its excellent charge carriers separation ability. Besides, the large specific surface area (703.27 m\textsuperscript{2} g\textsuperscript{-1}) and mesoporous structure (ca. 3–4.5 nm in diameter) of CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O can expose more active sites and serve as channels for the access of reactants, accelerating the water-cracking reduction reaction also. Furthermore, the H\textsubscript{2} evolution performances of CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O under visible light (λ > 400 nm) and full spectrum light are studied as well. On the basis of experiment and density functional theory (DFT) calculation results, a feasible mechanism is tentatively proposed. This work suggests the great application prospects of NiCo-MOF-based hybrid in water splitting.

KEYWORDS: CdS@Ni\textsubscript{x}Co\textsubscript{1-x}O, NiCo-MOF, CdS NPs, synergistic effect, photocatalytic H\textsubscript{2} production

INTRODUCTION

Light-driven H\textsubscript{2} production has been considered as one of the most promising strategies to convert solar power to green chemical energy.\textsuperscript{1–5} However, the key problem to realize H\textsubscript{2} production is preparing an efficient photocatalyst with high...
charge carriers separation capacity. Recently, metal–organic frameworks (MOFs), which are mainly constructed by metal clusters and organic moieties, have been proven to be intriguing templates for preparing various functional nanomaterials due to their tunable texture, multiple porosity, and chemical functionalities, etc. Besides, based on thermal decomposition strategy, the content of MOFs-based materials could be adjusted to be carbon, metal oxide, or their hybrids by the control of ingredients and calcination conditions. In fact, MOFs have been widely applied in the synthesis of various heterogeneous photocatalysts. The abundant 3D open-framework structure in MOFs allows the reactant to access active sites, thereby bestowing MOFs unique photocatalysis properties.

In the case of active sites, noble metal (e.g., Au, Pt, Ag) nanoparticles (NPs) may be the most efficient materials for water splitting due to their surface plasmon resonance effect and low overpotential. But the high prices and inadequate global reserve seriously limit their wide application in H2 production. Recent investigations reveal that some metal sulfides can serve as cocatalysts for proton reduction. As a typical transition metal sulfide, CdS, has been fostered as one of the most prominent photocatalytic materials because of its visible-light responsibility, suitable redox potentials, and befitting band gap (ca. 2.4 eV). Unfortunately, during the photocatalytic process, CdS NPs might agglomerate to reduce surface free energy, resulting in poor stability. To overcome this shortcoming, fabricating a CdS@MOFs heterostructure might be a judicious strategy. A MOF skeleton could serve as a host to control the growth of CdS NPs. On the basis of this principle, several CdS-decorated MOFs (such as ZIF-8, MIL-101, UiO-66, ZnCo-ZIF7, and MIL-53 (Fe)) were fabricated successfully. At the same time, they have proved Ni and Co elements tend to display unique H2 production enhancement. Up to now, Co(Ni)-MOF was approved to be an excellent functional material, but no CdS@NiCo-MOF heterostructure has been reported so far, let alone be applied to H2 production. Thus, there is reason to believe that efficient H2 production catalysts can be developed via constructing a CdS@NiCo-MOF hybrid.

Herein, we have for the first time successfully fabricated a porous CdS@NiCo1−xO nanohybrid with enhanced photocatalytic H2 production under visible-light irradiation (λ > 420 nm). The whole preparation process is pretty facile and can be generally divided into two steps as schematically presented in Figure 1. First, under N2 atmosphere conditions, porous NiCo1−xO skeleton, originating from NiCo-MOF, can be obtained by calcination. Second, via a hydrothermal method, light sensitive CdS NPs are decorated in the NiCo1−xO skeleton, constructing porous CdS@NiCo1−xO eventually.

Compared to pristine NiCo1−xO, the H2 production of CdS@NiCo1−xO heterostructure increased from ca. 0 to 2795.6 μmol h−1 g−1 dramatically, demonstrating the unique synergistic effect between NiCo1−xO skeleton and CdS. After modifying CdS NPs, NiCo1−xO exhibits typical semiconductor properties and the visible-light response region can be extended to ca. 550 nm. The high water splitting performance of CdS@NiCo1−xO can be ascribed to its enhanced electron–hole pairs generation and separation ability. Furthermore, the large specific surface area (703.27 m2 g−1) bestows CdS@NiCo1−xO a high mass transfer rate and more exposed active sites for the proton reduction reaction. Additionally, the prepared CdS@NiCo1−xO exhibited an excellent stability without obvious decrease in H2 production even after four cycles. This work would inspire growing interest in achieving various noble-metal-free NiCo-MOF-based photocatalysts for H2 evolution.

## EXPERIMENTAL SECTION

### Synthesis of CdS@NiCo1−xO

**CoCl2·6H2O (0.1 mmol), NiCl2·6H2O (0.05 mmol), and 1,4-dicarboxybenzene (0.15 mmol)** were evenly dispersed in a mixture of 2 mL of ethyl alcohol, 25 mL of dimethylformamide, 0.8 mL of triethylamine, and 2 mL of H2O under ultrasonic treatment for 1 h, to prepare NiCo-MOF facilely. The as-prepared NiCo-MOF was thermally treated in a tube furnace at 400 °C for 4 h in N2 to get the NiCo1−xO skeleton. A 0.61 g aliquot of CdCl2 and an appropriate amount of CH3CSNH2 (CdCl2/CH3CSNH2 mass ratio is 3:1) was mixed uniformly in 60 mL of water. Then, 0.1 g of NiCo1−xO and the above solution were transferred into a 100 mL Teflon-lined autoclave and maintained at 160 °C for 5 h. The final product (CdS@NiCo1−xO) was centrifuged, washed with ethanol, and dried under vacuum. To change the CdS content, the CdCl2 dosage was adjusted to 0.35, 0.43, 0.52, 0.61, 0.7, and 0.87 g. The corresponding samples were denoted as CdS@NiCo1−xO-1, CdS@NiCo1−xO-2, CdS@NiCo1−xO-3, CdS@NiCo1−xO-4, CdS@NiCo1−xO-5, and CdS@NiCo1−xO-6, respectively.

### Photocatalytic H2 Production Test

The H2 production test was investigated on CEL-PAEM-D6 (Beijing Ceaulight). Generally, 10 mg of CdS@NiCo1−xO nanocatalyst was evenly dispersed in an aqueous solution of 45 mL of deionized water and 5 mL of TEOA. Before H2 production, the reaction system was evacuated for 1 h and then exposed to irradiation by 300 W Xe lamp with a UV-light cutoff filter (λ > 420 nm). The volume of photogenerated H2 was measured by an online gas chromatograph (GC-7920, Beijing Ceaulight). The stability test of CdS@NiCo1−xO was studied by adding 5 mL of TEOA in the next cycle.
conditions (300 W Xe light source and a band-pass filter for 420 ± 10 nm). The AQY was calculated by the following equation:

\[
AQY(\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons} \times 100} \times \frac{\text{number of evolved } H_2 \text{ molecules} \times 2}{\text{number of incident photons} \times 100}
\]

## RESULTS AND DISCUSSION

The first step in this project was to investigate the morphology and structure of CdS@Ni$_x$Co$_{1-x}$O by SEM and TEM. As shown in Figure S1, both NiCo-MOF and Ni$_x$Co$_{1-x}$O presented an agglomeration structure of many tiny irregular particles (ca. 100 nm). After doping CdS NPs in the Ni$_x$Co$_{1-x}$O skeleton via the hydrothermal treatment, the agglomeration structure of Ni$_x$Co$_{1-x}$O remained (Figure 2a,b), and from Figure 2c,d, it could be observed that CdS NPs (ca. 24.9 ± 2.6 nm in diameter) exhibited an obvious dark appearance and decorated or were embedded in the Ni$_x$Co$_{1-x}$O framework. The high-resolution TEM image in Figure 2d showed a lattice fringe measured with the spacing of 0.358 nm, related to the (100) atomic plane of CdS (JCPDS No. 41-1049). Furthermore, from the elemental mapping analysis of CdS@Ni$_x$Co$_{1-x}$O Ni, Co, and Ni elements had a relatively uniform distribution, thereby further demonstrating the successful assembly of CdS NPs in the Ni$_x$Co$_{1-x}$O frame.

The crystalline structure of the as-prepared catalysts was investigated by XRD measurements. As shown in Figure 3a,b, Ni$_x$Co$_{1-x}$O presented an obvious diffraction peak at 2θ = 44.4°, corresponding to the (111) crystal plane. After introducing CdS NPs, the characteristic peaks of CdS at 24.9°, 26.6°, 28.1°, 36.6°, 43.9°, 47.8°, and 51.9° emerged clearly in all CdS@Ni$_x$Co$_{1-x}$O curve, and meanwhile, the diffraction peak of (111) disappeared gradually, which might be due to the potential interaction of the CdS NPs and Ni$_x$Co$_{1-x}$O skeleton structure. Furthermore, Fourier transform infrared spectroscopy (FTIR) was employed to characterize the chemical structures of all prepared photocatalysts. From Figure 3b, the specific absorption band at ~3430.7 cm$^{-1}$ corresponded to the breathing vibration mode of the hydroxyl functional group (O–H band). The emerging peaks at ~1626.7 and 1373.6 cm$^{-1}$ belonged to the stretching vibration of ν$_s$ (–COO) and ν$_s$ (–COO) of terephthalate anions, respectively. Besides, the weak peaks at ~2918.3, ~881.3, and ~799.8 cm$^{-1}$ originated from the para-aromatic C–H stretching bands. With an increase of the dosage of CdS solution, no new characteristic peaks emerged in the FT-IR spectra, thereby indicating that the doped CdS NPs had no effect on the chemical structures of Ni$_x$Co$_{1-x}$O. The optical properties of all Ni$_x$Co$_{1-x}$O-based samples were studied via UV–visible diffuse reflectance spectroscopy (Figure 3d). It was surprising to find that pristine Ni$_x$Co$_{1-x}$O did not exhibit a typical semiconductive curve. In comparison, when CdS NPs were introduced, all CdS@Ni$_x$Co$_{1-x}$O samples presented a basal absorption edge at ca. 550 nm, thereby indicating CdS exhibited remarkable photo properties in the Ni$_x$Co$_{1-x}$O skeleton. In addition, from the inset of Figure 3d, with increasing CdS dosage, the band gap of CdS in the CdS@Ni$_x$Co$_{1-x}$O samples changed apparently, and the CdS in the CdS@Ni$_x$Co$_{1-x}$O-4 showed the most narrowed band gap of ca. 1.54 eV.

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**Figure 2.** (a and b) SEM images of CdS@Ni$_x$Co$_{1-x}$O, (c and d) TEM images of CdS@Ni$_x$Co$_{1-x}$O, (e) elemental mapping analysis of Cd, S, Co, Ni.
Figure 3. (a) XRD patterns of all samples, (b) corresponding enlarged (111) crystal plane, (c) FT-I, and (d) UV-diffuse reflection spectra (inset is Kubelka–Munk transformed reflectance spectra) of series Ni\textsubscript{1-x}Co\textsubscript{x}O-based samples.

Figure 4. XPS spectra of (a) Ni 2p, (b) Co 2p, (c) Cd 3d, and (d) S 2p in CdS@Ni\textsubscript{1-x}Co\textsubscript{x}O.
XPS was employed to study the chemical valence states and elemental binding energies of CdS@Ni\textsubscript{x}Co\textsubscript{1−x}O. The appearance of Ni, Co, O, Cd, and S elements in the XPS survey spectrum of Figure S2 confirmed that CdS NPs was successfully loaded in the Ni\textsubscript{x}Co\textsubscript{1−x}O catalytic system. From Figure 4a, Ni presented two obvious peaks at 856.6 and 874.2 eV, related to Ni 2p\textsubscript{3/2} and Ni 2p\textsubscript{1/2}. Besides, the Ni 2p peaks have two shakeup satellites peaks (marked as Sat.) at 862.5 and 880.3 eV, which denote characteristic strips of Ni\textsuperscript{2+}. Similarly, in Figure 4b, Co showed the analogous spectrum (781.5 and 797.3 eV, Co\textsuperscript{2+}).\textsuperscript{22,24} In addition, the fitting peaks at 405.9 and 412.6 eV (Figure 4c) corresponded to Cd 3d\textsubscript{5/2} and 3d\textsubscript{3/2} spin orbits, respectively. S element exhibited two peaks at 163.4 and 162.2 eV, related to S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2}.\textsuperscript{23,25}

The pore structure of Ni\textsubscript{x}Co\textsubscript{1−x}O-based nanocatalysts were studied via N\textsubscript{2} adsorption−desorption measurement. From Figure 5a, pristine Ni\textsubscript{x}Co\textsubscript{1−x}O exhibited a high specific surface area (ca. 591.08 m\textsuperscript{2} g\textsuperscript{−1}), which is identical to other reports.\textsuperscript{10} When introducing a small amount of CdS NPs in Ni\textsubscript{x}Co\textsubscript{1−x}O through hydrothermal treatment, the specific surface area of CdS@Ni\textsubscript{x}Co\textsubscript{1−x}O-1 increased to 868.04 m\textsuperscript{2} g\textsuperscript{−1}. Furthermore, with a further increase in CdS NPs dosage, the specific surface area of serial CdS@Ni\textsubscript{x}Co\textsubscript{1−x}O samples decreased gradually to 703.27 m\textsuperscript{2} g\textsuperscript{−1}, which may have occurred because some tiny CdS blocked the pore structure in Ni\textsubscript{x}Co\textsubscript{1−x}O. Just as shown in Figure 5b, all the samples showed a mesoporous diameter distribution centered in the range of ca. 3−4.5 nm and, when the dosage of CdS increased from 0 to 23.58 atom %, the portion of mesoporous decreased apparently, thereby resulting in the decreased specific surface area. The abundant porous structures could serve as channels for the access of reactants to inner active sites, and each CdS@Ni\textsubscript{x}Co\textsubscript{1−x}O unit is an efficient nanoreactor with high photoactivity.
Hydrogen evolution catalysis under visible-light irradiation ($\lambda > 420$ nm) was implemented to investigate the catalytic performance of series Ni$_x$Co$_{1-x}$O-based nanocatalysts. From Figure 6a, no H$_2$ was generated over pristine Ni$_x$Co$_{1-x}$O, which may occur because Ni$_x$Co$_{1-x}$O failed to absorb visible light. After decorating small amounts of CdS NPs, CdS@Ni$_x$Co$_{1-x}$O started to exhibit a low H$_2$ production performance (ca. 800−900 µmol h$^{-1}$ g$^{-1}$) and, with a further increase of CdS dosage, the H$_2$ evolution of CdS@Ni$_x$Co$_{1-x}$O (CdS content is 23.58 at% Ni, Figure S3) increased sharply to ca. 2795.6 µmol h$^{-1}$ g$^{-1}$. What is more, we had found three other different synthesis strategies of NiCoO, the H$_2$ evolution of the above conventional CdS@NiCoO is ca. 1607.2, 0, and 0 µmol h$^{-1}$ g$^{-1}$ under the same conditions, respectively. Therefore demonstrating the structure advantages of NiCoO-MOF. Generally, the enhanced water splitting performance is closely related to efficient charge-hole pairs separation.

In contrast, with the doping of CdS NPs, the EPR signal intensity of CdS@Ni$_x$Co$_{1-x}$O increased significantly due to the abundant surface oxygen vacancy, thereby directly demonstrating the excellent synergistic effect of CdS and Ni$_x$Co$_{1-x}$O in charge carrier separation. PL quenching phenomenon is related to the recombination processes of charge carriers and a low PL emission intensity suggested a low recombination rate. Just as illustrated in the inset of Figure 6a, Ni$_x$Co$_{1-x}$O possessed a Lorentz shaped EPR resonance signal at $g = 2.002$. In contrast, the doping of CdS NPs caused a significant decrease of $g$ value to 1.995. Further, in comparison with Ni$_x$Co$_{1-x}$O, CdS@Ni$_x$Co$_{1-x}$O exhibited a much lower PL emission peak at about 430 nm, ulteriorly proving its efficient charge carrier separation. Furthermore, from the inset of Figure 6d, CdS@Ni$_x$Co$_{1-x}$O presented a slower charge carriers decay process than Ni$_x$Co$_{1-x}$O and, accordingly, the average fluorescence lifetime was prolonged from 0.317 to 0.528 ns.

To further evaluate the enhanced photovoltaic properties of CdS@Ni$_x$Co$_{1-x}$O, photocurrent responses were measured in a three-electrode cell. As illustrated in Figure 6c, CdS@Ni$_x$Co$_{1-x}$O showed an obvious stronger photocurrent response than Ni$_x$Co$_{1-x}$O and, meanwhile, the semicircular Nyquist plots of CdS@Ni$_x$Co$_{1-x}$O in electrochemical impedance spectra possessed a reduced diameter, confirming its high photogenerated electron−hole pairs separation efficiency and smaller charge transfer resistance.

The H$_2$ evolution performances of all CdS@Ni$_x$Co$_{1-x}$O catalysts were studied as well at visible-light of $\lambda = 420 \pm 10$ nm, $\lambda > 400$ nm, and full spectrum. As shown in Figure 6b, all the samples exhibited similar H$_2$ evolution changing trend with Figure 6a and CdS@Ni$_x$Co$_{1-x}$O-4 still showed the best catalytic activity in all kinds of lights ($\lambda = 420 \pm 10$ nm, $\lambda > 400$ nm, and full spectrum, the H$_2$ evolution is ca. 858.6, 3267, and 3851.8 µmol h$^{-1}$ g$^{-1}$, respectively). Besides, the AQY of CdS@Ni$_x$Co$_{1-x}$O-4 could reach up to 24.89%. These results provided solid evidence to confirm that CdS can dramatically enhance the light utilization in the Ni$_x$Co$_{1-x}$O-based catalytic system for photocatalysis.

The excellent stability of CdS@Ni$_x$Co$_{1-x}$O was demonstrated by a four recycle photocatalytic experiment (Figure S4). It could be found that, after four test cycles, no obvious decrease in hydrogen production was observed and the recycled sample exhibited no clear variation in crystal shape (Figure S5a). Besides, recycled CdS@Ni$_x$Co$_{1-x}$O showed a similar change trend in a UV-diffuse reflection curve (Figure S5b) with pristine CdS@Ni$_x$Co$_{1-x}$O, and at $\lambda > 570$ nm a straightforward rise in visible-light response occurred, which might due to the slight deviation from the bond of Ni$_x$Co$_{1-x}$O skeleton and CdS NPs. Furthermore, a comparison of the H$_2$ production rate of CdS@Ni$_x$Co$_{1-x}$O with that of the other NiO or CoO-based photocatalysts is necessary as well. From Table 1, the H$_2$ production performance of CdS@Ni$_x$Co$_{1-x}$O in this work is much higher than that of most reports (including complicated multiple systems), thereby proving the promising application of CdS in the Ni$_x$Co$_{1-x}$O-based catalytic system for water splitting.

To get insights into the excellent synergistic effect between Ni$_x$Co$_{1-x}$O and CdS in water splitting, density functional theory (DFT) calculations are employed. It can be concluded that CdS can not only enhance the low electron region of the adjacent Ni$_x$Co$_{1-x}$O but also make CdS act as an electron reservoir during H$_2$ evolution. Furthermore, from the density of states (DOS) of CdS, CdS@Ni$_x$Co$_{1-x}$O features a notably higher Fermi level than CdS. Therefore, it may be concluded that the decorated CdS NPs could narrow the band gap of Ni$_x$Co$_{1-x}$O-based catalytic system and further regulate its charge carrier distribution, which is consistent with the UV-diffuse reflection data in the inset of Figure 3d. The above experiment and DFT calculation results inspire us to propose a possible photocatalytic H$_2$ production mechanism for CdS@Ni$_x$Co$_{1-x}$O. Generally, the light sensitive CdS NPs can be photostimulated facilely to generate conduction band (CB) electrons ($e^-$) and valence band (VB) holes ($h^+$). The accumulated $e^-$ in CdS NPs would disperse and migrate to the low electron region of the adjacent Ni$_x$Co$_{1-x}$O, while the $h^+$ would react with the sacrificial reagent (TEOA), thereby inhibiting the recombination of electron−hole pairs and thus reducing H$^+$ into large volumes of H$_2$ (Figure 7f). Additionally, the excellent water splitting performance of CdS@Ni$_x$Co$_{1-x}$O is also consistent with its high specific surface (703.27 m$^2$ g$^{-1}$) area and enhanced light response ability (Figure 3d).

### Table 1. Comparison of H$_2$ Production for NiO or CoO-Based Photocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lighter Source</th>
<th>H$_2$ Evolution ($\mu$mol h$^{-1}$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS@Ni$<em>x$Co$</em>{1-x}$O</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>2795.6</td>
</tr>
<tr>
<td>CoO NW$^{29}$</td>
<td>$\lambda &gt; 250$ nm, 300 W Xe</td>
<td>17.76</td>
</tr>
<tr>
<td>CdS@CoO$^{30}$</td>
<td>$\lambda &gt; 400$ nm, 300 W Xe</td>
<td>33.4</td>
</tr>
<tr>
<td>NiO/TiO$_2$/ C$^{31}$</td>
<td>$\lambda &gt; 400$ nm, 350 W Xe</td>
<td>356</td>
</tr>
<tr>
<td>CdS@CoO$^{32}$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>360</td>
</tr>
<tr>
<td>C/N-NiO$^{33}$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>465</td>
</tr>
<tr>
<td>g-C$_3$N$_4$/CoO/Pt$^{34}$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>651.3</td>
</tr>
<tr>
<td>TiO$_2$/Pt-CoO$^{35}$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>3762.8</td>
</tr>
<tr>
<td>NiO/MIL-125-NH$_2$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>1084</td>
</tr>
<tr>
<td>CoO-Co$_3$O-SnO$_2$−TiO$_2$</td>
<td>$\lambda &gt; 420$ nm, 300 W Xe</td>
<td>1486.4</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

To sum up, we have fabricated a noble-metal-free CdS NPs decorated Ni$_x$Co$_{1-x}$O nanohybrid photocatalyst derived from NiCo-MOF for efficient visible-light H$_2$ production. The as-assembled CdS@Ni$_x$Co$_{1-x}$O composite exhibits distinguished visible-light photocatalytic hydrogen evolution rate of 2795.6
μmol g⁻¹ h⁻¹ (λ > 420 nm) due to enhanced electron–hole pairs generation and separation ability. The doped CdS NPs could extend the visible-light response region of NiₓCo₁₋ₓO to ca. 550 nm and the band gap of the CdS in the CdS@NiₓCo₁₋ₓO narrowed to ca. 1.54 eV. Moreover, the enhanced photoelectric properties of CdS@NiₓCo₁₋ₓO are directly demonstrated via photocurrent response, EPR, and PL, etc. The H₂ evolution rates of CdS@NiₓCo₁₋ₓO under λ = 420 ± 10 nm, λ > 400 nm and full spectrum are tested to be ca. 858.6, 3267, and 3851.8 μmol h⁻¹ g⁻¹, respectively. Moreover, the high H₂ evolution of CdS@NiₓCo₁₋ₓO also relates to the abundant mesoporous structure (ca. 3–4.5 nm in diameter) and large specific surface area (ca. 703.27 m² g⁻¹), which could serve as channels for the access of reactants to inner active sites. Furthermore, the prominent reusability of CdS@NiₓCo₁₋ₓO hybrid is confirmed via stability test. Lastly, a viable photocatalytic H₂ production mechanism for CdS@NiₓCo₁₋ₓO is proposed based on experiment and DFT calculation data. This work may highlight the privilege of establishing such architecture (CdS@NiₓCo₁₋ₓO) and providing a novel strategy for the synthesis of efficient H₂ production photocatalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.9b01983.

Characterization, chemicals, and materials, experimental comparisons, DFT calculation, SEM images of NiCo-MOF and NiₓCo₁₋ₓO, XPS spectra of CdS@NiₓCo₁₋ₓO (survey), EDS of the CdS@NiₓCo₁₋ₓO-4, photocatalytic stability test of CdS@NiₓCo₁₋ₓO under visible-light irradiation of λ > 400 nm, XRD and UV-diffuse reflection spectra of CdS@NiₓCo₁₋ₓO (before and after reaction) (PDF)

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Notes

The authors declare no competing financial interest.

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