Supporting Information

Well-designed honeycomb Co_3O_4@CdS photocatalyst derived from cobalt foam for high-efficiency visible-light H_2 evolution

Chao Zhang,[a, b, c] Baoquan Liu,[a] Weiping Li,[a] Xiangxue Liu,[a] Ke Wang,[a]
Yifeng Deng,[a] Zhenmei Guo,[a] and Zhiguo Lv[a, *]

a. State Key Laboratory Base for Eco-chemical Engineering, Key Laboratory of Multiphase Flow Reaction and Separation Engineering of Shandong Province, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

b. Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, Guangxi University, Nanning 530004, China

c. Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

Corresponding Author: Zhiguo Lv

E-mail: lvzhiguo@qust.edu.cn

---

[*] Corresponding author: Zhiguo Lv
E-mail: lvzhiguo@qust.edu.cn

Chemicals and materials.

All the reagents were of analytical grade and used without further purification. All experiments used deionized (DI) water. Cobalt foam was purchased from Taobao. Hydrochloric acid was purchased from Yantai far east fine chemical Co., Ltd. Ethyl alcohol was purchased from Tianjin fuyu fine chemical Co., Ltd. DETA (diethylenetriamine) and thioacetamide were purchased from Shanghai Macklin Biochemical Co., Ltd. Cadmium chloride was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Experimental

Preparation of photocatalyst

Preparation of Co_3O_4: Firstly, the CF (1 × 2 cm) was treated with 1 M HCl solution in the ultrasound system for 30 min. Secondly, the CF was washed with deionized water and ethyl alcohol in turn, and then dried at 80℃ under vacuum. Finally, the pre-treated CF was treatment at high-temperature processing in muffle furnace at 550℃ for 6 h under the atmospheric to get the Co_3O_4 black powder.

Preparation of H-Co_3O_4@CdS: H-Co_3O_4@CdS compound was synthesized *via* a facile one-step oil bath method. Briefly, 0.375 mmol $CdCl_2$ and 2.5 mmol thioacetamide were dissolved in 12 mL deionized water under ultrasonic treatment. Subsequently, 48 ml DETA (diethylenetriamine) was added to form a yellow-green solution. After mixing the above solution evenly, the mixed solution was transferred into 100 ml round-bottom flask and react at 80℃ for 6 h under constant agitation. After that, the prepared Co_3O_4 black powders were added and the reaction continued for 6 h. The end product was collected by centrifugation, washed with deionized water and ethanol, and dried at 60℃. As comparison, the Co_3O_4 dosage was adjusted to 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g. And the corresponding production was named as H-Co_3O_4@CdS-1, H-Co_3O_4@CdS-2, H-Co_3O_4@CdS-3, H-Co_3O_4@CdS-4, H-Co_3O_4@CdS-5 and H-Co_3O_4@CdS-6, respectively.

Preparation of CdS: CdS was prepared *via* a simple Oil Bath method. Firstly, $CdCl_2$ (0.0687g), thioacetamide (0.1876g), deionized water (12 mL) and DETA (48 mL) were added into a round-bottom flask. Then the mixture was stirred 15 min at room temperature. The round-bottom flask was installed in oil bath pan equipment and heated at 80℃ for 12 h. Finally, the yellow products were centrifuged, washed with deionized water and ethyl alcohol repeatedly and dried at 60℃.

Preparation of Co_3O_4/CdS. In a typical procedure, Co_3O_4 (0.2g) and a certain amount of CdS (0.0687g $CdCl_2$ and 0.1876g thioacetamide, oil bath, 80℃, 12h) was dissolved in 80 mL of deionized water, followedby, the mixed solution was maintained at 80℃ for 12 h under magnetic stirring, then cooled to room temperature.

The mixture was collected and washed with absolute alcohol and deionized water in sequence. Lastly, the final product was dried in vacuum at 60℃ for 6 h.

Photocatalytic measurement experiment

The H_2 evolution rate of all photocatalysts was researched on CEL-PAEM-D6 (Beijing CEAULIGHT). Typically, 20 mg of photocatalyst was dispersed into homogenous solution, which contained 40 ml deionized water and 10 ml triethanolamine. Then the solution was poured into a sealed quartz reaction cell and absolutely vacuumed for 1 hour in order to get rid of the interference terms. Using 300 W Xe-lamp with different cut-off filters as the light source. The photogenerated hydrogen was determined by an online gas chromatograph (GC-7920, Beijing CEAULIGHT). The apparent quantum yield (AQY) of H_2 production of all samples was tested by the same photocatalytic condition except cut-off filters was replaced by bandpass filters (420 ± 10 nm). The value of AQY was calculated by the following formula:

$$\begin{aligned}\mathrm{AQ}Y(\%) &= \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{\text{Number of evolved } \mathrm{H_2} \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\end{aligned}$$

Characterization.

The morphologies of samples were observed by Scanning electron microscopy (SEM, Hitachi S-4800). The crystal structure of all samples was recorded by X−ray diffraction (XRD) on ULTIMA IV (Rigaku Corporation) with Cu-Kα radiation, the range of 2 Theta from 10 to 90°, 40 kV of rated voltage and 40 mA of rated current. The Fourier transform infrared spectra (FT-IR) researched the chemical structure and performed on Nicolet IS10 (America). The X-ray photoelectron spectra (XPS) measurements were carried out using Thermo ESCALAB 250 instruments (USA) with non-monochromatic Al Kα 1486.6 radiation. The photoluminescence (PL) spectroscopy was measured using fluorescence spectrometer (Shimadzu RF-5301) at the excitation wavelength of 320 nm. The specific surface area was determined from the linear part of the BET equation (P/P_0 =0.05–0.25). The pore size distribution was derived from the desorption branch of the N_2 isotherm using the Barrett–Joyner–Halenda (BJH) method. UV-vis absorption spectra analysis was performed using a Shimadzu UV 3600 spectrometer. In photoelectrochemical measurements, $MgSO_4$ solution was used as electrolyte and the tests were performed by switching visual light ON/OFF with a duration of 30 s in a typical three-electrode cell.

DFT Calculations detail

The density functional theory (DFT) calculation was carried out using the Cambridge serial total energy package (CASTEP) code, in which a plane wave basis set was used. The model was established by the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) functional. The cutoff energy of the OTFG ultrasoft pseudopotential was 571.40 eV. The Brillouin zone integration was performed using 3×2×1 k-point sampling through all the computational process. Geometric convergence tolerances with maximum force and maximum displacement was 0.03 eV/Å and 10^{-3} Å. Self-consistent field (SCF) tolerance with high accuracy of 10^{-6} eV/atom for energy convergence.

The d band center (ε) was calculated based on the following equation:

$$\varepsilon = \frac{\int_{-\infty}^{\infty} \rho(x) x dx}{\int_{-\infty}^{\infty} \rho(x) dx}$$

where ρ(x) is the PDOS at the energy of x.

The detailed information about the structural model used in the DFT calculations as follow:

1. Co_3O_4 was cut with (311) surface, and CdS was cut with (002) surface.

2. The lattice parameters of H-Co_3O_4@CdS: a 9.349466Å, b 14.281718Å, c 30.000Å.

   α 90°, β 90°, γ 98.38933°.

3. The thickness of slab is 2 layers.

4. The matching between two surfaces is 92.15642%.

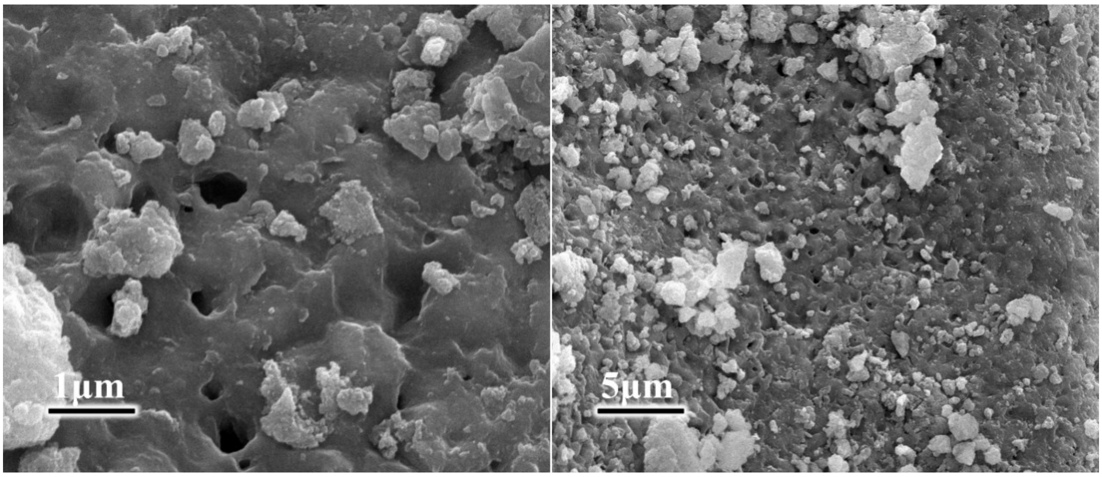


Fig. S1 SEM images of the H-Co_3O_4@CdS-3 samples.

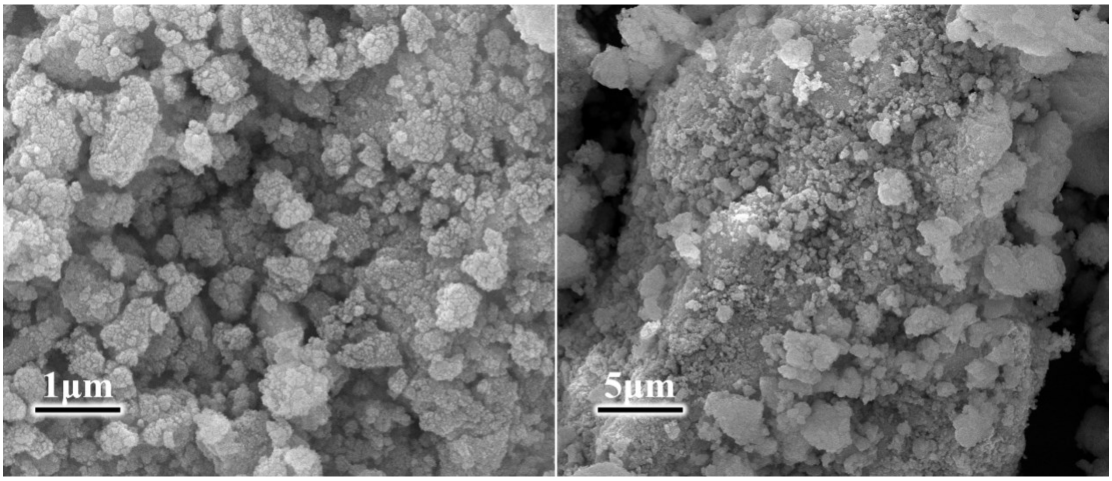
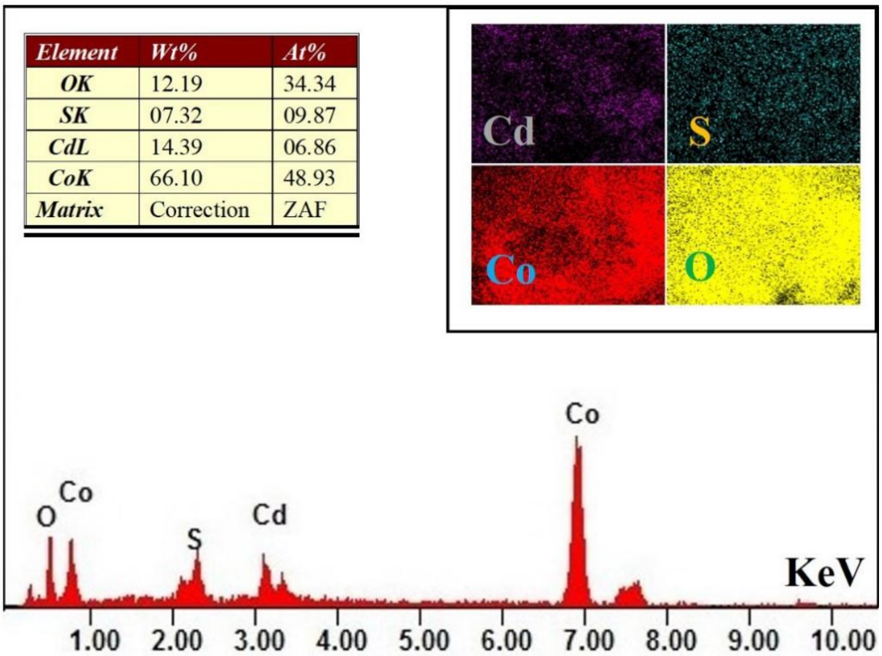


Fig. S2 SEM images of the H-Co_3O_4@CdS-5 samples.



Element	*Wt%*	*At%*
OK	12.19	34.34
SK	07.32	09.87
CdL	14.39	06.86
CoK	66.10	48.93
Matrix	Correction	ZAF

Fig. S3 EDS analysis and the element mapping results of the H-Co_3O_4@CdS-4 sample.

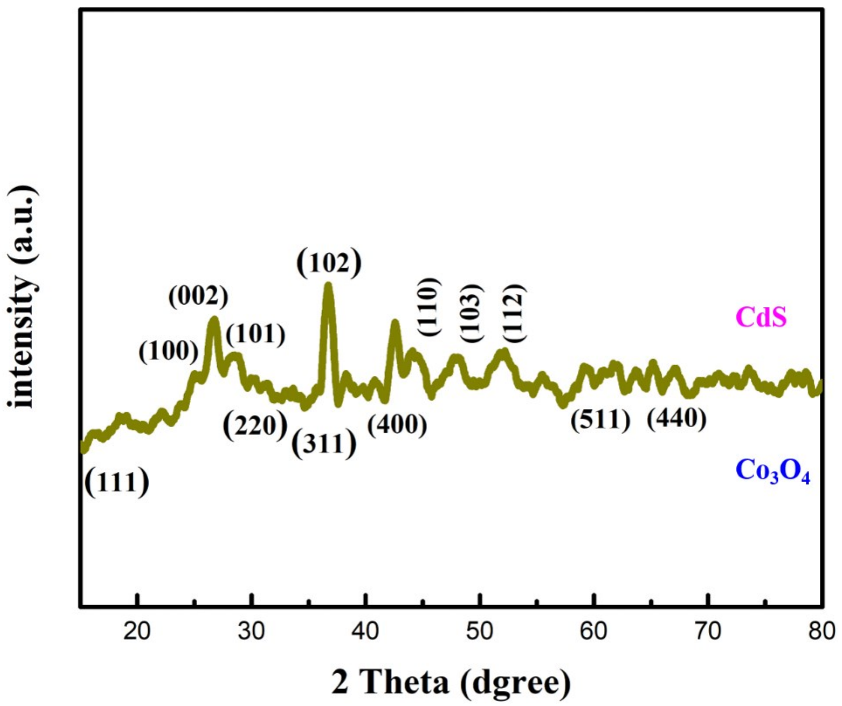


Fig. S4 XRD of the optimal Co_3O_4/CdS.

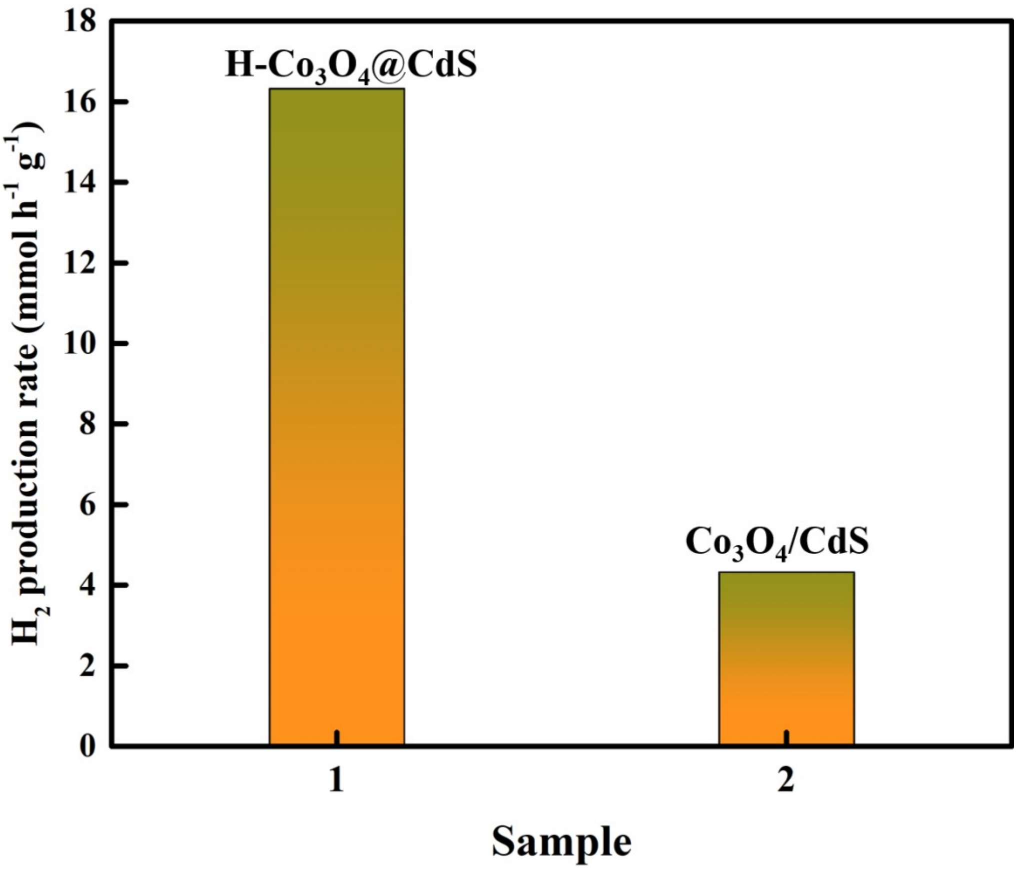


Fig. S5 The hydrogen production performance of H-Co$_3$O$_4$@CdS and Co$_3$O$_4$/CdS.

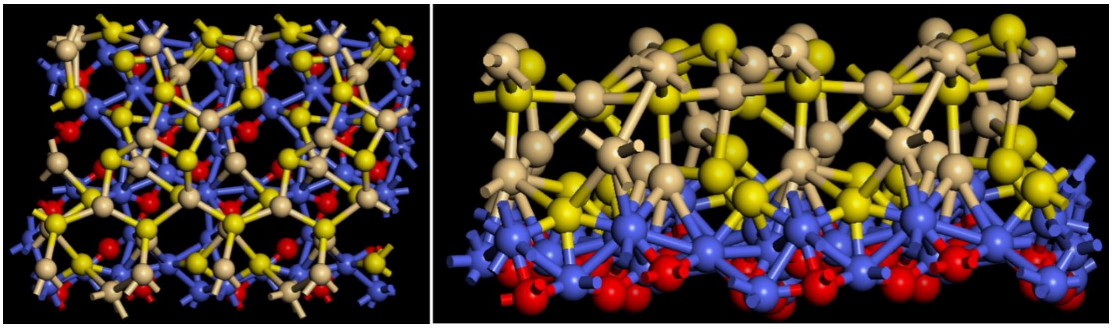


Fig. S6 The optimized model of Co_3O_4@CdS heterojunction.

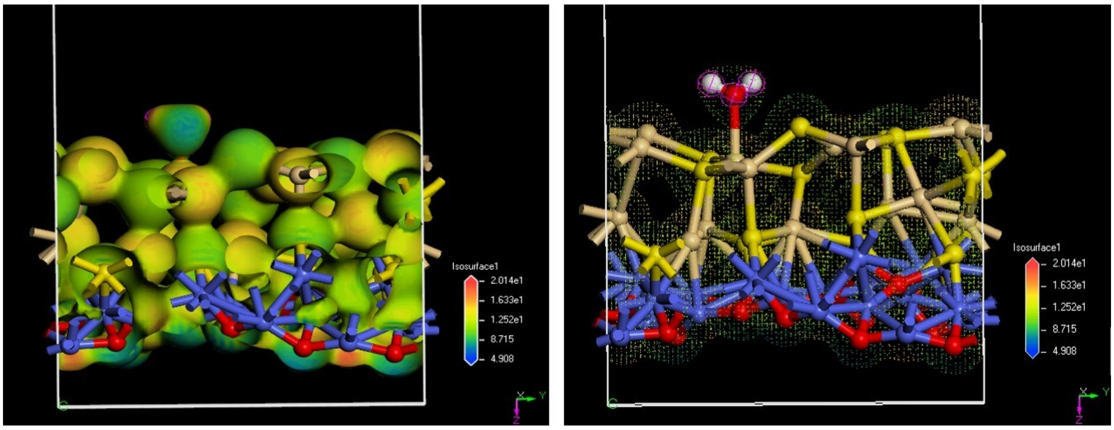


Fig. S7 The electrostatic potential of H-Co_3O_4@CdS-H_2O model.

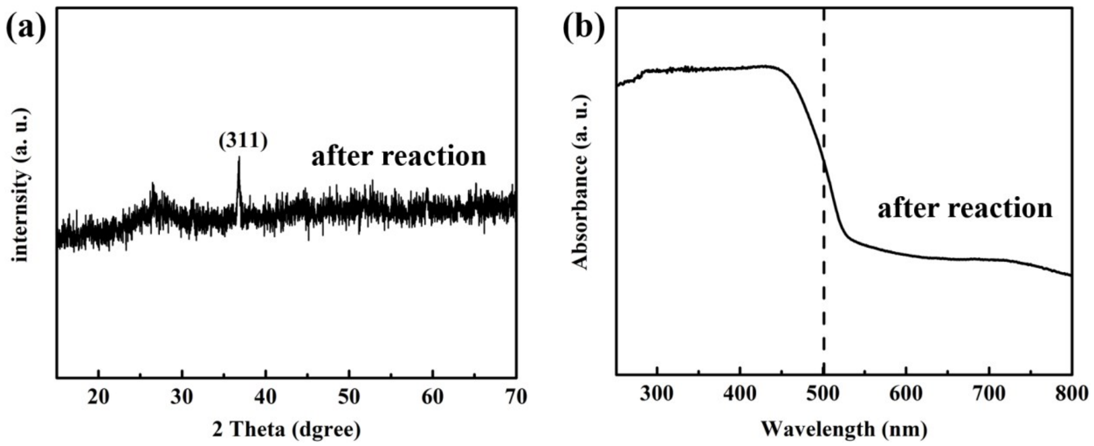


Fig. S8 (a) XRD and (b) UV-diffuse reflection spectra of H-Co_3O_4@CdS-4 (after photocatalytic reaction).

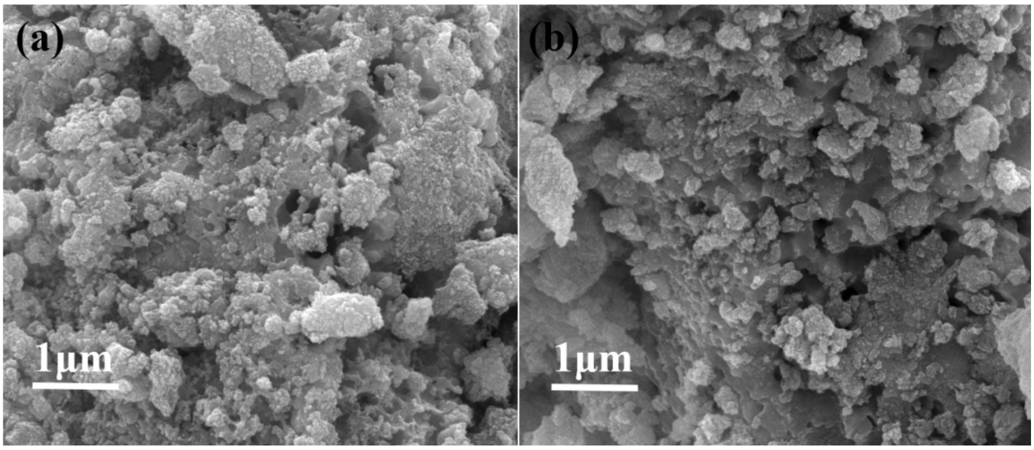


Fig. S9 (a) (b) SEM of H-Co_3O_4@CdS-4 (after photocatalytic reaction).

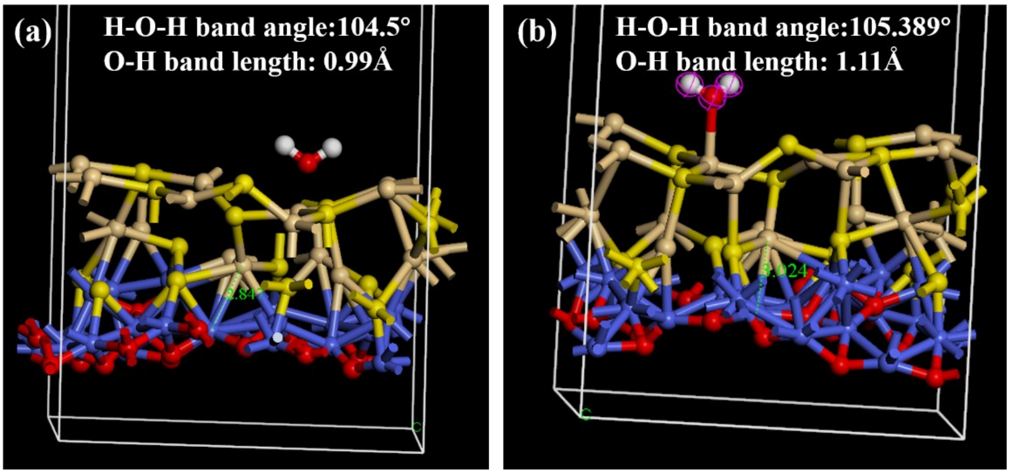


Fig. S10 The bond length and bond angle information of free H_2O and absorbed H_2O in Co_3O_4@CdS-H_2O model.

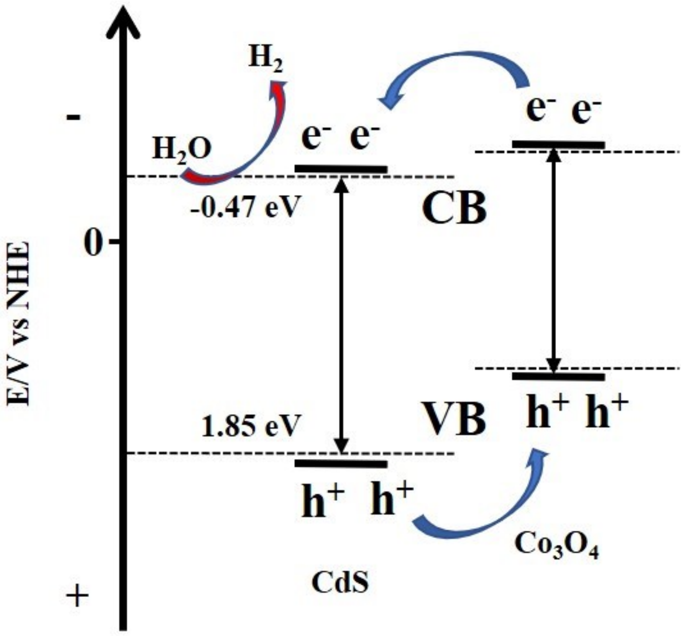


Fig. S11 The band structure diagram and H_2 evolution mechanism.[1, 2]

We labeled two different O-H bonds, O-H_1 and O-H_2. In the process of water splitting, the O-H_1 bond was more likely to break, resulting in H^* in the whole system.

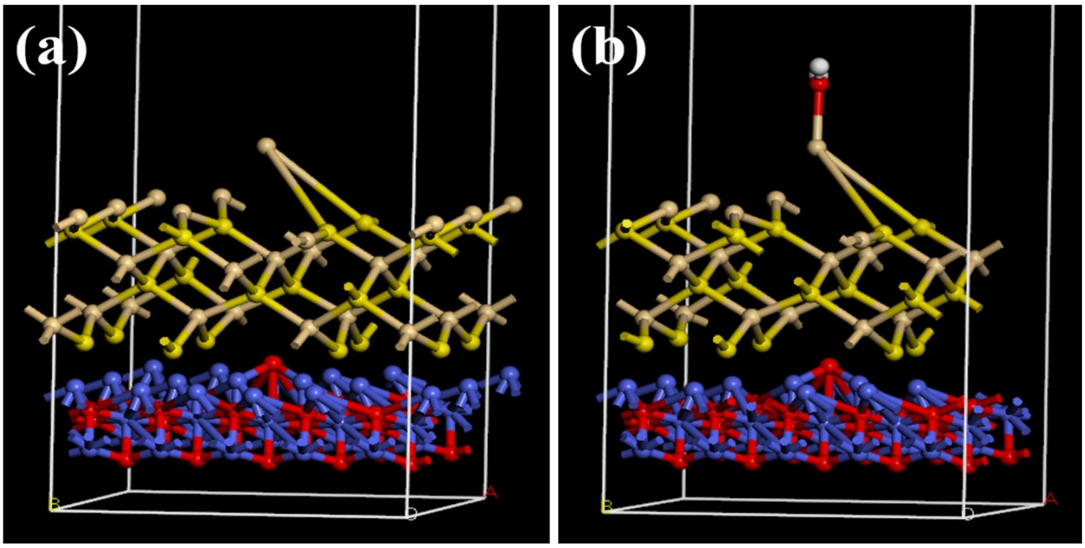


Fig. S12 The optimized models of Co_3O_4@CdS* (three layers) and Co_3O_4@CdS*-H_2O (three layers) heterojunction.

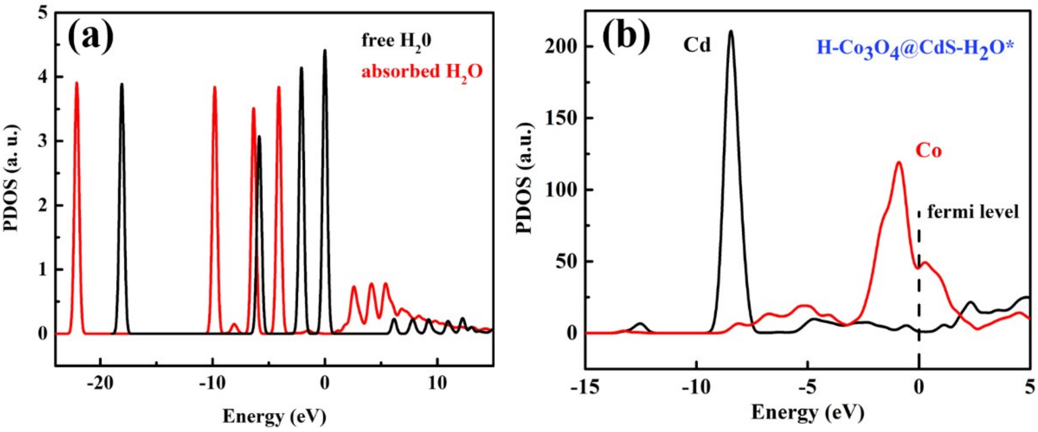


Fig. S13 PDOS of free H_2O and absorbed H_2O, (b) PDOS of d-orbitals (Cd and Co model) in H-Co_3O_4@CdS*(three layers).

References

1. T. Yu, Z. Li, Z. Lv, X. Liu, G. Wang, G. Xie, L. Jiang, *Appl. Surf. Sci.*, 2020, **509**, 145371.
2. J. Chu, G. Sun, X. Han, X. Chen, J. Wang, W. Hu, I. Waluyo, A. Hunt, Y. Du, B. Song, P. Xu, *Nanoscale*, 2019, **11**, 15633-15640.