Supporting Information

Noble-metal-free CdS decorated porous Ni_xCo_{1-x}O skeleton derived from

metal-organic framework for efficient visible-light H₂ production

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Chemicals and materials

All the reagents were of analytical grade and used without further purification. All experiments used deionized (DI) water. Nickel chloride hexahydrate (NiCl₂·6H₂O; 99.9%) and cobalt chloride hexahydrate (CoCl₂·6H₂O; 99%) were purchased from Tianjin hengxng chemical reagent manufacturing Co., Ltd. 1,4-dicarboxybenzene was purchased from was purchased from Shanghai Macklin Biochemical Co., Ltd. Dimethyl formamide (DMF) and triethylamine were purchased from Tianjin fuyu fine chemical Co., Ltd. Cadmium chloride and sodium thiosulfate pentahydrate were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

Characterization

The morphologies of samples were observed by Scanning electron microscopy (SEM, Hitachi S-4800) and Transmission Electron Microscopy (TEM, JEM 2100F, JEOL). 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 Ka 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/P₀ =0.05-0.25). The pore size distribution was derived from the desorption branch of the N₂ isotherm using the Barrett–Joyner–Halenda (BJH) method. UV-vis absorption spectra analysis was performed using a Shimadzu UV 3600 spectrometer. In photoelectrochemical measurements, MgSO₄ 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.

Comparing experimental

1、 NiCl₂ (1.189 g, 4.86 mmol) and CoCl₂ (2.312 g, 9.72 mmol) were dissolved in 40 mL of DMF. In a separate bottle, 2,5-dihydroxyterephthalic acid (0.24 g, 1.215 mmol) and PVP (4 g) were also dissolved in 40 mL of DMF. Then, the above two solutions were mixed and transferred into a stainless steel-lined Teflon autoclave and heated at 100 °C for 24 h. After cooling to room temperature, the resulting precipitate was collected and thoroughly washed with methanol for at least three times. Finally, the NiCo-MOF sample was obtained after drying at 60 °C for 24 h.

 $2 \$ 375 mg Ni(NO₃)₂·6H₂O, 375 mg Co(NO₃)₂·6H₂O and 175 mg hexamethylenetetramine (HMT) were dissolved into 200 mL 0.7 mM trisodium citrate solution. Then 50 mg sulfonated PNTs were dispersed into the above solution by sonication for 30 minutes. The reaction mixture was then transferred into a 500 mL round bottom flask. After stirring for 6 h at 90 °C, the flask was left to cool down to room temperature. The green precipitate was collected by centrifugation, washed thoroughly with ethanol, and dried at 60 °C overnight.

3, First, 1 mmol of Ni(NO₃)₂·6H₂O, 1 mmol of Co(NO₃)₂·6H₂O, and 15 mmol of urea were dissolved in deionized H₂O (40 mL), generating an intermediate complex. The obtained solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, which was heated to 200 °C and the temperature was maintained for 12h.

The DFT calculation

The density functional theory calculation was carried out using the Cambridge serial total energy package code, using the generalized gradient approximation. The Perdew–Burke–Ernzerhof functional was used to model the exchange and correlation interactions. A cutoff energy of 340 eV was used in the Vanderbilt ultraso pseudopotential process. Geometric convergence tolerances were set for the maximum force at 0.03 eV Å⁻¹, maximum energy change at 10⁻⁵ eV per atom,

maximum displacement at 0.001 Å and maximum stress at 0.5 GPa. Density mixing electronic minimisation was performed, and the self-consistent field tolerance was set to "fine" with a high accuracy of 10^{-6} eV per atom for energy convergence. Besides, the water adsorptions energies were calculated as follows: $E_{ads} = E_{adsorbate/slab}-E_{adsorbate}-E_{slab}$.

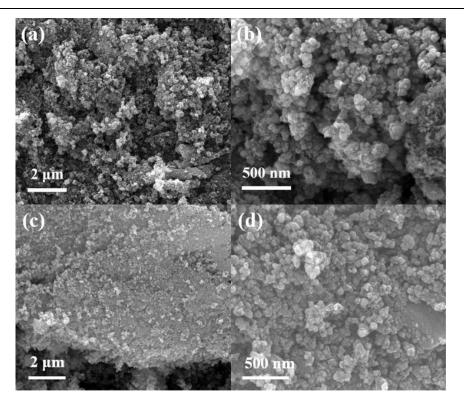


Figure S1. (a) and (b) SEM images of NiCo-MOF, (c) and (d) SEM images of Ni_xCo_{1-x}O.

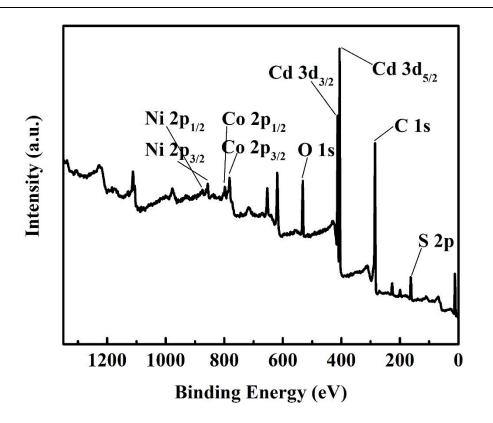


Figure S2. The XPS spectra of the CdS@NixCo1-xO (survey).

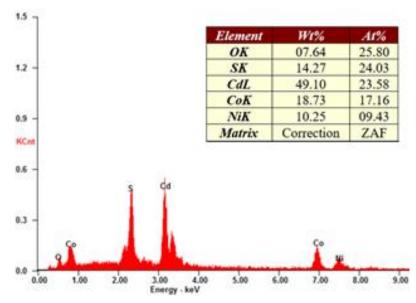


Figure S3. The EDS of the CdS@Ni_xCo_{1-x}O-4.

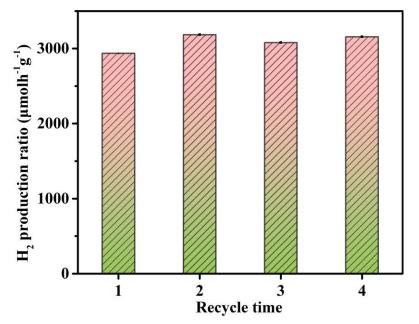


Figure S4. Photocatalytic stability test of CdS@Ni_xCo_{1-x}O under visible-light irradiation of λ >400 nm.

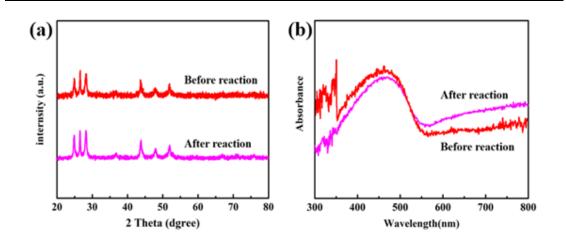


Figure S5. (a) XRD and (b) UV-diffuse reflection spectra of CdS@Ni_xCo_{1-x}O (before and after reaction).