Supplementary Information (SI) for Catalysis Science & Technology.

Hierarchical hollow UiO-66-NH_2/CdS heterostructure with synergistic mass transport and charge separation for enhanced photocatalytic hydrogen production

Yongling Liu, Zhaohui Huang, Senlin Zhang, Ruoning Zhan, Yingxinjie Wang, Xiuqiang Xie, and Nan Zhang*

[†] *College of Materials Science and Engineering, Hunan University, Changsha 410082, China*

[*]Corresponding author, E-mail: nanzhang@hnu.edu.cn (Nan Zhang)

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I. Experimental Section

Chemicals and Materials

All chemical reagents were obtained from commercial suppliers and used as received without further purification. Cadmium chloride hemipentahhydrate ($CdCl_2 \cdot 2.5H_2O$, 98%), elemental sulfur (S_8), N, N-dimethylformamide (DMF, analytical grade), acetic acid (CH_3COOH, AR), propionic acid (CH_3CH_2COOH, AR), acetonitrile (CH_3CN, AR), triethanolamine (TEOA, AR), and ethanol (C_2H_5OH, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Zirconium(IV) chloride ($ZrCl_4$, 98%) was acquired from Aladdin Industrial Inc., and 2-amino terephthalic acid (H_2ATA) was obtained from Shanghai Dibai Biotechnology Co., Ltd.

Synthesis of S-UiO-66-NH$_2$

The S-UiO-66-NH$_2$ was synthesized through an oil-bath-assisted solvothermal method. Typically, $ZrCl_4$ (233.1 mg, 1 mmol) and 2-amino terephthalic acid (181.2 mg, 1 mmol) were dissolved in 60 mL of DMF containing 6 mL of acetic acid as a structural modulator. The reaction mixture was transferred to a 100 mL round-bottom flask and maintained at 120° C for 24 h under continuous magnetic stirring in a silicone oil bath. After cooling to room temperature naturally, the resulting yellow crystalline product was collected by centrifugation at 8000 rpm for 5 min, followed by sequential washing with deionized water and anhydrous methanol (three cycles each) to remove unreacted precursors. The purified product was finally dried overnight in a vacuum oven at 60°C.

Synthesis of W-UiO-66-NH$_2$

W-UiO-66-NH$_2$ was prepared following a modified literature procedure. In brief, equimolar amounts of $ZrCl_4$ (233.1 mg, 1 mmol) and 2-amino terephthalic acid (181.2 mg, 1 mmol) were dissolved in a binary solvent system comprising acetic acid and deionized water (2:3 v/v). The mixture was maintained at 90° C with constant stirring for 24 h. The resulting product was isolated by centrifugation, thoroughly washed with deionized water and methanol (three cycles each), and vacuum-dried at 60°C overnight.

Synthesis of H-UiO-66-NH$_2$

The hierarchical H-UiO-66-NH$_2$ was obtained through acid etching of W-UiO-66-NH$_2$. Specifically, 500 mg of W-UiO-66-NH$_2$ was dispersed in 56 mL of a deionized water/propionic acid mixture (4:3 v/v) and stirred at 100° C for 12 h. The etched product was collected by centrifugation, washed repeatedly with deionized water and methanol, and dried under vacuum at 60° C.

Photodeposition of CdS

CdS was photodeposited on the X-UiO-66(NH_2) frameworks (X = S, W, H) through a light-driven process. In a typical procedure, 100 mg of X-UiO-66(NH_2) was dispersed in 26 mL of ethanol containing 12 mg S_8 and 91 mg $CdCl_2{\cdot}2.5H_2O$ (molar ratio 1:1). The suspension was purged with nitrogen for 30-60 min to establish an oxygen-free environment prior to illumination. Subsequently, the mixture was irradiated under Full-spectrum light ($\lambda \geq 200$ nm) using a 300 W Xe lamp with a 420 nm cutoff filter for controlled durations (10, 20, 30, and 60 min) to investigate the deposition kinetics.

Materials Characterization

The crystalline structure of synthesized materials was characterized by X-ray diffraction (XRD, X'Pert Pro, Philips) using Cu Kα radiation ($\lambda = 1.5406$ Å) with a Ni filter. Measurements were performed in Bragg-Brentano geometry with a 2θ range of 3-90° at a scanning rate of 10°/min. Fourier transform infrared spectroscopy (FT-IR) and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses were conducted on a Nicolet iS50 spectrometer (Thermo Fisher) equipped with a mercury cadmium telluride (MCT) detector. Elemental composition was determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 730). Optical properties were evaluated using UV-vis diffuse reflectance spectroscopy (DRS) on a Shimadzu UV-2600 spectrophotometer with an integrating sphere attachment. All electrochemical measurements were performed using a CHI 660E workstation (Chenhua Instruments).

Electrochemical and Photoelectrochemical Characterization

Electrochemical properties were evaluated using a standard three-electrode configuration in a quartz cell containing 40 mL of 0.2 M Na_2SO_4 electrolyte. A platinum plate (1 cm^2) served as the counter electrode, with Ag/AgCl (3 M KCl) as the reference electrode. Working electrodes were prepared by depositing catalyst inks onto fluorine-doped tin oxide (FTO) glass substrates. The FTO substrates (1 × 2 cm) were pre-cleaned by ultrasonication in ethanol for 30 min and dried at 60°C. A 0.25 cm^2 active area was defined using masking tape, onto which 50 μL of catalyst ink (5 mg sample in 1 mL DMF, sonicated for 30 min) was drop-cast. After air-drying, exposed conductive areas were insulated with epoxy resin. Photoelectrochemical measurements employed a 300 W Xe lamp (PLS-SXE300E, PerfectLight) with an AM 1.5G filter. Electrochemical impedance spectroscopy (EIS) was performed at open-circuit potential with a 10 mV amplitude from 100 kHz to 0.1 Hz. Mott-Schottky analysis was conducted at 1 kHz with a 10 mV AC amplitude. Linear sweep voltammetry (LSV) and chronoamperometry measurements were recorded at a 10 mV/s scan rate.

Photocatalytic Hydrogen Evolution

The photocatalytic hydrogen production experiments were conducted in a gas-closed circulation system (Labsolar-6A, PerfectLight) equipped with a 300 W Xe lamp and 420 nm cutoff filter. In a standard test, 2 mg photocatalyst was dispersed in 11 mL of aqueous solution containing deionized water (1 mL), acetonitrile (8 mL), and triethanolamine (2 mL) as a sacrificial agent. The suspension was degassed by argon purging for 30 min prior to illumination and maintained under continuous magnetic stirring during irradiation. Evolved hydrogen was quantified by gas chromatography (Shimadzu GC-2014) equipped with a 5 Å molecular sieve column and thermal conductivity detector (TCD), using argon as carrier gas. For stability tests, the catalyst was recovered after 2 h reaction cycles by centrifugation, washed thoroughly with acetone, and dried at 60°C under vacuum before reuse. Catalyst loss was compensated by adding fresh material to maintain constant loading.

Calculation of Apparent Quantum Yield of Syngas Production: The apparent quantum yield (AQY) is calculated. Monochromatic lights with wavelengths of 365, 450, 500, and 605 nm are used for irradiation for 2 h. The distance between the reactor and the light source is 8 cm during the photocatalytic process. The light intensity was measured using a calibrated portable optical power meter. The evolved hydrogen was quantified by gas chromatography and converted into the number of hydrogen molecules. The composition of the reaction solution and the catalyst loading were consistent with those used in the photochemical activity tests. The AQY value is calculated based on the following equations:

$$\mathrm{N} = \frac{I \times \mathrm{A} \times \mathrm{t} \times \lambda}{h \times c}$$

$$\mathrm{AQY} = \frac{2 \times \text{the number of evolved } hydrogen \text{ molecules}}{\mathrm{N}} \times 100\%$$

Where I is the measured light intensity of monochromatic light, A is the illumination area (3.92×10^{-4} m^2), t is the illumination time (7200 s), h is the Plank constant (6.62×10^{-34} J·s), c is the light speed (3×10^{8} m/s), and λ is the monochromatic light's wavelength, and 2 represents the number of consumed electrons of photolysis of water for the formation of hydrogen.

I. Results and Discussion

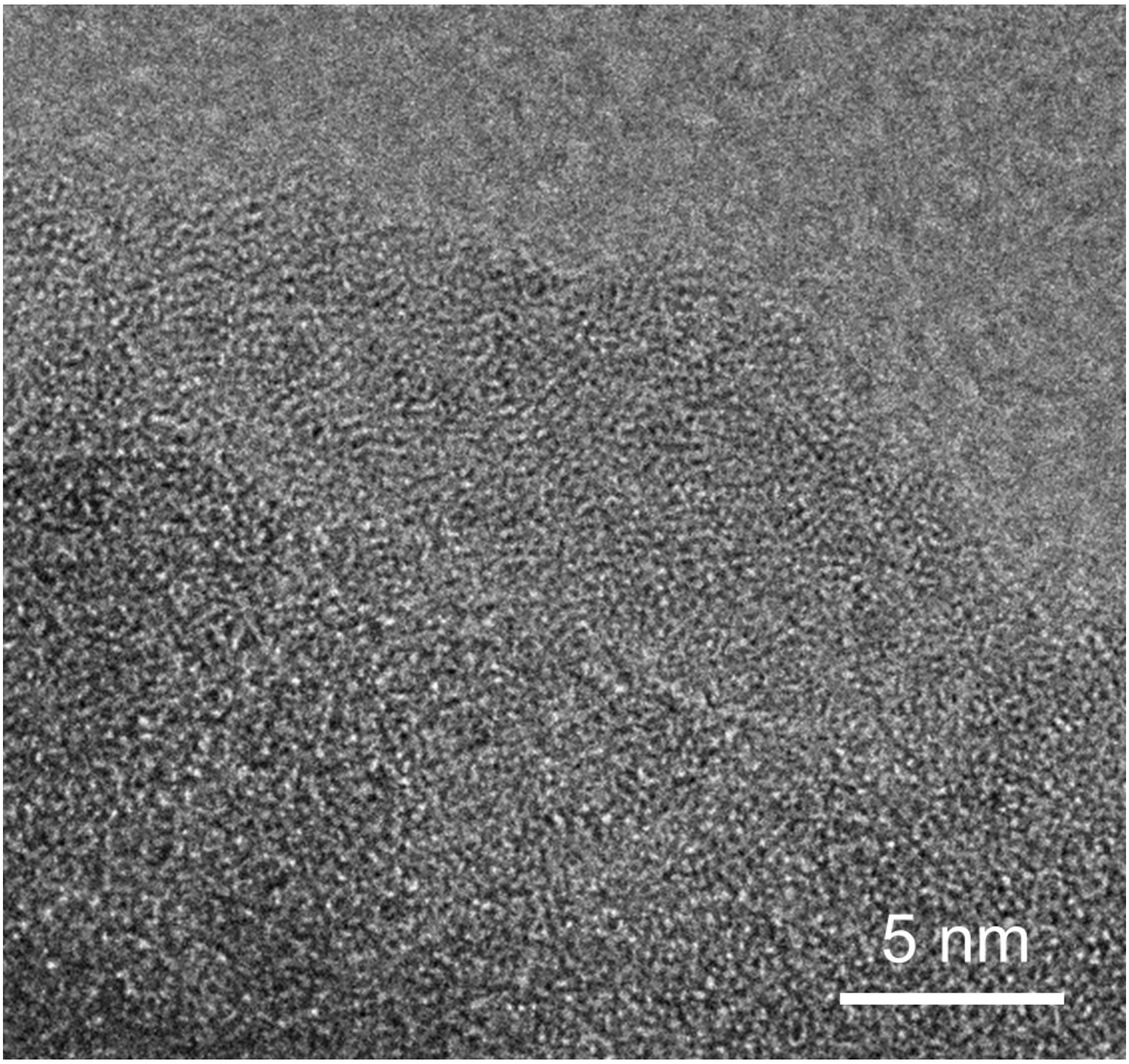

Fig. S1. HRTEM images of H-UiO/CdS-20min.

Supplementary Note: HRTEM analysis reveals no discernible lattice fringes corresponding to either UiO-66-NH_2 or CdS, indicating the poor crystallinity of both components and suggesting that CdS is not deposited as discrete nanoparticles or quantum dots.

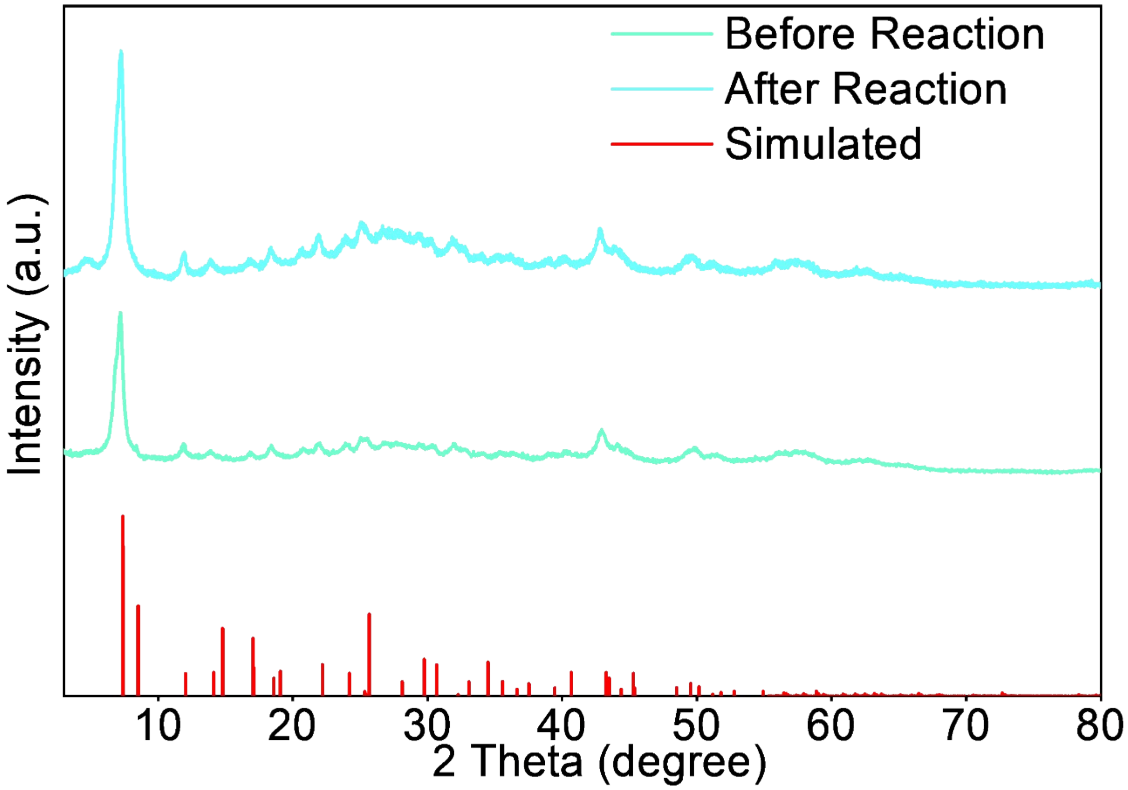

Fig. S2. XRD patterns of H-UiO/CdS-20min before and after photocatalysis reaction.

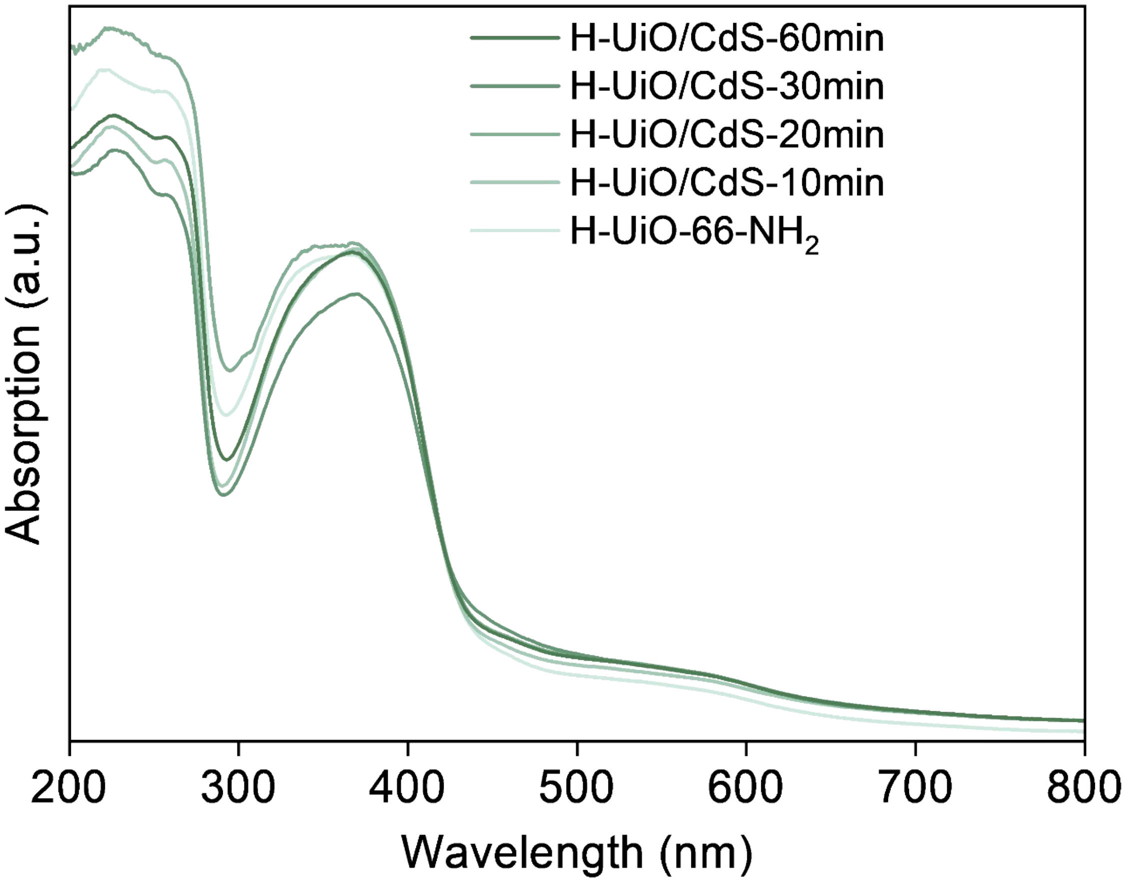

Fig. S3. DRS spectra of H-UiO/CdS with different deposition times.

Supplementary Note: Prolonged deposition durations do not induce significant variations in light absorption characteristics across the H-UiO/CdS series. This observation manifests through three key spectral features: (1) nearly identical absorption edge positions, and (2) consistent line shapes without new absorption peaks emerging. These results indicate that while CdS loading amounts increase with deposition time, the fundamental light-harvesting properties remain essentially unchanged.

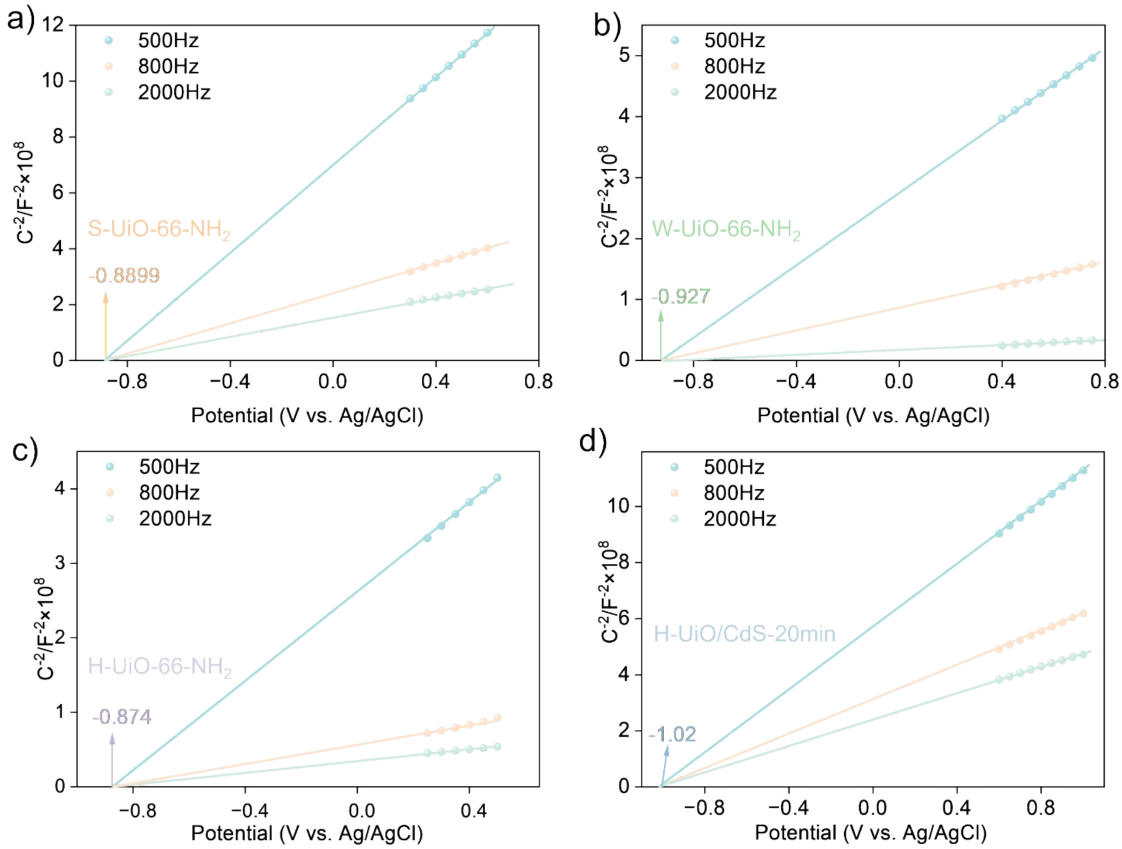

Fig. S4. Mott-Schottky plots of a) S-UiO-66-NH$_2$, b) W-UiO-66-NH$_2$, c) H-UiO-66-NH$_2$ and d) H-UiO/CdS-20min.