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1. Introduction

Nowadays, pollution degradation and energy production have become major problems that should be solved to meet the energy crisis and environmental issues.^{1–3} Among other energy sources, solar energy is a highly abundant and environmentally clean energy source. Consequently, light-driven technologies such as photocatalytic hydrogen production by water splitting and pollutant photodegradation have attracted great attention.^{4–6} Generally, efficient photocatalysts for both of these processes need to absorb light in the full range of the solar spectrum and to rapidly separate photo-produced electrons (e) and holes (h).^{7–9} Visible light accounts for about 43% of the total solar spectrum

A hierarchical hollow Pt@H-UiO-66-NH₂/CdS ternary catalyst for efficient visible light prompted photocatalysis[†]

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Metal–organic frameworks (MOFs) have great potential for producing photoelectrocatalyzed hydrogen and degrading pollutants, owing to several factors such as high porosity and tunable semiconductor-like properties. Wide band gaps, which restrict their use to only UV light induced reactions, and low efficiencies for the separation of photogenerated charge carriers (electrons and holes) pose significant challenges to the widespread applications of MOFs. In this study, a hierarchical hollow Pt@H-UiO-66-NH₂/CdS ternary catalyst was designed and synthesized. The immobilized CdS nanoparticles (NPs) in this catalyst endow the MOF H-UiO-66-NH₂ with high visible light absorption ability and the Pt NPs serve as electron sinks to improve charge carrier separation. Furthermore, the hierarchical hollow structure of H-UiO-66-NH₂ in the composite contributes to boosting light absorption and shortening the distance for charge transfer. As a proof of principle, Pt@H-UiO-66-NH₂/CdS catalyzes methylene blue (MB) degradation with a high rate constant of 1.025×10^{-2} and hydrogen production with a rate of 12810μ mol g⁻¹ h⁻¹, the latter of which is about 2.3, 11.7 and 173 times higher than those of Pt@UiO- $66-NH_2/CdS$, H-UiO-66-NH₂/CdS and Pt@H-UiO-66-NH₂, respectively.

while UV light constitutes only 4%. Therefore, by extending their light absorption capabilities into the visible region, photocatalysts will have significantly improved water splitting and pollutant photodegradation performances.^{10,11} Moreover, photocatalysts with enhanced activities must have high rates of separation of the photogenerated electrons and holes for participation in subsequent redox reactions.^{12,13} Though significant progress has been made, developing new photocatalysts that have enhanced visible light absorption and charge carrier separation is still a highly challenging task.

Metal-organic frameworks (MOFs), a class of crystalline porous materials composed of metal ions/clusters and organic ligands,¹⁴ have great potential for use in photocatalytic processes. The relevant properties that make MOFs attractive for this purpose include: (1) large surface areas and high porosities that cause exposure of numerous active sites, facilitated substrate transport and accelerated photogenerated e-h separation, (2) crystalline structures that lead to greatly suppressed charge carrier recombination and (3) frameworks that enable flexible positioning of photosensitizers or cocatalysts to enhance photocatalytic performances.¹⁵⁻¹⁹ However, most MOFs have high energy conduction bands (CBs) and low energy valence bands (VBs) that translate into wide band gaps. Although wide band gaps are important for enhancing the redox abilities of charge



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carriers in order to promote direct oxidation of some pollutant dyes, they restrict light absorption to the UV region, a property that limits solar energy utilization.^{20,21}

A variety of studies targeted at expanding visible light absorption propensities and mitigating charge carrier recombination have focused on complexing MOFs with semiconductors that absorb light in the visible region and with cocatalysts that act as electron sinks to rapidly capture electrons to create free holes. Among the semiconductors employed for this purpose, cadmium sulfide (CdS) is greatly preferred because of its high visible light absorption ability and band gap (2.4 eV) suitable for H₂ production and pollutant degradation.²²⁻²⁶ Nevertheless, the tendency to form bulk particles, the toxicity of photo-corrosion produced Cd²⁺ and the limited number of surface catalytic sites of single nanoparticles (NPs) have limited direct applications of CdS as a photocatalyst.²⁷⁻²⁹ Therefore, loading highly dispersed CdS NPs on porous MOFs is an approach that we anticipated would not only extend absorption into the visible light region, but also prevent agglomeration of CdS NPs. For example, earlier studies have shown that MOF composites CdS/MIL-53(Fe),³⁰ CdS/Ni-MOF,³¹ and CdS/NH₂-MIL-125(Ti),³² containing a CdS heterojunction have high catalytic activities in visible-light induced H₂ production reactions. Electron sinks like Pt NPs, which have high electron capturing abilities as well as high work functions (5.65 eV for Pt), have been utilized to elevate charge carrier separation and improve photocatalytic activity.33-35 Moreover, owing to the confinement effect of porous MOFs, encapsulated Pt NPs are stabilized and well dispersed.13,36

In addition to the composition modulation strategy, the morphology also plays a vital role in governing photocatalytic efficiencies of MOFs. MOFs with morphologies, such as 2D nanosheets³⁷⁻⁴³ and hollow structures,⁴⁴⁻⁴⁷ have gained extensive attention due to their unique physicochemical properties. In particular, hollow structured MOFs show enhanced photocatalytic performances relative to those of traditional bulk MOFs. The properties responsible for the enhancement include: (1) hollow structures that shorten diffusion pathways of photogenerated charge carriers, (2) multiple reflection sites inside the hollow interior that enhance the use of light and (3) large surface areas and porosities that give rise to more redox active catalytic sites. One example of the enhancement effect of morphology is found in a new H₂ evolution reaction photocatalyst developed by He et al. in which zirconiumporphyrinic MOF hollow nanotubes (HNTMs) are used as anchors for noble metal single atoms. As a consequence of its unique hollow structure, the new catalyst, HNTM-Ir/Pt, has a H₂ production rate (201.9 μ mol g⁻¹ h⁻¹) that is about 6 times higher than that of its bulk counterpart, bulk-Ir/Pt (31.7 $\mu mol~g^{-1}~h^{-1})\!.^{45}$

Guided by the considerations described above, we designed and evaluated a new photocatalyst that is composed of the hierarchical hollow MOF, H-UiO-66-NH₂. This material was prepared using a top-down acid etching strategy starting with the original pristine UiO-66-NH₂, their interiors were adorned with Pt NPs using an *in situ* method and their outer shells were loaded with CdS NPs using a post-supporting technique.



Scheme 1 Illustration of the route used for the synthesis of Pt@H-UiO-66-NH₂/CdS.

We anticipated that the novel hierarchical hollow Pt@H-UiO-66-NH₂/CdS ternary catalyst (Scheme 1) generated in this manner would have an expanded light absorption range owing to the presence of CdS, an accelerated rate of electron-hole transfer and separation caused by electron capture by Pt NPs, and a high number of exposed active sites and decreased charge transfer distances arising from the hollow structure. As described below, Pt@H-UiO-66-NH₂/CdS has a high MB degradation rate constant of 1.025×10^{-2} and a hydrogen production rate of 12 810 µmol g⁻¹ h⁻¹. Furthermore, the photocatalytic performance of Pt@H-UiO-66-NH₂/CdS is maintained for the most part during three hydrogen production cycles, suggesting it is stable.

2. Experimental details

2.1. Chemicals

All chemicals were purchased from commercial sources and used without further purification. Cadmium acetate ($(CH_3COO)_2Cd$, 99.99%) and sodium sulfide nonahydrate ($Na_2S\cdot9H_2O$, 98%) were purchased from Aladdin Industrial Inc; thioacetamide (CH_3CSNH_2 , 99%) was purchased from Innochem; methylene blue (MB, \geq 90%), chloroplatinic acid hexahydrate (H_2PtCl_6 , Pt content \geq 37.5%), 2-aminoterephthalic acid ($CR_4T_7NO_4$, 98%), zirconium tetrachloride ($ZrCl_4$, 98%), acetic acid (CH_3COOH , AR) and propionic acid (CH_3CH_2COOH , AR) were purchased from Macklin Biochemical; sodium sulfite (Na_2SO_3 , 98%), polyvinylpyrrolidone (PVP), ethylene glycol (($CH_2OH)_2$, AR), *n*-hexane (C_6H_{14} , AR), acetone (CH_3COCH_3 , AR), ethanol (CH_3CH_2OH , AR) and methanol (CH_3OH , AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of Pt@UiO-66-NH₂ and UiO-66-NH₂

Typically, 233.1 mg (1 mmol) of $ZrCl_4$ and 181.2 mg (1 mmol) of 2-amino-1,4-benzenedicarboxylic acid (H₂BDC-NH₂) were

dissolved in a mixed solution containing 8 mL of an aqueous dispersion of 3 wt% Pt NPs (the synthesis of Pt NPs is shown in the ESI[†]), 10 mL of deionized water and 12 mL of acetic acid. The mixture was sealed and incubated at 90 °C for 24 h. The product was collected by centrifugation and the precipitate was washed with deionized water and methanol three times, respectively. Finally, the obtained powder, Pt@UiO-66-NH₂, was dried using a vacuum dryer overnight. For comparison purposes, the same procedure was used for the synthesis of UiO-66-NH2 with the exception that Pt NPs were omitted.

2.3. Synthesis of Pt@H-UiO-66-NH2 and H-UiO-66-NH2

Typically, 100 mg of Pt@UiO-66-NH2 was dispersed in an 11 mL mixed solution of 3:4 v/v of propanoic acid and deionized water within a 20 mL glass bottle. The bottle was sealed and incubated at 100 °C for 12 h. The precipitate was collected by centrifugation and washed with deionized water and methanol three times, respectively. Finally, the obtained powder, Pt@H-UiO-66-NH₂, was dried using a vacuum dryer overnight. For comparison purposes, the same procedure was used for the synthesis of H-UiO-66-NH2 except that 100 mg of Pt@H-UiO-66-NH₂ was replaced by 100 mg of UiO-66-NH₂.

2.4. Synthesis of Pt@H-UiO-66-NH2/CdS and Pt@UiO-66-NH2/ CdS

CdS was loaded on MOF-based materials according to the reported method with some modifications.²⁷ Typically, 80 mg of Pt@H-UiO-66-NH2 was added to a solution of 16.2 mg of Cd(CH₃COO)₂·2H₂O in 20 mL of ethanol. Following sonication for 30 min, the suspension was incubated at 80 °C for 10 min. Then, 10 mL of aqueous thioacetamide (TAA, 4.6 mg) was added dropwise to the intensely agitated mixture and incubated at 80 °C for 60 min. The precipitate was isolated by filtration and repeatedly rinsed with deionized water and ethanol three times, respectively. Finally, the obtained powder was dried at 60 °C under vacuum for 12 h. For comparison purposes, the same procedure was used for the synthesis of Pt@UiO-66-NH2/CdS except that Pt@H-UiO-66-NH2 was replaced by Pt@UiO-66-NH2.

2.5. Characterization

The surface morphologies were determined using a field emission scanning electron microscope (FESEM, S-4800, HITACHI) and a transmission electron microscope (TEM, JEOL-2100F). Energy-dispersive X-ray spectra (EDS) and elemental mapping images were collected using an EDAX Genesis spectrometer. Power X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer with Cu-Ka radiation (D8 Advance, Bruker, $\lambda = 1.5418$ Å). N₂ adsorption–desorption isotherms were determined at 77 K using a Tristar II 3020 surface area analyzer on samples that were activated at 120 °C for 12 h before analysis. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were made using a Prodigy7 instrument. For chemical composition determination, X-ray photoelectron spectroscopy (XPS) was performed using a PHI Quantera II spectrometer, (ULVAC-PHI, Japan), and all binding energies were calibrated using the C 1s peak at 284.8 eV.

Photoluminescence spectra (PL) of solid samples were recorded using a F-7000 spectrophotometer. A Shimadzu UV-2700 spectrophotometer and a white standard of BaSO₄ as a reference were employed to generate UV-Vis diffuse reflectance spectra.

2.6. Photocatalytic procedure

Methylene blue (MB) was used as a model pollutant to investigate the photoactivity of the samples. For the MB photodegradation test, 20 mg of catalysts were added into 100 mL of a MB aqueous solution (20 mg L^{-1}). A 300 W xenon lamp (PLS-SXE-300C, Beijing PerfectLight Technology Co., Ltd) was used. The solution was stirred in the dark for 60 minutes until the concentration of MB remained unchanged, indicating that the adsorption of MB in the MOF of the catalyst was saturated. During the photocatalytic reaction, 2 mL of the suspension was taken out every 20 minutes. The catalysts in the suspensions were removed by centrifugation and the supernatant liquids were tested by UV-vis spectroscopy. Photocatalytic H₂ production was performed in a closed circulation system using a PLS-SXE-300C lamp (Beijing PerfectLight Technology Co., Ltd) with UV-vis spectroscopy. 20 mg of the sample was suspended in 80 mL of an aqueous solution (0.1 mol L^{-1} Na₂S, 0.1 mol L^{-1} Na₂SO₃). The mixture was sealed in a quartz vessel and evacuated for 10 min to remove the dissolved oxygen, continuous magnetic stirring during the experiment. The produced H₂ was analyzed using an Agilent 7890 A gas chromatograph (GC) with a thermal conductivity detector (TCD).

2.7. Photoelectrochemical measurements

An electrochemical workstation (Autolab PGSTAT302N) was used to carry out the photoelectrochemical measurements, including the photocurrent tests and electrochemical impedance spectra (EIS). Photocurrent tests were conducted utilizing a conventional three electrode cell consisting of Ag/AgCl (reference electrode), Pt foil (counter electrode) and a working electrode, prepared by drop-casting 25 µL of a suspension containing 5 mg of the photocatalyst in 250 µL of 3:2 v/v DMF and ethanol, on the surface of a fluorine-doped tin oxide (FTO) glass with a covering of approximately 1 cm². The electrolyte was 0.5 mol L^{-1} aqueous Na₂SO₄.

Results and discussion

The pathway used to prepare the hierarchical hollow Pt@H-UiO-66-NH₂/CdS ternary composite is shown in Scheme 1. Briefly, the reaction of Pt NPs, zirconium tetrachloride and 2aminoterephthalic acid in an H2O/acetic acid solution resulted in the formation of Pt@UiO-66-NH2, which was acid etched to produce Pt@H-UiO-66-NH2. The obtained Pt@H-UiO-66-NH2 was then hybridized with CdS to form the ternary target composite, Pt@H-UiO-66-NH2/CdS.

The microstructures and morphologies of all of the MOFbased materials explored here were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1a, UiO-66-NH₂ microcrystals



Fig. 1 SEM micrographs of (a) UiO-66-NH₂, (b) Pt@UiO-66-NH₂, (c) Pt@H-UiO-66-NH₂ and (d) Pt@H-UiO-66-NH₂/CdS. TEM micrograph of (e) Pt@H-UiO-66-NH₂/CdS. HRTEM micrographs of (f) CdS and Pt NPs in Pt@H-UiO-66-NH₂/CdS. (g) and (h) EDS mappings of C, N, Pt, Cd and S. (i) Powder XRD patterns of UiO-66-NH₂, H-UiO-66-NH₂, H-UiO-66-NH₂/CdS, Pt@H-UiO-66-NH₂, Pt@H-UiO-66-NH₂/CdS and CdS. (j) Nitrogen adsorption (filled)–desorption (empty symbols) isotherms of UiO-66-NH₂, H-UiO-66-NH₂, H-

synthesized from ZrCl₄ and H₂BDC-NH₂ under aqueous acid conditions have a rough surface and a well-defined octahedral shape. Moreover, the morphology of Pt@UiO-66-NH₂ is not significantly different from that of UiO-66-NH₂ (Fig. 1b). During acid etching, wrinkles are formed on the surface of Pt@H-UiO-66-NH₂ particles, which have hollow structures (Fig. 1c) evidenced by their broken shells (Fig. S1b, ESI[†]). In Fig. 1e, a TEM image is displayed which shows that the formed Pt@H-UiO-66-NH₂/CdS has not only an octahedral morphology, but also a hollow structure, along with evenly dispersed CdS and Pt NPs. Importantly, the HRTEM image (Fig. 1f) reveals the existence of 0.33 nm and 0.23 nm lattice stripes that are associated with CdS and Pt NPs, respectively. The corresponding EDS element mapping indicates that Cd, S and Pt are homogeneously dispersed within the Pt@H-UiO-66-NH2/CdS particles (Fig. 1g). Analysis of the spatial distributions of pertinent elements (Fig. 1h) shows that Pt is mainly located in the hollow H-UiO-66-NH₂ core region and CdS is positioned on the shell surrounding the core.

The crystallinity and phase purity of all explored materials were determined and confirmed by using powder XRD measurements (Fig. 1i). The diffraction peaks of H-UiO-66-NH₂ match with those of the pristine counterpart, indicating that acid etching has no effect on the crystal structure. The presence of CdS peaks at 26.5°, 43.9° and 52.1° in the diffraction patterns of Pt@H-UiO-66-NH₂/CdS and H-UiO-66-NH₂/CdS shows that CdS NPs are loaded in these materials (9.2 wt% measured by ICP-AES). For comparison purposes, the absence of the Pt diffraction peak in the pattern of Pt@H-UiO-66-NH₂/CdS and Pt@H-UiO-66-NH₂ is probably caused by a low crystallinity of the Pt NPs or low Pt content (0.8 wt% measured by ICP-AES).

The porosities of the materials were evaluated utilizing nitrogen adsorption–desorption isotherms (Fig. 1j). The findings show that UiO-66-NH₂ exhibits a type I isotherm which indicates that it has a microporous structure, while that of H-UiO-66-NH₂ contains a hysteresis loop due to the mesoporous character caused by acid etching. The hysteresis loop in the isotherm of Pt@H-UiO-66-NH₂/CdS indicates that it retains the mesoporous structure of its precursor H-UiO-66-NH₂, indicating that the loading of Pt NPs and CdS has almost no influence on the mesoporous structure of H-UiO-66-NH₂. However, Pt@H-UiO-66-NH₂/CdS has a BET surface area of 351 m² g⁻¹ that is slightly lower than that of H-UiO-66-NH₂ (471 m² g⁻¹) owing to the presence of Pt NPs and CdS (Table S1, ESI[†]).

UV-vis diffuse reflectance spectroscopy (DRS), photoluminescence (PL), transient photocurrent response and electrochemical impedance (EIS) were employed to determine the optical and photoelectrochemical properties of Pt@H-UiO-66-NH₂/ CdS. The UV-vis DRS spectra of the materials are displayed in Fig. 2a. Compared to the pristine MOF H-UiO-66-NH₂, the absorption edge of H-UiO-66-NH2/CdS is at a longer wavelength (500 nm) than before the introduction of CdS, indicating that, as anticipated, CdS enhances the light absorption capacity. In addition, the absorbance of H-UiO-66-NH₂ is higher than that of UiO-66-NH₂, suggesting that the hollow structure improves light scattering and harvesting.46 As expected, compared with the binary composites H-UiO-66-NH2/CdS and Pt@H-UiO-66-NH₂ and the single component H-UiO-66-NH₂, the ternary composite Pt@H-UiO-66-NH2/CdS has a broader absorption edge and increased absorbance owing to the presence of both CdS and the hollow structure.



Fig. 2 (a) UV-vis DRS, (b) photoluminescence (320 nm excitation), (c) transient photocurrent response spectroscopy and (d) EIS Nyquist plots at light of UiO-66-NH₂, H-UiO-66-NH₂, H-UiO-66-NH₂/CdS, Pt@H-UiO-66-NH₂ and Pt@H-UiO-66-NH₂/CdS.

When recombination of photogenerated carriers occurs, energy is released in the form of light emission. Therefore, the magnitude of the PL intensity is a measure of the efficiency of photogenerated carrier separation. As can be seen by viewing the PL spectra in Fig. 2b, H-UiO-66-NH₂ displays less intense emission than does UiO-66-NH2, indicating that the hollow structure enhances the transfer and separation of charge carriers by shortening the charge transfer path. The emission intensity of Pt@H-UiO-66-NH2/CdS is significantly lower than that of UiO-66-NH₂ and the other MOF-based materials, which demonstrates that interactions among the three components at the formed heterojunction greatly enhance the transfer and separation of charge carriers. The results verify that recombination of photogenerated e-h pairs is lowered and charge transfer is increased due to the hollow structure, together with CdS and Pt NPs.

Photocurrent density intensities (Fig. 2c) also follow the same trend (Pt@H-UiO-66-NH₂/CdS > H-UiO-66-NH₂/CdS > $Pt@H-UiO-66-NH_2 > H-UiO-66-NH_2 > UiO-66-NH_2)$, revealing again that the rate of charge carrier transfer in Pt@H-UiO-66-NH₂/CdS benefits from both the ternary heterojunction and the hollow morphology. Electrochemical impedance spectrometry was employed to determine the charge transfer resistance of these materials. As shown in Fig. 2d, the presence of Pt or CdS somewhat reduces the Nyquist radius of Pt@H-UiO-66-NH₂ and H-UiO-66-NH₂/CdS compared to that of the pristine MOF. Furthermore, Pt@H-UiO-66-NH2/CdS displays the smallest Nyquist radius, which supports the conclusions arising from the PL and transient photocurrent response results that it has the lowest charge transfer resistance and the best photoelectronic properties among the investigated MOF-based catalytic materials.

The electronic properties of key elements in the materials were evaluated using X-ray photoelectron spectroscopy (XPS). The full XPS spectra (Fig. S4a, ESI⁺) of the MOF-based catalysts reveal that they contain the appropriate C, N, O, Pt, Cd and S elements. The N 1s binding energy of H-UiO-66-NH₂ derived from the spectrum in Fig. 3a is 399.3 eV. After incorporation of Pt NPs, the N 1s binding energy increases. Also, the N 1s binding energy of Pt@H-UiO-66-NH₂/CdS is higher than that of H-UiO-66-NH₂/CdS, showing that inclusion of Pt NPs causes an appreciable change in the electronic environment around N. The Pt 4f binding energy of Pt@H-UiO-66-NH2/CdS is lower than that of Pt@H-UiO-66-NH₂ (Fig. 3b). This finding clearly demonstrates that the role of Pt NPs in the ternary system is to attract electrons. Finally, the slight differences in O 1s binding energies of Pt@H-UiO-66-NH2/CdS and hollow H-UiO-66-NH2, and the S 2p binding energies between Pt@H-UiO-66-NH2/CdS and H-UiO-66-NH₂/CdS indicate that an interaction occurs between CdS, Pt NPs and H-UiO-66-NH₂. Although the results indicate that interactions take place between the ternary components, the complexity of the system makes it difficult to elucidate the exact nature of charge transfer that occurs between the elements.

The observations outlined above clearly show that the Pt@H-UiO-66-NH₂/CdS ternary composite has a hierarchical



Fig. 3 High resolution XPS spectra of (a) N 1s, (b) Pt 4f, (c) O 1s and (d) S 2p.

hollow structure and a hierarchical heterojunction which lead to strong light absorption and improved electron transfer. In the next phase of this investigation, we evaluated the role that these properties play in governing photocatalytic activities. First, Pt@H-UiO-66-NH₂/CdS was employed as a catalyst for visible-light promoted degradation of the model pollutant methylene blue, MB. The results shown in Fig. 4a in the form of C/C_0 vs. the time plot show that the hollow structure containing H-UiO-66-NH₂ has higher degradation efficiency than does UiO-66-NH₂. Incorporation of Pt NPs in the catalysts to produce Pt@UiO-66-NH₂ and Pt@H-UiO-66-NH₂ leads to significant elevation of the degradation efficiency compared



Fig. 4 (a) Photocatalytic degradation of MB, (b) photocatalytic degradation rate constant of MB and (c) photocatalytic H_2 production rate of MOFbased materials. (d) Three continuous cycles of the photocatalytic H_2 production of Pt@H-UiO-66-NH₂/CdS.

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to that of the corresponding pristine MOF. Moreover, the catalytic activities of UiO-66-NH₂/CdS and H-UiO-66-NH₂/CdS are further enhanced owing to the visible-light absorption properties of CdS. As expected, the MB degradation activity of Pt@H-UiO-66-NH₂/CdS is the highest among all catalysts tested which is attributed to the effects of the hollow structure, CdS and Pt NPs on facilitating the capturing of light and separation of photogenerated electron-hole pairs. The graph in Fig. 4b contains the rate constants of the MB photocatalyzed degradation process (Fig. S5 and Table S2, ESI[†]). The results show that Pt@H-UiO-66-NH₂/CdS has the highest rate constant of 1.025 × 10⁻², which is about 1.5, 2.1, 4.5 and 10 times greater than those of Pt@UiO-66-NH₂/CdS, H-UiO-66-NH₂/CdS, Pt@H-UiO-66-NH₂/CdS, Pt@H

The propensities of the photocatalysts to promote the hydrogen producing water splitting reaction were also evaluated. The overall results show that hydrogen production performances of the photocatalysts (Fig. 4c) lie in the following order: Pt@ $H-UiO-66-NH_2/CdS > Pt@UiO-66-NH_2/CdS > H-UiO-66-NH_2/$ $CdS > Pt@H-UiO-66-NH_2 > H-UiO-66-NH_2 > UiO-66-NH_2$ Among these catalysts, Pt@H-UiO-66-NH2/CdS has the highest H_2 production rate of 12 810 µmol g⁻¹ h⁻¹, which is higher than those of the binary composites and the single component MOFs. In addition, the significance of morphology is demonstrated by the observation that the rate of H₂ production promoted by hollow Pt@H-UiO-66-NH₂/CdS (12 810 μ mol g⁻¹ h⁻¹) is higher than that of pristine Pt@UiO-66-NH₂/CdS (5505 μ mol g⁻¹ h⁻¹), as well as the finding that the rate of H₂ production catalyzed by the hollow H-UiO-66-NH₂ (69 μ mol g⁻¹ h⁻¹) is higher than that of the pristine UiO-66-NH₂ (24 μ mol g⁻¹ h⁻¹). Compared to those of other MOFbased catalysts described in the literature, the rate of H₂ production with Pt@H-UiO-66-NH2/CdS also shows high performance (Table S3, ESI⁺). As a demonstration of its stability, Pt@H-UiO-66-NH₂/CdS (Fig. 4d and Fig. S5, ESI⁺) shows no significant decline after three test cycles. When combined, the results of this study demonstrate the advantageous effects on catalytic activity arising from incorporating a ternary heterojunction structure and a hollow morphology into a simple MOF.



4. Conclusions

Chao Liu: methodology, investigation, and writing – original draft. Gang-Gang Chang: conceptualization and writing – review and editing. Ting-Ting Luo, Yi-Tian Wang, and Shi-Tian Xiao: investigation. Yao Yao and Hong-Jian Xu: formal analysis. Ge Tian, Christoph Janiak, and Hai-Hu Yu: resources and supervision. Xiao-Yu Yang: conceptualization and writing – review and editing.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.





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The results and discussion above enable us to propose a

plausible mechanism that explains how the Pt@H-UiO-66-NH₂/

CdS heterojunction enhances the photocatalytic performance. In

the pathway depicted in Fig. 5, CdS absorbs visible light to elevate

an electron from the valence band (VB) to the conduction (CB)

band. Owing to the existence of a Z-scheme heterojunction

between H-UiO-66-NH2 (band gap 2.77 eV, Fig. S6, ESI⁺) and

CdS, the photogenerated electron is transferred to the LUMO of H-UiO-66-NH₂, and then captured by Pt which functions as a proton reduction H₂ producing site.^{48–50} The hole created in the

VB of CdS is reduced by S^{2-} and SO_3^{2-} that serve as sacrificial

agents. In this process, the hollow structure and heterojunction

accelerate transfer of charge carriers and thereby inhibit e-h

recombination. In the process of MB degradation, the photogen-

erated electron combines with oxygen (O_2) to form superoxide

anion radicals ($^{\bullet}O_2^{-}$), and simultaneously photogenerated holes oxidize a hydroxyl anion (OH⁻) to form a hydroxyl radical ($^{\bullet}OH$). It

should be noted that ${}^{\bullet}O_2^{-}$, ${}^{\bullet}OH$ and holes have high oxidation

In summary, a ternary hierarchical hollow Pt@H-UiO-66-NH2/CdS

heterostructure, consisting of a MOF and highly dispersed CdS

and Pt NPs, was designed and synthesized. Studies demonstrated

that this material serves as an effective catalyst in photocatalytic

H₂ production and MB degradation. Among the materials pre-

pared in this effort, Pt@H-UiO-66-NH2/CdS displays the highest

photocatalytic activity towards the degradation of MB and hydro-

gen evolution (12810 μ mol g⁻¹ h⁻¹) under solar irradiation

conditions. The superiority of Pt@H-UiO-66-NH2/CdS is attributed

to the (1) acceleration of photogenerated electron and hole

transfer and separation by the Pt NP cocatalyst, (2) expansion of

the light absorption range by CdS and (3) increase in the exposure

of active sites and the capturing light ability, and decrease in

distances for charge transfer caused by the hollow H-UiO-66-NH₂

structure. Moreover, Pt@H-UiO-66-NH2/CdS also displays excel-

lent stability during photocatalytic hydrogen evolution. We believe that this effort will aid the design of highly efficient, hollow and

hierarchical nanostructured MOF-based photocatalysts.

potential required for oxidative degradation of pollutants.

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