Electronic Supplementary Information

A unique coordination-driven route to precise nanoassembly of metal sulfides onto metal–organic frameworks

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Contents

1. Experimental Procedures	2/19
2. Additional Characterizations	5/19
3. Growth Mechanism Studies for MIL-101@metal sulfides composites	10/19
4. Photocatalytic Mechanism Study	17/19
5. References	19/19

1. Experimental Procedures

Chemicals and materials: Chromium (III) chloride hexahydrate (CrCl₃·6H₂O, 98%), terephthalic acid (C₈H₆O₄, H₂BDC, 98%) and cysteamine (NH₂(CH₂)₂SH, 97%) were supplied by Sigma-Aldrich. Thioacetamide (CH₃CSNH₂, TAA, AR), cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O, AR), zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, AR), copper acetate monohydrate (Cu(CH₃COO)₂·H₂O, AR), silver nitrate (AgNO₃, AR), polyvinylpyrrolidone (PVP, AR), anhydrous ethanol (CH₃CH₂OH, AR), 4-nitroaniline (C₆H₆N₂O₂, AR), 4-nitrophenol (C₆H₅NO₃, AR), 4-nitrotoluene (C₇H₇NO₂, AR), and ammonium formate (HCOONH₄, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All materials were used as received without further purification. Deionized (DI) water used in the synthesis process was obtained from local sources.

Methods:

Synthesis of MIL-101: MIL-101 microcrystals were synthesized according to the literature with some modification. In a typical procedure, 266.5 mg of CrCl₃ 6H₂O (1.0 mmol) and 166.1 mg of terephthalic acid (H₂BDC) (1.0 mmol) were dispersed in 7.2 mL of DI water. After sonication at room temperature for 15 min, the mixed solution was transferred into a 25 mL Teflon-lined autoclave and heated at 210 \degree C for 24 h. When completing the reaction and slowly cooling to room temperature, a certain amount of recrystallized H₂BDC was formed in the green solution. The solution was then centrifuged at 2900 rpm for 3 min for three times to remove H₂BDC precipitates. Subsequently, the reserved green solution containing MIL-101 was collected by centrifugation at 8500 rpm for 5 min and washed twice with DI water and anhydrous ethanol. To remove the residual H₂BDC existed in the pore of MIL-101 microcrystals, the obtained MIL-101 was redispersed in 200 mL of anhydrous ethanol and kept at 80 °C for 12 h, during which the activation solvent was decanted and freshly replenished two times.

Synthesis of CdS particles: CdS particles were prepared by a simple solvothermal method. Typically, 44.2 mg of Cd(CH₃COO)₂·2H₂O was added into 20 mL of anhydrous ethanol in a 40 mL glass vial and kept reflux at 80 °C under magnetic stirring. Then, 12.4 mg of TAA was added and kept reflux for 10 h. The obtained CdS particles were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101@CdS and MIL-101/CdS composites: In detail, 40 mg of activated MIL-101, which was dehydrated at 120 °C for 12 h beforehand, was suspended in 20 mL of anhydrous ethanol. To this suspension, 40 mg of cysteamine was added, and then the mixture was stirred with heating to reflux at 80 °C for 4 h to obtain the cysteamine-grafted MOF (named MIL-101-S). After that, 44.2 mg of Cd(CH₃COO)₂·2H₂O was added and kept reflux for 2 h. Subsequently, 12.4 mg of TAA was added and kept reflux for 10 h. The obtained MIL-101@CdS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C. For comparison, MIL-101/CdS was fabricated *via* the same preparation process as that for MIL-101@CdS except for the addition of cysteamine.

Synthesis of MIL-101-CdS: The preparation of MIL-101-CdS was the same with that of MIL-101@CdS except for substituting anhydrous ethanol for DI water. In a typical procedure, 40 mg of MIL-101, which was dehydrated at 120 °C for 12 h beforehand, was suspended in 20 mL of DI water. To this suspension, 40 mg of cysteamine was added, and then the mixture was stirred with heating to reflux at 80 °C for 4 h. Afterwards, 44.2 mg of Cd(CH₃COO)₂·2H₂O was added and kept reflux for 2 h. Subsequently, 12.4 mg of TAA was added and kept reflux for 10 h. The obtained MIL-101-CdS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101/CdS-PVP: The preparation of MIL-101/CdS-PVP was the same with that of MIL-101@CdS except for substitution of cysteamine for polyvinylpyrrolidone. In a typical procedure, 40 mg of MIL-101, which was dehydrated at 120 °C for 12 h beforehand, was suspended in 20 mL anhydrous ethanol. To this suspension, 40 mg PVP was added, and then the mixture was stirred with heating to reflux at 80 °C for 4 h. Afterwards, 44.2 mg of Cd(CH₃COO)₂·2H₂O was added and kept reflux for 2 h. Subsequently, 12.4 mg of TAA was added and kept reflux for 10 h. The obtained MIL-101/CdS-PVP composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of ZnS particles: ZnS particles were prepared by a simple solvothermal method. Typically, 45 mg of $Zn(CH_3COO)_2 \cdot 2H_2O$ was added into 20 mL of anhydrous ethanol and kept reflux at 80 °C under magnetic stirring. Then, 16 mg of TAA was added and kept reflux for 4 h. The obtained ZnS particles were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101@ZnS: In a typical procedure, 20 mg of dehydrated MIL-101 was suspended in 20 mL of anhydrous ethanol. To this suspension, 20 mg of cysteamine was added, and then the mixture was stirred with heating to reflux at 80 °C for 4 h. After that, 45 mg of $Zn(CH_3COO)_2 \cdot 2H_2O$ was added and kept reflux for 2 h. 16 mg of TAA was added and kept reflux for 4 h. The obtained MIL-101@ZnS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101/ZnS: 20 mg of dehydrated MIL-101 was suspended in 20 mL of anhydrous ethanol. To this suspension, 45 mg of $Zn(CH_3COO)_2 \cdot 2H_2O$ was added and kept reflux at 80 °C for 2 h. Then, 16 mg of TAA was added and kept continuously reflux for 4 h. The obtained MIL-101@ZnS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of CuS particles: CuS particles were prepared by a simple solvothermal method. Typically, 10 mg of $Cu(CH_3COO)_2 \cdot H_2O$ was added into 20 mL of anhydrous ethanol and kept reflux at 80 °C under magnetic stirring. Then, 4.2 mg of TAA was added and kept reflux for 4 h. The obtained CuS particles were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101@CuS: 20 mg of dehydrated MIL-101 was suspended in 20 mL of anhydrous ethanol. To this suspension, 20 mg of cysteamine was added and stirred with heating at 80 °C for 4 h. After that, 10 mg of $Cu(CH_3COO)_2 \cdot H_2O$ was added and kept reflux for 2 h. Then 4.2 mg of TAA was added and kept continuously reflux for 4 h. The obtained MIL-101@CuS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101/CuS: 20 mg of dehydrated MIL-101 was suspended in 20 mL of anhydrous ethanol. To this suspension, 10 mg of $Cu(CH_3COO)_2 \cdot H_2O$ was added and kept reflux at 80 °C for 2 h. After that, 4.2 mg of TAA was added and kept reflux for 4 h. The obtained MIL-101@CuS composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of Ag₂S particles: Typically, 15 mg of AgNO₃ was added into 20 mL of anhydrous ethanol and kept reflux at 80 °C under magnetic stirring. Then, 4 mg of TAA was added and kept continuously reflux for 1 h. The obtained Ag2S particles were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101@Ag₂S: In a typical procedure, 20 mg of dehydrated MIL-101 was mixed with 20 mL of anhydrous ethanol in a 40 mL glass vial. To this suspension, 20 mg of cysteamine was added and stirred with heating at 80 °C for 4 h. After that, 5 mL of ethanol solution of AgNO₃ (15 mg) was injected into the glass vial and kept reflux at 80 °C for another 1 h. Then, 2 mL of ethanol solution of TAA (4 mg) was added dropwise with agitation and kept continuously reflux for 1 h. The obtained MIL-101@Ag₂S composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Synthesis of MIL-101/Ag₂S: In a typical procedure, 20 mg of dehydrated MIL-101 was suspended in 20 mL of anhydrous ethanol. To this suspension, 15 mg of AgNO₃ was added and kept reflux at 80 °C for 1 h. After that, 4 mg of TAA was added and kept reflux for 1 h. The obtained MIL-101@Ag₂S composites were collected by centrifugation and washed with DI water twice and dried at 60 °C.

Characterization: The Powder X-ray diffraction (XRD) patterns of samples were collected on a Japan Rigaku MiniFlex 600 equipped with graphite-monochromated Cu K α radiation ($\lambda = 1.54178$ Å). The diffraction patterns in the 2 θ range from 1° to 20° were recorded on Xpert-3 diffractometer. The morphology of samples was determined by field emission scanning electron microscopy (FESEM) on a Hitachi New Generationcold field emission SEM SU-8010 spectrophotometer. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and elemental mapping results were obtained by a JEOL model JEM 2010 EX instrument at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCA Lab 250 spectrometer, which was made of a monochromatic Al K α as the X-ray source, a hemispherical

analyzer, and a sample stage with multiaxial adjustability to obtain the surface composition of the samples. All of the binding energies were calibrated by the C 1s peak at 284.6 eV. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy (DRS) using a UV-vis spectrophotometer (Cary 500, VarianCo.), in which BaSO₄ was employed as the internal reflectance standard. The Fourier transformed infrared spectroscopy (FT-IR) was performed on a Nicolet Nexus 670 FT-IR spectrophotometer at a resolution of 4 cm⁻¹. The Raman spectra were recorded at room temperature using a RenishawinVia Raman System 1000 with a 633 nm Nd:YAG excitation source. The laser power incident on the samples was 10 mW. The Nitrogen adsorption-desorption isotherms of samples were determined at liquid nitrogen temperature (77 K) after degassing at 393 K for 6 h using Micromeritics ASAP 2460 equipment. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method by choosing N₂ adsorption points in the p/p₀ range of 0.05 - 0.3. Pore size distribution analysis was based on the density functional theory (DFT) method, and pore sizes were obtained from the peak positions of the distribution curves. The thermogravimetric analysis (TGA) was conducted on a TGA/DSC apparatus (TGA/DSC 3⁺, METTLER TOLEDO) under N₂ atmosphere.

Photoelectrochemical measurements were carried out on an electrochemical workstation (MUTI AUTOLAB M204) with a conventional three electrode cell, which uses a Pt plate as the counter electrode and an Ag/AgCl electrode as the reference electrode. The working electrode was prepared on fluorine doped tin oxide (FTO) glass that was cleaned by sonication in ethanol and dried at 80 °C for 2 h. The boundary of FTO glass was protected using scotch tape. The 5 mg of sample was fully dispersed in 0.5 mL of DMF by sonication to get slurry. The slurry was spread onto the pre-treated FTO glass. After air drying, the working electrode was further dried at 80 °C for 2 h to improve adhesion. Then, the scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of the working electrode was 0.25 cm². The photocurrent measurement was taken on the workstation with bias of 0.1 V under visible light irradiation and the electrolyte was 0.2 M Na₂SO₄ aqueous solution (pH = 7). The electrochemical impedance spectroscopy (EIS) measurement was measured via an EIS spectrometer (MUTI AUTOLAB M204) in the three-electrode cell in the presence of 0.5 M KCl solution containing 5.0 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] by applying an AC voltage with 5 mV amplitude in a frequency range from 1 Hz to 100 kHz under open circuit potential conditions. Mott-Schottky plots were measured in a standard three-electrode system at frequencies of 500 and 1000 Hz, respectively. A 0.2 M Na₂SO₄ solution was used as the electrolyte.

Photocatalytic selective reduction of aromatic nitro compounds measurements: 10 mg of photocatalysts and 50 mg of HCOONH₄ were added into 20 mL of aromatic nitro compounds solution (20 ppm) in a glass vial. The mixture was stirred for 0.5 h in dark to blend well and establish the adsorption-desorption equilibrium before the irradiation. A 300W Xe arc lamp (PLS-SXE 300C, Beijing Perfect light Co., Ltd.), emitting visible light ($\lambda \ge 420$ nm) with an energy output of 0.8 W cm⁻² measured by a Thorlabs PM100 optical power and energy meter, was placed at a distance of approximate 5 cm from the reactor to be the irradiation source to trigger the photocatalytic reaction. At a certain irradiation time interval during the experiment, 1.5 mL of sample solution was drawn from the system and centrifuged at 10000 rpm for 5 min to remove catalyst particles completely. The reduction amount of aromatic nitro compounds in the solution was analyzed on Varian ultraviolet-visible-light (UV-vis) spectrophotometer (Cary-50, Varian Co.). The whole experimental process was conducted under N₂ bubbling at a flow rate of 80 mL min⁻¹. Conversion of aromatic nitro compounds after the establishment of adsorption desorption equilibrium before irradiation and C_r is the concentrations of reactant aromatic nitro compounds at a certain time during the photocatalytic reaction.

2. Additional Characterizations



Fig. S1 Scanning electron microscopy (SEM) image of bare CdS particles.



Fig. S2 (A) SEM and (B and C) transmission electron microscopy (TEM) images of MIL-101.



Fig. S3 (A-C) SEM and TEM images of MIL-101@CdS, and (D) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping results of MIL-101@CdS.

Note: The high-resolution TEM image reveals a lattice fringe with an interplanar spacing of 0.33 nm, corresponding to the (111) face of cubic CdS (inset in **Fig. S3C**).¹



Fig. S4 Additional (A) SEM and (B) TEM images of MIL-101/CdS.



Fig. S5 (A) SEM image of bare ZnS, (B and C) TEM images of MIL-101@ZnS, and (D) SEM image of MIL-101/ZnS. Inset in (C): HRTEM, scale bar, 5 nm.

Note: The lattice fringe of 0.31 nm is attributed to the (111) crystal plane of ZnS (**Fig. S5C**).²



Fig. S6 (A) SEM image of bare CuS, (B and C) TEM images of MIL-101@CuS, and (D) SEM image of MIL-101/CuS. Inset in (C): HRTEM, scale bar, 5 nm.

Note: The lattice fringe of 0.27 nm is indexed to the (006) plane of CuS (**Fig. S6C**).³



Fig. S7 SEM and TEM images of (A) bare Ag_2S , (B and C) MIL-101@Ag_2S and (D) MIL-101/Ag_2S. Inset in (C): HRTEM, scale bar, 5 nm.

Note: The lattice fringe of 0.28 nm is indexed to the (-112) facet of Ag₂S (**Fig. S7C**).⁴

3. Growth Mechanism Studies for the MIL-101@metal sulfides composites



Fig. S8 Representation of the hierarchical structure of MIL-101. (A) Perspective view of the mesoporous cage of MIL-101 with hexagonal windows, (B) super tetrahedrons in MIL-101, (C) chromium trimers with water molecules occupied on the coordinatively unsaturated metal sites (CUSs) and (D) structural model of the coordinatively unsaturated metal sites.



Fig. S9 Thermogravimetric analysis (TG) of MIL-101. (A) TG curve of MIL-101 with heating rate of 5 °C/min, (B) and (C) the TG and first derivative thermogravimetry (DTG) curves of MIL-101 with heating rate of 5 °C/min and 2 °C/min, respectively.

Note: TG curve of MIL-101 is shown in **Fig. S9A**. Two steps of weight loss are obtained in the range below 150 °C. First step corresponds to the removal of adsorbed water, which exhibits weak interactions (e.g., Van Der Waals force) with MIL-101 microcrystals. Second step corresponds to the removal of coordinated water, which exhibits stronger interactions (e.g., coordination bond) with MIL-101 microcrystals than that of adsorbed water. The different weight losses of these two types of water are due to the different interactions with MIL-101 microcrystals, which could be distinguished carefully by derivative thermogravimetry (DTG) analysis. As shown in **Fig. S9B**, under the constant heating treatment, there are two troughs of the rate of weight losses in DTG curve of MIL-101, implying two kinds of interactions with MIL-101 microcrystals. And it becomes more apparent when the heating rate decreases (**Fig. S9C**). These observations provide a qualitatively accessible route for the recognization of CUSs.



Fig. S10 XRD pattern of MIL-101-CdS composite prepared in water. No apparent XRD peaks of MIL-101 can be found in the red circled area, which indicates that the introduction of water will damage the crystal structure of MIL-101 during the cysteamine-enabled assembly process.



Fig. S11 Digital photo of MIL-101/CdS-PVP.



Fig. S12 Fourier-transform infrared (FT-IR) spectra of MIL-101, MIL-101-S and MIL-101@CdS.

Note: The peaks of MIL-101-S at approximately 3227 and 1590 cm⁻¹, resulting from the characteristic stretching vibration and scissoring vibration of the N-H (v_s (N-H) and δ (N-H)), indicate the existence of cysteamine.^{5, 6}



Fig. S13 Survey XPS spectra of MIL-101 and MIL-101-S.

Note: As compared to MIL-101, the survey XPS spectrum of MIL-101-S shows the peaks in the region of N 1s, S 2s and S 2p, which indicates the existence of the N and S elements of the cysteamine molecule in MIL-101-S.



Fig. S14 Time-dependent monitoring of nucleation of CdS on MIL-101 (MIL-101/CdS) without the addition of cysteamine.



Fig. S15 (A) TEM and (B) HRTEM images of MIL-101@CdS with the addition of excessive amount of cysteamine.

Note: Fig. S15 shows the TEM and HRTEM images of the sample of MIL-101@CdS, which was obtained by decreasing the ratio of S^{2-} sources to cysteamine via adding excessive amount of cysteamine. Compared to the size of CdS NPs on composites of MIL-101/CdS and MIL-101@CdS (Fig. S3 and S4), it can be seen that the size of CdS NPs is obviously decreased as the incressed addition amount of cysteamine (Fig. S15B). This result suggests the competition between cysteamine and S^{2-} for Cd²⁺, in which the thiol group of cysteamine coordinates to Cd²⁺ and subsequently obstructs the combination of Cd²⁺ and S²⁻ for the nucleation of CdS, thereby resulting in slowing down the nucleation rate of CdS NPs onto MIL-101-S. In this way, the size of as-formed CdS NPs becomes much smaller.



Fig. S16 (A) N_2 adsorption-desorption isotherms (solid symbols: adsorption curve; open symbols: desorption curve) and (B) Brunauer-Emmett-Teller (BET) surface area of MIL-101, MIL-101-S, MIL-101@CdS and MIL-101/CdS, respectively.



Fig. S17 Pore size distribution analysis for MIL-101, MIL-101-S, MIL-101@CdS, and MIL-101/CdS based on the density functional theory (DFT) method.

Note: Compared with bare MIL-101, MIL-101-S and MIL-101@CdS composites exhibit a significant decrease of the N₂ amount, which is owing to the stepwise loading of cysteamine and CdS to MIL-101.⁷ The decreased pore width by a sequence of MIL-101@CdS < MIL-101-S < MIL-101/CdS < MIL-101 further reveals that the cysteamine grafting and S²⁻ anion exchange process happen in the cavities of MIL-101 for synthesis of MIL-101@CdS, by which then the uniform coating of CdS NPs onto the surface of MIL-101. However, for MIL-101/CdS, CdS particles are formed outside of MIL-101, thus displaying obvious heterophase separation.

4. Photocatalytic Mechanism Study



Fig. S18 The formula for photocatalytic reduction of 4-NA.



Fig. S19 Photocatalytic reduction of (A) 4-nitrotoluene, (B), 4-nitroanisole and (C) 4-nitrophenol under visible light irradiation.



Fig. S20 (A) Mott-Schottky plots for MIL-101 in a 0.2 M Na_2SO_4 aqueous solution (pH = 7) and (B) UV-vis diffuse reflectance spectrum (DRS) of MIL-101.

Note: The flat band position which refers to the lowest unoccupied molecular orbital (LUMO) of MIL-101 was estimated at -0.66 V according to the Mott-Schottky analysis. When a normal hydrogen electrode (NHE) is used as the standard, the LUMO of MIL-101 is about -0.05 V vs. NHE,⁸ which is referenced by following calculation: E (vs. NHE) = E (vs. Ag/AgCl) + 0.197 + 0.059 × pH. With the band gap of 2.21 eV determined from DRS result (**Fig. S20B**), the highest occupied molecular orbital (HOMO) of MIL-101 is then calculated with the value of 2.16 V vs. NHE.

5. References

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