INORGANIC CHEMISTRY







FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue



Cite this: *Inorg. Chem. Front.*, 2024, **11**, 5484

Exposing coordination-unsaturated Co sites in Co-MOF for efficient photocatalytic water oxidation†

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Water oxidation to molecular dioxygen driven by visible light is essential but difficult in solar fuel production due to its sluggish reaction kinetics. Although the catalytic process is highly dependent on the coordination-unsaturated metal sites in coordination catalysts, the controllable design of catalysts with such catalytic sites remains challenging. Herein, we report two new Co-MOFs (CoBIM-1 and CoBIM-2) for photocatalytic water oxidation under visible light. The coordination environment of Co in Co-MOFs can be easily manipulated by changing the atmosphere and concentration of deprotonated solvent during synthesis. CoBIM-1 with coordinatively unsaturated Co sites showed good performance with an O_2 production of 2.0 mmol $g^{-1} h^{-1}$, in sharp contrast to its counterpart CoBIM-2. Furthermore, through isotope tracing experiments, we confirmed that the dioxygen was produced from water oxidation. This work highlights that the atmosphere during synthesis and solvent selection greatly regulate the crystal structures of MOFs and further manipulate their photocatalytic performance.

Received 17th April 2024, Accepted 20th July 2024 DOI: 10.1039/d4qi00968a

rsc.li/frontiers-inorganic

Introduction

With the depletion of fossil fuels and increasing environmental problems, it is urgent to look for clean and renewable energy sources that can replace traditional fossil energy. Photosynthesis in nature is the process by which green plants convert carbon dioxide and water into food using energy obtained from sunlight. Fortunately, mimicking natural photosynthesis in plants, artificial photosynthesis, a promising strategy for storing solar energy, is being explored to produce solar fuel. ¹⁻³ In both natural and artificial photosynthesis, the water oxidation half-reaction is essential and more challenging compared to the reductive ones. It requires the transfer of 4e⁻ and 4H⁺ with the concomitant formation of an O=O bond, leading to high energy barriers and slow kinetics in addition to uphill reaction thermodynamics. ⁴ In natural photosynthesis, the

heart of the photosystem II with an active Mn₄CaO₅ core is responsible for biocatalytic water oxidation, and the accessible metal sites in this active Mn₄CaO₅ center are regarded as active sites.⁵⁻⁷ To mimic natural photosynthesis, precious metal oxides such as IrO₂ and RuO₂ have been proven to be the most effective water oxidation catalysts (WOCs), but catalysts with low-cost elements are more attractive.⁸⁻¹⁰ Recently, cobalt-based catalysts have shown potential as WOCs, such as Co₃O₄, Co(PO₃)₂, Li₂Co₂O₄, Co-polyoxometalate, Co-based metal-organic cages, *etc.*¹¹⁻¹⁵ Due to the lack of porosity of these photocatalysts, typically only surface cobalt sites can be utilized to catalyse water oxidation reactions, thereby limiting their catalytic efficiency.

Metal-organic frameworks (MOFs) composed of metal ions or clusters and polytopic organic linkers have been widely investigated for gas storage and separation, sensors, drug delivery, and catalysis, *etc.*, due to their large surface areas, high porosity, and easy structural and functional adjustment. 16-29 In recent years, through rational design or post-synthetic modification, functionalized MOFs have been endowed with potential applications in artificial photosynthesis. 30-37 However, most of those works focus on the reductive half-reaction but not the water oxidative half-reaction. As one of the important branches of MOFs, zeolitic imidazolate frameworks (ZIFs) are composed of metal ions and imidazole ligands. 38 Their structure and physical and chemical properties have many similarities with zeolite, such

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[†]Electronic supplementary information (ESI) available. CCDC 2203264 and 2204131. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d4qi00968a

as good thermal stability and chemical stability. Unfortunately, most of the ZIFs are constructed using metal ions with a tetrahedral coordination geometry that mimics the SiO₄ tetrahedral units in zeolites, resulting in only coordination-saturated metal centers within them. This is not beneficial for further applications in catalysis. The incorporation of unsaturated metal sites inside ZIFs is still challenging. 39-41

In this work, we reported a solvent/atmosphere-assisted method to construct a new ZIF with coordinated unsaturated metal sites by manipulating the atmosphere and concentration of deprotonated solvent. The ZIF named CoBIM-1, constructed 1,2-bis((5*H*-imidazol-4-vl)methylene)hydrazine (H₂BIM) ligand and cobalt(II) nitrate, was synthesized under low concentration of deprotonated solvent and inert atmosphere. As a control, CoBIM-2 with coordination-saturated Co sites was also synthesized using a higher concentration of deprotonated solvent and an air atmosphere. Compared with CoBIM-2, CoBIM-1 could efficiently photocatalyze water oxidation with Ru(bpy)₃Cl₂ (bpy, 2,2'-bipyridine) as the photosensitizer and Na₂S₂O₈ as the sacrificial electron acceptor in a borate buffer solution. An O₂ production of 2.0 mmol g⁻¹ h⁻¹ was observed in a borate buffer solution at pH of 8.4. Through isotope tracing experiments, it was confirmed that the produced dioxygen came from water oxidation.

Results and discussion

The reaction of the ligand BIM with cobalt(II) nitrate in a mixed solvent (DMF/methanol, 1/4, v/v) under a nitrogen atmosphere produces purple polyhedral crystals denoted as CoBIM-1. When the same ligand and metal salt are used but under an air atmosphere and with a higher concentration of DMF (DMF/methanol, 4/1, v/v), the reaction produces orange cubic crystals denoted as CoBIM-2. Single crystal X-ray diffraction (SCXRD) studies revealed that CoBIM-1 crystallizes in space group Ia3d, featuring a gie topology (Fig. 1d).39 The coordination environment of the Co1 ion in CoBIM-1 adopts an octahedral geometry, coordinating with 5 nitrogen atoms (from BIM) and 1 oxygen atom (from H₂O) (Fig. 1a). In contrast, CoBIM-2 crystallizes in space group Im3, featuring a pcu topology (Fig. 1e, S1, and S2†). There are two types of cobalt ion centers with different coordination environments in CoBIM-2 (Fig. 1b and c). The Co2 ion adopts an octahedral geometry, coordinating with 6 nitrogen atoms from six imidazole parts of BIMs, while the Co3 ion adopts an octahedral geometry, coordinating with 6 nitrogen atoms from one BIM and one undeprotonated H₂BIM. The H₂BIM ligands are hung in the pores and do not participate in the expansion to form the three-dimensional structure (Fig. 1e).

The structural differences between CoBIM-1 and CoBIM-2 are reflected in the following two aspects: (1) different length of Co-N coordination bonds; (2) difference valence state of cobalt ions. In the CoBIM-1, the Co1-N bond distances are in the range of 1.918(5)-1.998(15) Å and the Co-O bond distance is 1.986(7) Å. In contrast, distances of all Co2-N bonds in

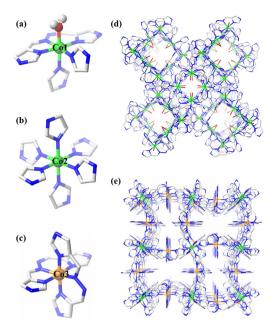


Fig. 1 Crystal structure of CoBIM-1 and CoBIM-2. The coordination environment of cobalt ions in (a) CoBIM-1 and (b, c) CoBIM-2, respectively. The three-dimensional structure of (d) CoBIM-1 and (e) CoBIM-2 along a axis, respectively. Colour codes: Co^{II} green, Co^{III} orange, N blue, O red, C grey, and H white.

CoBIM-2 are 2.147(4) Å, while the Co3-N bond distances are in the range of 1.872(18)-1.914(8) Å. The obviously longer Co1-N bonds in CoBIM-1 and Co2-N bonds in CoBIM-2 than that of Co3-N bonds indicate that the Co1 and Co2 centers tend to have +2 oxidation states, while Co3 centers have +3 oxidation states.42 Based on the above information and the results of elemental analysis, the chemical formulas of CoBIM-1 and CoBIM-2 are [Co^{II}(BIM)(H₂O)]·CH₃OH·4.5H₂O and [Co₃^{III}Co^{II}(BIM)₃(H₂BIM)₃]·5NO₃·4CH₃OH, respectively.

Thermogravimetric analysis (TGA) showed that CoBIM-1 was stable up to around 250 °C (Fig. 2a). In situ variable temperature powder X-ray diffraction (PXRD) patterns further confirmed the high temperature tolerance of CoBIM-1 (Fig. S5†). CoBIM-1 was also quite stable in common organic solvents (e.g., CH₃OH, CH₃CN) and water for one month at room temperature (Fig. S6†). Moreover, CoBIM-1 showed good stability after being soaked in aqueous solutions over a wide pH range for one week (Fig. 2b). All of the above reflect that CoBIM-1 has good thermal and chemical stability. In addition, the data from the TGA plot (Fig. S7†) and the PXRD patterns after being soaked in water for a week (Fig. S8†) also confirm that CoBIM-2 has good thermal and hydrolytic stability.

To confirm the permanent porosity of CoBIM-1 and CoBIM-2, N2 adsorption/desorption isotherm measurements at 77 K were carried out. The N2 adsorption isotherm of CoBIM-1 showed a type-I isotherm for microporous materials (Fig. 2c). The BET and Langmuir surface areas of CoBIM-1 were calculated to be 752 and 853 m² g⁻¹, respectively. The pore size distribution of CoBIM-1 calculated by the DFT model showed that

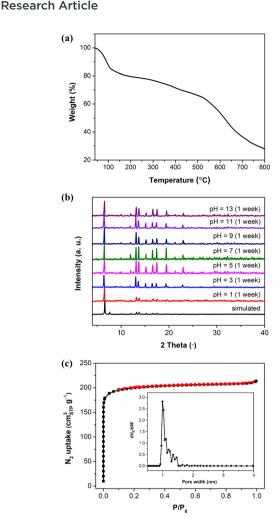
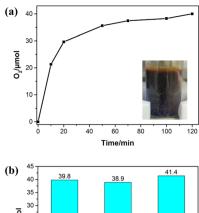


Fig. 2 (a) TGA plot under a N₂ atmosphere of CoBIM-1. (b) PXRD patterns of CoBIM-1 in H₂O with different pH for one week. (c) The N₂ adsorption (black dotted line) and desorption (red dotted line) isotherms at 77 K of CoBIM-1. The inset is the DFT pore size distributions.

its pores range from 9.9 to 14.5 Å (inset of Fig. 2c). Moreover, the water vapor adsorption isotherm of CoBIM-1 at 298 K displayed a type-I characteristic and an uptake of 268 cm³ g⁻¹ (Fig. S9†), confirming the hydrophilic nature of internal pore surface. 41 Additionally, the porosity of CoBIM-2 was confirmed by N2 adsorption isotherm at 77 K (Fig. S10†), and its BET surface area was 66 m² g⁻¹. The reason for its small surface area may be that the H₂BIM ligands hung in the pore channels occupy most of the cavities.

In order to determine whether the coordinated unsaturated Co sites in Co-ZIF are beneficial for photocatalytic water oxidation reaction, both CoBIM-1 and CoBIM-2 are used as catalysts for evaluation. The solid-state UV-vis absorption spectrum showed that CoBIM-1 had a broader light absorption range in the visible light area than that of CoBIM-2 (Fig. S11†). Next, A 10.0 mL degassed borate buffer solution (pH = 8.2) containing 10 mg of CoBIM-1 or CoBIM-2, 30.0 mM of Na₂S₂O₈, and 6.0 mM of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) was irradiated using a 470 nm light-emitting diode (LED) lamp. The photoca-



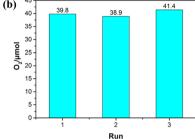


Fig. 3 (a) The time-dependent photocatalytic O₂ evolution and (b) recycling performance of CoBIM-1.

talytically produced O2 was quantified using gas chromatography (GC). As shown in Fig. 3a, in the system with CoBIM-1 as the catalyst, the generated O2 increased with time and almost reached a plateau after two hours of reaction. Around 40.0 μmol of O₂ was generated with a production of 2.0 mmol g^{-1} h⁻¹. This O₂ production capacity is better than some reported MOF materials, 43 e.g., [Ru(tpy)(dcbpy)(OH2)]2+ doped UiO-67 (0.04 mmol g⁻¹ h⁻¹), 44 [Bi(BTC)(DMF)]·DMF(CH₃OH)₂ (0.8 mmol g⁻¹ h⁻¹),⁴⁵ Bi-MOF (1.1 mmol g⁻¹ h⁻¹),⁴⁶ Cd-TBAPy $(1.6 \text{ mmol g}^{-1} \text{ h}^{-1})$, 47 etc. Moreover, based on the amount of Na₂S₂O₈ used, the yield of O₂ in this system was calculated to be 26.7%. No O_2 evolution was observed without $Ru(bpy)_3Cl_2$, Na₂S₂O₈, or CoBIM-1 during the photocatalytic process (Table 1). The control experiments indicated that CoBIM-1 was indeed active towards water oxidation reaction. To prove that the O₂ was produced by water oxidation, an isotope-labelling water oxidation experiment was performed with CoBIM-1 as the photocatalyst and H₂¹⁸O as the solvent. As shown in Fig. S12,† 18O2 was detected, confirming the above conclusion.

Table 1 The amount of O2 evolution of CoBIM-1 and CoBIM-2 as photocatalysts, respectively

Catalysts	$Ru(bpy)_3Cl_2(mM)$	$Na_2S_2O_8$ (mM)	$O_2\left(\mu mol\right)$
CoBIM-1	_	30	None
CoBIM-1	6	_	None
_	6	30	None
CoBIM-1	6	30	40.0
CoBIM-2	6	30	None

Conditions: degassed borate buffer solution, 10.0 mL; catalysts, 10 mg; reaction time, 2 h; pH, 8.2; light source, 470 nm LED.

Notably, CoBIM-2 showed no activity towards water oxidation due to the lack of coordinatively unsaturated Co sites.

The cyclic catalytic testing of **CoBIM-1** showed that its catalytic activity could be well maintained after at least three runs (Fig. 3b and S13†). The retained PXRD pattern further indicated that the crystal structure remained intact after three rounds of the photocatalytic process (Fig. S14†). We also found the size of **CoBIM-1** can influence the catalytic performance and the smaller crystals are benefit for the catalytic activity toward water oxidation (Fig. S15, S16 and Table S2†). It may be that the smaller size of **CoBIM-1** is more conducive to the exposure of catalytic sites.

Based on the above experimental results, CoBIM-1 can indeed decompose H_2O into O_2 in the $[Ru(bpy)_3]^{2+}$ - $Na_2S_2O_8$ system with visible light irradiation. According to previous reports on the mechanism of the photocatalyzed water oxidation reaction using cobalt-containing MOF catalysts, 48 we speculate the possible mechanism of the photocatalytic water oxidation reaction of **CoBIM-1** as follows. (1) The photosensitizer $[Ru(bpy)_3]^{2+}$ is excited by visible light to form [Ru(bpy)₃]^{2+*} (* represents an excited state). (2) After transferring electrons to S₂O₈²⁻, the active [Ru $(bpy)_3]^{2+\star}$ is oxidized to $[Ru(bpy)_3]^{3+}$. The sacrificial agent $S_2O_8^{2-}$ is reduced to SO_4^{2-} and SO_4^{*-} radicals as well. (3) The electrode potential of the SO₄ radical is higher than the electrode potential of $[Ru(bpy)_3]^{2+}/[Ru(bpy)_3]^{3+}$. As a result, two molecules of the SO_4 radical can oxidize $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$. (4) $[Ru(bpy)_3]^{3+}$ (bpy)₃³⁺ can accept electrons from CoBIM-1 and is reduced to $[Ru(bpy)_3]^{2+}$. The oxidized **CoBIM-1** can then catalyze the water oxidation reaction to produce O2.

Conclusions

In summary, we have synthesized two new Co-ZIFs (CoBIM-1 and CoBIM-2) using the same cobalt salt and BIM ligand. The coordination-unsaturated Co sites inside Co-ZIF can be achieved by manipulating the atmosphere and concentration of deprotonated solvent during the synthesis process. Under reaction conditions of a high concentration of deprotonated solvent and an inert atmosphere, CoBIM-1 with coordinationunsaturated Co sites was obtained. In contrast, the case of CoBIM-2 with coordination-saturated Co sites was obtained under a lower concentration of deprotonated solvent and an air atmosphere. Both CoBIM-1 and CoBIM-2 exhibited good chemical and thermal stability. Compared with CoBIM-2, CoBIM-1, with coordination-unsaturated Co sites, exhibited good performance in photocatalytic water oxidation with an O2 production of 2.0 mmol g⁻¹ h⁻¹ under 470 nm light irradiation. Besides, CoBIM-1 also showed good recyclability. The isotope-labelling water oxidation experiment further proved that O2 was produced by the photocatalytic water oxidation reaction. This work provides an interesting method for synthesizing MOF materials with coordination-unsaturated metal sites and applying them to photocatalytic water oxidation, which is inspiring for the synthesis of similar photocatalysts for water splitting.

Experimental

Synthesis of CoBIM-1

In a nitrogen atmosphere, the reaction of ligand BIM (0.03 mmol) with cobalt(II) nitrate hexahydrate (0.03 mmol) in a mixed solvent (DMF/methanol, 1/4, v/v) under solvethermal conditions (110 °C, 72 h) afforded purple polyhedral crystals denoted as **CoBIM-1**. In order to obtain high yields of samples, degassing conditions are necessary. The samples were soaked in methanol for solvent exchange, and fresh methanol was replaced every day for three days. The solid sample was collected by filtration. Elemental analysis (CHN), $CoC_9H_{21}N_6O_{6.5}$ (corresponding to $[Co^{II}(BIM)(H_2O)]$ - CH_3OH - $4.5H_2O$), calculated (%): C, 28.73; H, 5.63; N, 22.34. Found (%): C, 28.60; H, 4.48; N, 22.34.

Smaller purple polyhedral crystals of **CoBIM-1**, all less than 10 μ m in size, were obtained by the following method. The entire mixture, including BIM (0.06 mmol), cobalt(II) nitrate hexahydrate (0.06 mmol), and DMF/methanol solvent (1/4, v/v), was reacted under stirring (200 rpm) with a magnetic bar for 24 hours. Additionally, samples with a size of about 5 μ m could be produced by increasing the stirring speed to 400 rpm. Lastly, nanoscaled **CoBIM-1** was obtained by grinding the sample in a ball mill with a rotation speed of 1200 rpm.

Synthesis of CoBIM-2

The ligand BIM (0.03 mmol) was reacted with cobalt(II) nitrate hexahydrate (0.02 mmol) in a mixed solvent (DMF/methanol, 4/1, v/v) under solvethermal conditions (110 °C, 72 h), resulting in the formation of orange cubic crystals as a product (denoted as **CoBIM-2**). The samples were soaked in methanol for solvent exchange, and fresh methanol was replaced every day for three days. The solid sample was collected by filtration. Elemental analysis (CHN), $\text{Co}_4\text{C}_{52}\text{H}_{58}\text{N}_{41}\text{O}_{19}$ (corresponding to $[\text{Co}_3^{\text{III}}\text{Co}^{\text{II}}(\text{BIM})_3(\text{H}_2\text{BIM})_3] \cdot 5\text{NO}_3 \cdot 4\text{CH}_3\text{OH}$), calculated (%): C, 34.76; H, 3.25; N, 31.96. Found (%): C, 37.49; H, 3.24; N, 32.37.

Photocatalytic water oxidation experiments

The photocatalytic water oxidation experiments were conducted in a quartz tube using the WP-TEC-1020H system. Specifically, CoBIM-1 or CoBIM-2, Ru(bpy) $_3$ Cl $_2$, and Na $_2$ S $_2$ O $_8$ were added to the quartz tube along with 10 mL of degassed borate buffer solution (pH = 8.2). The mixture in the tube was then bubbled with argon for half an hour before starting the reaction by turning on the LED lamp. The generated gas was analysed by gas chromatography (GC9790II) with a TCD detector.

Data availability

The data supporting this article have been included as part of the ESI. \dagger

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 22171106, 21871172, 22201101, and 22001094), the Guangdong Major Project of Applied Research (No. 2019B030302009), Basic and Guangdong Natural Science Foundation (No. 2022A1515011937), the Fundamental Research Funds for the Central Universities (No. 21622103), the Guangdong Basic and Applied Basic Research Foundation (No. 2022A1515110523), open fund of Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications (No. 2022A06), and Jinan University.

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