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Syntheses, structures and catalytic mechanisms of three new MOFs for aqueous Cr(VI) reduction and dye degradation under UV light

Liwen Wang[†], Tianyu Zeng[†], Guiying Liao[‡], Qingrong Cheng^{* †‡,} Zhiquan Pan[†] [†] School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, 693 Xiongchu Avenue, Wuhan 430073, China

[‡] Engineering Research Center, Nano-Geo Materials of Ministry of Education, China University of Geosciences, 388 Lumo Avenue, Wuhan 430073, China

Abstract

Three novel metal-organic frameworks (MOFs) photocatalysts with different structures $[Cd(4-Hptz)_2(H_2O)_2Cl_2](4-Hptz = 4-(1H-tetrazol-5-yl)-pyridine) (1), [Cu(btx)_2$ $(ClO_4)_2]_n(btx = 1,4-bis(triazol-1-ylmethyl)benzene) (2), and [Cu(btx)(ClO_4)]_n (3) have$ been synthesized by solvothermal reaction successfully. All samples were characterized by X-ray, FT-IR, XPS and UV-vis diffuse reflectance spectra. The photocatalystic properties were investigated by degradation of methylene blue(MB) dye andreduction of Cr(VI) to Cr(III) in aqueous solution under UV light. Controlexperiments show that the pH value is vital for Cr(VI) reduction, and meanwhile, theuse of hole scavenger of methanol promotes the photocatalytic reduction significantly.It has been also demonstrated that photocatalysts 1 and 2 are efficient for MBdegradation. The cyclic experiments indicated three photocatalysts are stable andreusable, enabling them to be the potential candidate in environment governance.

Keywords MOFs, photocatalysis, Cr(VI) reduction, dye degradation, mechanism

Introduction

Nowadays, there is growing concern about environmental protection and human health because more and more areas of the earth are facing serious water pollution. A great deal of industrial wastewater is generated in many industrial processes. The wastewater often contains many inorganic heavy metal ions and organic pollutants¹. The main reason is that inorganic heavy metal ions ^{2, 3} and organic dyes ^{4, 5} are usually highly toxic which are not easy to be degraded biologically directly. For example, inorganic hexavalent chromium Cr(VI) is with high levels of toxicity and nonbiodegradable, and it could also cause DNA damage and cancers⁶⁻¹⁰. Because Cr(VI) in water is difficult to be gathered and removed, and Cr(III) exhibits low

toxicity in contrast to Cr(VI), the reduction of Cr(VI) to Cr(II) is an effective technique in the process of sewage treatment¹¹. Among organic pollutants, organic dyes are notorious for causing environmental deterioration and negative impact on ecosystems such as toxicity and perturbation in aquatic life.

Among the various methods, photocatalysis is an economic, green and effective way¹². Since semiconductor TiO_2^{13} was initially discovered for pollutants degradation in the photocatalytic system, many semiconductor photocatalysts have been reported, such as SnO_2 , WO_3 , Bi_2O_3 , ZnO, CdS and so on^{14-16} . There is a typical drawback of these photocatalysts, they are not very stable under irradiation. For example, transition metal sulfides are highly unstable semiconductors with narrow band-gap, and their often dissolve in the solvent under irradiation. Other metal oxides, such as iron oxides, silver oxide, and copper oxides are also affected by photo corrosion.

MOFs, a class of newly-developed inorganic-organic solid-state porous materials, have generated a rapid development due to their large surface area, diverse structural topologies and rich active site, as well as various potential applications, such as in gas storage¹⁷, separation¹⁸, heterogeneous catalysis^{19, 20}, and so on. Some MOFs show their semiconductors behavior under irradiation, implying that they are potentially useful as photocatalysts. The porous structure of MOFs promote the diffusion of substrates and products through MOF channels, making MOFs an ideal platform to reach catalytic centers. In 2007, MOF-5 was first proposed to behave as a photocatalyst. MOF-5 as a reverse size-selective photocatalysis was observed for phenol and 2,6-di-tert-butylphenol, while the smaller molecule phenol was able to diffuse freely into the interior of MOF-5, leading to a lower degradation rate, while the bulkier molecule DTBP(2,6-di-tert-butylphenol) remained on the external surface of the MOF-5, exhibiting a higher degradation rate.

Presently, as photocatalysts, photoactive MOFs have been used to eliminate the organic pollutants^{21, 22}. 4-Hptz²³ and btx²⁴ obtain p- π conjugate effect and π - π conjugated effect, respectively. Their conjugated structures are helpful to electron transfer, implying that they have remarkable advantages in the separation of photogenerated electron and hole. This material contains a three-dimensional pore structure, noteworthy features of this catalyst are good substrate-size-selectivity, consistent with channel localized catalysis. For big substrate (organic dyes), it could not enter the channels of material, implying that catalysis takes place chiefly on the

surface of material. For small substrate (inorganic ions), mostly it could easily access the channels of material, indicating that the catalysis occur within the channels and pores of material²⁵⁻²⁷. In this article, three new complexes $[Cd(4-Hptz)_2(H_2O)_2Cl_2]_n$ (1), $[Cu(btx)_2(ClO_4)_2]_n$ (2), and $[Cu(btx)(ClO_4)]_n$ (3) have been synthesized. These Cu(I)-MOFs, Cu(II)-MOFs, and Cd(II)-MOFs as photocatalysts have not been reported. Moreover, complex 1 and complex 2 both exhibit cages together with open channels running along some certain directions, contributing to surface areas for sufficient contact with substrate in photocatalytic reaction. Based on the above characteristics, we have studied the active photocatalytic performance of these complexes for MB dye degradation and reduction of Cr(VI) to Cr(III) in aqueous solution under ultraviolet light. As far as we know, although the photocatalysis of MOFs has been researched for many years, the researches about the impacts of their band gaps and the structure of ligand on the photocatalytic activity remain limited. Moreover, the catalytic kinetic and the photocatalytic mechanism have not been reported in detail, and the first case is reported by our group²⁸.

Experimental section

Materials and methods

The ligands 4-Hptz = 4-(1H-tetrazol-5-yl)-pyridine and btx = 1,4-bis(triazol-1-ylmethyl)benzene were synthesized according to the reported procedures(The details of the synthesized are given in Supplementary information. All other reagents and solvents for syntheses were purchased from commercialsources and used without further purification.

Synthesis of the complexes

Cd(4-Hptz)₂·(**H**₂**O**)₂**Cl**₂]_{**n**}(**1**) A mixture of Cd(NO₃)₂·4H₂O 0.0308 g(0.1 mmol), 4-Hptz 0.0148 g(0.1 mmol), and 5 mL deionized water was mixed in a 10 mL vial by ultrasonic dispersion method at room temperature. After a few minutes, the mixed solution was put into 20 mL Teflon lined stainless steel autoclave and heated at 140°C for 2 days. For obtaining crystals, the hydrothermal reaction was set as the following temperature control program: heating from room temperature to 140 °C for 30 min and cooling for 24 h, respectively. After cooling to room temperature, complex **1** was washed with water and DMF twice. Colorless block-shaped crystals of **1** were collected in a 56% yield based on Cd(II). The phase purity of compound was checked by powder X-ray diffraction. Anal. Calcd for C₁₂H₁₂CdN₁₀O₂: C, 32.70; H,

7.260; N, 31.78. Found: C, 32.67; H, 2.640; N, 31.58. IR (KBr, cm⁻¹) for 3233.72s, 2069.05m, 1685.50w, 1619.95s, 1376.92m, 1315.03s, 1133.68m, 866.54m, 839.36m, 755.83m, 728.14m (Fig S1).

[Cu(btx)₂(ClO₄)₂]_n(2) A mixture of Cu(ClO₄)₂·6H₂O 0.0195 g(0.05 mmol), btx 0.0248 g(0.1 mmol), and 5.00 mL deionized water was mixed in a 10 mL vial by ultrasonic dispersion method at room temperature. After a few minutes, the mixed solution was put into 20 mL Teflon lined stainless steel autoclave and heated at 140°C for 2 days. The hydrothermal reaction was set as the following temperature control program: heating from room temperature to 140 °C for 30 min and cooling for 24 h, respectively. After cooling to room temperature, complex **2** was washed with water and DMF twice. Blue block-shaped crystals of **2** were collected in a 66% yield based on Cu(II). The phase purity of compound was checked by powder X-ray diffraction. Anal. Calcd for C₂₄H₂₄Cl₂Cl₁₂CuN₁₂O₈: C, 39.44; H, 1.650; N, 23.00. Found: C, 39.54; H, 1.580; N, 23.75. IR (KBr, cm⁻¹) for 3441.81w, 3041.00w, 1619.18w, 1481.08m, 1426.93m, 1360.84m, 1291.08m, 1274.81m, 1222.43w, 1136.20s, 768.63m, 733.50m (Fig. S2).

[Cu(btx)(ClO₄)]_n(**3**) A mixture of Cu(ClO₄)₂·6H₂O 0.0375 g (0.100 mmol) , btx 0.0248 g (0.100 mmol), and 5.00 mL deionized water was mixed in a 10.0 mL vial by ultrasonic dispersion method at room temperature. After a few minutes, the mixed solution was put into 20.0 mL Teflon lined stainless steel autoclave and heated at 140 °C for 2 days. After cooling to room temperature, complex **3** was washed with water and DMF twice. Orange block-shaped crystals of **3** were collected in a 66% yield based on Cu(II). The phase purity of compound was checked by powder X-ray diffraction. Anal. Calcd for $C_{12}H_{12}CuN_6ClO_4$: C, 35.74; H, 3.000; N, 20.84. Found: C, 35.69; H, 2.950; N, 20.91. IR (KBr, cm⁻¹) for 3438.47m, 3138.31m, 1622.21w, 1346.56w, 1285.31m, 1130.61s, 881.41w, 731.54m, 673.38m, 622.54m (Fig S3).





4-(2*H*-tetrazol-5-yl)pyridine

1,4-bis((1*H*-1,2,4-triazol-1-yl)methyl)benzene

Scheme 1. The structures of N - donor ligands used in this work

Photocatalytic experiments.

The photocatalytic experiments for aqueous Cr(VI) reduction were carried out in open air and at room temperature. A 125 W Hg lamp with a 365 nm cutoff filter provided ultraviolet light irradiation. The suspensions were irradiated by The photocatalysts 7mg were dispersed into 40.0mL of Cr(VI) aqueous solution (10.0 mg/L) which were prepare by potassium dichromate(K₂Cr₂O₇). The suspensions were magnetically stirred for 60 min in the dark to reach an adsorption-desorption equilibrium. In the reaction, 6 M H₂SO₄ was used to adjust the acidity. During the photoreduction reaction, stirring was maintained all the time to keep the mixture in suspension. The concentration of Cr(VI) in the solution was monitored colorimetrically using an UVvis spectrophotometer by the diphenylcarbazide method (DPC). The relative intensity of absorption peaks (λ =540 nm for Cr(VI)) was compared to value the degradation. The reduction ratio of Cr(VI) = (C₀ - C₁)/C₀ × 100%.

The photocatalytic experiments for the degradation of dyes of MB were carried out at room temperature. A 125 W Hg lamp with a 365 nm cutoff filter provided ultraviolet light irradiation. 7.00 mg of photocatalyst and 40.0 mL of MB (10.0 ppm) were added in a 50ml quartz tube. The suspensions were magnetically stirred for 60 min in the dark to reach an adsorption-desorption equilibrium. Samples were withdrawn at regular intervals under UV-light irradiation. The MB concentration changes were monitored by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 662$ nm using a UV-visible spectrophotometer. The fractional degradation efficiency (DR) of MB can be calculated by the following eq 1:

$$DR = (C_0 - C_t)/C_0 \times 100\%$$
 (1)

where C_0 is the initial concentration of MB and C_t is the concentration at a definite interval of time, respectively.

Results and discussion

Description of the crystal structure

 $1.[Cd(4-Hptz)_{2} \cdot (H_{2}O)_{2}]_{n}$

Complex 1 crystallized in the monoclinic space group $P2_1/n$. The structure of 1 is an square grid 2D(4,4) network. The asymmetry unit consists of one Cd(\mathbf{I}) atom, two 4-Hptz, two H₂O molecules (Fig.1a). Within the present complex molecule, the metal atom adopts a significantly octahedral coordination geometry. The basal coordination plane is composed of four N atoms of four 4-Hptz ligands with the Cd-N distances in the range of 1.911-1.954 Å, and the apical position is occupied by two O atoms arising from two H₂O molecules with a Cd-O distance of 2.794 Å (Fig.1b). The two crystallographically independent Cd(II) ions are linked together by two N atoms of pyridine and tetrazole from the same ligand 4-(1H-tetrazol-5-yl)pyridine ligand (Fig.1c). The distance of Cd1…Cd1 is 8.211(4) Å. The Cd–O bond distances lie in 2.326(2) Å, which are comparable to reported Cd-O bond distance²⁹, and the distances are conformed to the normal range The N-Cd-N geometry angles are in the range of 92.55(9)-87.45(9)° and the N-Cd-O geometry angles are in the range of 94.60(9)-82.84(8)°. The 20-member ring has the dimensionalities of 14.3643(8) Å ×7.9574(6) Å (diagonal metal-metal distances). The porous structure of MOFs as the photocatalysts facilitates the diffusion of substrates and products through MOFs channels, making MOFs an ideal platform to incorporate catalytic centers. Herein, if each Cd(II) ion is simplified as a 4-connected node, complex 1 can be topologically classified as a 2D network (Fig.1d) with sql topology represented by a Schläfli symbol of $\{4^4.6^2\}$ (Fig.1e).



Figure 1. View of (a) The asymmetry unit with one Cd(\mathbb{I}) atom; (b) the coordination environment of Cd(\mathbb{I}) ions; (c) Coordination geometry of the four Cd(\mathbb{I}) centers; (d)

the 2D layer structure, and (e) the sql topological net of complex 1.

$2 [Cu(btx)_2(ClO_4)_2]_n(2)$

On the basis of single crystal X-ray analysis, 2 crystallized in the monoclinic space group $P2_1/n$. The asymmetry unit consists of one Cu(II) ion, two btx molecules, two ClO₄⁻ anions (Fig. 2a). Within the present complex molecule, the metal atom adopts a significantly octahedral coordination geometry, in which the basal coordination plane is composed of four N atoms arising from four btx ligands with the Cu-N distances in the range of 1.911-1.954 Å, and the apical position is occupied by two O atoms arising from two ClO₄⁻ anions with a Cu-O distance of 2.794 Å (Fig. 2b). The two crystallographically independent Cu(II) ions are linked together by N····N atom from the same btx ligand forming 2D layer structure, the 54-member ring consists of six btx ligands and six Cu(II) ions (Figs. 2c, 2d). The distance of Cu···Cu is 14.088(16) Å. The values of N1-Cu-N1, N1-Cu-N4 and N4-Cu-N4 were found to be 180.0(3)°, 91.7(3) - 88.3(3)° and 180.0°, respectively. The Cu-N1 and Cu-N4 distance were found to be 2.015(7) and 2.028(7) Å, respectively. The 54-member ring has the dimensionalities of 32.016(45) Å ×14.0881(16) Å (diagonal metal-metal distances). The porous structure of MOFs as the photocatalyst facilitates the diffusion of substrates and products through MOF channels, making MOFs an ideal platform to incorporate catalytic centers. Simplifying Cu(II) ions as 4-connected nodes, the complex would produce a 3D CdS-type net (Fig. 2e) with a Schläfla symbol of $\{6^{5}\cdot 8\}$ (Fig. 2f). The distances of C3-N3 (1.457 Å) and C3-C4 (1.512 Å) are shorter than the distances of C-N covalent bonds(1.470 Å) and C-C covalent bonds(1.540), respectively, which proves that there are conjugation action between C3-N3 and C3-C4.



Figure 2. Views of (a) The asymmetry unit with one Cu(II) atom; (b) the coordination environment environment of Cu(II) and linkage modes of the ligands, (c) Coordination geometry of the six Cu(II) centers; (d) the 2D layer structure, (e) the 3D net structure, and (f) the topogical net of complex 2

$3.[Cu(btx)(ClO_4)]_n$

X-ray diffraction analysis shows that complex **3** is comprised of undulated 1D network. The present complex molecule consists of four Cu(I) ions, four btx ligand molecules and four ClO₄⁻ anions. Each Cu1(I) ion displays a plane triangle coordination geometry, coordinated by two nitrogen atoms from btx ligand and one oxygen atoms from ClO₄⁻ anion, respectively. The values of Cu1-N distance and Cu1-O distance are in the range of 1.863(5)-1.868(6) Å and 2.826(5) Å, respectively. Each Cu2(I) atom displays a linear coordination geometry, coordinated by two nitrogen atoms from two btx ligand molecules with the values of Cu2-N distance are 1.858(5) Å. Each Cu3(I) atom displays a tetrahedron coordination geometry, coordinated by two nitrogen atoms from two btx ligand molecules and two oxygen atoms from two ClO₄⁻ anions, respectively. The values of Cu3-N distance are in the range of 1.862(6)-2.805(5)Å. The values of Cu1-N distance and Cu1-··Cu3 distance are 13.344(11) and 13.149(11) Å, respectively. The two crystallographically independent Cu(I) ions are linked together by two N atoms from the one btx ligand molecule (Fig.3a). The adjacent benzene rings of btx ligands in the double-layers

overlap parallel to each other with a suitable space (3.628 Å) to form the $\pi \cdots \pi$ stacking interactions(Fig.3b).



Figure 3. View of (a) the coordination environment of Cu(I) ions, (b) the 2D structure of complex 3.

Physical characterizations.

Thermal analyses

The thermal property of complex **1** has been analysed by TGA under N_2 atmosphere with a heating rate of 10 °C min⁻¹, and are shown in Fig. S4. Complex **1**, has no weight loss up to 224 °C, followed by a sharp weight loss of 8.2% to 264 °C. This weight loss can be assigned to the loss of the coordination water(calcd. 7.70%). Then the weight loss 61.8% from 264°C to 524°C, including loss weight 29.7% from 264 to 351°C to release one ligand (calcd.30.7%) and loss weight 31.5% from 351°C to 524 °C, to release another ligand(calcd.30.7%).

The thermal properties of complexes 2 and 3 have not been analysed because of the explosiveness of ClO_4^- .



Figure 4. UV-Visible absorption spectra complex of 1(a), complex 2(b) and complex 3(c); The valence band XPS pattern of complex 1(d), complex 2(e) and complex 3(f)

UV-Vis diffuse reflectance spectroscopy(DRS)

Photoelectron spectroscopy(XPS) Valence band spectrum

The optical absorptions of these complexes were investigated by DRS and XPS. The optical HOMO/LOMO gap of samples can be estimated by the absorption spectra using the equation, $\alpha hv = (hv - E_g)^{1/2}$, where α , h, and E_g are the absorption coefficient, Planck constant, and HOMO/LOMO gap, respectively. As shown in Fig 4a, 4b, and 4c, the E_g value of samples were determined by measuring the x-axis intercept of an extrapolated tangential line from the linear regime of the curve. The HOMO/LOMO gap energies are estimated to be 4.12 eV, 3.58 eV, 2.59 eV for complexes 1, 2 and 3, respectively. And the main absorption bands are 261 nm, 245

nm, 283 nm for complexes 1, 2 and 3, respectively. Apart from appropriate HOMO/LOMO gap, proper matching of valence band (E_v) and conduction band (E_c) sites is also important for evaluating photocatalysis.

The E_v positions of samples are determined by linear extrapolation of the leasing edges of VB-XPS spectra to the base lines. As shown in Fig. 4d, 4e, and 4f, the E_v values are 2.98 eV, 3.20 eV and 1.72 eV for complexes **1**, **2** and **3**, respectively. MOFs have some semiconductors behaviors, in order to the convenience of compare the three complexes, the conduction band level of these complexes are estimated by the equation, $E_c = (E_v - E_g)^{30}$. Then we can get the conduction band level (-1.14 eV for **1**, -0.38 eV for **2**, -0.87 eV for **3**).

Photocatalytic reduction of Cr(VI).

To investigate the photocatalytic efficiency of three complexes in this work, the photoreduction of Cr(VI) was performed as a standard protocol during inorganic pollutant under dark and light conditions. As shown in Figs. 5a, 6a, and 7a, the photoreduction efficiencies of Cr(VI) were very low in the dark or in the absence of a photocatalysts. The previous study reported that the reduction rate of aqueous Cr(VI) over photocatalysts is greatly influenced by pH values of the solution. We adjust the different pH values by using 6 M H₂SO₄. As shown in Figs. 5b, 6b and 7b. it can be seen that the photoreduction efficiencies of Cr(VI) were greatly improved by the decreasing the pH values. Different from other catalysts, the reduction process over complex **2** was slowly accelerated by decreasing the pH values. This result of the experiment is consistent with other reports on aqueous reduction of Cr(VI) by MOFs photocatalysts³¹⁻³³. Under acid conditions, the $Cr_2O_7^{2-}$ anion is predominant in the solution, and the reduction proceeds as eq 2:

$$14H^{+} + Cr_{2}O_{7}^{2^{-}} + 6e^{-} \rightarrow 2Cr^{3^{+}} + 7H_{2}O$$
 (2)

To obtain the optimum the photocatalytic reduction condition, methanol was added as a hole scavenger in the reaction. As shown in Figs. 5c, 6c and 7c, different dosage methanol were added where the reactions were all in acid condition with the same pH value of 3.0. The addition of methanol indeed promotes the photocatalytic activity for the reduction of Cr(VI). Experiments show that the higher the amount of methanol

was added, the faster the reduction of Cr(VI) is. Results show that the addition of 200 uL methanol is befitting for the reaction. Figs. 5d, 6d and 7d display the timedependent absorption spectra for the reaction of photocatalytic reduction Cr(VI) under pH 3.00 and 200 uL of methanol. Result show that about 100% of Cr(VI) in the photocatalytic reaction over complex 1 could be reduced after 50 min. About 92.17% of Cr(VI) in the photocatalytic reaction over complex 2 could be reduced after 70 min, and about 82.92% of Cr(VI) in the photocatalytic reaction over complex 3 could be reduced after 60 min at the same condition. Figs. 8a, 8b and 8c show a linear relationship between $\ln(C_0/C_t)$ and the irradiation time for MB degradation. The rate constants for Cr(VI) reduction with 1, 2 and 3 under UV light are 0.04818 min⁻¹, 0.02953 min⁻¹, and 0.02175 min⁻¹, respectively. As shown in Fig. 8d, the photocatalytic acitivity of complex 1 is the best in these three photocatalysts. The hole scavenger of methanol significantly promotes the photocatalytic reaction, which limit the recombination between photoinduced electrons and holes to accelerate the target reaction³⁴. Moreover, the E_g values of complexes 1, 2 and 3 are bigger than the E_g value of reduction Cr(VI), indicating that those complexes are able to reduce Cr(VI). The higher Eg value of samples is helpful for suppressing recombination between photoinduced electrons and holes³⁵. Therefore, complex **1** has the best photocatalytic activity. Compared with some photocatalysts which have been reported (Table S5), complexes 1 and 2 have the advantage, for example, the dosage of photocatalyst is less than TiO₂ (1.00 g/L, 300min) to the same effect of reduction within shorter time³⁶. Xinjuan Liu and co-workers reported ZnO-RGO composites spent more energy by using UV light (500W high pressure Hg lamp) than the complexes in this paper (125 W Hg lamp)³⁷. Moreover, the dosage of the photocatalyst G-TiO₂ was about 4 times as much as we used. And there was not any analysis about the underlying mechanism of the reduction of $Cr(VI)^{38}$.



Figure 5. View of (a)time-dependent absorption spectra for the reaction of photocatalytic reduction of Cr(VI) with methanol (2.00 mL) at pH 3.0; (b)Control experiments for the reduction of Cr(VI) under different conditions; (c) photocatalytic reduction of Cr(VI) over complex 1 at different pH values; (d) photocatalytic reduction of Cr(VI) with different methanol addition of complex 1



Figure 6. View of (a)time-dependent absorption spectra for the reaction of photocatalytic reduction of Cr(VI) with methanol (2.00 mL) at pH 3.0; (b)Control experiments for the reduction of Cr(VI) under different conditions; (c) photocatalytic reduction of Cr(VI) over complex 2 at different pH values; (d) photocatalytic reduction of Cr(VI) with different methanol addition of complex 2.



Figure 7. View of (a) time-dependent absorption spectra for the reaction of photocatalytic reduction of Cr(VI) with methanol (2.00 mL) at pH 3.0; (b) Control experiments for the reduction of Cr(VI) under different conditions; (c) photocatalytic reduction of Cr(VI) over complex 3 at different pH values; (d) photocatalytic reduction of Cr(VI) with different methanol addition of complex 3



Figure 8. psudo-first-order kinetics curves of photocatalytic Cr(VI) reduction over different photocatalyst, (a), (b) and (c) are for complexes 1, 2 and 3, respectively; (d) the bar of psudo-first-order kinetics curves of photocatalytic Cr(VI) reduction over different photocatalysts.

Mechanism of reduction Cr(**VI**)

Based on the experiment results of Cr(VI) reduction, a potential mechanism of photocatalysis for complexes 1, 2 and 3 is proposed and illustrated in Fig.9. The organic linkers serve as sensor to absorb light and transfer the photoexcited charge carriers to the central metal clusters (LCCT mechanism) upon light excitation³⁹⁻⁴¹. The detailed process is as follows, upon UV light irradiation (hv $\geq E_g$), the photogenerated electron-hole pairs would separate through the ligand to metal charge transfer (LMCT) process^{42, 43}, complexes 1-3 can be excited to generate photoinduced electrons (e⁻) in the conduction band and photoinduced holes in the valence band by the ligand to metal charge transfer. The photogenerated electrons (e⁻) in the LOMO can directly attack Cr(VI) ions (eq 3), the holes oxidize the hole scavenger (methanol) to form CO₂ and H₂O and other minerals(eq 4). The LOMO edges of 1, 2 and 3 locate at ~-1.14eV, ~-0.38 eV and ~-0.87eV(all values are less than 0.51 eV), indicating that the photoexcited electron possess fixed reducing capacity for Cr(VI) reduction.

$$\{MOFs\} + hv \rightarrow \{MOFs\}(h^+ + e^-\}$$
(3)
methanol + h⁺ \rightarrow CO₂ + H₂O + others (4)



Figure 9. A schematic illustration of the energy position and Cr(VI) reduction over three complexes

Stability and reusability

The stability and reusability of MOF photocatalyst in aqueous solution are necessary in following photocatalysis study. As shown in Fig.10, photocatalytic acitivities of three complexes have been evaluated by recycling reactions for Cr(VI) under UV light. And it is easy to see that the photocatalytic activity of these three photocatalysts do not obviously decrease after four recycles for the reduction of Cr(VI), indicating that these three catalysts are with good stability in the photoreaction, which is demonstrated by XRD.



Figure 10. (a) The photocatalytic Cr(VI) reduction during four consecutive runs over photocatalyst 1; (b) The PXRD patterns for photocatalyst 1 before and after Cr(VI)reduction; (c) The photocatalytic Cr(VI) reduction during four consecutive runs over photocatalyst 2;(d) The PXRD patterns for photocatalyst 2 before and after Cr(VI)reduction photocatalyst 2; (e) The photocatalytic Cr(VI) reduction during four consecutive runs over photocatalyst 3; (f) The PXRD patterns for photocatalyst 3 before and after Cr(VI) reduction

Photocatalytic degradation of dyes.

MB is chosen as representative dye to evaluate the capability of three MOFs for organic pollutions degradation. As shown in Fig.11, there is no significant degradation in the dark. About 93.43%, 47.32% and 14.60% MB degradation were achieved after 100 min for complexes **1**, **2** and **3**, respectively. Without photocatalyst, the photocatalytic activity is very poor with 15.53% degradation of MB. Those results suggest that complex **3** has hardly any photocatalytic activity for MB, Complex **1** has comparative predominance for photocatalysis over complex **2**. Compared with some MOFs which have reported(Table 6S), complex **1** also has the preponderance, for example, the dosage of photocatalyst $[Cd_4(L)_2(BIME)_{0.5}(\mu_3-OH)_2(H_2O)_{1.5}] \cdot 2H_2O$ was ten times as much as we used for the same effect of degradation within the same time⁴⁴. Another MOFs photocatalyst $[Zn_2(fer)_2] \cdot 0.5H_2O$, in spite of lower irradiation (15W high pressure Hg lamp) within shorter time, the dosage of the photocatalyst was 21 times as much as complex **1**. Moreover, there was not any analysis about the underlying mechanism of the degradation of MB⁴⁵.

Mechanism of degradation MB

The photocatalytic mechanism of complexes **1** and **2** in dye molecule degradation is similar to those of reported photocatalyst⁴⁶ (Fig. S5). According to LCCT mechanism, we can know how it occurs. Irradiated by UV light, the photocatalysts get into excited state {Cat}(e^{-} + h^{+}) with photogenerated electron and hole are formed (eq 3). The water molecule was then captured by the photogenerated (h^{+}) for production of \cdot OH (eq 5). And O₂ can capture electrons from the conduction band to form \cdot O₂⁻ (eq 6). The generated O₂⁻ and \cdot OH can convert MB molecules into CO₂, H₂O and so on (eq 7). The process of photocatalytic reaction is as shown equation 5-7:

$$h^+ + H_2O \rightarrow \bullet OH + H^+$$
 (5)

$$O_2 + e^- \rightarrow \bullet O_2^- \tag{6}$$

$$MB + \bullet OH + \bullet O_2^{-} \rightarrow CO_2 + H_2O + Others$$
(7)



Figure 11. The MB degradation with different photocatalytic conditions

Several experiments were carried out to explore the photodegradation of MB. It is known that ·OH reacts with terephthalic acid (TA) in basic solution to generate 2-hydroxyterephthalicacid (TAOH), which emits a unique fluorescence signal with its peak centered at ca. 426 nm^{47, 48}. As shown in Fig.12, significant fluorescent signals associated with TAOH were generated upon both UV irradiation in a TA solution for 60 min.



Figure 12. The photoluminescence spectra of TAOH formed by the reaction of TA with ·OH radicals generated from different photocatalytic systems under UV-light for 60 min

Table 1. The fluorescence intensities (a.u.) at 426 nm in different systems at the different reaction times under UV- light

			6	
Time	1	2	No Cat	

0	6.575	6.488	4.189	
10	30.48	20.08	44.47	
20	102.3	19.31	56.97	
30	108.7	36.21	138.7	
40	251.6	30.44	126.1	
50	245.8	52.93	288.8	
60	824.7	38.28	248.1	

We can see that H_2O molecule can generate OH under UV-light irradiation. Compared with the system without photocatalyst, the system with 1 has a stronger fundamental signal, while the system with 2 has a weaker signal. These results clearly suggest that the photoexcited holes in the valence band of complex 1 are powerful enough to oxidize water to generate OH radicals. The fluorescence intensity can not significant prove what the main active component in 1 and 2 systems is.

In order to find out the truth of the matter, the effects of radical scavengers on the degradation of MB have been examined in an attempt to elucidate the reaction mechanism. Triethanolamine (TEOA) was chosen as an effective hole scavenger for the photocatalysis system, and tert-Butyl alcohol (t-BuOH) was chosen as OH scavenger because it reacts with \cdot OH radicals with a high rate constant (k = 6×10^{8})⁴⁹⁻ ⁵⁰. The results are shown in Fig.13a and 13b for 1 and 2, respectively. For 1, the degrading rate of MB increased to about 98.47% when the TEOA (10 mM) was added into the reaction solution after 50 min under UV light irradiation, while about 60.07% MB degradation was achieved when the t-BuOH (10 mM) was added into the reaction solution after 100 min under UV light irradiation. Compared with the system without scavenger, the degrading rate of MB increased significantly in the system with TEOA (10.0 mM), while decreased significantly in the system with t-BuOH (10.0 mM). These results clearly suggest that the main active component is OH radical for 1 system, which was consistent with the PL experiments. However, the reason why degrading rate of MB has increase after addition of hole scavenger TEOA is that TEOA has the ability to restrain charge recombination thereby increasing photocatalytic efficiency. For 2, the addition of t-BuOH and TEOA has led to 73.64% after 100 min and 78.52% after 70 min quenching in the system, respectively. Compared with three different systems, the addition of hole scavenger of TEOA and OH radical scavenger of t-BuOH significantly promotes the photocatalysis. Obviously, active component is neither \cdot OH radical nor hole in the system with 2. According to reports, the main active component of degradation MB is $\cdot OH$, $\cdot O_2^-$, and



hole, therefore we can draw the conclusion from the results that the main active component is $\cdot O_2^{-}$.

Figure 13. Effect of photocatalytic reaction as different trapping agents were added to the system. (a) and (b) are for 1 and 2, respectively.

Conclusions

In summary, three metal-organic frameworks using nitrogen heterocyclic ligands were synthesized by a facile solvothermal crystallization method and structurally characterized. The photocatalytic activities of these three complexes were evaluated using Cr(VI) reduction and dye degradation in aqueous solution under UV light irradiation. All of the complexes had high photocatalytic activity in Cr(VI) reduction. The rate constants of complexes 1-3 were 0.04818 min⁻¹, 0.02953 min⁻¹ and 0.02175 min⁻¹, respectively, which were higher than other photocatalysts. The experiments displayed that the photocatalytic reduction reaction of Cr(VI) to Cr(III) was superiorly accelerated by decreasing the pH values, indicating that three photocatalysts had strong acid-resistivity. And the addition of methanol can enhance the Cr(VI) reduction by retraining the recombination of photogenerated electron and photogenerated hole pairs. The cyclic 4 times experiments also indicated three photocatalysts are stable and reusable, enabling them to be potential candidates for wastewater treatment. Moreover, complexes 1 and 2 have been proved to be effective to enhance the photocatalytic degradation of MB under UV light irradiation. The mechanism research indicated that the main active component of 1 and 2 are \cdot OH and \cdot O₂, respectively. It can be concluded that photocatalytic Cr(VI) reduction and dve degradation from colored wastewater can be carried out by the complexs 1-3 as the environmentally friendly photocatalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Cr(III) H_2O OH . O2 Cr(VI) e UV light MOFs h^+ LUMO Degradation products 4.12V 3.58V 2.59V MOFs-1 MOFs-2 MOFs-3 номо

Abstract Graphic

The three novel coordination polymers were efficient, stable and reusable photocatalyst in degradation of MB dye and reduction of Cr(VI) aqueous solution.

Abstract Graphic



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Graphical Abstract-Synopsis

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