

基于2,6-二(4-羧基苯亚甲基)环己酮的金属-有机 框架化合物的合成与表征

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摘要: 以2,6-二(4-羧基苯亚甲基)环己酮(H_2L)为配体得到一例锰金属-有机框架化合物 $[MnL]_n$, 并运用红外、热重、循环伏安、固体紫外、X射线光电子能谱和X射线单晶衍射对其进行表征。单晶衍射分析表明该配合物属于三斜晶系, 空间群 $P\bar{1}$, 不对称单元由Mn(II)离子和一个 L^{2-} 配体组成。配体两端的羧基均为单齿配位, 配体中间羰基上的氧参与配位, 每个配体 L^{2-} 和3个Mn(II)离子配位, 形成相对稳定的三角形配位构型。配合物中的Mn(II)与氧原子形成六配位构型, 其中赤道面中的4个氧原子来自4个配体 L^{2-} 中单齿配位的羧基, 上下顶点的2个氧原子分别来自配体 L^{2-} 中的羰基, 从而形成八面体构型 $[MnO_6]$ 。拓扑分析表明该金属-有机框架化合物具有二维 kfd 结构特征。循环伏安测试表明在扫速为 $30\text{ mV}\cdot\text{s}^{-1}$ 时, 半波电位为171 mV, 固体紫外光谱表明该化合物的带隙为1.76 eV。该化合物在染料分子如亚甲基蓝、甲基橙的降解过程中, 具有一定的光催化活性。

关键词: 2,6-二(4-羧基苯亚甲基)环己酮; 锰配合物; 晶体结构; 拓扑分析

中图分类号: O614.71^{†1}

文献标识码: A

文章编号: 1001-4861(2021)05-0953-08

DOI: 10.11862/CJIC.2021.106

Synthesis and Characterization of Metal-Organic Framework Based on 2,6-Bis(4-carboxybenzylidene)cyclohexanone

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Abstract: By virtue of 2,6-bis(4-carboxybenzylidene)cyclohexanone (H_2L) as the ligand, metal-organic framework $[MnL]_n$ has been successfully fabricated. This compound has been characterized by FT-IR, powder X-ray diffraction, cyclic voltammogram, solid UV, X-ray photoelectron spectroscopy and single-crystal X-ray diffraction. It crystallizes in triclinic system with space group $P\bar{1}$, and the asymmetric unit is composed of one Mn(II) ion and one ligand. The

收稿日期: 2020-12-07。收修改稿日期: 2021-01-21。

国家自然科学基金(No.21771088)、浙江省自然科学基金(No.LY20B010005)、江苏省自然科学基金(No.BK20181374)和无机合成与制备化学国家重点实验室开放基金(No.2020-9)资助。

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carboxyl groups at both ends of the ligand are monodentate coordination, and the oxygen on the carbonyl group in the middle of the ligand coordinate with the central ion as well. Each ligand is coordinated with three Mn(II) ions and consequently, achieving a relatively stable triangular coordination configuration. The Mn(II) ion forms a six-coordinated configuration with oxygen atoms from six different ligands, *i.e.*, those four O atoms in the equatorial plane derived from four different ligands' carboxyl groups, the other two O atoms on the two vertices from the different ligands' carbonyl groups, respectively. As a consequence, the octahedral configuration $[\text{MnO}_6]$ unit is formed. Based on the topological analysis, its two-dimensional (2D) *kgd* structural character could be observed. The cyclic voltammogram showed that the half-wave potential, $E_{1/2}=(E_{\text{cp}}+E_{\text{ap}})/2$, was 171 mV when the sweep speed was $30 \text{ mV} \cdot \text{s}^{-1}$. The solid UV absorption spectra showed the band gap was $\sim 1.76 \text{ eV}$. Photocatalytic activity has been observed in the process of degrading of dye molecules such as methylene blue and methyl orange. CCDC: 2045728.

Keywords: 2,6-bis(4-carboxybenzylidene)cyclohexanone; manganese compound; crystal structure; topology structure

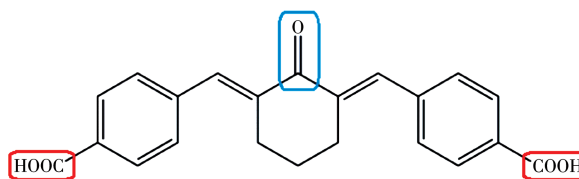
0 Introduction

As a type of functional crystalline material, metal-organic frameworks (MOFs) has developed rapidly and it could be exploited in the fields of gas adsorption and separation, electrochemistry, catalysis, ion exchange and sensors^[1-6]. Recently, Zang's group used highly ordered macro-micropore zeolitic imidazolate framework-8 (ZIF-8) to encapsulate enzyme such as horseradish peroxidase (HRP) and notably, the HRP enzyme not only maintained its activity, but also exhibited stability, recyclability, low leakage as well as resistance to chelating compounds. This work demonstrated the great potential of MOFs materials to help to fabricate biocatalysts^[7]. By using the multifunctional ligand of 3-(3,5-dicarboxylphenyl)-5-(4-carboxylphenyl)-1-*H*-1,2,4-triazole (H_3DBPT) to bridge hexanuclear $[\text{Cd}_6]$ clusters, a chemical-stable and thermal-stable luminescent metal-organic framework (MOF), $[\text{Cd}_3(\text{DBPT})_2(\text{H}_2\text{O})_4] \cdot 5\text{H}_2\text{O}$, has been reported by Liu et al. The resulting material has shown sensitivity and selectivity toward nitroaromatic compounds and nitroimidazole-based drug molecules^[8]. Taking advantage of the ligand 2,6-bis(((2-hydroxybenzyl)(2-hydroxyethyl)amino)methyl)-4-methylphenol, a fluorescent tetranuclear $[\text{Zn}_4(\text{L}-3\text{H})_2](\text{ClO}_4)_2 \cdot 3.5\text{H}_2\text{O}$ could bind to phosphate backbones of DNA covalently. And this complex exhibited its optimal DNA hydrolytic activity, indicating the potential application in the field of biological chemistry^[9].

During the process of achieving MOFs materials with aesthetical structural characters, organic ligands

that containing versatile coordination sites have important roles. We have embarked on several kinds of MOFs materials by using the 2,6-bis(4-carboxybenzylidene)cyclohexanone (H_2L) ligand (Scheme 1)^[10-11]. The H_2L ligand contains one keto and two carboxylic acid groups, which make it a suitable candidate to combine with oxophilic metal ions to achieve MOFs. Various structural characters have been explored in our laboratory: (a) when using lanthanide metals such as La, Ce, Pr, Nd, Sm, Eu and Gd, three-dimensional (3D) metal-organic frameworks with honeycomb cavities have been obtained^[10]; (b) when using transition metals such as Zn and Cd, two-dimensional (2D) metal-organic frameworks with structural diversity have been observed^[11]. It is believed that more elegant structural characters could be observed and in any case, experimental conditions such as pH, temperature, solvent type, reaction duration, template, auxiliary ligands and reaction type (batch or flow type) play important role in the process of achieving the final product.

The overarching aim of this research is to broaden MOFs chemistry and in this contribution, $[\text{MnL}]_n$ has been achieved in a feasible way. The described (3,6)-connected *kgd* topological character with schläfli sym-



Scheme 1 Ligand H_2L with potential coordination sites

bol (4^3)₂($4^6 \cdot 6^6 \cdot 8^3$) adds value to the research field.

1 Experimental

1.1 Materials and measurements

All the chemicals were received as reagent grade and used directly without further purification. The ligand H₂L was synthesized via Claisen-Schmidt condensation reaction. IR spectrum was recorded on a Varian 640 FT/IR spectrometer with KBr powder in a range of 4 000~500 cm⁻¹. Powder X-ray diffraction (PXRD) pattern was collected on a DX-2600 spectrometer with Mo K α radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293 K (Voltage: 40 kV, Current: 30 mA, Scan range: 0°~60°). Thermal gravimetric analyses (TGA) were carried out under N₂ flow on an SDT 2960 differential thermal analyzer at a heating rate of 10 °C·min⁻¹. Cyclic voltammograms (CVs) were obtained with a CHI 440A electrochemical workstation at room temperature. Platinum wire was used as a counter electrode and Ag/AgCl electrode was used as a reference electrode. Chemically bulk-modified carbon paste electrode (CPE) was used as the working electrode. The diffuse reflectance spectra (DRS) of the crystalline solid was recorded by the UV-Vis-NIR spectrophotometer (Cary 5000). The UV-Vis measurements of solution were carried out on a Thermo EV 201CP. X-ray photoelectron spectroscopy (XPS) analyses was carried out with a Kratos Axis Ultra

spectrometer using a monochromatic Al K α source (15 mA, 14 kV).

1.2 Syntheses of Mn-MOF [MnL]_n

A mixture of MnCl₂·4H₂O (9.89 mg, 0.05 mmol), H₂L (18.1 mg, 0.05 mmol), DMF (4 mL), C₂H₅OH (2 mL) and H₂O (1 mL) was placed in a 10 mL glass bottle and then under ultrasonic for 30 minutes. The mixture was heated in an oven at 80 °C for 20 hours. After slowly cooling to room temperature, dark brown block crystals were obtained by filtering and washing (Yield: 68%, based on Mn). IR (KBr, cm⁻¹): 3 425(m), 2 925(s), 1 624(vs), 1 405(s), 1 266(m), 1 139(m), 779(s). Elemental analysis Calcd. for C₂₂H₁₆MnO₅(%): C, 63.63; H, 3.88. Found(%): C, 62.76; H, 3.91.

1.3 X-ray crystallography

The suitable crystal of Mn-MOF was selected and characterized on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo K α ($\lambda=0.071\ 073\ \text{nm}$) at 293(2) K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package^[12-13]. The hydrogen atoms attached to carbon atoms were placed at geometrically estimated positions. A summary of the crystal data and structure refinements of the compound is provided in Table 1 and the selected bond lengths and angles are given in Table 2.

CCDC: 2045728.

Table 1 Crystal data and structure refinements for Mn-MOF

Empirical formula	C ₂₂ H ₁₆ MnO ₅	V / nm^3	0.856 2(2)
Formula weight	775.63	Z	1
Temperature / K	293(2)	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.504
Crystal system	Triclinic	μ / mm^{-1}	0.452
Space group	$P\bar{1}$	$F(000)$	401
a / nm	0.913 56(10)	Reflection collected	3 492
b / nm	1.010 99(11)	Independent reflection	2 135
c / nm	1.095 10(14)	R_{int}	0.017 3
$\alpha / (^\circ)$	64.975(12)	Goodness-of-fit on F^2	1.053
$\beta / (^\circ)$	70.872(11)	$R_1, wR_2 [I > 2\sigma(I)]$	0.035 1, 0.082 8
$\gamma / (^\circ)$	74.562(9)	$R_1, wR_2 (\text{all data})$	0.045 2, 0.087 2

Table 2 Selected bond distances (nm) and bond angles (°) for Mn-MOF

Mn—O1	0.220 6(2)	Mn1—O3 ^{iv}	0.218 4(2)	O2—C1	0.125 7(3)
Mn1—O1 ⁱ	0.220 6(2)	Mn1—O3 ^v	0.218 4(2)	O3—Mn1 ^{vii}	0.218 4(2)
Mn1—O1 ⁱⁱ	0.220 6(2)	Mn1—O3	0.218 4(2)	O3—C22	0.123 7(3)

Continued Table 2

Mn1—O2 ⁱⁱⁱ	0.211 18(16)	O1—Mn1 ^{vi}	0.220 64(19)	O2—C1	0.127 1(3)
Mn1—O2	0.211 18(16)	O1—C14	0.124 5(3)	O4—C22	0.129 1(3)
O1 ⁱ —Mn1—O1 ⁱⁱ	180.0	O2—Mn1—O3 ^{vi}	93.82(8)	O3 ^{iv} —Mn1—O3 ^v	180.00(7)
O2—Mn1—O1 ⁱ	90.82(7)	O2 ⁱⁱⁱ —Mn1—O3 ^v	86.18(8)	C1 ^{iv} —O1—Mn1 ^{vi}	147.05(18)
O2 ⁱⁱⁱ —Mn1—O1 ⁱ	89.18(7)	O2 ⁱⁱⁱ —Mn1—O3 ^{iv}	93.82(8)	C1—O2—Mn1	131.79(15)
O2 ⁱⁱⁱ —Mn1—O1 ⁱⁱ	90.82(7)	O3 ^{iv} —Mn1—O1 ⁱ	86.23(8)	C22—O3—Mn1 ^{vii}	145.2(2)
O2—Mn1—O1 ⁱⁱ	89.18(7)	O3 ^{iv} —Mn1—O1 ⁱⁱ	93.77(7)	O1—C14—C9	120.6(2)
O2—Mn1—O2 ⁱⁱⁱ	180.0	O3 ^v —Mn1—O1 ⁱ	93.77(7)	O1—C14—C13	118.9(3)
O2—Mn1—O3 ^{iv}	86.18(8)	O3 ^v —Mn1—O1 ⁱⁱ	86.23(8)		

Symmetry codes: ⁱ 1-x, 1-y, 2-z; ⁱⁱ -1+x, y, 1+z; ⁱⁱⁱ -x, 1-y, 3-z; ^{iv} 1-x, 2-y, 1-z; ^v -1+x, -1+y, 2+z; ^{vi} 1+x, y, -1+z; ^{vii} 1+x, 1+y, -2+z.

1.4 Photocatalytic degradation of organic pollutants by Mn-MOF

In this contribution, methylene blue (MB) and methyl orange (MO) were selected as model pollutants to explore their degradation process in the presence of Mn-MOF. Mn-MOF (20 mg) was added into 50 mL aqueous solution of MB or MO, then the obtained suspension was magnetically stirred in the dark for 15 minutes to ensure the equilibrium. The solution was exposed to UV irradiation from a 100 W Hg lamp ($\lambda = 365$ nm) and it was kept stirring. At given time intervals, 3 mL of sample was taken out for UV-Vis measurements.

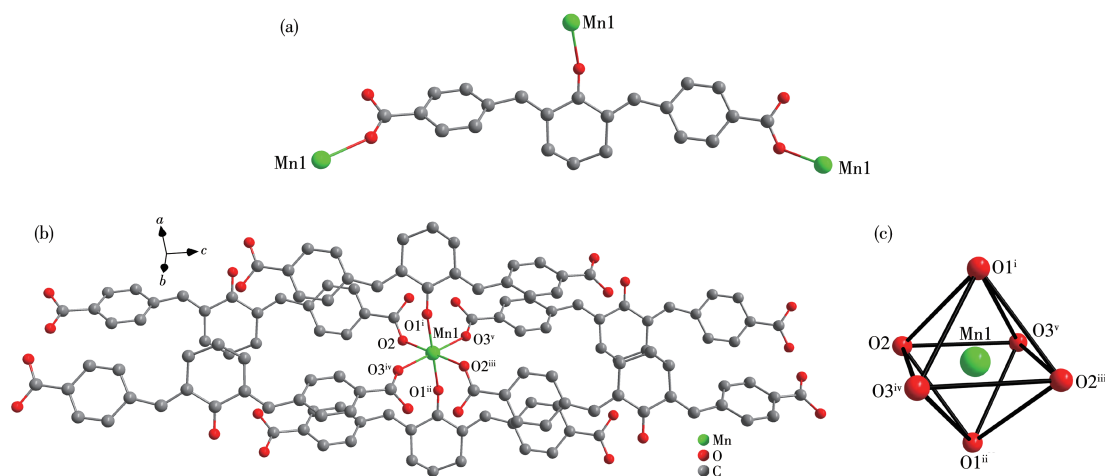
2 Results and discussion

2.1 Structural analysis of Mn-MOF

Crystallographic analysis reveals that Mn-MOF

crystallizes in the triclinic crystal system with space group $P\bar{1}$. The two carboxyl groups in the L^{2-} ligand are deprotonated, and the coordination mode is shown in Fig. 1. The carboxyl groups at both ends of the ligand are monodentate coordination, and the oxygen on the carbonyl group in the middle of the ligand participates the coordination as well. Each ligand is coordinated with three Mn(II) ions, thus forming a relatively stable triangular coordination configuration. The Mn(II) ion is coordinated with six O atoms from different ligands to form an octahedral $[MnO_6]$ unit (Fig. 1c). The four O atoms in the equatorial plane are derived from four different L^{2-} ligands' carboxyl groups (O2, O2^v, O3^{iv}, O3ⁱⁱⁱ), and the other two O atoms on the two vertices from the two ligands' carbonyl groups (O1ⁱ, O1ⁱⁱ), respectively.

The $[MnO_6]$ unit bridged each other through the O atoms on the carboxyl groups and four Mn(II) ions, gen-



Symmetry codes: ⁱ 1-x, 1-y, 2-z; ⁱⁱ -1+x, y, 1+z; ⁱⁱⁱ -x, 1-y, 3-z; ^{iv} 1-x, 2-y, 1-z; ^v -1+x, -1+y, 2+z

Fig.1 (a) Coordination mode of L^{2-} ligand in Mn-MOF; (b) Coordination environment of Mn(II) ion; (c) Coordination mode of Mn(II) ion

erating a one-dimensional (1D) chain along c axis direction with the Mn $\cdots$ Mn distance of 1.990 17(36) nm. Based on the one-dimensional (1D) chain (Fig.2a), the oxygen atoms and Mn(II) ions in b axis direction connect the one-dimensional chain with each other, forming a two-dimensional (2D) layered structure (Fig.2b). In addition, the two-dimensional (2D) plane has a hexagonal channel in c axis direction and a rectangular-like window perpendicular to a axis.

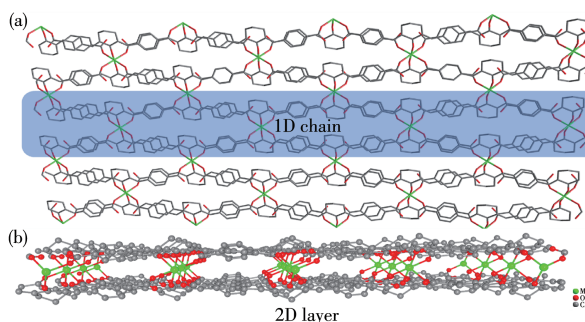


Fig.2 (a) One-dimensional chain structure and (b) 2D layer structure of Mn-MOF

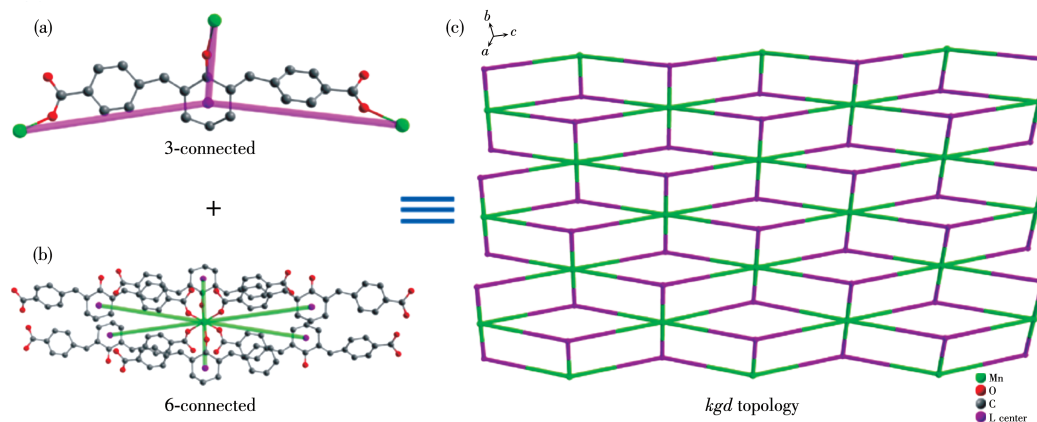


Fig.3 Topological simplification diagram of Mn-MOF

2.2 IR spectrum and PXRD of Mn-MOF

As shown in Fig.4a, the weak absorption peak at $2\,944\text{ cm}^{-1}$ is assigned to the C—H stretching vibration of cyclohexanone ring. A strong band at $1\,635\text{ cm}^{-1}$ can be attributed to the C=O stretching vibration of the carbonyl group. Two absorption peaks at $1\,599$ and $1\,404\text{ cm}^{-1}$ are assigned to the asymmetric and symmetric stretching vibration of carboxyl group, respectively. The peak at $1\,280\text{ cm}^{-1}$ can be assigned to the C—O stretching vibration. In addition, the peak at 975 cm^{-1} is the characteristic absorption peak of C=C, while a peak at 785 cm^{-1} arises from the para-substituted char-

Regarding its structural character, the topological structure is described in Fig.3. Each ligand is coordinated with three Mn atoms, which can be simplified as a three-connected node, namely node 1 (Fig.3a), and each Mn atom is connected to six ligands, which can be simplified as a six-connected node, namely node 2 (Fig.3b). The Mn-MOF can be simplified to the classic 2D (3,6)-connected *kgd* topology by TOPOS (Fig.3c) and its Schläfli symbol is $(4^3)_2(4^6\cdot6^6\cdot8^3)$.

acteristic peak of phenyl ring.

To test the phase purity of Mn-MOF, PXRD experiment was carried out (Fig.4b). The diffraction peaks of both simulated and experimental patterns matched well in the key positions, indicating that the powders of the compound are single phase. The intensity differences may arise from the different orientation of the samples.

2.3 TGA analysis and electrochemical property of Mn-MOF

The thermal stability of Mn-MOF has been investigated. The TGA curve showed one step of weight loss (Fig.5a). The whole skeleton began to collapse at about

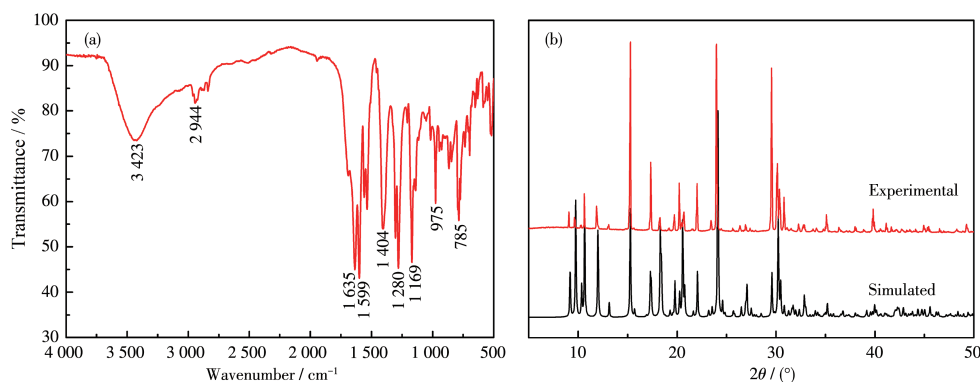


Fig.4 (a) IR spectrum and (b) PXRD patterns of Mn-MOF

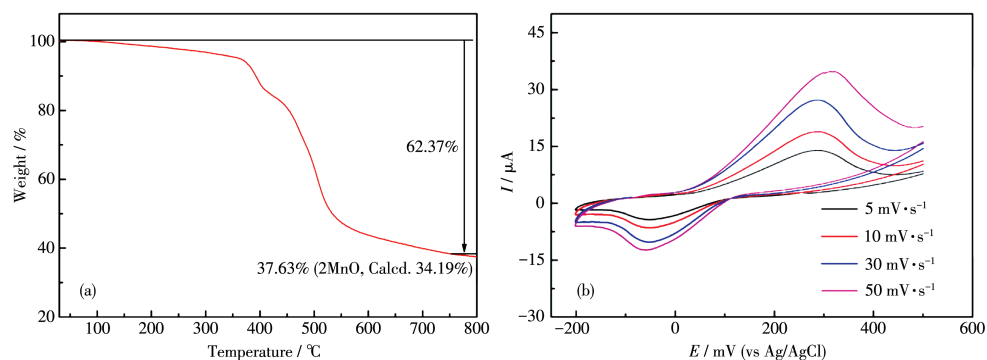


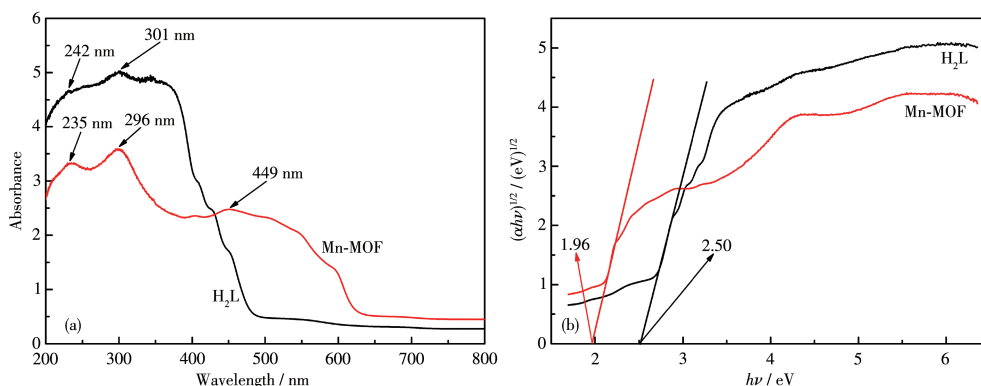
Fig.5 (a) TGA curve and (b) CV curves of Mn-MOF

375 °C with the weight loss being 62.37%, indicating that this MOF has relatively high thermal stability. The structure became stable after 700 °C, and the final residue was MnO (37.63%).

The electrochemical property of Mn - MOF has been investigated in detail in 0.5 mol·L⁻¹ Na₂SO₄+0.1 mol·L⁻¹ H₂SO₄ aqueous solution. In a potential range of -200~500 mV, there was a pair of reversible redox peak. The half-wave potential $E_{1/2}$ was 171 mV (Scan rate: 30 mV·s⁻¹) (Fig.5b).

2.4 DRS of Mn-MOF

The absorption data of H₂L and Mn-MOF were calculated from reflectance data by using the Kubelka-Munk function. BaSO₄ powder was used as reference (100% reflectance)^[14]. Compared with H₂L ligand, the red shift of Mn - MOF has been observed. The peak around 450 nm may arise from the metal - to - ligand charge transfer (MLCT)^[15], while those two absorptions at 235 and 296 nm might originate from the $\pi \rightarrow \pi^*$ absorption of the phenyl ring and double bond unit

Fig.6 (a) UV-Vis DRS spectra and (b) band gaps of H₂L and Mn-MOF

(Fig.6a). The estimated band gap of H_2L and Mn-MOF samples were ~ 2.50 and ~ 1.96 eV, respectively (Fig.6b).

Apparently, compared with the ligand, Mn-MOF exhibited absorbance around 450 nm. It may act as photocatalyst and its activity has been explored^[16-17].

2.5 XPS of Mn-MOF

To further clarify the valence of Mn ion in Mn-MOF, the Mn2p XPS spectrum was recorded and fitted (Fig.7). Analysis of Mn2p XPS spectrum show that the binding energies of $Mn2p_{3/2}$ (640.9 eV) and $Mn2p_{1/2}$ (653.5 eV) and their spin energy difference (12.6 eV) are consistent with the Mn(II). Moreover, the unique satellite peak could further confirm that Mn ion is divalent^[18-20].

2.6 Photocatalytic activities

MOFs materials could be exploited as green photocatalysts for the removal of organic pollutants from water^[11]. So, the degradation of MB and MO is used to

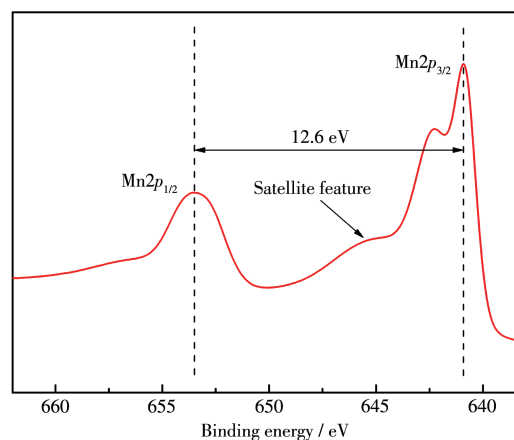
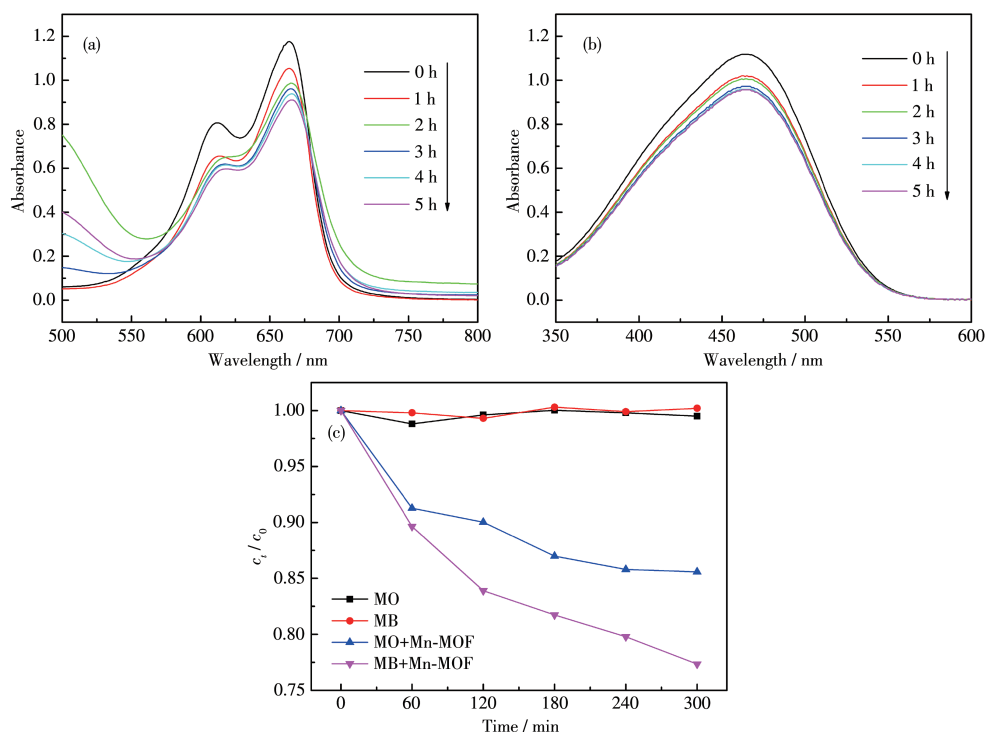


Fig.7 XPS spectrum of Mn2p in Mn-MOF

evaluate the photocatalytic activity of Mn-MOF. Fig.8 shows the photocatalytic effect of Mn-MOF and its degradation efficiency for MB is better than MO. The calculation results show that the conversion of MB and MO under irradiation after 5 h was 23% and 14%, respectively (Fig.8c).



c_t : dye concentration at time t , c_0 : dye concentration at the beginning of photocatalytic degradation reaction

Fig.8 UV-Vis spectra varying with light time of (a) MB and (b) MO dye in the presence of Mn-MOF;
(c) Degradation rates of MB/MO in the absence and presence of Mn-MOF

3 Conclusions

Using 2, 6-bis(4-carboxybenzylidene)cyclohexanone (H_2L) as organic ligand, one 2D Mn-MOF with

kgd topology has been fabricated and characterized by IR, PXRD, TGA, CV, solid UV, XPS and X-ray crystal structure analysis. Those O atoms of L^{2-} and Mn(II) ions

connect the one-dimensional chain with each other, forming the 2D layered structure. Currently, we are actively pursuing along this research line as following: (1) apart from the main ligand, we aim to construct diverse types of structures by introducing various auxiliary ligands; (2) we are using the emergent technique, flow chemistry, and taking advantage of its impressive abilities such as high effective mass- and heat-transfer to synthesize MOFs and hopefully, we could finely control reaction rate, speed up the synthetic process and obtain target molecules with high yields^[21-24].

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