https://doi.org/10.31871/IJNTR.8.4.9 International Journal of New Technology and Research (IJNTR)
ISSN: 2454-4116, Volume-8, Issue-4, April 2022 Pages 26-28

Synthesis and Characterization of A Fluorescent Metal-Organic Framework: Zn-MOF

Su-ke Lan

Abstract—**Metal-organic frameworks (MOFs), as unique hybrid porous materials composed of metal ions or clusters self-assembled with organic linkers, have attracted wide attention for their unique physical and chemical properties, especially for the fluorescent MOFs. In this article, a fluorescent zinc MOF (Zn-MOF) material was successfully prepared with Zn as the central ion at room temperature. It was characterized by fluorescence (FL) spectrometer, dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and X-ray diffractometer (XRD). The material exhibits bright red fluorescence under ultraviolet light, which can be used as a promising candidate for fluorescent sensor.**

Index Terms— **Zn-MOF, fluorescent, XPS, ultraviolet light.**

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline hybrid materials over the last 20 years. Due to the desirable properties, MOFs are widely used in many chemical fields such as catalysis, sensing, gas storage, and biomedical applications [1-6]. MOFs can be one-, two-, or three-dimensional structures containing inorganic units called primary building units or metal cation clusters called secondary building units, formed by linkage to organic polydentate ligands. By changing the type, length, function, and charge of the linkages between ligands or metals, or the nodal components within the material framework, different MOF structures with multiple functions can be obtained. Among them, fluorescent MOFs are widely used in the field of fluorescence sensing due to their high sensitivity and special selectivity. So far, many strategies for preparing fluorescent MOFs have been studied, which can be divided into three methods: (1) encapsulating fluorophores as the intrinsic structural components of MOFs during the synthesis process; (2) soak the synthesized MOF in the imaging agent solution to load it into the hole through size effect, ion exchange or post-synthesis modification, collectively referred to as the post-insertion method; (3) the developer is attached to the MOF surface by covalent conjugation, electrostatic or hydrophobic interactions.

Compared to conventional fluorescent reagents, it has reported that, fluorescent MOFs materials are a promising fluorescent probe, such as for the detection of metal ions, organics, the biomarkers [7-9]. Some MOFs with good water stability and chemical stability can be used to detect inorganic ions [10]. In attention, some toxic and harmful gases, such as carbon disulfide, can also be detected by MOFs sensors with dual emission wavelengths [11-12].

Su-ke Lan, College of Chemical and Environment Protection, Southwest Minzu University, Chengdu, China

Therefore a Zn-based dual-emission fluorescent MOF (Zn-MOF) with good luminescence properties was designed in this study.

In this paper, a novel fluorescent MOF, Zn-MOF, has been prepared, and chemical and physical properties of the Zn-MOFs has been characterized. In the Zn-MOF, meso-Tetra(4-carboxyphenyl)porphine (TCPP) was used as a fluorescent group, and Zn was used as the metal center for. The characterization results indicated that the fluorescent Zn-MOF was successfully prepared, which could be a potentially applicable fluorescent probe.

EXPERIMENTAL

Materials

Terephthalic acid (99%), zinc nitrate hexahydrate (99%), sodium hydrate (NaOH), hydrochloric acid, anhydrous ethanol and meso-Tetra(4-carboxyphenyl)porphine (TCPP) used in this study were of analytical grade.

Synthesis of Materials

The precursor material $[Zn(BDC)(H_2O)_2]$ was prepared according to the literature method [13]. First, 0.5540 g of terephthalic acid has been added into a beaker containing 25 mL of 1 mol/L NaOH solution, and stirred until terephthalic acid was dissolved completely. The mixture was dropwise to 1 mol/L hydrochloric acid solution with a pipette, and then pH was adjusted to neutral. 2.9750 g of $Zn(NO_3)_2{\cdot}6H_2O$ was dissolved in 25 mL of pure water. After that, the above two solutions were mixed thoroughly with a magnetic stirrer for stirring 20 min at room temperature. The white solids in the mixture were filtered and vacuum dried for 4 hours to obtained $Zn(BDC)(H_2O)_2$. After that, the $[Zn(BDC)(H_2O)_2]$ and TCPP were transferred to 5 mL of ethanol solution. After magnetic stirring at room temperature for 4 hours, a reddish-brown powder has been obtained, which is Zn-MOFs.

RESULTS AND DISCUSSION

Characterization of Zn-MOFs

Fluorescence spectrometer were used to identify the properties Zn-MOFs. The representative fluorescence spectrum of the Zn-MOFs was shown in Figure 1a. The fluorescence spectrum was carried out to verify the MOF fluorescence property, it can be seen that, the fluorescence spectra of the Zn-MOF aqueous solution shows a characteristic absorption peak at ~610 nm and ~662 nm. The DLS was utilized to measure the nanoparticle size of Zn-MOFs, as shown in Figure 1b. The average hydrodynamic diameter of Zn-MOF was approximately 122 nm via DLS measurements.

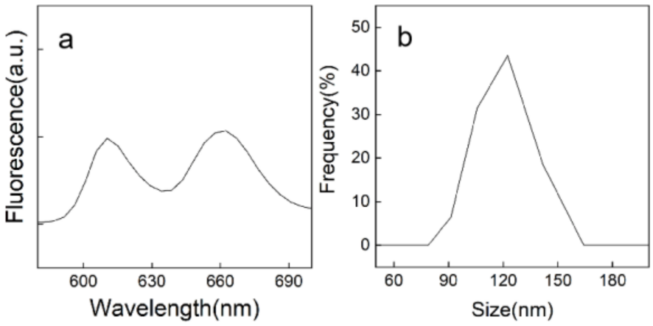

Figure 1 Fluorescence spectrum of Zn-MOFs (a); hydrated particle size of Zn-MOFs (b).

X-ray photoelectron spectroscopy (XPS) is widely used to analyze the elemental composition of samples as well as the chemical states and molecular structures of elements. As shown in Figure 2, chemical composition of Zn-MOFs was analyzed by XPS. Typical C 1s, O 1s and Zn 2p XPS spectra were recorded, indicating the presence of C, O and Zn in the Zn-MOFs. C 1s spectrum is used to analyze the chemical state of C element. As shown in Figure 2b, the content of C-C (284.8 eV) is greater than that of C=O (288.5 eV), indicating that the C element in Zn-MOF mainly exists in the form of C-C. As shown in Figure 2c, O element has only one valence state, namely -2 valence, because there is only one peak in the O 1s spectrum. As shown in Figure 2d, the binding energy of 1022.91 eV is Zn $2p^{3/2}$ and the binding energy of 1046.01 eV is Zn $2p^{1/2}$.

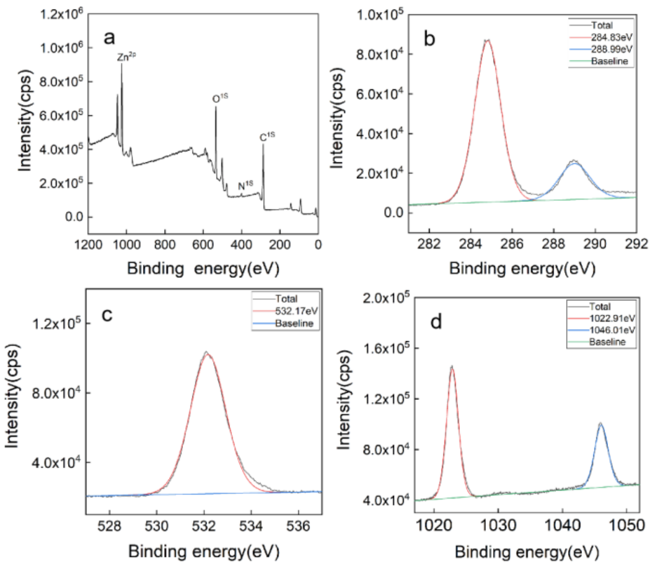

Figure 2 Full spectrum of XPS scans (a); C 1s XPS spectrum (b); O 1s XPS spectrum(c); Zn 2p XPS spectrum (d).

Transmission electron microscopy (TEM) is an electronic optical instrument with high resolution and high magnification, which is widely used in materials science and other research fields. Fine flake-like particles of Zn-MOF were observed by TME, as shown in Figure 3a. X-ray diffraction (XRD) technology has become the most basic and important method for structural testing, XRD spectrum of Zn-MOF has been shown in Figure 3b. There are diffraction peaks at 12.18°, 16.90° and 25.52° in XRD spectrum of Zn-MOFs (Figure 3b), due to the higher peak intensity of XRD spectrum, it shows that the crystallinity of Zn-MOF is better.

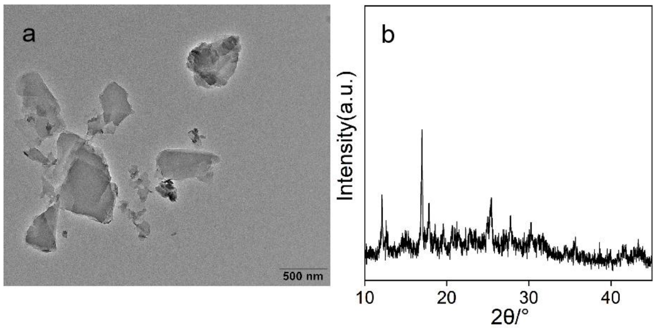

Figure 3 TEM image of Zn-MOFs (a); XRD spectrum of Zn-MOFs (b).

Under the irradiation of UV (λex = 365nm), the fluorescence properties of Zn-MOF were displayed bright red emission at room temperature (Figure 4), which indicated that Zn-MOFs have excellent fluorescence properties.

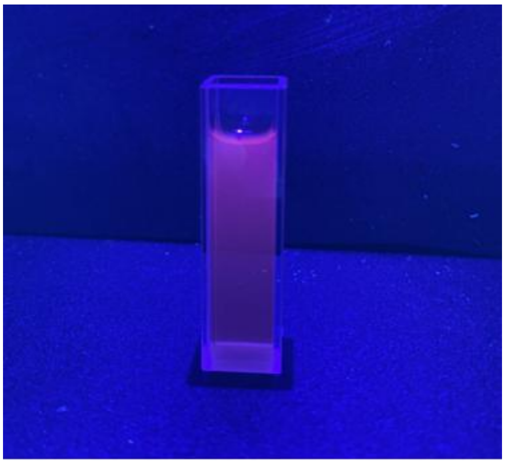

Figure 4 Image of Zn-MOFs under UV light.

CONCLUSION

In conclusion, a novel kind fluorescent organometallic framework material for sensing was prepared. The prepared Zn-MOFs has good stability in water, and the hydrated particle size is about 93 nm. Fluorescence properties were studied in a fluorescence spectrometer and under the excitation of UV light. The elemental composition of Zn-MOFs was determined by XPS, and the crystallinity and crystal structure were determined by XRD. Based on the above experimental results, the prepared Zn-MOFs are considered as a potential fluorescence sensor.

REFERENCES

[1] Wang H, Chen L, Pang H, et al. MOF-derived electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions[J]. Chemical Society Reviews, 2020, 49:1414-1448.
[2] Haque E, Jun J, Jhung S. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235)[J]. Journal of Hazardous Materials, 2011, 185(1):507-511.
[3] Li Y, Yang R. Gas adsorption and storage in metal-organic framework MOF-177.[J]. Langmuir the Acs Journal of Surfaces & Colloids, 2007, 23(26):12937-44.
[4] Liu T, Li P, Yao N, et al. CoP-Doped MOF-Based Electrocatalyst for pH-Universal Hydrogen Evolution Reaction.[J]. Angewandte Chemie, 2019.131(14):4727-4732.
[5] Alezi D, Belmabkhout Y, Suyetin M , et al. MOF Crystal Chemistry Paving the Way to Gas Storage Needs: Aluminum-Based soc-MOF for CH4, O2, and CO2 Storage.[J]. Journal of the American Chemical Society, 2015, 137(41):13308-13318.

[6] Wu M, Yang Y. Metal–OrganicFramework (MOF)-Based Drug/Cargo Delivery and Cancer Therapy[J]. Advanced Materials, 2017, 29(23):1606134.
[7] Liu Q, X Li, Wen Y, et al. Twofold Interpenetrated 2D MOF Nanosheets Generated by an Instant In Situ Exfoliation Method: Morphology Control and Fluorescent Sensing[J]. Advanced Materials Interfaces, 2020, 7(16):2000813.
[8] Liu X, Zhang X, Li R, et al. A highly sensitive and selective "turn off-on" fluorescent sensor based on Sm-MOF for the detection of tertiary butylhydroquinone[J]. Dyes and Pigments, 2020, 178(28):108347.
[9]Guo L, Liu Y, Kong R, et al. Turn-on fluorescence detection of β-glucuronidase using RhB@MOF-5 as an ultrasensitive nanoprobe[J]. Sensors and Actuators, 2019, B295(SEP.):1-6.
[10] Liu Q, Zhang S, Yang J, et al. A water-stable La-MOF with high fluorescence sensing and supercapacitive performances[J]. The Analyst: The Analytical Journal of the Royal Society of Chemistry: A Monthly International Publication Dealing with All Branches of Analytical Chemistry, 2019, 144(15):4534-4544.
[11]Wu Z, Tan B, Feng M, et al. A magnesium MOF as a sensitive fluorescence sensor for CS2 and nitroaromatic compounds[J]. Journal of Materials Chemistry A, 2014, 2(18):6426-6431.
[12] Fu H, Yan L, Wu N, et al. Dual-emission MOFdye sensor for ratiometric fluorescence recognition of RDX and detection of a broad class of nitro-compounds[J]. Journal of Materials Chemistry A, 2018, 6:9183-9191.
[13] Li Z, Zhang M, Qiu L. Synthesis and Fluorescent Property of Metal-organic Frameworks [Zn(BDC)(H2O)2-2x·(8-Hq)] with Tunable Fluorescence[J]. Chinese Journal of Luminescence, 2010, 3:421-426.