Ultrasonic assisted solvothermal synthesis of CaCO$_3$-Ni-MOF and its application in removing heavy metal ions

Jie Yang$^{1,2}$, Guangchao Qin$^1$, Qihong Li$^3$, Huabin Huang$^3$, Yun Wu$^1$, *, Xiuxiu Zuo$^1$

$^1$School of Energy Materials and Chemical Engineering, Hefei University, Hefei, China
$^2$CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, China
$^3$Cologne Powder Co., Ltd., Hezhou, Guangxi, China

*Corresponding author’s e-mail: 542529829@qq.com

Abstract. The effect of CaCO$_3$-Ni-MOF synthesized by different ratio between Ni$^{2+}$ and organic ligand terephthalic acid on the removal of heavy metal ions was studied. CaCO$_3$-Ni-MOF was synthesized by ultrasonic and solvothermal methods. The crystal structure and morphology of the material were characterized by XRD and SEM. TG curve was used to test the thermal stability of the material. In addition, the experimental study also found that CaCO$_3$-Ni-MOF can remove heavy metal ions. The adsorption capacity of Cu$^{2+}$ was found to be 16.96mg/100mg by energy spectrum analysis. And the amount of lead also has a certain amount of adsorption. The results show that the performance of the CaCO$_3$-Ni-MOF material in the water environment has not been destroyed, and the heavy metal ions in the water can be effectively separated.

1. Introduction
With the rapid development of global industrialization, more and more people are aware of the harm of environmental pollution to life. Over the past decade, heavy metal pollution in water has seriously affected the quality of life of the people. The incidence of cancer in various regions has increased dramatically, causing a certain degree of panic. It is urgent to solve this problem by means of science and technology. This has prompted researchers to pay great attention to this. However, air pollution is also very serious at present. Smog and haze appear in different degrees in major cities [1-4]. This is largely due to the exhaust gas from the combustion of industrial fuels such as petroleum kerosene. This makes the use of clean energy more important. It can ease the tension of the use of non-renewable resources such as petroleum. For example, H$_2$ and other clean energy only generate water after burning, which will not cause any harm to the air. But at present, the problem of clean energy storage is facing. Although hydrogen is environmentally friendly, it is difficult to transport and store because of its explosion, which limits its wide application. Here, we will introduce a new class of micro mesoporous solid state crystal materials [5-7]. Metal-organic-framework (MOF) materials have attracted great interest in chemistry, materials science and some engineering applications. Because of its complex structure, high specific surface area and pore size, especially the excellent controllability of pore chemical properties and size at the molecular level, it has many unique advantages, such as gas-phase
and liquid-phase adsorption separation in energy gas storage, heterogeneous catalysis, biomedicine and so on [8-11]. It has broad application prospects in many fields such as optical and electromagnetic, sensing and so on. However, because of its instability in performance and energy consumption, the development of industrialization is hindered [12-14].

Most of the MOF materials reported so far have low stability, especially for water. MOF series were designed and synthesized by Yaghi research group in the United States. On this basis, Yaghi research group carried out chemical modification of the pore channels and pore size expansion. Although the MOF series had better thermal stability than before, the water-borne was still very poor. This also limits the application of MOF materials in water environment [15-16].

To solve this problem, MOF materials with strong water stability have been developed, which can be used not only in non-aqueous environment such as gas adsorption, but also in the separation of heavy metal ions in water environment. This will bring a new world to the treatment of body weight and metal pollution.

2. Experimental Section

The main chemical reagents and raw material parameters are as follows: P- phthalic (C₈H₈O₄), P-hydroxybenzoic Acid (C₇H₉O₃), Acetic Acid (C₂H₄O₂), N, N-Dimethylformamide (C₆H₁₂N), Ethanol (C₂H₅OH), Nickel Nitrate (Ni(NO₃)₂·6H₂O), these reagents are produced by Shanghai Chemical Reagent Company Guo Yao Group Chemical Reagent Co., Ltd. Heavy Calcium Carbonate (CaCO₃) is produced by Cologne Powder Co., Ltd.

The target product CaCO₃-Ni-MOF was synthesized by ultrasonic wave and solvothermal method on the basis of existing literature. The specific steps are as follows:

(1) 20 ml DMF and 10ml EtOH were selected as solvents.

(2) Terephthalic acid 2.00 g was used as an organic ligand and Heavy Calcium Carbonate(CaCO₃) 0.6g, Ni(NO₃)₂·6H₂O 1.74 g as the coordination metal ion.

(3) With acetic acid 1ml and benzoic acid 0.01g as molecular size modifier, the aim is to synthesize smaller size CaCO₃-Ni-MOF.

(4) After all the drugs are added, they are stirred with a magnetic stirrer until they are completely dissolved, and then placed in an ultrasonic instrument for 80 minutes to make the drugs disperse evenly and promote crystallization. Finally, the mixture was poured into the PTFE lined reactor and reacted at 160 °C for 24 hours in a constant temperature drying box. After the reaction is cooled down to room temperature. Wash 3 times, wash alcohol 3 times, wash DMF 1 times, remove unreacted drugs. Activation process: the filtered and washed samples were soaked in DMF for one day and dried in ethanol for two days. Considering the synergistic effect of metal ions and organic ligands, we investigated the structure, morphology and properties of different molar ratios of nickel to terephthalic acid. When the molar ratio of Calcium Carbonate, Ni(NO₃)₂·6H₂O to terephthalic acid is 1:1, the excess of Ni²⁺ is considered to be saturated, and when the molar ratio of CaCO₃-Ni(NO₃)₂·6H₂O to terephthalic acid is 1:2, the coordination of Ni²⁺ is thought to be 4 in theory, and the molar ratio is just 1:2. When the molar ratio of CaCO₃-Ni(NO₃)₂·6H₂O to terephthalic acid is 1:3, it is considered that Ni²⁺ is not enough to satisfy all the carboxyl coordination, that is, the carboxyl coordination is not saturated.

3. Results and Discussion

Structural characterization of CaCO₃-Ni-MOF: It can be seen from Figure 1 that the diffraction peaks of the samples synthesized with different ratios are all located at 2 theta=8 degrees, and the hetero-peaks are less, the ratios are 1:1, 1:2, 1:3, 1:4, respectively. It shows that the four samples have similar crystal structure, but the figure shows that when the ratio of CaCO₃, Ni²⁺ to terephthalic acid is 1:2, the peak appears most.
Figure 1. XRD curves of synthetic ratios of CaCO₃-Ni-MOF.

It can be seen that the morphologies of the CaCO₃-Ni-MOF samples with different proportions are honeycomb porous, with large surface area, clear pore size and no collapse. The morphology of the sample with 1:2 ratio is regular spherical and porous, which is in good agreement with the XRD spectrum in Figure 1. The crystallinity of the samples with 1:2 ratio is the best. This spherical porous crystal provides intuitive evidence for subsequent adsorption experiments.

Figure 2. (a)–(d) SEM with a ratio of 1:1–1:4 of the CaCO₃-Ni-MOF samples.

Compared with the four ratios of SEM, it was found that the structure collapsed more seriously with the decrease of metal ions. Therefore, the optimum synthesis ratio was 1:2. The structure was uniform and regular spherical cage.

After synthesis, the material was kept in a common reagent bag without any drying measures. The infrared spectra were measured one month later. It was found that there was only a very small absorption peak at 3680 cm⁻¹, whereas the absorption peak was here. The absorption peak of crystalline water shows that CaCO₃-Ni-MOF has good water stability and can be preserved in common environment for a long time without destroying its structure.
Figure 3. FT-IR curves of synthetic ratios of CaCO$_3$-Ni-MOF.

Figure 4 shows the TG curves of 1:1 and 1:2 ratios of CaCO$_3$-Ni-MOF, respectively. It can be seen from the graphs that the weight loss temperature of CaCO$_3$-Ni-MOF material is about 400 °C, and the weight loss temperature of CaCO$_3$-Ni-MOF material is 1:2 TG curve. It can be seen that the weight loss temperature of 1:2 CaCO$_3$-Ni-MOF is slightly higher than that of CaCO$_3$-Ni-doped 1 (1:1), but this temperature is suitable for most cases. The scope of use is broader.

Figure 4. TG curves of MOF synthetic ratios of doped 1:1 (1#), 1:2 (2#).

CaCO$_3$-Ni-MOF performance test: The synthesized CaCO$_3$-Ni-MOF samples were added to the solution containing Cu$^{2+}$ and Pt$^{4+}$ respectively. After 12 hours, the precipitates were filtered, washed, dried and tested. The contents of elements in the samples were determined by Emax spectroscopy. Fig. 5 (a) is the EDS(Energy Dispersive Spectrometer) spectra of the samples before adsorption. Fig. 5 (b) (c) is the EDS spectra and the element content table after adsorption of Cu$^{2+}$. Fig. 5 (d) (e) is the Emax spectra after adsorption of Pt$^{4+}$. It is found that CaCO$_3$-Ni-MOF has a certain degree of adsorption to Cu$^{2+}$ and Pt$^{4+}$. Among them, the adsorption of Cu$^{2+}$ is more obvious.

| Element | Weight Percentage | Atom Percentage |
|---------|------------------|----------------|
| C K     | 38.28            | 56.61          |
| O K     | 50.94            | 34.34          |
| Ca K    | 0.50             | 0.28           |
| Ni K    | 13.31            | 4.03           |
| Cu L    | 16.96            | 4.74           |
| Total   | 100.00           | 100.00         |

| Element | Weight Percentage | Atom Percentage |
|---------|------------------|----------------|
| C K     | 35.99            | 55.42          |
| O K     | 29.77            | 34.40          |
| Ni K    | 31.49            | 9.92           |
| Pt M    | 2.76             | 0.26           |
| Total   | 100.00           | 100.00         |

Figure 5. Certain element percentage of adsorption of synthetic ratios of CaCO$_3$-Ni-MOF.
4. Conclusion
CaCO$_3$-Ni-MOF was synthesized by ultrasonic and solvothermal methods. The experimental study also found that CaCO$_3$-Ni-MOF can remove heavy metal ions. The adsorption capacity of Cu$^{2+}$ was found to be 16.96mg/100mg by energy spectrum analysis. And the amount of lead also has a certain amount of adsorption. The results show that the performance of the CaCO$_3$-Ni-MOF material in the water environment has not been destroyed, and the heavy metal ions in the water can be effectively separated.

Acknowledgments
This work was supported by the Foundation of the Key Natural Science Research Projects in Universities of Anhui Province (KJ2018A0549), the Nature Science of Hefei University (17ZR02ZDA, 18ZR17ZDA, 18ZR18ZDA), the Natural Science Foundation of Anhui Province (1708085ME112), the Excellent Young Talents Fund Program of Higher Education Institutions of Anhui Province (GXYQ2018072).

References
[1] Furukawa H, Cordova K E, O Keeffe, Yaghi O M. (2013) The Chemistry and Applications of Metal-Organic Frameworks, Science, 341(6149):1230444.
[2] Rowsell J L C, Yaghi O M. (2004) Metal-Organic Frameworks: a New class of Porous Materials. Johnson Matthey Technol Rev, 59(2):123-125.
[3] Long J R, Yaghi O M. (2009) The Pervasive Chemistry of Metal-Organic Frameworks. Chem Soc Rev, 38: 1213-1214.
[4] Zhou H, Long J R, Yaghi O M. (2012) Introduction to Metal-Organic Frameworks[J].Chem Rev, 112: 673-674.
[5] Ferey G. (2007) Hyrid porous solids: past, present, future. Chem Soc Rev, 37:191.
[6] Murray L J, Dinca M, Long JR. (2009) Hydrogen Storage in Metal-Organic Frameworks. Chem Soc Rev, 38:1294-1314.
[7] Makal T A, Li J, Lu W, Zhou H. (2012) Methane Storage in Advanced Porous Msterials. Chem Soc Rev, 41: 7761.
[8] Li J, Kuppler R J, Zhou H. (2009) Selective Cas Adsorption and Separation in Metal-Organic Frameworks. Chem Soc Rev, 38: 1477-1504.
[9] Li J, Sculley J, Zhou H. (2012) Metal-Organic Frameworks for Separations. Chem Rev, 112(2): 869-932.
[10] Cychosz K A, Ahmad R, Matzger A J. (2010) Liquid Phase Separations by Crystalline, Microporous Coordination Polymers. Chem Sei, 1:293.
[11] Tong Minman, Zhao Xudong, Xie Liting, Liu Dahuan, Yang Qingyuan, Zhong Chongli. (2012) Metal-Organic Framework Materials for Wastewater Treatment. Chemical Progress, 1646-1655.
[12] Lee J, Farha O K, Roberts J, Scheidt K A, Nguyen S T, Hupp J T. (2009) Metal-Organic Framework Material as Catalysts. Chem Soc Rev, 38:1450.
[13] Yoon M, Srirambalaji R, Kim K. (2012) Homochiral Metal-Organic Frameworks for Asymmetric Heterogeneous Catalysis. Chem Rev, 112:1196-1231.
[14] Corma A, Garca H, Llabres I, Xamena F X. (2010) Engineering Metal-Organic Frameworks for Heterogeneous Catalysis. Chem Rev, 2010, 110:4606-4655.
[15] Cui Y, Yue Y, Qian G, Chen B. (2012) Luminescent Functional Metal-Organic Frameworks. Chem Rev, 112(2): 1126-1162.
[16] Zhang W, Xiong R. (2012) Ferroelectric Metal-Organic Frameworks. Chem Rev, 112:1164-1195.