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Fabrication of the Novel Uio-66-Go/Pvdf Composite Membrane

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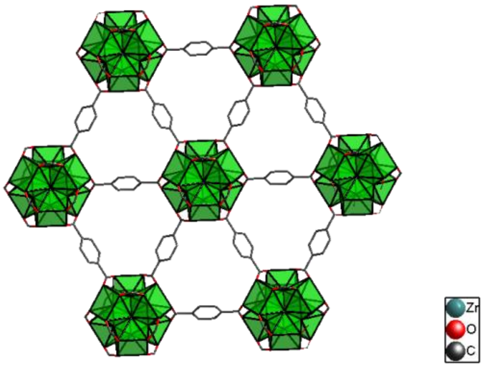
ABSTRACT. *In this work, the UiO-66-GO/ Polyvinylidene fluoride (PVDF) flat membranes were prepared by nonsolvent-induced phase separation (NIPS), the synthesis of the UiO-66-GO composites were carried out through hydrothermal and Solvothermal method[1-4]. The effect of the contents of GO was studied. Additionally, the novel membranes were characterized by XRD, FTIR and AFM. The XRD demonstrates that GO did not influence the crystal structure of UiO-66, the FTIR shows that there is no new chemical bonds between UiO-66 and GO, and the AFM exhibits that surface roughness was reduced to 46.5nm. Specifically, the membranes exhibited high flux and rejection when the contents of the GO were 6wt%, the water flux was enhanced to 88.42%, the rejection of BSA was increased to 95.77%, the water contact angle was decreased to 62.21 °, The good properties of the UiO-66-GO/PVDF composite membranes make it possible to be a good potential candidate for water treatment.*

KEYWORDS: *Uio-66-go/pvdf, Composite membrane, Antifouling property, Metal-organic frameworks*

1. Introduction

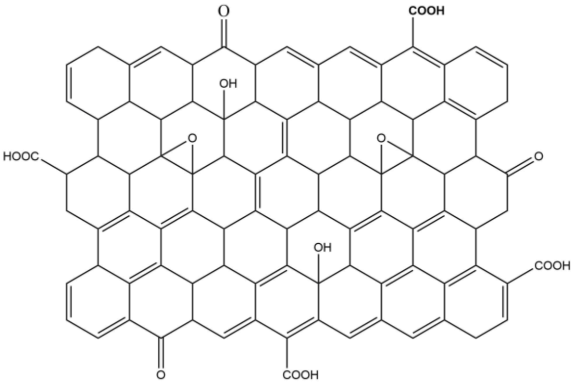
The UiO is a kind of MOFs has Zr atom in it which was first invented by Lillerud in 2008, and the UiO-66 is the superstar of it, which is the three dimensional topological structure of porous crystal materials through the octahedrons and tetrahedrons are connected alternately that the [Zr6O4(OH)4] and terephthalic acid connected by twelve coordination[5-7]. As is shown in the picture, UiO-66 exhibites excellent thermal and chemical stability because of the amount of coordination numbers and the strong bond energy of Zr-O, which make it stable even when it was immersed in strong acid and strong base solutions[8]. UiO-66 is considered as one of the most potential materials of MOFs[9-10], with the development of the study, the central metal atom could be replaced by Ti or Hf or others.

There are some kinds of Synthetic methods can be used to make MOFs, which are shown in the followings: hydrothermal and Solvothermal method, microwave method, electrochemical synthesis, ultrasonic method, diffusion method, the hydrothermal and solvothermal method are the most commonly methods, which are synthesis method that original stock for chemical reaction in the certain solvent at ta certain high temperature and pressure in the reactional still, which make the solubility of the refractory material increased, which is good for the experiment.



Scheme. 1 Crystal structure of UiO-66 (Zr) material

Graphene oxide(GO)is one ramification of graphene, the C molecule is modified by oxygen-containing groups, which can not only enlarge the distance of lawyers, but also make the molecules more hydrophilia, which provide a lot of binding sites for the grow up of MOFs, at the same time, the amount of hydrophilia functional groups can be improved due to the dispersibility of the materials[25].



Scheme. 2 Molecular structure of graphene oxide (GO)

Although some defects of MOFs by GO-MOFs composite materials have been modified by Petitand and his colleges, the specific theory of the molecule is still unknown, the composite material is so complex because of its uncertainty. Thus, have a more particular knowledge of composite materials is significant for its application and future.

Since the UiO-66-GO composite materials were composited and added into PVDF casting membrane solution to fabricate UiO-66-GO composite membranes, additionally, we evaluated it's performance though SEM,XRD,AFM,Flux and Rejection.

2. Experiment

2.1 Materials

All chemicals and solvents were purchased from commercial suppliers and used without further purification. ultrapure water was used throughout the experiment. Polyvinylidene Fluoride 6010(PVDF 6010) was purchased from Solvay. N,N-dimethylformamide(DMF) and terephthalic acid(H_2BDC) were purchased from Tianjin guangfu fine chemical research institute. zirconium tetrachloride($ZrCl_4$) was purchased from Shanghai Aladdin biochemical technology co. LTD. graphene oxide(GO) was purchased from Tangshan jianhua technology development co. LTD. Glycerinum was purchased from Tianjin third chemical reagent factory. Bovine serum albumin (BSA)was purchased from Beijing puboxin biotechnology co. LTD. sodium hypochlorite (NaClO) was purchased from Tianjin kemeiou chemical reagent co. LTD. absolute ethyl alcohol(C_2H_6O) was purchased from Tianjin fengchuan chemical reagent technology co. LTD. Allochroic silicagel was purchased from Qingdao ocean chemical co. LTD.

2.2 Preparation of Modified Pvdf Composite Membranes Use Uio-66-Go

2.2.1 Synthesis of Uio-66-Go Composites

Because of the addition of GO, we need to figure out the content of GO in the PVDF blend system to modify the property of the PVDF membrane better. The specific experimental procedure is as followings: firstly, disperse a certain amount of GO in the DMF through ultrasound, secondly, $ZrCl_4$ and H_2BDC were added in to the solvent in turn, stirring the solvent to make the $ZrCl_4$ and H_2BDC dissolve at a certain temperature and pressure in the reaction still, then, the UiO-66-GO composites was received, finally, we got UiO-66-GO powder through centrifugation and dry of the supernatant. the content of the GO were 0 wt%,1 wt%,2 wt%,4 wt%,6 wt% and 8 wt% respectively, which were labeled by UG-0,UG-1,UG-2,UG-3,UG-4 and UG-5, severally. the mass fraction of GO in the composites is as following:

$$\omega = \frac{\mathrm{m(GO)}}{\mathrm{m(ZrCl_4 + H_2BDC + GO)}} \cdot 100\%$$

m(GO) is referred to the quality of GO;

m(ZrCl4+H2BDC+GO) is referred to the total quality of $ZrCl_4$ and H_2BDC

and GO

2.2.2 Preparation of the Uio-66-Go/Pvdf Composite Membranes

After vacuum drying, the mass fraction of 1.67% of UiO-66-GO composites were put into the mixed system of PVDF as well as DMF, then transferred it into oil bath pan and stirred it for 12h at a certain temperature, until the casting membrane solution became a stabilized homogenous phase, finally, let it stand for deaeration for at least 24h, when the casting membrane solution cold to indoor temperature, put the appropriate amount of the casting membrane on the clean glass pane, then used the 200 μm scraping membrane rods to knifing, next, put the membrane into the deionized water for solidification, afterwards, transferred it into deionized water for removing the solvent, renewed the deionized water every 4h in order to extract the solvent adequately. in the end, immersed the membrane into the glycerinum for 24h, in order to prevent the collapse of the membrane pore[14-17].

2.3 Testing and Characterization

The surface morphologies were observed by FESEM(Hitachi S-4800, Hitachi, Japan). The surface roughness was measured by Otomic force microscope(Agilent-S5500, AGILENT, America). The water contact angles were measured by a contact angle goniometer(DSA-100, Kruss, Germany) at room temperature. The tensile strength of the membrane samples were determined by a tensile testing machine(CMT4503, Meitesi Industry Co. Ltd, China). The Fourier transform infrared spectroscopy (FT-IR) spectra of the membrane surfaces were conducted on a spectrometer(Bruker TERSOR37, German) in the range of 4000–800cm^{-1}. The specific surface area was measured by Physicochemical adsorption apparatus(Autosorb-iQ-C, U.S.A.).

3. Results and Discussion

3.1 Characterization of Uio-66-Go Composites

3.1.1 Xrd of Uio-66-Go Composite Material

The appropriate amount of the GO needed to be figured out. As is shown in the figure1, each composites is accordant to the standard spectra of the UiO-66, additionally, the characteristic diffraction peaks of the GO which is 10.7 ° is not shown in it, the possible reason of this phenomenon is as followings: one is that absorption spectra of the addition of GO is too small to seen in the XRD test pattern, the other is that GO was fully dispersed in the DMF composite solvent so that the diffraction peak of the GO is not shown in the XRD spectrum, nonetheless, we did prepare the UiO-66-GO composites from the appearance of the materials[18-20].

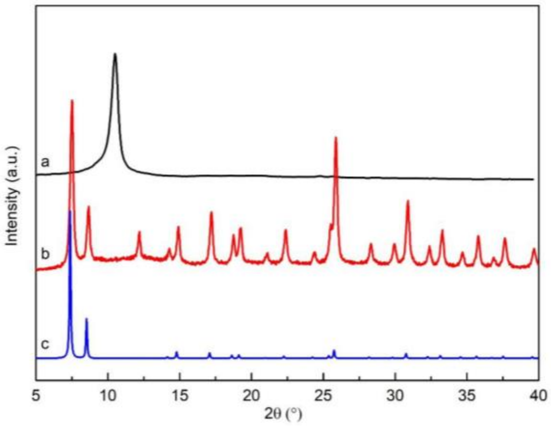


Fig.1 Xrd Patterns of Go(a), Uio-66-Go(B) and Uio-66(C)

3.1.2 Infrared Spectroscopic Analysis of the Uio-66-Go Composites

In order to figure out that if new chemical bond existed in the UiO-66-GO composites through the infrared spectroscopic analysis. As is shown in the picture: in the 4a, 1725cm^{-1} is the Stretching vibration peak of the C=O of GO, the absorption peak of 1637cm^{-1} of the C=C is the bending vibration absorption peak of C-OH, the peak of 1110cm^{-1} is the absorption peak of C-O-C, in the 4-2c, the absorption peak of the 744cm^{-1},663cm^{-1},53cm^{-1} and 477cm^{-1} are all belonging to the vibrational expansion peak of the Zr-O in the UiO-66. in the figure2, the absorption peak contains both the vibrational expansion peak of the UiO-66 and GO, and there is no new diffraction peak, which means that no new chemical bond is shown in the composite materials.

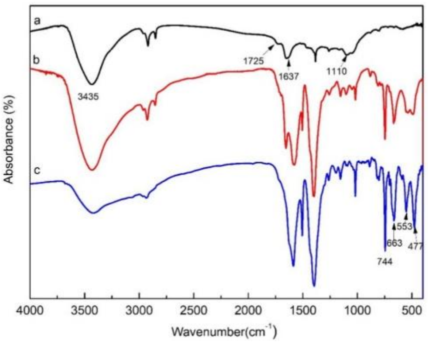


Fig.2 Ftir of Go(a), Uio-66-Go(B) and Uio-66(C)

3.2 The Impact of the Capacity of the Go of the Structure and Characterization of the Composite Membranes

3.2.1 The Microtopography of the Uio-66 Composite Membranes

The microtopography of the UiO-66-GO composite membranes were achieved by SEM, from the figure3, in terms of the surface, no matter what the capacity of the GO is, there is no obvious difference between the UiO-66 composite membranes and the UiO-66-GO composite membranes. from the fracture surface of the membranes, the two both have the asymmetric structure, with the increase of the content of GO, the fingerlike pores become longer and wider, the reason is maybe that the hydrophilic group of the GO make the diffusion rate faster of the solvent and the non-solvent in the phase transformation process, which make the consolidation forming of membranes fast[21-22], so that bigger pores were achieved. At the same time, with the increase of the quality of GO, the sponge pores are bigger at the first and smaller in the next.

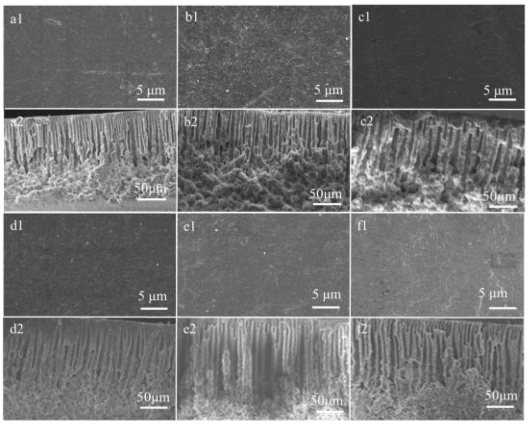


Fig.3 Microscopic Morphology of the Surface and Section of Uio-66-Go/Pvdf Blend Membranes

(a: UG-0; b: UG-1; c: UG-2; d: UG-3; e: UG-4; f: UG-5)

3.2.2 The Flux and Rejection of the Uio-66-Go Composite Membranes

We studied the flux of the pure water and the rejection of BSA of the UiO-66-GO /PVDF composite membranes. As is shown in the figure 4, the flux of the composite membrane is 120.23L(㎡ h) without GO, in addition, with the increase of the capacity of GO, the flux of the composite membrane tends to increase first and decrease next, the flux of 142.38(㎡ h) is the best when the capacity of GO is 6wt%, we speculate that the capacity of GO over 6wt%, which would limit the UiO-66 to grow up, which made the crystal size and porosity smaller, thus the rejection decreased also.

When GO has the low load, which has little impact on the UiO-66,the synergistic effect between GO and UiO-66 could better the property of the composite membranes, which is in the result of the increase of the porosity of the membranes, the decrease of the specific surface area.

Table 1 Viscosity and Porosity of Uio-66-Go/Pvdf Blend Membranes

sample	viscosity(pa s)	porosity(%)
UG-0	0.543	78.32±1.2
UG-1	0.535	79.72±0.9
UG-2	0.539	81.46±1.0
UG-3	0.541	83.29±0.8
UG-4	0.544	84.2±0.9
UG-5	0.538	82.89±1.1

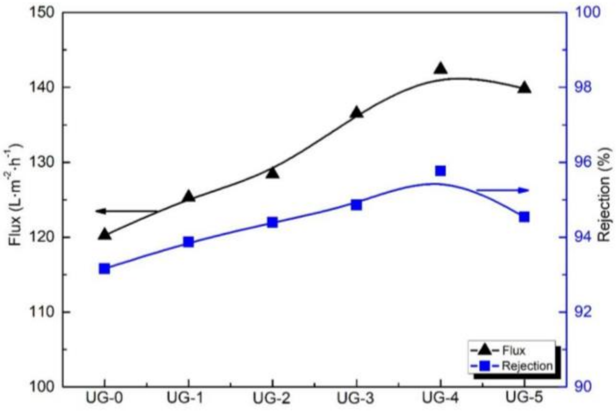


Fig.4 Water Flux and Rejection of Uio-66-Go/Pvdf Blend Membranes

3.2.3 The Hydrophilia of the Composite Uio-66-Go/Pvdf Membrane

As what is shown in the figure 5,the hydrophilia of the composite membrane has been improved within limits, specifically, the smallest water contact angle is 62.21° with the capacity of 6wt% of GO, which is mainly because the increase of the hydrophilic group of the composites, which lower the water contact angle, however, when the load of GO over 6wt%, there will be hinder between GO and UiO-66, which decline the hydrophilia of the membrane.

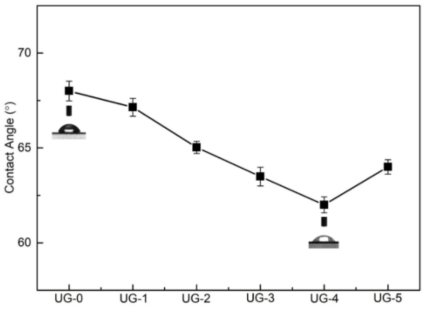


Fig.5 Water Contact Angle of Uio-66-Go/Pvdf Blend Membranes

3.2.4 Antifouling Property of the Uio-66-Go/Pvdf Composite Membranes

The surface roughness of the composite membrane was tested by AFM, which is shown in the chart2 based on the 5.01μm×5.01μm, according to figure 6, the bigger roughness is because of the sunken of the composite membranes, opportunely, these sunken can be nicely filled by GO, which could decline the roughness of the composite membrane down to 46.5nm with the load of GO of 6wt%.

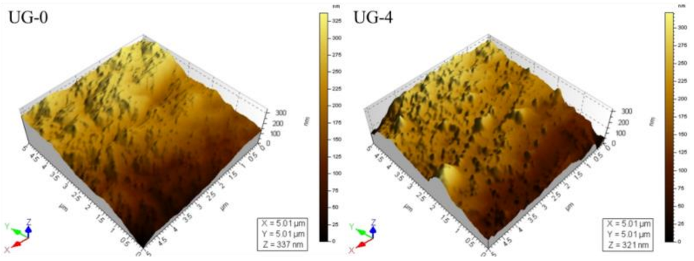


Fig.6 Afm of the Original Membrane and Uio-66-Go/Pvdf Blend Membranes

Table 2 Roughness Parameters Of Original Membrane and Uio-66-Go/Pvdf Blend Membranes

Sample	Average roughness Sa(nm)	RMS ridge height Sq(nm)	Maximum ridge height Sz(nm)
UG-0	59.7	71.2	337
UG-4	46.5	56.9	321

In the figure7 and figure8, the membranes were polluted by BSA first and to then washed by NaClO. in the figure 8, all the BSA flux are lower than the water flux because of the adsorption of the protein, due to the BSA can be easily stuck in the pores, so that the FRR is hard to 100%, fortunately, the FRR is higher than 89%, which means that the composite membranes have a good antifouling property.

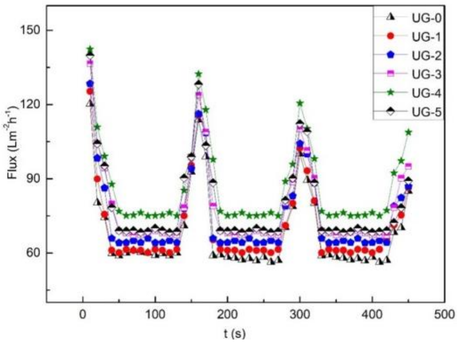


Fig.7 Three Consecutive Pollution-Flux Changes in the Cleaning Cycle

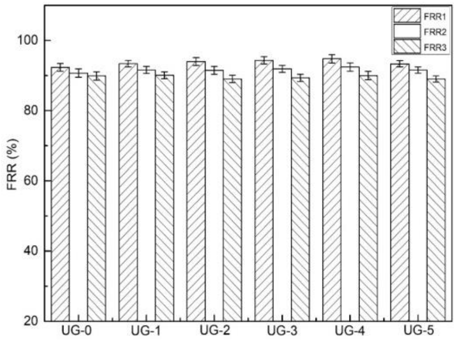


Fig.8 Changes in Flux Recovery Rate during Three Pollution-Wash Cycles

3.2.5 Mechanical Property of the Uio-66-Go Composite Membrane

The tensile strength and breaking elongation of the composite membrane is shown in the figure 9,which increased and then decreased with the amount of GO, additionally, it reaches the largest 4.52MPa with the GO of 6wt%, the tensile strength and the breaking elongation is enhanced by 9.44% and 8.41% respectively compared with the UiO-66-GO/PVDF composite membrane and the UiO-66/PVDF composite membrane.

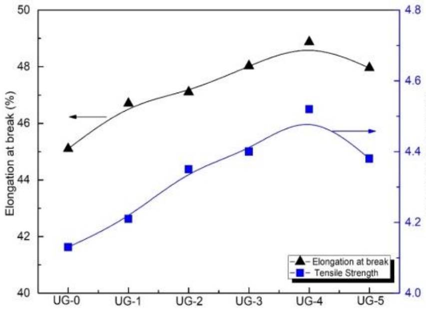


Fig.9 Tensile Strength and Elongation At Break of Uio-66-Go/Pvdf Blend Membranes

4. Conclusion

In this work, UiO-66-GO composites were synthesized through hydrothermal and Solvothermal method, which were used to fabricate the UiO-66-GO/PVDF membranes by NIPS, we evaluated the impact of the content of GO of its performance though flux ,rejection,hydrophilia and mechanical property.

(1)The XRD demonstrates that GO did not influence the crystal structure of UiO-66, the FTIR shows that there was no new chemical bonds between UiO-66 and GO.

(2)We prepared the UiO-66-GO/PVDF composite membranes through NIPS method, the best performance of the membrane shows when the load of GO is 6wt%, specifically, the water flux is enhanced by 18.42%, the rejection of BSA is increased from 93.16% to 95.77%, the water contact angel is decreased from 68 °to 62.21 °, and the surface roughness is reduced from 59.7nm to 46.5nm.

5. Acknowledgement

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References

[1] N. Zhang, L.Y. Yuan, W.L. Guo, S.Z. Luo, Z.F. Chai, W.Q. Shi, Extending the use of highly porous and functionalized MOFs to Th (IV) capture, ACS Appl. Mater. Inter. 9(2017) 25216-25224.
[2] Wu, Y. Gao, W. Zhang, Y. Tan, A. Tang, Y. Men, B. Tang, Deep desulfurization

by oxidation using an active ionic liquid-supported Zr metal–organic framework as catalyst, Appl. Organomet. Chem. 29 (2015) 96-100.

[3] JI G L, ZHU L P, ZHU B K, et al. Structure formation and characterization of PVDF hollow fiber membrane prepared via TIPS with diluent mixture[J]. Journal of Membrane Science, 2008, 319(1):264-270.

[4] Q. X. Luo, B.W. An, M. Ji, S.E. Park, C. Hao, Y.Q. Li, Metal–organic frameworks HKUST-1 as porous matrix for encapsulation of basic ionic liquid catalyst: effect of chemical behaviour of ionic liquid in solvent, J. Porous Mat. 22 (2015) 247-259.

[5] K. Zhao, D. Liu, H. Huang, C. Zhong, Highly selective and sensitive metal-organic framework fluorescent probe for Cu^{2+} through rational design of binding sites,Microporous Mesoporous Mater. 224 (2016) 149-154.

[6] DENG B, YU M, YANG X, et al. Antifouling microfiltration membranes prepared from acrylic acid or methacrylic acid grafted poly (vinylidene fluoride) powder synthesized via pre-irradiation induced graft polymerization. [J]. Journal of Membrane Science, 2010, 350(1):252-258.

[7] W. Liu, S. Liu, D. He, N. Li, Y. Ji, Z. Zheng, F. Luo, S. Lin, Z. Shi, C. Hu, Crystal facets make a profound difference in polyoxometalate-containing metal-organic frameworks as catalysts for biodiesel production, J. Am. Chem. Soc. 137 (2015)12697-12703.

[8] PEZESHK N, RANA D, NARBAITZ R M, et al. Novel modified PVDF ultrafiltration flat-sheet membranes[J]. Journal of Membrane Science, 2012, 389:280-286.

[9] RAJASEKHAR T, TRINADH M, VEERA B P, et al. Oil–water emulsion separation using ultrafiltration membranes based on novel blends of polyvinylidene fluoride(PVDF) and amphiphilic tri-block copolymer containing carboxylic acid functional group[J]. Journal of Membrane Science, 2015, 481:82-93.

[10] ZHANG J, XU Z, MAI W, et al. Improved hydrophilicity, permeability, antifouling and mechanical performance of PVDF composite ultrafiltration membranes tailored by oxidized low-dimensional carbon nanomaterials[J]. Journal of Materials Chemistry A, 2013, 1(9):3101-3111.

[11] DENG L, YE H, LI X, et al. Self-roughened omnipotent coatings on nanofibrous membrane for membrane distillation[J]. Separation and Purification Technology, 2018, 206: 14-25.

[12] E. Zhang, Y. Jin, J. Shi, Y. Zhong, W. Zhu, M.S. El-Shall, Polyoxometalates confined in the mesoporous cages of metal-organic framework MIL-100 (Fe): efficient heterogeneous catalysts for esterification and acetalization reactions, Chem. Eng. J.269 (2015) 236-244.

[13] WANG C, XIE Z, DEKRAFFT K E, et al. Doping metal-organic frameworks for water oxidation, carbon dioxide reduction, and organic photocatalysis[J]. Journal of the American Chemical Society, 2011, 133(34):13445-13454.

[14] J. Wu, Y. Gao, W. Zhang, Y. Tan, A. Tang, Y. Men, B. Tang, Deep desulfurization by oxidation using an active ionic liquid-supported Zr metal–organic framework as catalyst, Appl. Organomet. Chem. 29 (2015) 96-100.

[15] KAYE S S, DAILLY A, Yaghi O M, et al. Impact of preparation and handling

on the hydrogen storage properties of Zn_4O(1,4-benzenedicarboxylate)$_3$ (MOF-5) [J]. Journal of the American Chemical Society, 2007, 129(46):14176-14177.
[16] Q. X. Luo, B.W. An, M. Ji, S.E. Park, C. Hao, Y.Q. Li, Metal-organic frameworks HKUST-1 as porous matrix for encapsulation of basic ionic liquid catalyst: effect of chemical behaviour of ionic liquid in solvent, J. Porous Mat. 22 (2015) 247-259.
[17] TAKAISHI S S, HOSODA M M, KAJIWARA T T, et al. Electroconductive porous coordination polymer Cu[Cu(pdt)$_2$] composed of donor and acceptor building units[J]. Inorganic Chemistry, 2009, 48(19):9048-9050.
[18] OHBA M, YONEDA K, GLORIA A, et al. Bidirectional chemo-switching of spin state in a microporous framework[J]. Angewandte Chemie, 2010, 121(26):4746-4746.
[19] LI H, EDDAOUDIM, OKEEFFE M, et al. Design and synthesis of an exceptionally stable and highly porous metal-organic framework[J]. Nature, 1999, 402(6759): 276-279.
[20] STEPHEN S Y C, SAMUEL M F. L, JONATHAN P H C. A chemically functionalizable nanoporous material [Cu3(TMA)2(H2O)3]n[J]. Science, 1999, 283(5405):1148-1150.
[21] EDDAOUDI, M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage[J]. Science, 2002, 295(5554):469-472.
[22] J. Zhao, D. Liu, H. Huang, C. Zhong, Highly selective and sensitive metal-organic framework fluorescent probe for Cu^{2+} through rational design of binding sites, Microporous Mesoporous Mater. 224 (2016) 149-154.
[23] W. Wang, Q. Chen, Conversion of 5-hydroxymethylfurfural into 5-ethoxymethylfurfural and ethyl levulinate catalyzed by MOF-based heteropolyacid materials, Green Chem. 18 (2016) 5884-5889.
[24] ZHANG X F, FENG Y, WANG Z, et al. Fabrication of cellulose nanofibrils/UiO-66-NH_2 composite membrane for CO_2/N_2 separation[J]. Journal of Membrane Science, 2018, 568:10-16.
[25] W. Xie, M. Huang, Immobilization of Candida rugosa lipase onto graphene oxide Fe_3O_4 nanocomposite: characterization and application for biodiesel production, Energy Convers. Manage. 159 (2018) 42-53.
[26] A.H. Chughtai, N. Ahmad, H.A. Younus, A. Laypkov, F. Verpoort, Metal-organic frameworks: versatile heterogeneous catalysts for efficient catalytic organic transformations, Chem. Soc. Rev. 44 (2015) 6804-6849.
[27] J.R. Li, J. Sculley, H.C. Zhou, Metal-organic frameworks for separations, Chem. Rev.112 (2012) 869–932.
[28] W.B. Huang, J. Liang, X.S. Wang, R. Cao, Multifunctional metal-organic framework catalysts: synergistic catalysis and tandem reactions, Chem. Soc. Rev. 46 (2017)126-157.
[29] E.Rafiee, S. Eavani, Polyoxometalates as heterogeneous catalysts for organic reactions, Curr. Org Chem. 21 (2017) 752-778.