Encapsulation of metal-organic cage-based porous salt in silica nanopores

Liang-Hua Wu†, Shu-Na Liu†, Bing-Xun Zhou, Song-Liang Cai,* Wei-Guang Zhang, Sheng-Run Zheng*

DMPA Key Laboratory for Process Control and Quality Evaluation of Chiral Pharmaceuticals, and Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine, School of Chemistry, South China Normal University, Guangzhou 510006, China

* Corresponding author: Prof. Sheng-Run, Zheng; Dr. Song-Liang Cai

E-mail address: zhengsr@scnu.edu.cn; songliangcai@m.scnu.edu.cn

Tel./Fax.: +86-20-39310187

Supporting Information

EXPERIMENTAL SECTION

Materials and Measurements

Zirconocene dichloride, 2-Aminoterephthalic acid, and 5-Sulfoisophthalic acid sodium salt were of analytical grade and were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The other chemicals were of analytical grade and were purchased from Guangzhou Chemical Reagent Factory. Fourier transform infrared spectra (FTIR, Platinum Elmer Spectrum) were measured with the KBr pressed-disc method in the range 4000 to 400 cm^{-1}. Powder X-Ray diffraction (PXRD) data were collected using Cu Kα radiation (k = 1.5406 Å) at 40 kV and 40 mA at room temperature on a Ultima IV X-ray powder diffractometer. Thermogravimetric analysis (TGA) curves were taken on a NETZSCH TG 209 system heated from room temperature to 800 °C with a heating rate of 10 °C/min under air. Raman spectroscopy measurements were performed on a Renishaw inVia Reflex Raman spectrometer with a laser radiation line at 785 nm. X-ray photoelectron spectra (XPS) were recorded on a Thermofly EscaLab 250Xi X-ray photoelectron spectrometer. Inductively coupled

plasma (ICP) data were obtained on a Pastor Spectro Arcos MV Plasma Emission Spectrometer. EDS images were recorded on a Zeiss Gemini 500 Field Emission Scanning Electron Microscop at 15.0 kV.

Synthesis of Zr-MOC

The Zr-MOC was synthesized according to literature.[1] Firstly, 0.054 mg of 2-aminoterephthalic acid and 0.0175 g of zirconium dichloride were mixed in a 20 mL glass bottle, then 5 mL of DMAc and 1 mL of deionized water were added to the mixture. The mixture was dissolved under ultrasound, and heated at 60 ° C for 12 hours to obtain yellow cubic crystals. The crystals were washed with DMAc three times and dry under vacuum at 80 °C. Secondary, methanol (20 mL) was added to the mixture of the above product powder (200 mg) and silver trifluoromethylsulfonate (70 mg). The mixture was stirred in darkness for 3 days. Then, the precipitate was removed and the obtained clear yellow solution was evaporated to obtain the resulting yellow Zr-MOC powder. The product was dried under vacuum at 80 ℃ for 24 h. Yield: 65%.

Synthesis of Cu-MOC

The synthesis of Cu-MOC was based on the method described in the reference.[2] 200 mg of copper acetate was dissolved in a mixed solvent of DMAc and methanol ($v_{methanol}$: v_{DMAc} = 1:1, 15 mL). Then, 5-Sulfoisophthalic acid sodium salt (269 mg) methanol solution (8 mL) was added to the above solution. 5 mL of DMAc and 40 uL of nitric acid was further added and the resulting solution was sat for one week to obtain blue crystals of Cu-MOC. Yield: 60%.

Synthesis of bulk Zr-MOC/Cu-MOC

Firstly, 3 mL of Zr-MOC methanol solution (0.6 mM) and 3 mL of Cu MOC methanol solution (0.1 mM) were prepared, respectively. Then, these two solutions were added simultaneously to a glass bottle (with 2 mL of methanol solution in the bottle) with strong stirring. After 6 hours, the mixture was centrifuged to obtain a green powder. The powder was washed with methanol three times and dry it under vacuum at 80 ℃ to obtain Zr-MOC/Cu-MOC powder. Yield of 70%. The ICP results are showed in Tab. S1, and the XPS full spectra was showed in Fig. S1.

Syntheses of MS-Cu_x (x = 0.15, 0.30, 0.45)

MS-Cu_x was synthesized using the method described in the reference with some modification.[3] Dissolve 15 mg, 30 mg, and 45 mg of Cu-MOC samples in 10 mL of methanol to obtain three Cu-MOC solutions with different concentrations. Then, 85

mg, 70 mg, and 55 mg of SBA-15 were added to the above three solutions under stirring. After stirring the mixtures for 4 hours, the solvent was removed by vacuum rotary evaporation to obtain blue powders. The powders were vacuum dried overnight at 80 ℃, and the products were denoted as MS-$Cu_{0.15}$, MS-$Cu_{0.3}$, and MS-$Cu_{0.45}$, respectively.

Syntheses of MS-Cu_xZr_y (y = 1, 2, 4)

Three Zr-MOC solutions with different concentrations of 1, 2 and 4 mg/mL were prepared by dissolve 5 mg, 10 mg, and 20 mg of Zr-MOC in MeOH (5mL), respectively. Then, 30 mg of MS-$Cu_{0.15}$ powder was added to the above solution under stirring. After 6 hours, the green powder was obtained. The powder was washed with methanol three times and drying at 80 ℃ under vacuum overnight. Three products were obtained and denoted as MS-$Cu_{0.15}$-Zr_1, MS-$Cu_{0.15}$-Zr_2, and MS-$Cu_{0.15}$-Zr_4, respectively. The MS-$Cu_{0.3}$-Zr_4 and MS-$Cu_{0.6}$-Zr_4 were prepared under similar condition, except for replacing MS-$Cu_{0.15}$ with MS-$Cu_{0.30}$ and MS-$Cu_{0.45}$.

Iodine Capture from Vapor.

Fifteen milligrams of samples were placed in a small glass bottle (3 mL), which was attached to a larger glass bottle (20 mL) containing 250 mg nonradioactive iodine crystals without any physical contact between samples and iodine. The whole setup was placed in the oven and heated at 80 °C. Then, the weight of samples was measured at regular intervals until it was constant.

Table S1 ICP data summary of MS-$Cu_{0.15}$-Zr_4, MS-$Cu_{0.30}$-Zr_4, and MS-$Cu_{0.45}$-Zr_4, and bulk Zr-MOC/Cu-MOC.

sample	element	Concentrations of detected solutions (mg/L)	Ratio (Zr : Cu)	Ratio (Na : Cu)	Ratio (S : Cu)
MS-$Cu_{0.15}$-Zr_4	Cu	5.004	2.86:1	0.096:1	0.88:1
	Zr	20.380			
	Na	0.172			
	S	2.195			
MS-$Cu_{0.30}$-Zr_4	Cu	3.32	1.85:1		
	Zr	8.82			
MS-$Cu_{0.45}$-Zr_4	Cu	8.42	1.46:1		
	Zr	17.56			
Zr-MOC/Cu-MOC	Cu	2.40	2.80:1	0.080:1	0.80:1
	Zr	9.52			
	Na	0.069			
	S	1.000			

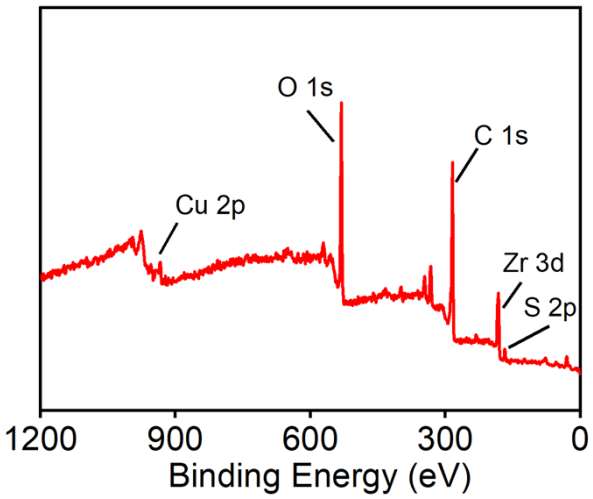


Fig. S1 XPS full spectrum of bulk Zr-MOC/Cu-MOC.

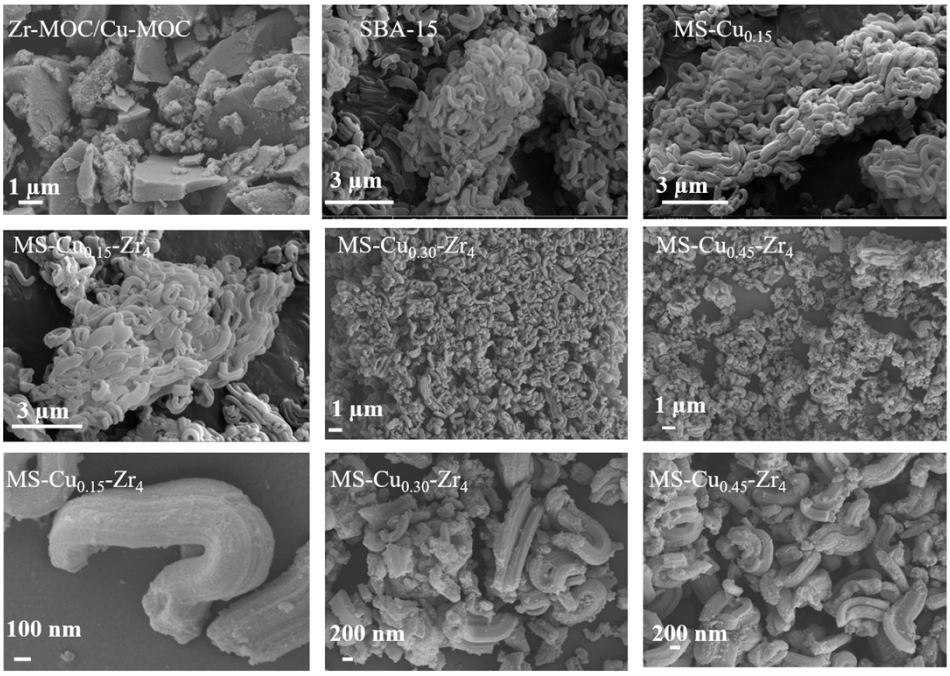
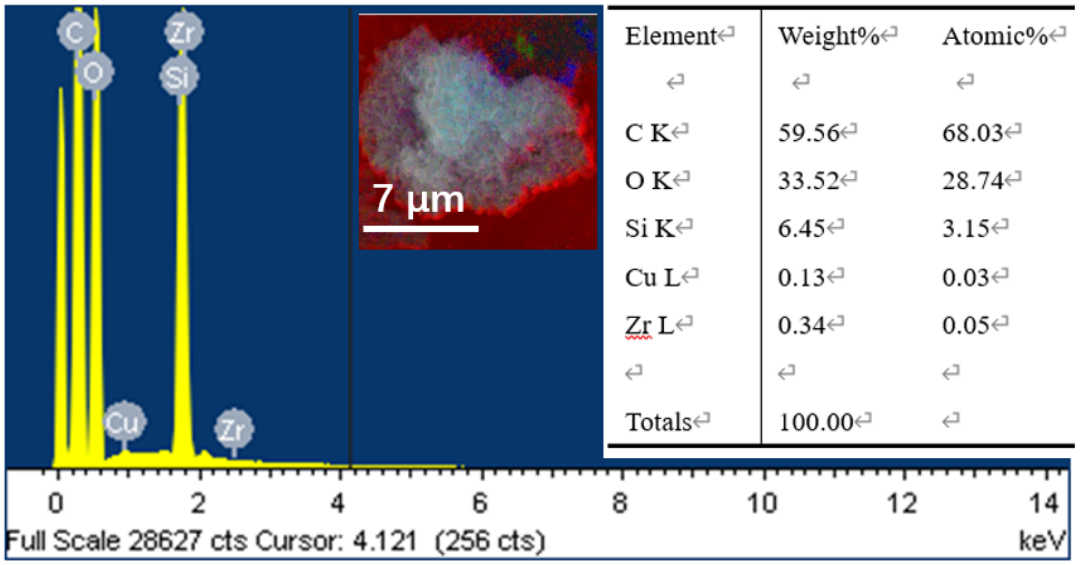


Fig. S2 SEM of bulk Zr-MOC/Cu-MOC, SBA-15, MS-$Cu_{0.15}$-Zr_4, MS-$Cu_{0.30}$-Zr_4, and MS-$Cu_{0.45}$-Zr_4.



Element	Weight%	Atomic%
C K	59.56	68.03
O K	33.52	28.74
Si K	6.45	3.15
Cu L	0.13	0.03
Zr L	0.34	0.05
Totals	100.00	

Fig. S3 SEM-EDS mapping of MS-$Cu_{0.15}$-Zr_4.

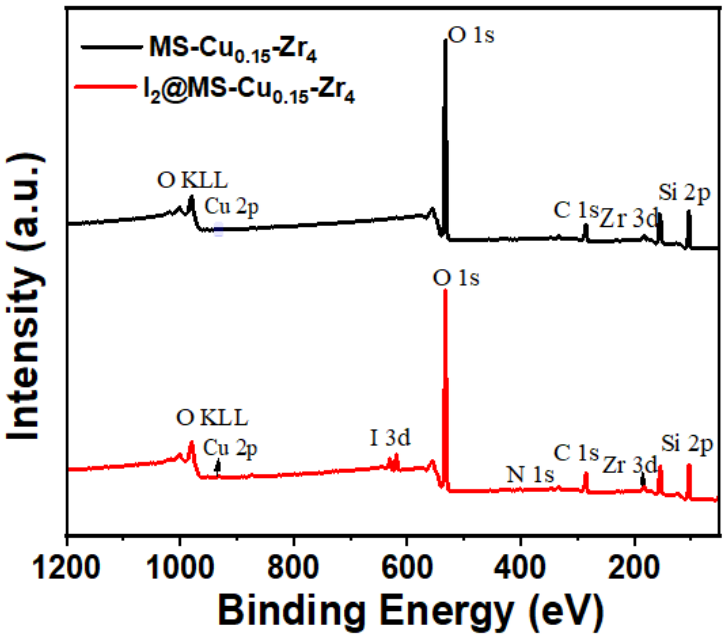


Fig. S4 XPS full-survey scan spectrum of MS-$Cu_{0.15}$-Zr_4 and I_2@MS-$Cu_{0.15}$-Zr_4.

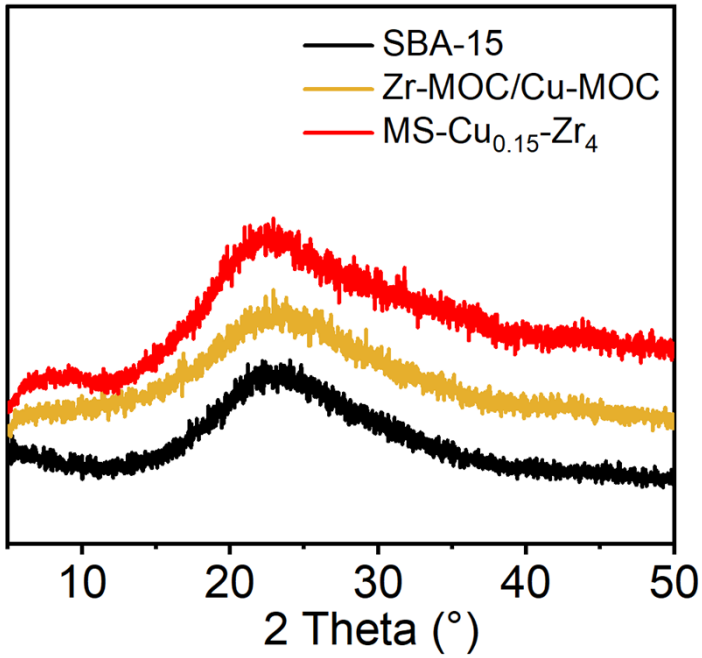


Fig. S5 PXRD of SBA-15, MS-$Cu_{0.15}$-Z_4 and bulk Zr-MOC/Cu-MOC.

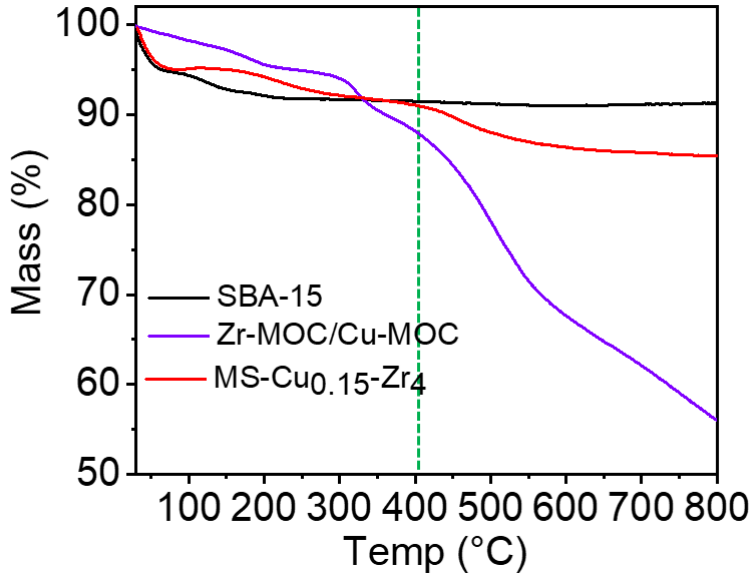


Fig. S6 TG curves of SBA-15, MS-$Cu_{0.15}$-Z_4 and bulk Zr-MOC/Cu-MOC.

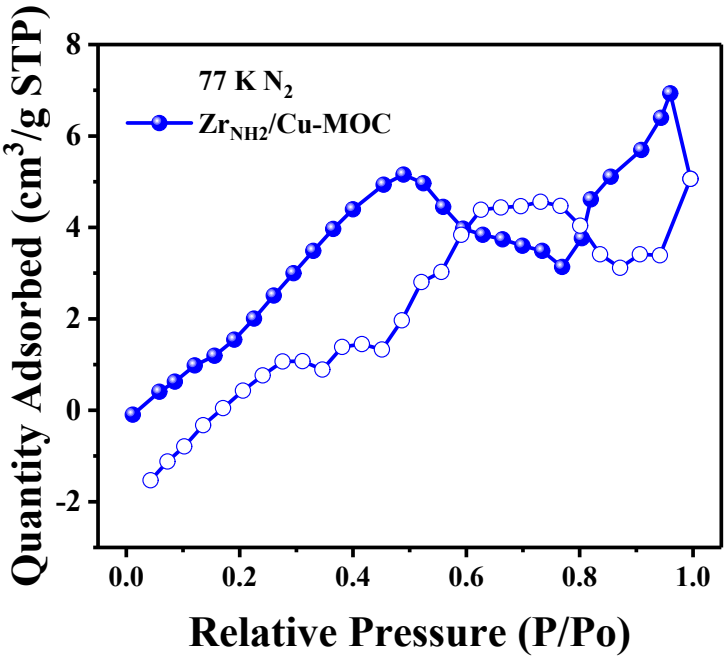


Fig. S7 N_2 adsorption-desorption isotherms for Zr-MOC/Cu-MOC at 77 K.

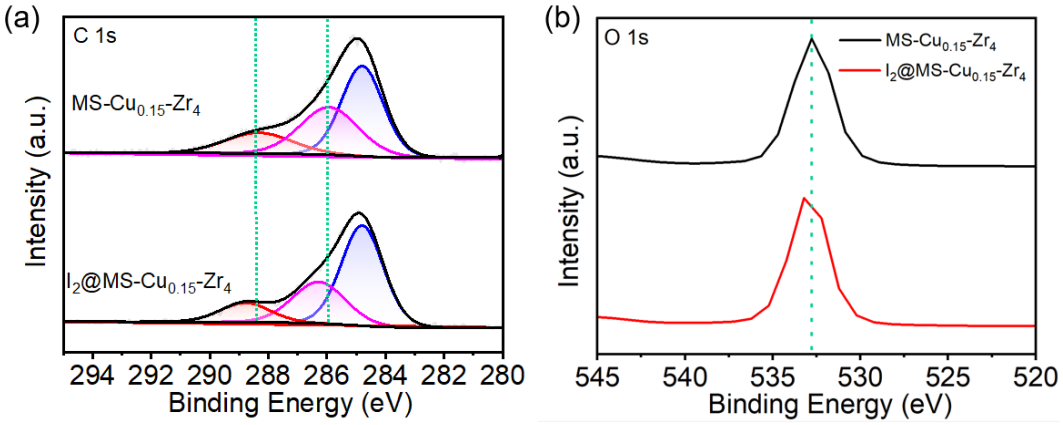


Fig. S8 (a) C 1s and (b) O 1s XPS spectra of MS-$Cu_{0.15}$-Zr_4 and I_2@MS-$Cu_{0.15}$-Zr_4.

References

1 D. Nam, J. Huh, J. Lee, J. H. Kwak, H. Y. Jeong, K. Choi and W. Choe, *Chem. Sci.*, 2017, **8**, 7765–7771.

2 J.-R. Li and H.-C. Zhou, *Nat. Chem.*, 2010, **2**, 893-898.

3 L.-B. Sun, J.-R. Li, W. Lu, Z.-Y. Gu, Z. Luo and H.-C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 15923−15928.