

Supporting Information

Ultrafast and Efficient Extraction of Uranium from Seawater Using an Amidoxime Appended Metal-Organic Framework

Long Chen,[†] Zhuanling Bai,[†] Lin Zhu,[†] Linjuan Zhang,[#] Yawen Cai,[†] Yuxiang Li,[†] Wei Liu,[†] Yanlong Wang,[†] Lanhua Chen,[†] Juan Diwu,[†] Jianqiang Wang,[#] Zhifang Chai,[†] and Shuaowang Wang^{*,†}

[†]School for Radiological and Interdisciplinary Sciences (RAD-X) and Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, 199 Ren'ai Road, Suzhou 215123, P. R. China

[#]Shanghai Institute of Applied Physics and Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences, 201800, Shanghai, P. R. China

* E-mail: shuaowang@suda.edu.cn

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1. General Information

All reagents and solvents were obtained from commercial suppliers and were used as received. 2-Bromoterephthalic acid was purchased from Chemsoon and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer for Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with a scan speed of $2.3^\circ \text{ min}^{-1}$ and step size of 0.02° in 2θ from 5° to 50° . The elemental analyses (C, H, and N) were carried out on a Vario EL CHNOS elemental analyzer. Scanning electron microscopy images and energy dispersive spectroscopy spectra were collected by FEI Quanta 200FEG with 30 kV electron beam. The samples were sputtered with Au before imaging by a SCD 040 Balzers Union. The spectra were acquired in 100 s. Fourier transform infrared (FT-IR) spectra were collected on a Thermo Nicolet iS50 spectrometer. N₂ adsorption curves were obtained by a Quantachrome Autosorb Gas Sorption analyzer IQ₂. Gas adsorption measurements for UiO-66 MOFs were carried out at 77 K in a liquid nitrogen bath with the pressure range from 0 to 760 Torr. Inductively coupled plasma mass spectrometry (ICP-MS) experiments were performed on a Thermo Finnigan high resolution magnetic sector Element 2 ICP-MS instrument. The extended X-ray adsorption fine structure (EXAFS) analyses were performed on beamline BL14W1 at Shanghai Synchrotron Radiation Facility and processed by the Demeter software suite of the IFEFFIT 1.2.10. The sample was prepared by soaking UiO-66-AO in uranyl solution overnight. The EXAFS data were collected at the uranium L_{III}-edge (17.166 keV).

2. Synthesis of UiO-66 MOFs

UiO-66-Br The synthesis of UiO-66-Br was according to a modified literature procedure.¹ 2-Bromoterephthalic acid (556 mg, 2.27 mmol), ZrCl₄ (529 mg, 2.27 mmol) and benzoic acid (5.5 g, 45.0 mmol) were dissolved in 57 mL of N, N'-dimethylformamide (DMF) at ambient temperature. After sonication for 10 min, the reaction mixture was sealed and put into an oven at 120 °C for 24 h. After cooling to room

temperature, the obtained white solid was isolated by centrifugation, washed with DMF (3×20 mL) and ethanol (3×20 mL), respectively, and then dried in an oven at $50\text{ }^{\circ}\text{C}$ for 12 h in vacuum.

UiO-66-CN The synthesis of UiO-66-CN was following by literature procedure.² UiO-66-Br (500 mg) and CuCN (150 mg) were suspended in 15 mL of N-methyl pyrrolidone (NMP) in a microwave tube. The original green mixture was sonicated for 20 min and heated by a microwave reactor for 20 min twice. After cooling the reaction mixture to ambient temperature, the solid was acquired by centrifugal separation, and washed by NMP (3×10 mL), dimethylsulfoxide (3×10 mL), DMF (3×10 mL) and ethanol (3×10 mL), respectively. The solid was dried in a vacuum oven at $50\text{ }^{\circ}\text{C}$ for 12 h.

UiO-66-AO UiO-66-CN (552 mg), hydroxylamine hydrochloride (1.29 g, 18.6 mmol) and triethylamine (1.88 g, 18.6 mmol) were dissolved in 50 mL of absolute ethanol.³ After stirring the mixture at $75\text{ }^{\circ}\text{C}$ for 24 h, the gray solid was isolated by centrifugation and washed by ethanol (3×15 mL). The solid was dried at $50\text{ }^{\circ}\text{C}$ for 12 h in vacuum.

3. Experimental and measurements procedures

Sorption kinetics of UiO-66-AO from seawater 50 mg of UiO-66-AO was added to 50 mL of seawater (pH = 8.23). After shanking for the desired time, 0.5 mL of sampling solution was sucked out and filtered by a 220 nm nylon membrane filter. The sorption experiment was carried out in a time range from 0.5 min to 300 min. The concentrations of uranium sampling at different time were determined by ICP-MS.

Desorption experiment 40 mg of UiO-66-AO was dispersed in 40 mL of seawater containing extra 500 ppb uranium. After shaking the solution for 2 h, the uranium-loaded UiO-66-AO was isolated by centrifugation and washed by ethanol (2×5 mL). The sample was dried in a pre-heated oven at $50\text{ }^{\circ}\text{C}$ for 5 h and eluted by 40 mL of HNO_3 solution at pH 2 for another 0.5 h. The eluent was filtered with a 220 nm nylon membrane filter and the concentration of uranium was measured by ICP-MS. The desorption ratio was calculated based on the sorption amount in each cycle.

Determination of adsorption capacity of uranium onto UiO-66-AO from seawater 1 mg of UiO-66-AO encapsulated in a dialysis bag was put into 1 L of natural seawater. After stirring for 3 days at room temperature, uranyl-adsorbed UiO-66-AO was isolated by filtration and washed with deionized water (2×2 mL) and ethanol (2×2 mL). After dried at $50\text{ }^{\circ}\text{C}$ for 5 h, 0.6 mg of UiO-66-AO was recovered and digested in 0.5

mL of HF (40% aqueous solution). The digestion solution was diluted with 5% HNO₃ and the concentration of uranium was determined by ICP-MS. 1.61 µg of uranium was adsorbed in 0.6 mg of UiO-66-AO according to the ICP-MS result. In other words, the maximum adsorption capacity of uranium from seawater for UiO-66-AO is 2.68 mg/g.

Determination of the concentration of uranium in seawater 5% HNO₃ was prepared by diluting 70% HNO₃ (99.99%) with ultrapure water. Indium (10 ppb) and uranium solution (1 ppb) were diluted from standard solution of indium (10⁴ ppm) and uranium (10² ppm) with 5% HNO₃, respectively. The concentration of uranium in seawater was determined by the standard addition method using ICP-MS. In a typical experiment, a series of solutions were prepared according to **Table S1**. Indium solution (10 ppb) was the internal standard and uranium solution (1 ppb) was used as the standard addition solution.

A plot was constructed after determination by using the concentration of adding uranium as x-axis and the intensity of uranium after background correction as y-axis. The intercept in x-axis is the concentration of uranium in the dilute seawater.

Table S1. A series of solutions were prepared to determine the concentration of uranium in seawater.

entry	seawater / mL	U (1 ppb) / mL	In (10 ppb) / mL	5% HNO ₃ / mL
1	0.2	0	0.4	3.4
2	0.2	0.2	0.4	3.2
3	0.2	0.4	0.4	3.0
4	0.2	0.6	0.4	2.8
5	0.2	0.8	0.4	2.6
6	0.2	1.0	0.4	2.4

4. SEM images of UiO-66 MOFs

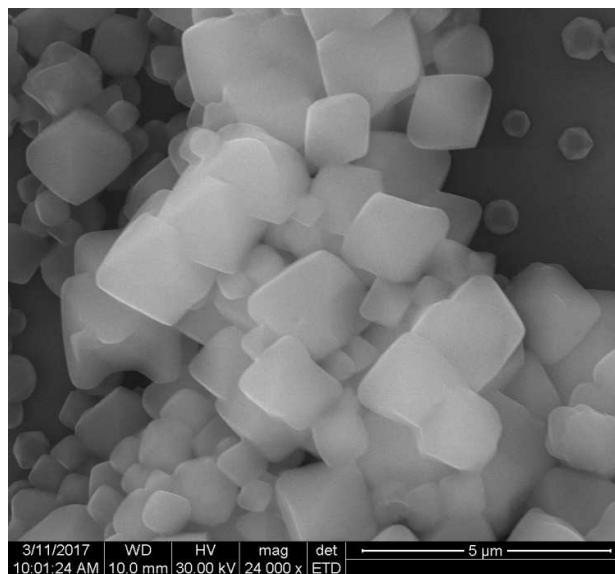


Figure S1. SEM image of UiO-66-Br

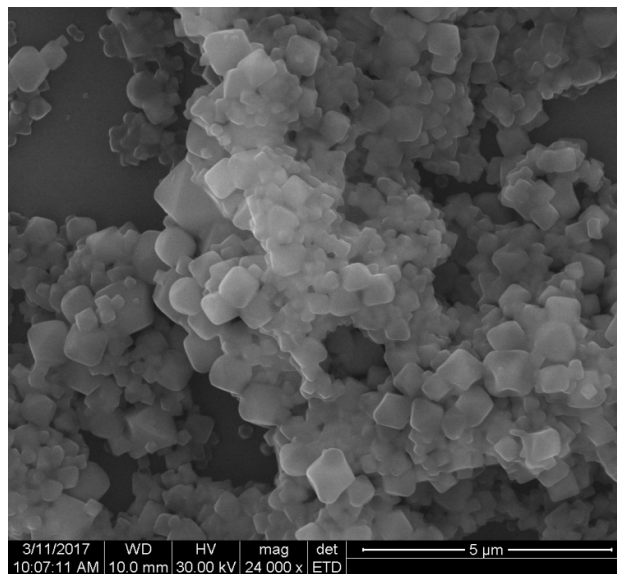


Figure S2. SEM image of UiO-66-CN

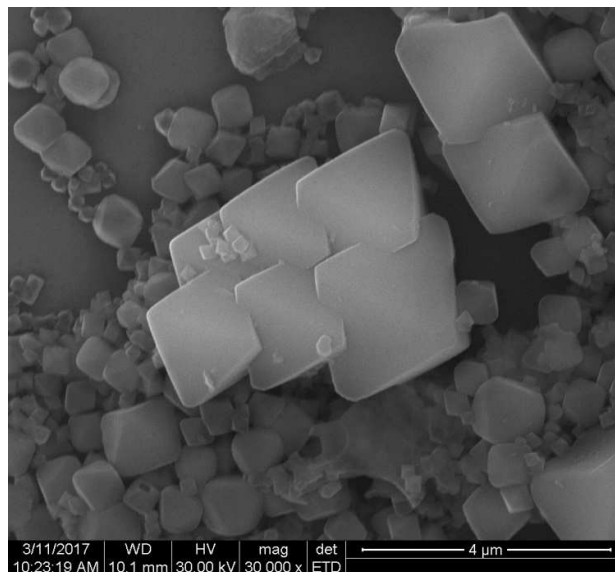


Figure S3.SEM image of UiO-66-AO

5. Elemental analysis for UiO-66 MOFs

Table S2. Elemental analysis results for UiO-66 MOFs.

Name	Weight. [mg]	Date Time	Content [%]	Peak Area	Daily Factor
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UiO-66-Br	2.9730	01.03.17 15:09	N: 0.000	391	0.9287
			C: 25.65	19938	0.9546
			H: 2.050	4765	1.0077
UiO-66-CN	2.8530	01.03.17 15:18	N: 3.116	3156	0.9287
			C: 28.83	21505	0.9546
			H: 2.585	5814	1.0077
UiO-66-AO	2.7610	01.03.17 15:28	N: 3.662	3610	0.9287
			C: 25.23	18202	0.9546
			H: 2.698	5876	1.0077

6. EDS spectra for UiO-66 MOFs

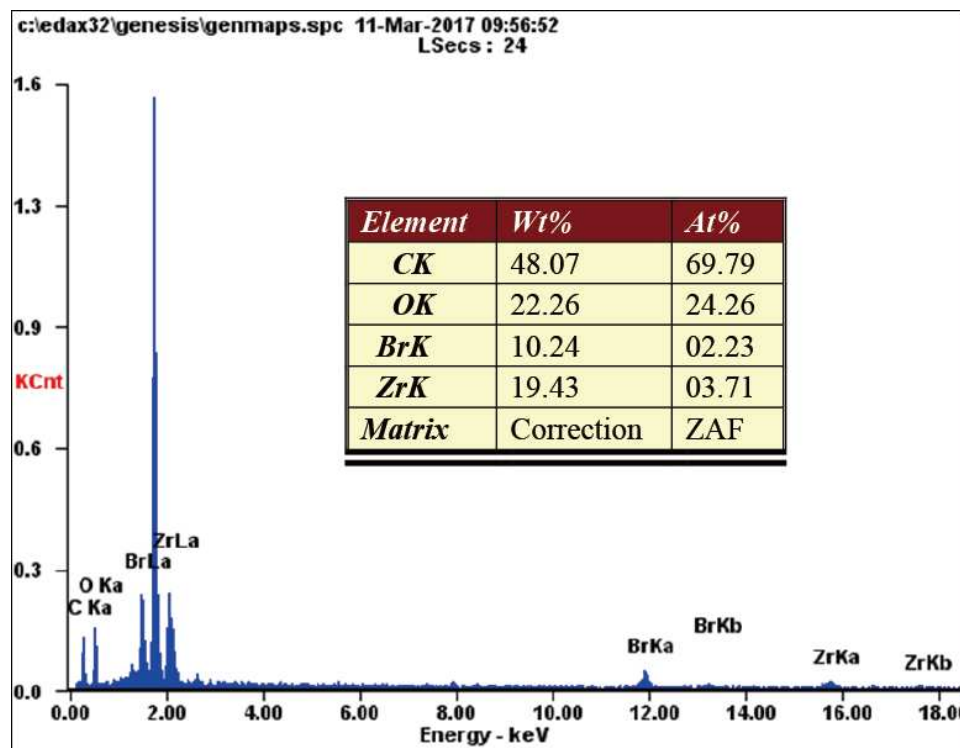


Figure S4. EDS spectrum of UiO-66-Br.

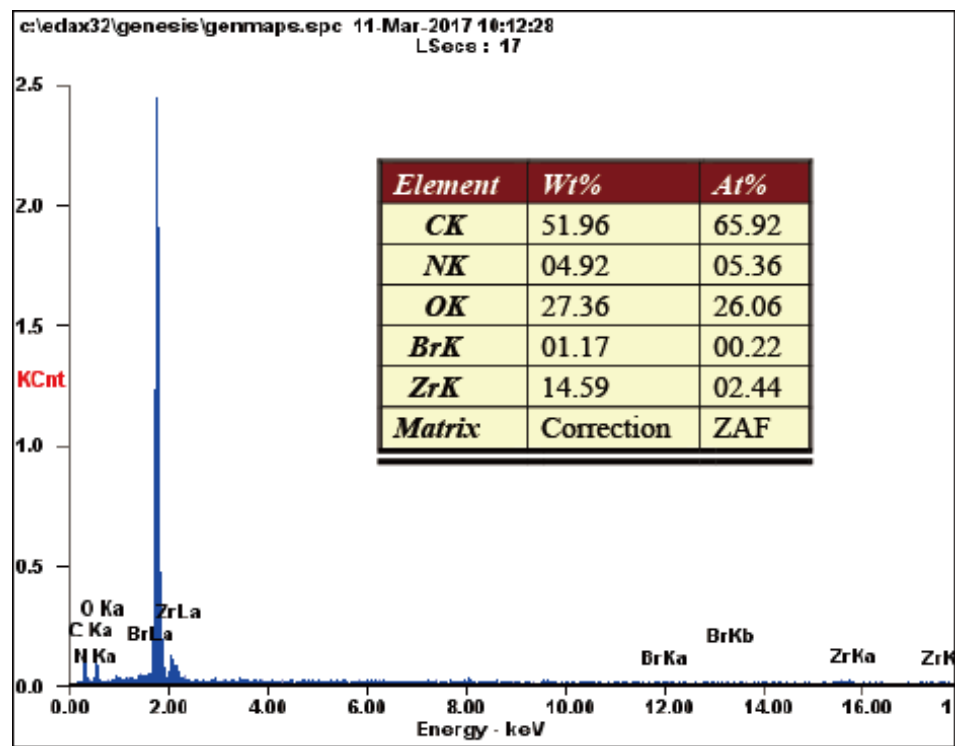


Figure S5. EDS spectrum of UiO-66-CN.

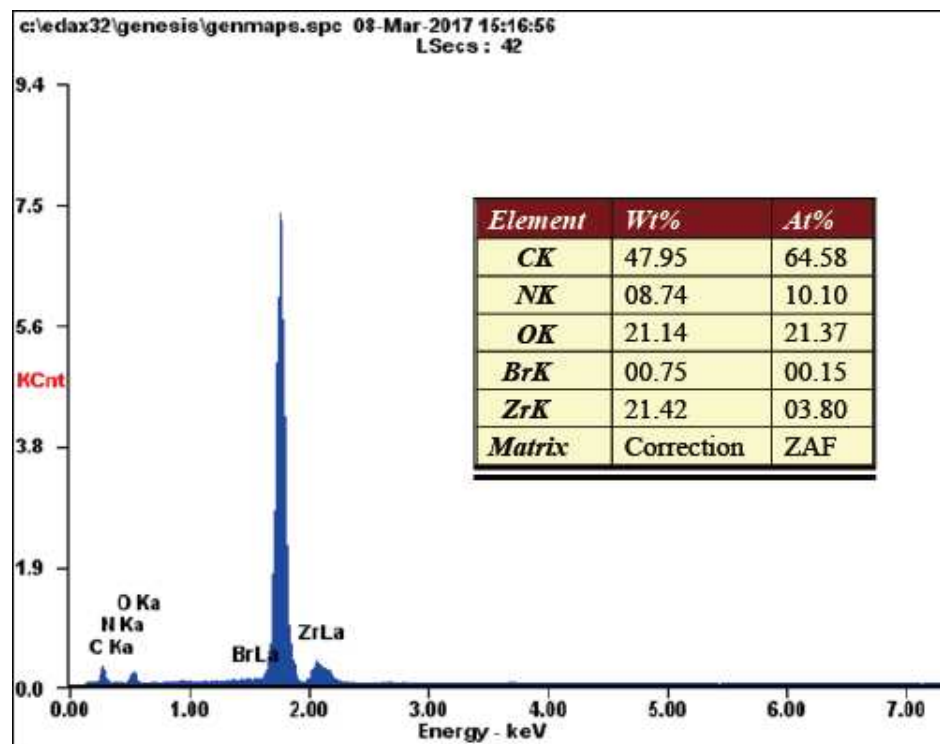
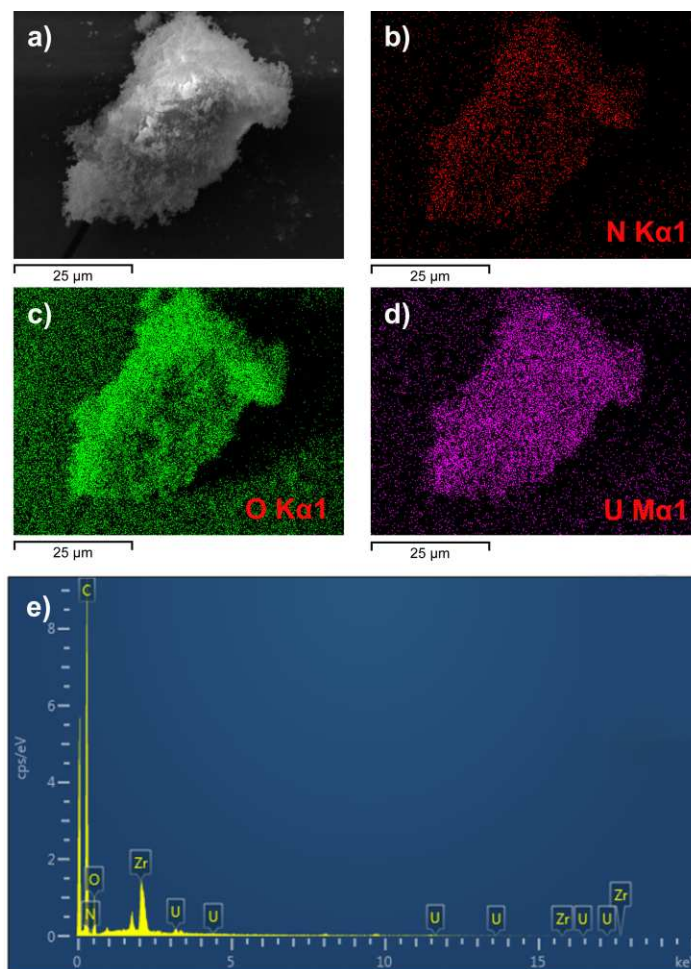


Figure S6. EDS spectrum of UiO-66-AO.



showing their distribution on the surface of UiO-66-AO. e) EDS spectrum of UiO-66-AO after loading uranyl.

7. Stability of UiO-66-AO in 0.01 M HNO₃

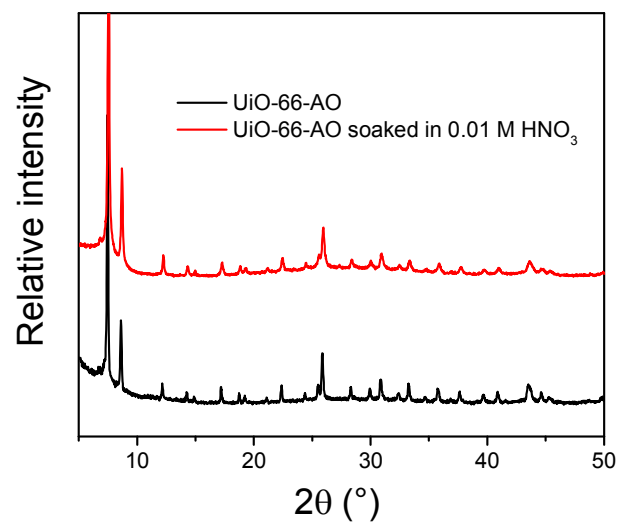


Figure S8. Powder X-ray diffraction (PXRD) patterns of UiO-66-AO as-synthesized as well as the one of immersing in 0.01 M HNO₃ for 4 h.

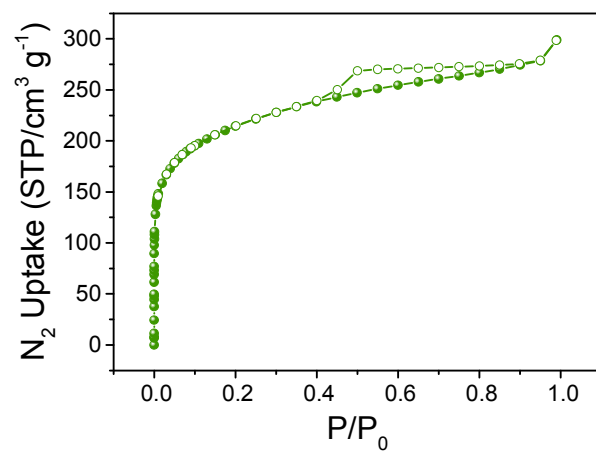


Figure S9. Nitrogen adsorption isotherm curve of UiO-66-AO immersed in 0.01 M HNO₃ for 4 h.

8. Influence of solid-to-liquid ratio

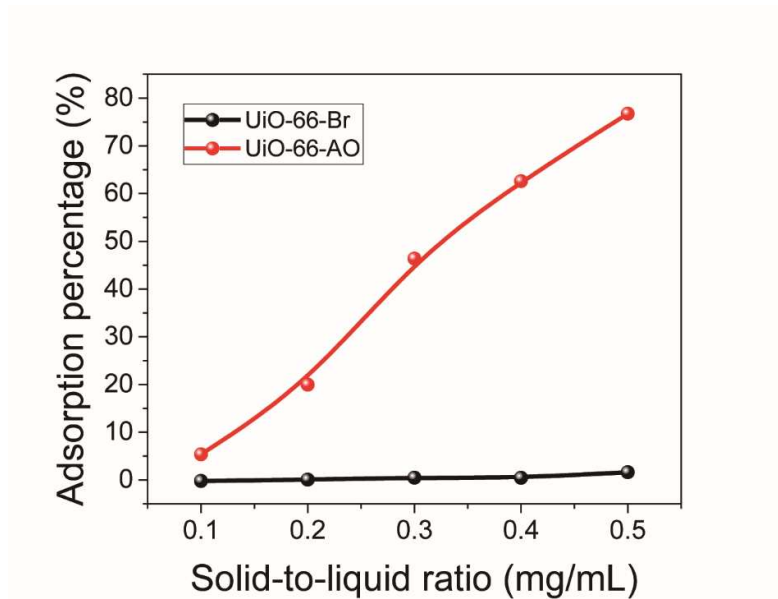


Figure S10. The adsorption percentage for uranium by UiO-66-Br and UiO-66-AO in various solid-to-liquid ratios ($[U(VI)]_{\text{initial}} = 9.82 \text{ mg/L}$, $\text{pH} = 4$).

9. Adsorption kinetics of seawater containing 500 ppb uranium

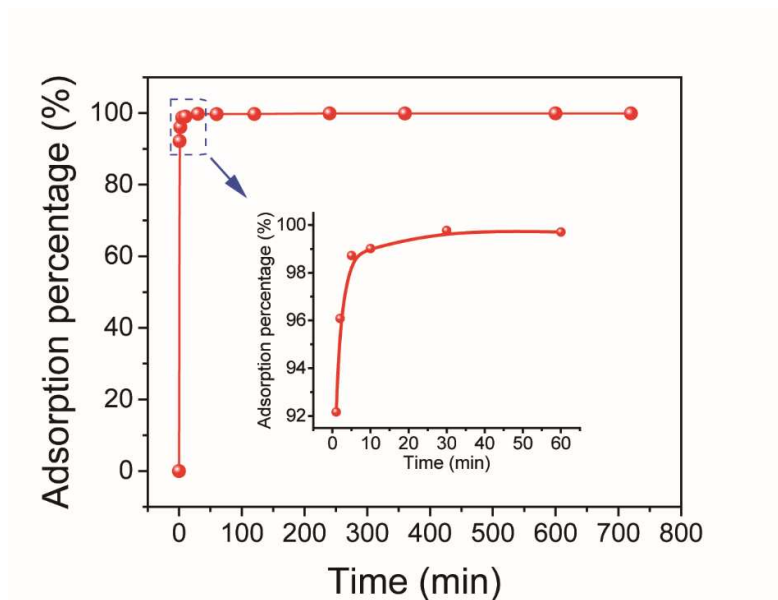


Figure S11. The effect of contact time on the sorption of Bohai seawater containing extra 500 ppb uranium by UiO-66-AO (pH = 8.25, $m_{\text{sorbent}}/V_{\text{solution}} = 1 \text{ mg/mL}$). The inserting graph shows the adsorption kinetics from 1 to 60 minutes.

10. Pseudo-first-order and pseudo-second-order kinetics models

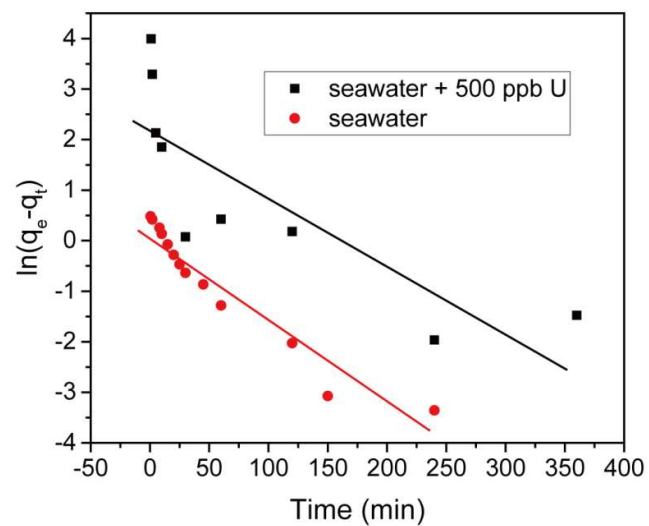


Figure S12. The pseudo-first-order kinetic model linearized plots for uranium adsorption on UiO-66-AO in different aqueous phases.

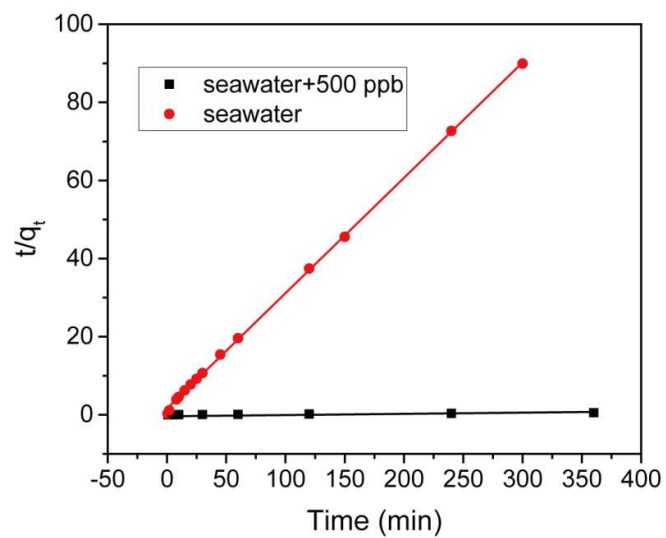


Figure S13. The pseudo-second-order kinetic model linearized plots for uranium adsorption on UiO-66-AO in different aqueous phases.

Table S3. Kinetic model constants and correlation coefficients for uranium adsorbed by UiO-66-AO in different aqueous phases.

	kinetic model			
	pseudo-first-order		pseudo-second-order	
	k_1 (min ⁻¹)	R^2	k_2 (g mg ⁻¹ min ⁻¹)	R^2
seawater	0.0171	0.920	0.0589	0.999
seawater + 500 ppb U	0.0131	0.624	0.0160	1

11. Comparison of adsorption kinetics for uranium

Table S4. Comparison of adsorption kinetics for uranium among reported materials and UiO-66-AO as sorbents.

Materials	Concentration (ppb)	L/S ratio (mL/g)	Adsorption (%)	Time (min)	Reference
SAX resin	57	10000	< 90	> 1000	Dalton Trans. 2016, 45, 11312–11325
SCX resin	57	10000	> 95	> 1000	
Activated carbon	57	10000	> 60	> 1000	
3,4 HOPO-nanoporous silica	57	10000	> 98	10	
Fe-MnO ₂ nanoporous composite	Natural seawater	10000	c.a.80	240	Ind. Eng. Chem. Res. 2016, 55, 4195-4207
8 nm Mn-Fe ₃ O ₄ magnetic nanoparticle	Natural seawater	10000	c.a.70	240	
MnO ₂ nanoporous composite	Natural seawater	10000	< 40	240	
8 nm Fe ₃ O ₄ magnetic nanoparticle	Natural seawater	10000	< 10	240	
PP-g-PVIm ⁺ Br ⁻ AO	1.7	25000	< 90	7200	Ind. Eng. Chem. Res. 2015, 54, 8699-8705
S ₄ -LDH	7	100	95	180	J. Am. Chem. Soc. 2015, 137, 3670-3677
UiO-66-AO	Natural seawater	1000	95	120	this work

12. References

- (1) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, Carlo.; Bordiga, S.; Lillerud, K. P. A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850-13851.
- (2) Kim, M.; Garibay, S. J.; Cohen, S. M. Microwave-assisted Cyanation of an Aryl Bromide Directly on a Metal-organic Framework. *Inorg. Chem.* **2011**, *50*, 729-731.
- (3) Vörös, A.; Mucsi, Z.; Baán, Z.; Timári, G.; Hermecz, I.; Mizsey, P.; Finta, Z. An Experimental and Theoretical Study of Reaction Mechanisms between Nitriles and Hydroxylamine. *Org. Biomol. Chem.* **2014**, *12*, 8036-8047.