Supporting Information

Ion-selective Uranium Capture from Seawater by UiO-66 Metal-organic Framework Modified with Amidoxime Groups

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1. Chemical reagents

All chemicals from commercial sources were reagent grade and used without further purification. Zirconium tetrachloride ($ZrCl_4$, 98%), N, N-Dimethylformamide (DMF, 99%), 2-Aminoterephthalic acid (BDC-NH_2, 98%), acrylonitrile stabilized with MEHQ (AN, 99%), hydroxylamine hydrochloride ($NH_2OH\cdot HCl$, 98%), triethylamine (99%), ethanol (99%), sodium hydroxide (NaOH, 96%), hydrochloric acid (HCl, 36~38%), sodium carbonate (Na_2CO_3, 99%), sodium bicarbonate ($NaHCO_3$, 99%), sodium chloride (NaCl, 99%) were obtained from Sinopharm chemical reagent company. The U and competing ions standard solution were purchased from Beijing North Weiye Metrology Technology Research Institute.

2. Material characterizations

Fourier transform infrared spectroscopy (FT-IR) were collected on a Thermo Nicolet iS50 spectrometer. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.54056 Å) and a step size of 0.02° in 2θ from 5 to 50°. The morphologies of synthesized MOFs were observed using a transmission electron microscope (JEOL JEM 2100F) and a scanning electron microscope (Merlin). Thermogravimetric analysis (TG) was carried out on a NETZSCH TG 209 F3 Tarus Thermo Microbalance. Nitrogen (N_2) adsorption curves were obtained using a Quantachrome Autosorb Gas Sorption analyzer IQ station 2. Gas adsorption measurements for MOFs were carried out at 77 K in a liquid nitrogen bath. X-ray photoelectron spectroscopy (XPS) was obtained using a Thermo Scientific K-Alpha spectrometer. The near-edge X-ray absorption fine structure (NEXAFS) of N K-edge, O K-edge were measured at the soft X-ray magnetic circular dichroism end station (XMCD) of the National Synchrotron Radiation Laboratory (NSRL) in University of Science and Technology of China (USTC). Inductively coupled plasma mass spectrometry (ICP-MS) experiments were performed on a NexION 300D instrument. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed using an Optima 8000 instrument.

3. Preparation of UiO-66-NH_2, UiO-66-CN and UiO-66-AO

UiO-66-NH_2 was synthesized by hydrothermal method according to literature reports and slightly modified.[1] There were two kinds of UiO-66-NH_2 with different molar ratios of $ZrCl_4$ and BDC-NH_2, which were $ZrCl_4$: BDC-NH_2 = 1:1.5 and 1:1.0. 0.40 g $ZrCl_4$ (1.72 mmol), 3.08 g, 5.14 g, 8.00 g or 12.36 g acetic acid (1.0, 1.7, 2.6, 4.1 M) were added to 24 mL DMF, which was recorded as A. 0.46 g BDC-NH_2 (2.54 mmol) was added to 24 ml DMF, which was recorded as B. A and B were sonicated for 10 minutes (min) to obtain the homogenous solution. Next, B was poured into A and sonicated for another 10 min. Then, the solution was heated at 120 °C for 24 hours (h). After the mixture was cooled to the ambient temperature, the yellow solid was collected by centrifuging at 8000 r min^{-1} for 10 min and washed with DMF (3 × 20 mL) and ethanol (3 × 20 mL), respectively. The sample was soaked in ethanol at 60 °C for 12 h. Upon cooling down the samples to room temperature, UiO-66-NH_2 were collected using centrifugation and dried in an oven at 55 °C for 12 h. As mentioned above, the mass of BDC-NH_2 was changed to 3.10 g and other conditions were unchanged when $ZrCl_4$: BDC-NH_2 = 1:1.0. The yield of UiO-66-NH_2 was 80%, which was calculated using Eq. S1.

$$Yield\ (\%) = actual\ quality\ (mg)/theoretical\ quality\ (\mathrm{mg}) \tag{S1}$$

0.60 g UiO-66-NH_2 above products (0.3 mmol) were added into the solution of 15 mL AN (0.227 mol) and 15mL DMF, respectively. The mixture was stirred and heated at 120 °C for 12 h. After cooling to ambient temperature, the yellow solid was acquired by centrifugation (8000 r min^{-1}), and washed by DMF (3 × 20 mL) and ethanol (3 × 20 mL), respectively. The solid was dried in oven at 55 °C overnight and UiO-66-CN was obtained. The yield of UiO-66-CN was 64%, which was calculated by Eq. S1.

0.20 g the above products UiO-66-CN (0.1 mmol), 1.29 g $NH_2OH{\cdot}HCl$ (18.6 mmol) and 1.88 g triethylamine (18.6 mmol) were dissolved in 50 mL of absolute ethanol refluxing for 24 h, the yellow solid was isolated by centrifugation (8000 r min^{-1}) and washed by ethanol (3 × 15 mL). UiO-66-AO was dried at 55 °C for 12 h in oven. The yield of UiO-66-AO was 78%, which was calculated by Eq. S1.

4. Batch adsorption experiments

The effects of acetic acid concentration, ligand concentration, anion (Cl^-) concentration, contact time, the initial concentration and pH on adsorption of UO_2^{2+} were investigated. Typically, the ratio of adsorbent mass to solution volume (m/V) was 0.02 mg/mL, an amount of the adsorbent (2.0 mg) was added to 100 mL UO_2^{2+} solution of given concentration and pH value in a plastic bottle. But, the volume of UO_2^{2+} solution was 500 mL when the effect of contact time was experimented, which was convenient for sampling and reduced experimental errors. The pH was adjusted by 0.1 M or 1 M HCl and NaOH solution. After being stirred at 100 rpm and 25 °C for 24 h, 2 mL sample solution was sucked out and filtered by a 0.2 μm nylon membrane filter. The sample was diluted by a certain multiple used 2% HNO_3, and the concentration of UO_2^{2+} was determined by ICP-AES or ICP-MS. The adsorption capacity of UO_2^{2+} was calculated using Eq. S2.

$$q_t = (c_0 - c_t) \times V/m \tag{S2}$$

where q_t (mg/g) is the adsorption amount of UO_2^{2+} after a contact time t (min), c_0 (mg/L) is the initial UO_2^{2+} concentration, c_t (mg/L) is the UO_2^{2+} concentration at t (min). V (L) is the volume of UO_2^{2+} solution, and m (g) is the weight of the adsorbent.

The removal rate of UO_2^{2+} was calculated using Eq. S3.

$$\text{removal rate (\%)} = (c_0 - c_t)/c_0 \times 100\% \tag{S3}$$

where c_t (mg/L) is the UO_2^{2+} concentration after adsorption; c_0 (mg/L) is the initial UO_2^{2+} concentration.

5. Adsorption test in simulated seawater

Simulated seawater was formulated according to previous study, and was consisted of ions as table S1, and 35 g/L sea salt. The pH value was adjusted to 7.8 ± 0.1 with Na_2CO_3. The initial concentrations of UO_2^{2+} was 330 ppb and competing ions, Pb, Zn, Cu, Ni, Co, Fe, V, Na and Ca in the simulated seawater system were about 100 times higher than those in natural seawater[2,3]. The mixture was stirred for 24 h at 25 °C. The MOFs were filtered by a 0.2 μm nylon membrane filter and digested. Dilute the digestion solution to 100 mL. The concentration of each ion concentration in the solution was determined by ICP-AES and calculated using Eq. S4.

$$q_t = c_t \times V/m \tag{S4}$$

where q_t (mg/g) is the adsorption amount of UO_2^{2+}, c_t (mg/g) is the UO_2^{2+} concentration measured by ICP-AES, V (L) is the volume of digestion solution, and m (g) is the weight of the adsorbent.

6. Adsorption test in seawater

Seawater was collected from Qingdao, China and adsorbed under laboratory conditions. 37 mg UiO-66-AO was soaked in 18.66 L seawater and stirred at room temperature at 100 rpm for 16 days. 2 mL sample solution was sucked out and filtered by a 0.2 μm nylon membrane filter in different time, and the MOFs were filtered by a 0.2 μm nylon membrane filter after 16 days. Dilute the sample 40 times with 2% HNO_3. Analyze the UO_2^{2+} content in seawater samples using ICP-MS and calculate the adsorption capacity for U using Eq. S2.

7. Adsorption kinetics and adsorption isotherms

The pseudo first-order model could indicate the initial stage of adsorption process, which is expressed by the following Eq. S5.

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{S5}$$

Where q_e (mg/g) and q_t (mg/g) are the equilibrium adsorption capacity and the specific adsorption capacity at any time of UO_2^{2+} (mg/g), respectively. Besides K_1 is the equilibrium rate constant of the pseudo first-order sorption (1/min).

The equation of pseudo second-order model is illustrated as Eq. S6:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 \times q_e^2} \tag{S6}$$

Where K_2 ($g \cdot mg^{-1} \cdot h^{-1}$) is the equilibrium rate constant of pseudo second-order. q_e (mg/g) and q_t (mg/g) are the maximum adsorption capacity and the adsorbing capacity at time t (min), respectively.[4]

The linear equation of Langmuir model is expressed as Eq. S7.

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{\mathrm{b} \times q_\mathrm{max}} + \frac{c_\mathrm{e}}{q_\mathrm{max}} \quad \text{(S7)}$$

Where q_e (mg/g) is the equilibrium adsorption capacity of UO_2^{2+} and c_e (mg/L) is the UO_2^{2+} concentration. q_max (mg/g) represents the maximum capacity of UO_2^{2+} adsorbed per unit mass of samples, and b (L/mg) is a constant related to the adsorption energy. Through linear fitting the plots $c_\mathrm{e}/q_\mathrm{e}$ as a function of c_e, a straight line with the slope $1/q_\mathrm{max}$ and intercept $1/(\mathrm{b}\times q_\mathrm{max})$ is made so as to obtain the q_max and b.

The Freundlich model in linear form is based on the assumption that the adsorption process on heterogeneous surface with different adsorption energies. This model is expressed by Eq. S8.

$$\ln q_\mathrm{e} = \ln \mathrm{K_F} + \frac{1}{n} \ln c_\mathrm{e} \quad \text{(S8)}$$

Where $\mathrm{K_F}$ is a constant related to adsorption capacity (mg/g) and $1/n$ is an empirical parameter corresponding to surface heterogeneity or adsorption intensity. Generally n in the range 2-10 means the adsorption is easy, 1-2 means relatively difficult, and less than 1 means the difficult adsorption process. The Freundlich constants $\mathrm{K_F}$ and $1/n$ can be determined from the intercept and slope of linear plot of $\ln q_\mathrm{e}$ against $\ln c_\mathrm{e}$, respectively.[4]

8. Supplementary Figures S1-S5 and Table S1, S2.

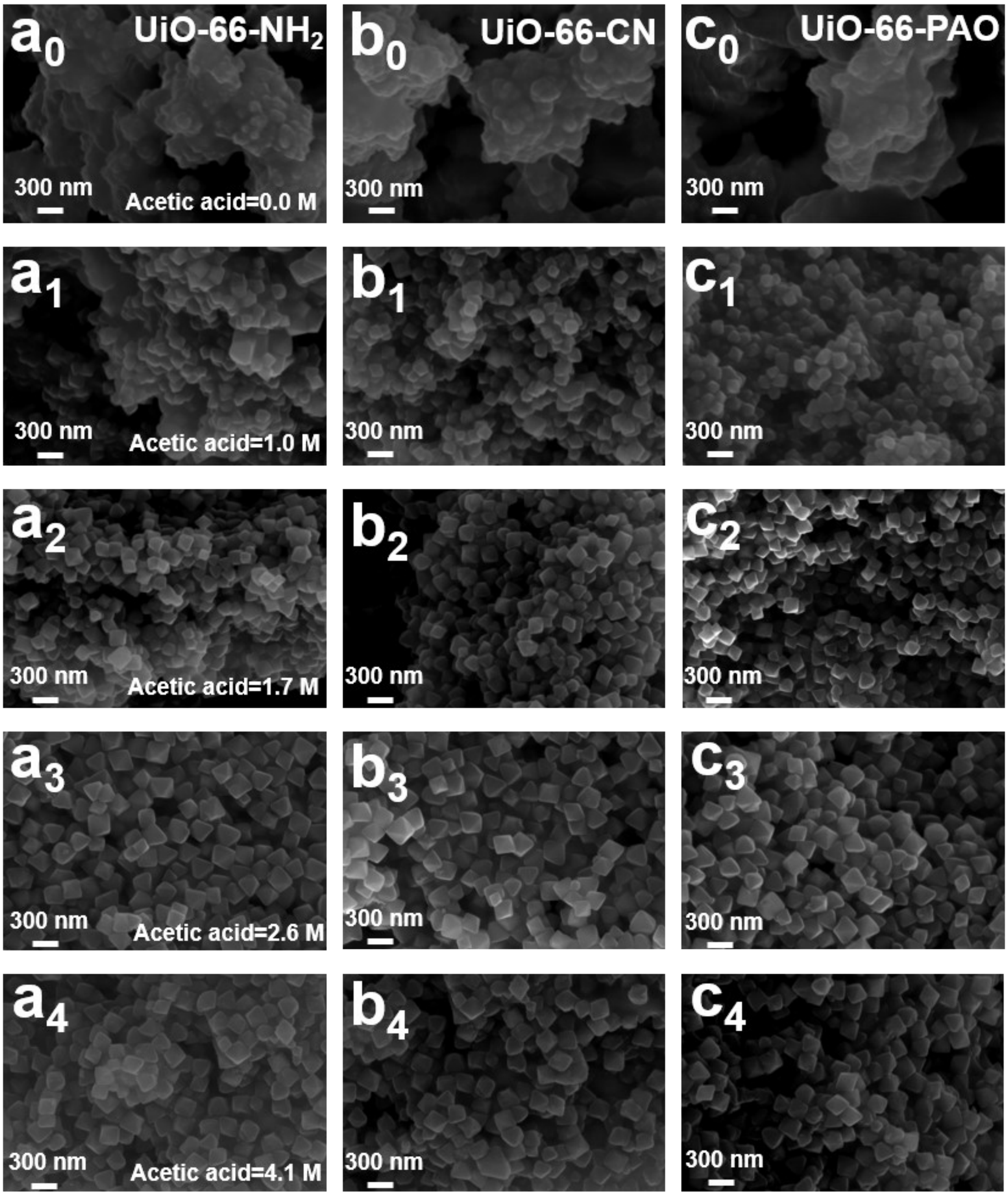

Fig. S1 (a_0-a_4) UiO-66-NH_2 prepared with the concentration of $ZrCl_4$: BDC-NH_2 =1.0 : 1.5, and the concentration of acetic acid are 0.0, 1.0, 1.7, 2.6, 4.1 M, respectively. (b_0-b_4) UiO-66-CN introduced with cyanide group from UiO-66-NH_2 under different acetic acid concentration. (c_0-c_4) UiO-66-AO prepared by amidoximation from UiO-66-CN under different acetic acid concentration.

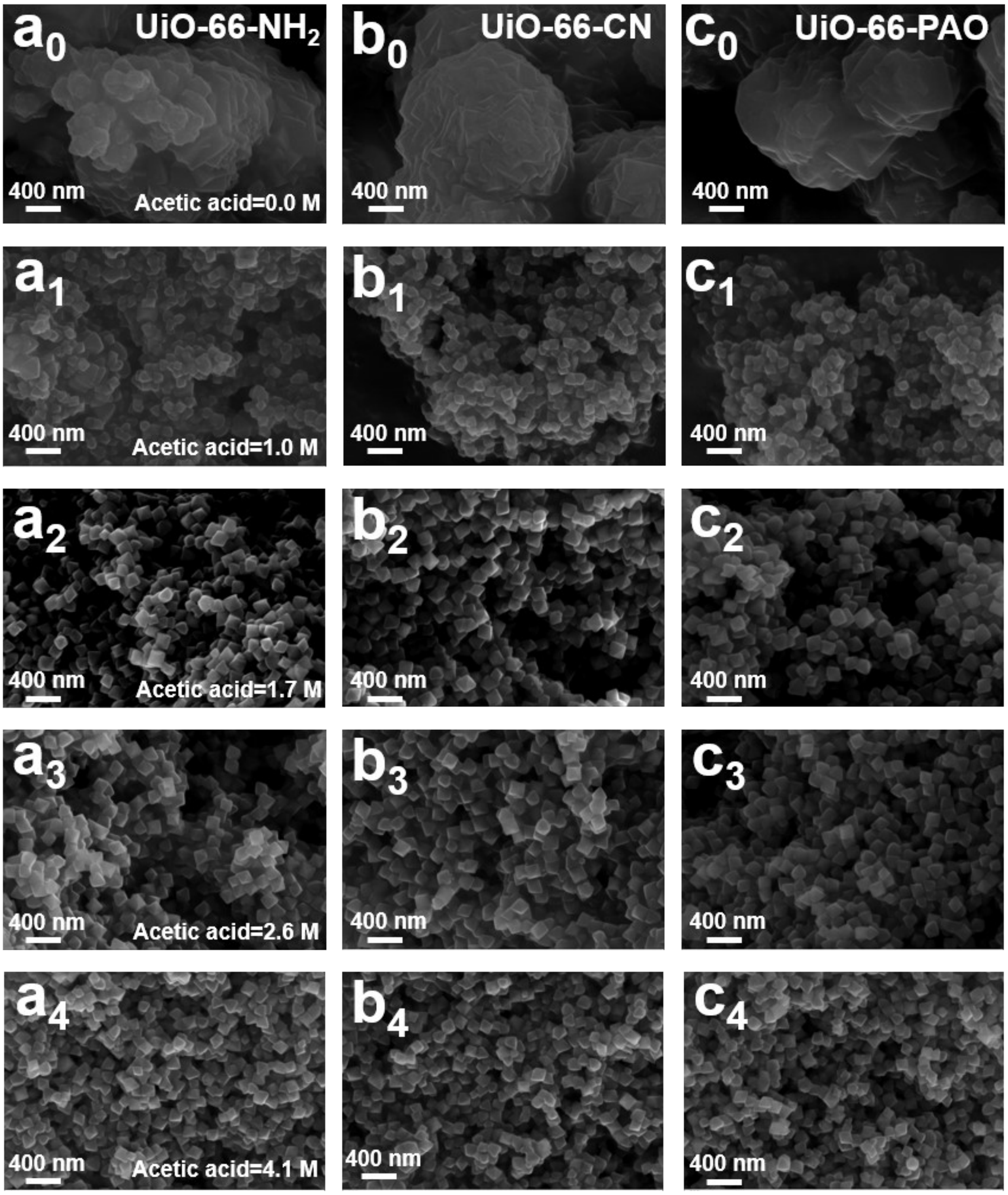

Fig. S2 (a_0-a_4) UiO-66-NH_2 prepared with the concentration of $ZrCl_4$: BDC-NH_2 =1.0: 1.0, and the concentration of acetic acid are 0.0, 1.0, 1.7, 2.6, 4.1 M, respectively. (b_0-b_4) UiO-66-CN introduced with cyanide group from UiO-66-NH_2 under different acetic acid concentration. (c_0-c_4) UiO-66-AO prepared by amidoximation from UiO-66-CN under different acetic acid concentration.

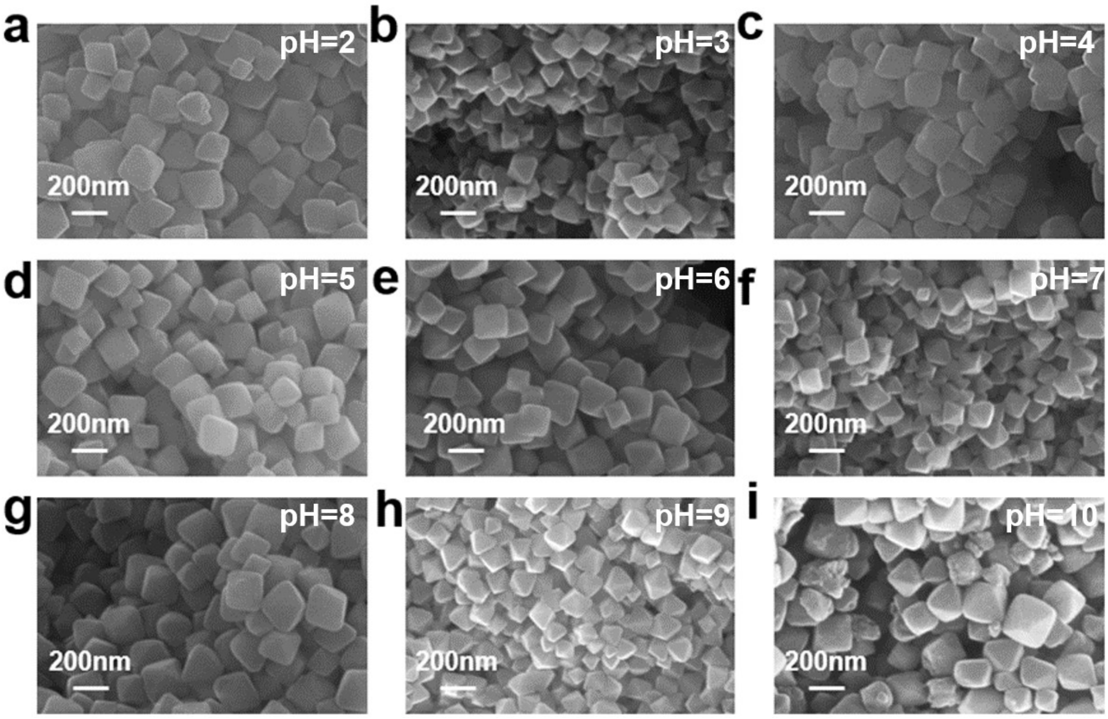

Fig. S3 (a-i) SEM of UiO-66-AO in pH 2.0-10.0 aqueous solution with 24 h.

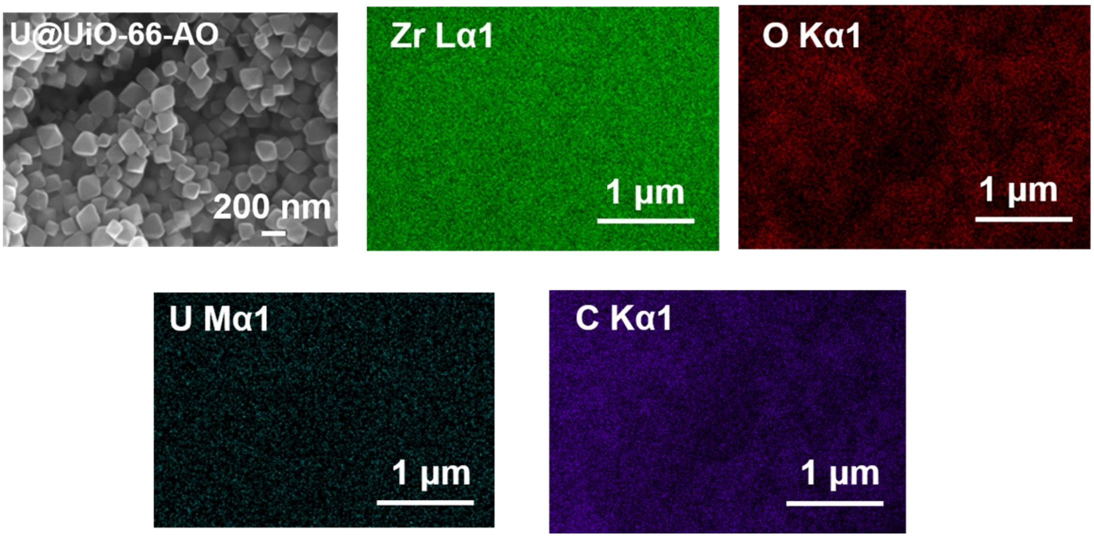

Fig. S4 SEM of UiO-66-AO after UO_2^{2+} adsorption in simulated seawater (U@UiO-66-AO), and Zr, O, U and C elemental mapping photographs of U@UiO-66-AO.

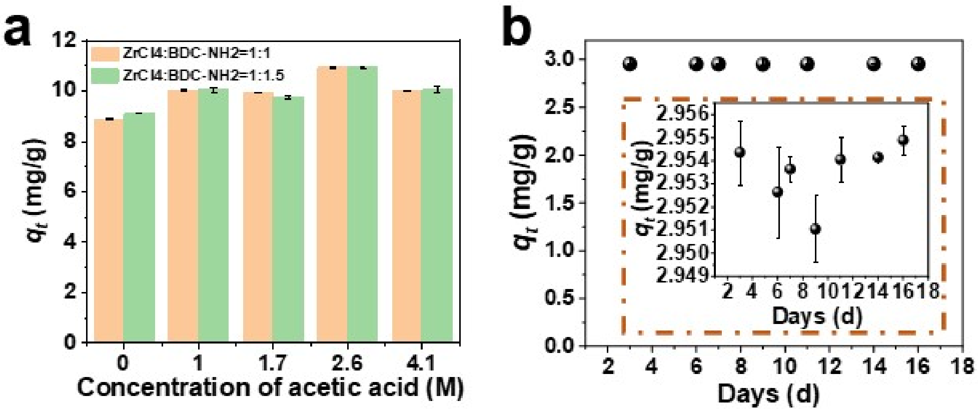

Fig. S5 (a) The effects of acetic acid concentration and ligand concentration on UO_2^{2+} adsorption (c_0=200 ppb, t=24h), (b) adsorption in seawater (m/V=2.0 mg/L in 18.7 L seawater).

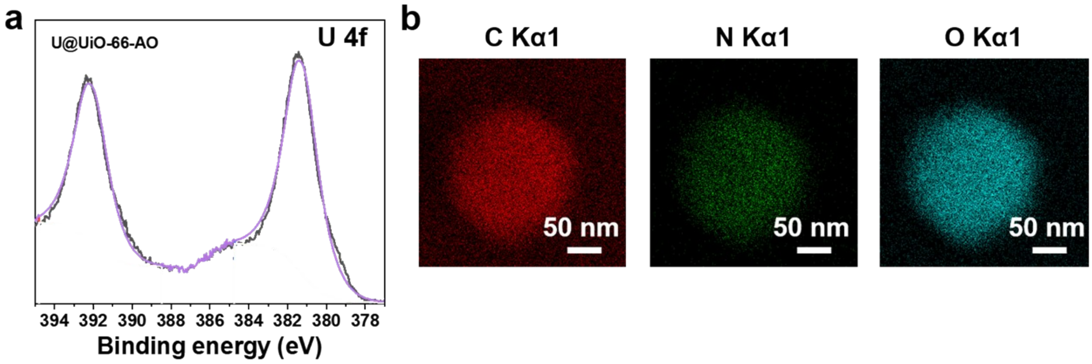

Fig. S6 (a) U 4f spectrum of U@UiO-66-AO, (b) C, N and O elemental mapping photographs of UiO-66-AO after adsorbing UO_2^{2+} from seawater.

Table.S1 Ions concentration in natural seawater and simulated seawater.[3,5]

Element	U	V	Fe	Co	Ni	Cu	Zn	Pb	Mg	Ca
Natural Seawater (ppb)	3.3	1.5-2.5	1.0-2.0	0.05	1.0	0.6	4.0	0.03	1.3×10^6	0.4×10^6
Simulated Seawater (ppb)	330	150-250	100-200	5	100	60	400	300	1.2×10^5	0.6×10^5

Table.S2 MOFs for uranium extraction from seawater.

MOFs	Seawater Volume and adsorbent dosage	Adsorption Time	Adsorption Capacity(mg/g)	Ref.
UiO-66-AO	19 L the Bohai Sea water； 2.0 mg/L	3 days	3.0	this work

UiO-66-NH-(AO)	25 L the South China Sea water； 0.2 mg/L	8 days	5.2	6
Co-SLUG-35	1 L actual seawater with 5.35 ppb U; 10 mg/L	--	1.0	7
UiO-66-AO	1 L Bohai seawater； 1 mg/L	3 days	2.7	8
UiO-66-neomycin	10 L actual seawater; 0.5 mg/L	30 days	4.6	9
UiO-66-3C4N	100 L the South China Sea water with a flow rate of 10 L/h; 0.2 mg/L	28 days	6.9	10
BP@CNF-MOF	100 L the South China Sea water with a flow rate of 1 L/h; 1 mg/L	6 weeks	4.4 (dark) 6.8 (light)	11

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