

Electronic Supplementary Information

Simple Small Molecule Carbon Source Strategy for Synthesis of Functional Hydrothermal Carbon: Preparation of Highly Efficient Uranium Selective Solid Phase Extractant

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Experimental Section

Section 1. Preparation of U(VI) stock solution and multi-ion solution

A stock solution of uranium(VI) ($\sim 1000 \text{ mg L}^{-1}$) was prepared by dissolving appropriate amounts of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water. The pure uranium working solutions (25–300 mg L^{-1}) were prepared by appropriate dilution of the stock solution. Similarly, the multi-ion solution containing 12 competing ions besides U(VI) as listed in Supporting Information, Table S1, was prepared by dissolving the metal oxides or nitrates in nitric acid aqueous solution with the concentration of about 0.84 mmol L^{-1} .

Section 2. Batch sorption studies

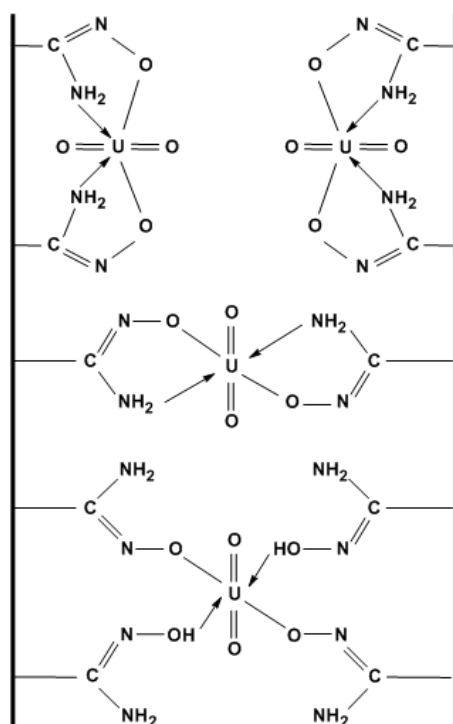
10 mg HTC-AO was added into a 50 mL Erlenmeyer flask along with 25 mL of either pure uranium solutions or multi-ion test solution at a given pH. The pH of each test solution was adjusted to the required value with dilute and concentrated HNO₃ and NaOH solutions. The flasks were shaken for specified time (t , min) at desired temperatures (T , K). Then the sorption systems were centrifuged, and the concentrations of metal ions in the supernatant, before and after sorption, were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or atomic absorption spectroscopy (AAS).

Section 3. Boehm titrations

A series of Boehm titrations were conducted in order to obtain information about the content of oxygen-containing groups of HTC samples. 20 mL of 0.1 mol L⁻¹ base solution (NaOH, Na₂CO₃, NaHCO₃) was pipetted slowly into a 250 mL Erlenmeyer flasks containing 0.025 g HTC samples. The Erlenmeyer flasks were sealed and placed in a shaking incubator (25 °C) at 120 rpm for 24 h. Samples were then filtered and 5 mL aliquots were removed along with 50 mL deionized water and titrated with standard HCl (0.1 mol L⁻¹), recorded the amount of consumed HCl solution. A blank sample which contained no HTCs was also titrated as described. The following formula was used to calculate the amount of the oxygen-containing groups of HTCs:

$$\text{Mass of SAFG} = \frac{(T_b - T) \times C}{w} \quad (1)$$

Where T_b (mL) is the amount of consumed hydrochloric acid in the blank titration; T (mL) are the amount of consumed HCl of different HTCs after oscillation; C (mol L⁻¹) is the concentration of HCl used; w (g) is the amount of added HTCs. The amount of various types of surface acid groups are calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; whereas Na₂CO₃ neutralizes carboxylic and lactonic groups; and NaHCO₃, only neutralizes carboxylic group.



Scheme S1. Classic coordination modes between amidoxime groups and uranyl ions.

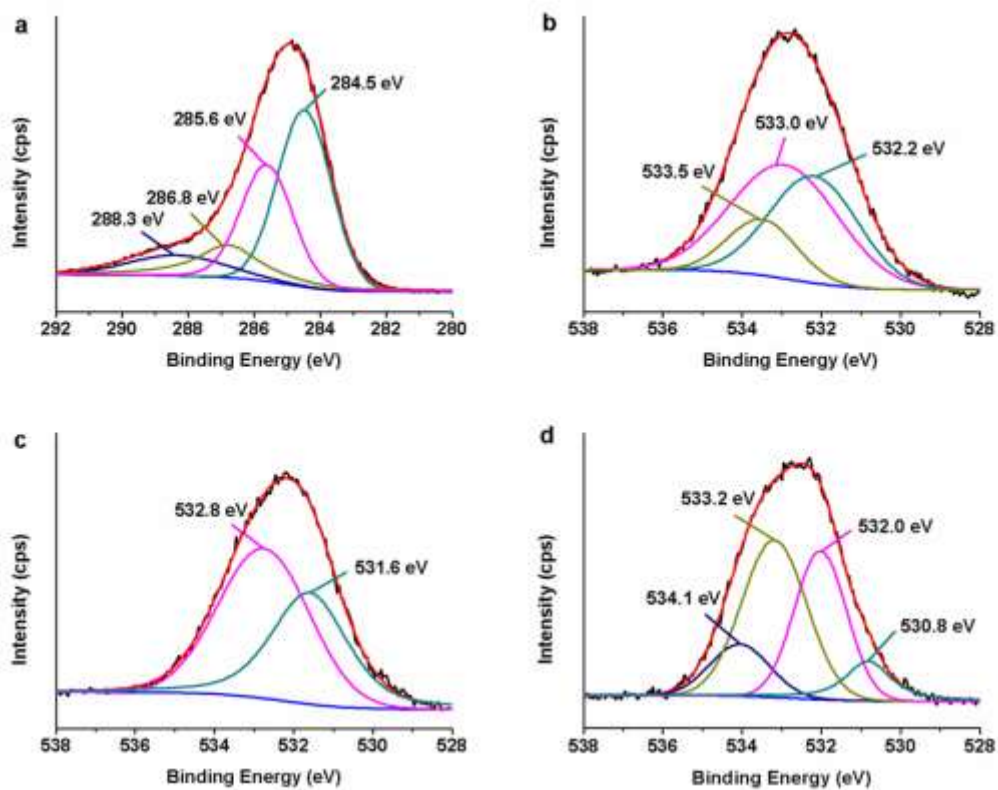


Figure S1. The XPS spectra of C 1s for (a) HTC-gly and O 1s for (b) HTC-gly, (c) HTC-CN and (d) HTC-AO.

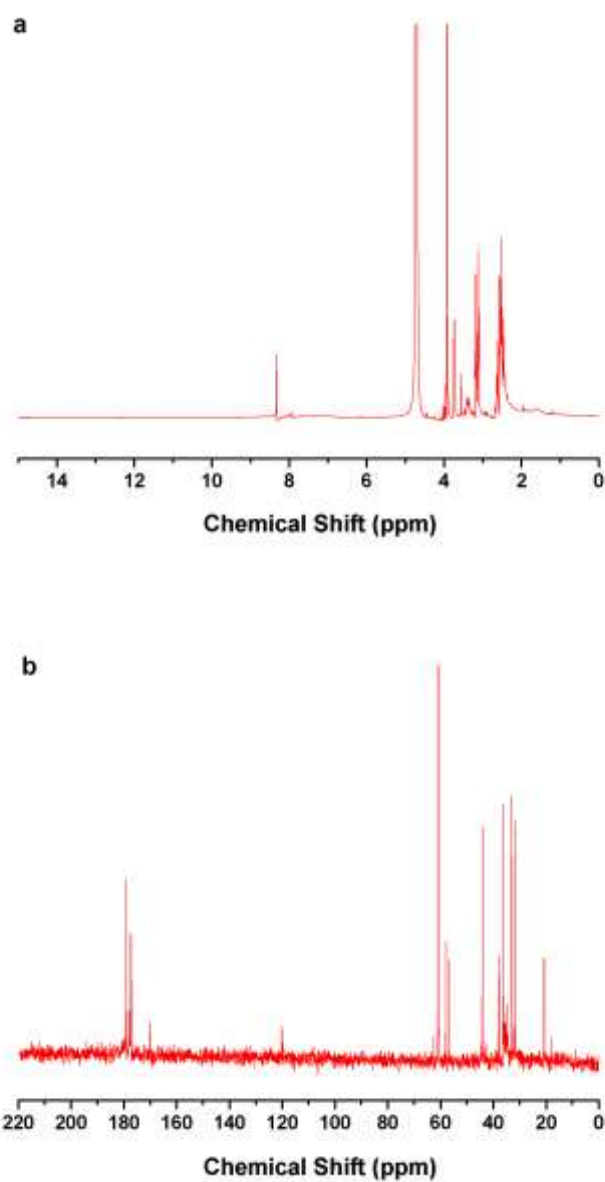


Figure S2. (a) Typical ^1H and (b) ^{13}C NMR spectra (400 MHz) of reaction solution corresponding to the synthesis process of HTC-gly.

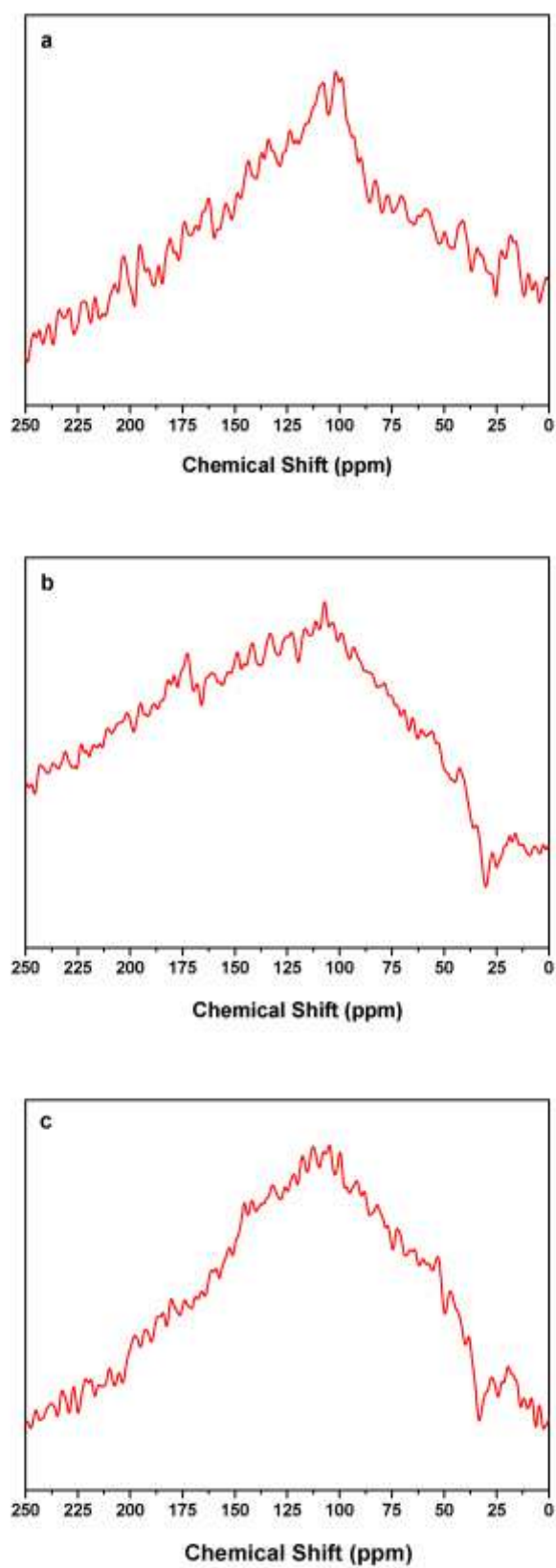


Figure S3. The ^{13}C solid-state CP-MAS NMR spectra (500 MHz) of (a) HTC-gly, (b) HTC-CN, and (c) HTC-AO.

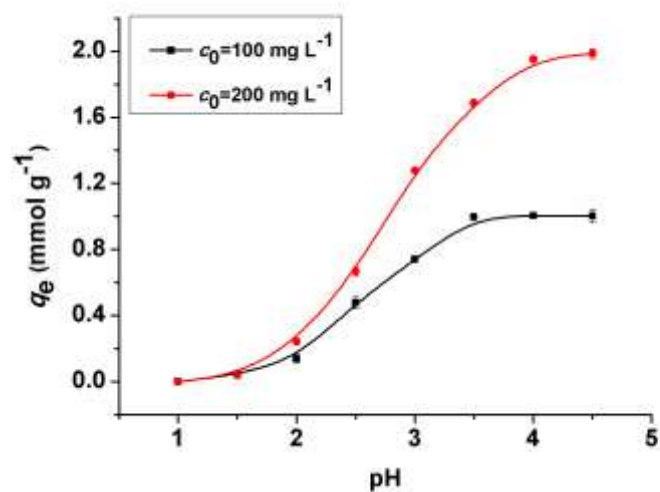


Figure S4. Effect of pH on the sorption of U(VI) onto HTC-AO in pure U(VI) solution ($t = 120 \text{ min}$, $V = 25 \text{ mL}$, $T = 298.15 \text{ K}$, and $w = 10 \text{ mg}$).

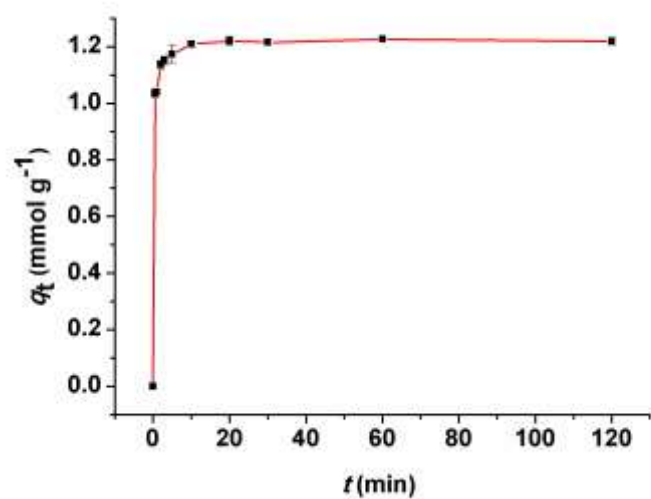


Figure S5. The effect of contact time on the sorption of U(VI) onto HTC-AO ($c_0 = 0.5$ mmol L⁻¹, pH = 4.5, $T = 298.15$ K, $V = 25$ mL, $w = 10$ mg).

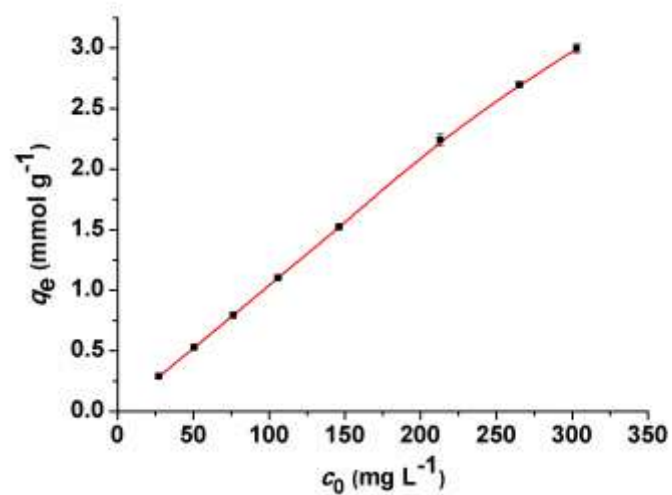


Figure S6. The effect of initial uranium concentration on the sorption of U(VI) onto HTC-AO (pH = 4.5, t = 120 min, T = 298.15 K, V = 25 mL, w = 10 mg).

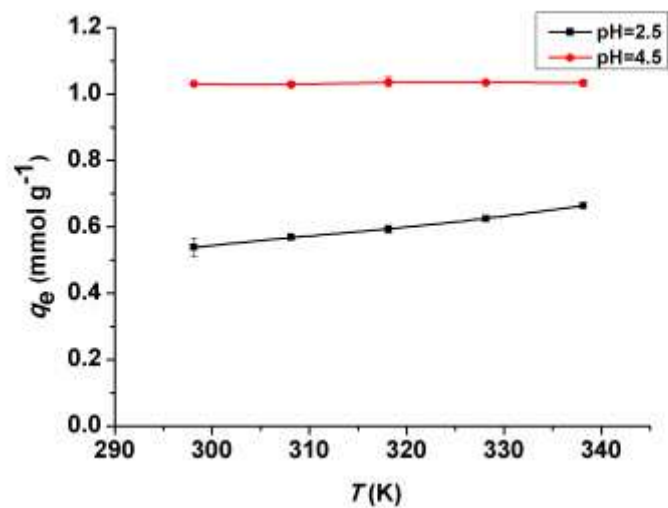


Figure S7. The effect of temperature on the sorption of U(VI) onto HTC-AO ($c_0 = 0.5 \text{ mmol L}^{-1}$, $t = 120 \text{ min}$, $V = 25 \text{ mL}$, $w = 10 \text{ mg}$).

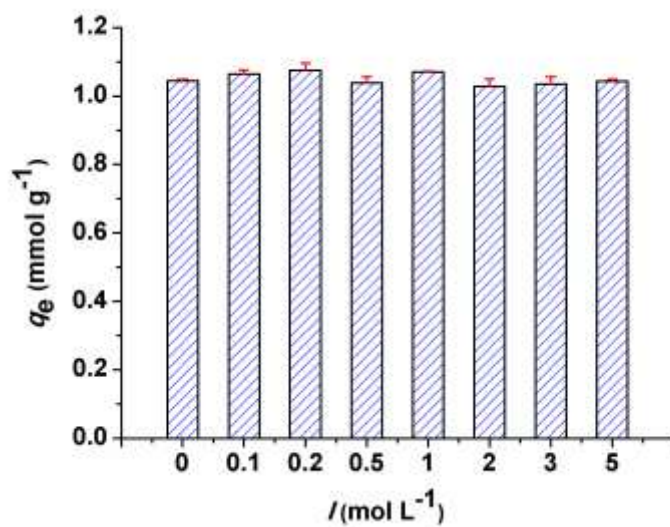


Figure S8. The effect of ionic strength on the sorption of U(VI) onto HTC-AO ($c_0 = 0.5$ mmol L⁻¹, pH = 4.5, $t = 120$ min, $T = 298.15$ K, $V = 25$ mL, $w = 10$ mg).

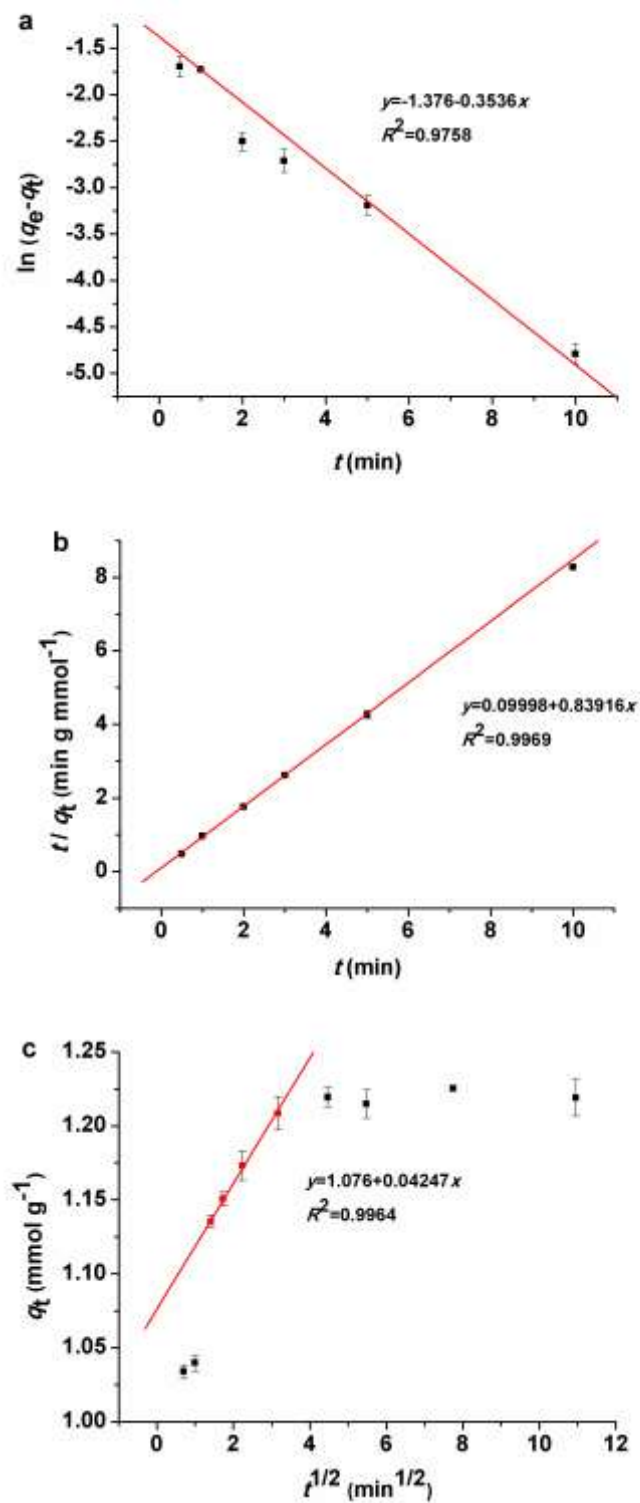


Figure S9. (a) Pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion plots for the sorption of U(VI) onto HTC-AO.

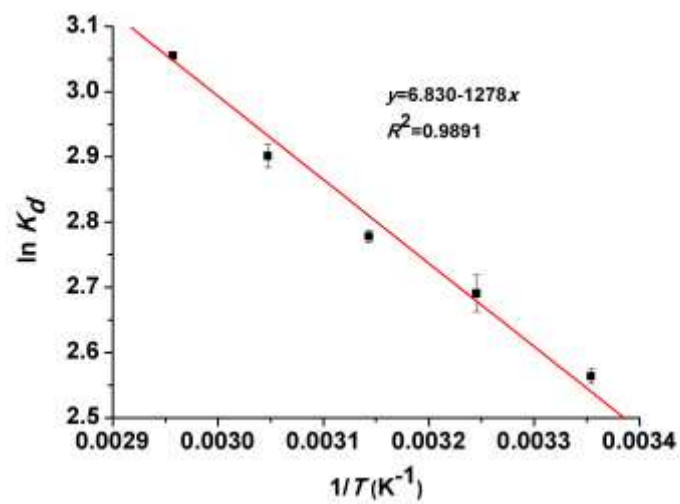


Figure S10. Plot of $\ln K_d$ vs. $1/T$ for the sorption of U(VI) onto HTC-AO.

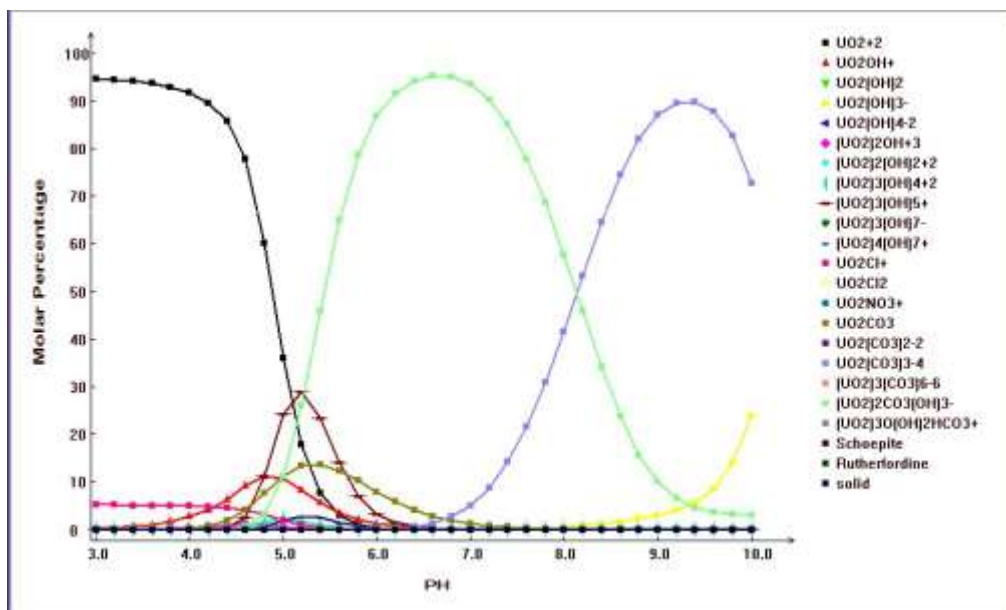


Figure S11. Distribution of uranium(VI) species in aqueous solution with a total concentration of 300 mg L^{-1} and pH values ranging from 3 to 10. Calculated by using a CHEMSPEC (C++) program.

Table S1. Compositions of the simulated nuclear industrial effluent.

Coexistent ion	Added as	Reagent purity
UO_2^{2+}	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Standard reagent
La^{3+}	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.9% metal basis
Ce^{3+}	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.99% metal basis
Nd^{3+}	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	AR
Sm^{3+}	$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	AR
Gd^{3+}	$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	AR
Mn^{2+}	MnO	99.5%
Co^{2+}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99.99% metal basis
Ni^{2+}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Spectrum pure
Zn^{2+}	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99.99% metal basis
Sr^{2+}	$\text{Sr}(\text{NO}_3)_2$	99.99% metal basis
Ba^{2+}	$\text{Ba}(\text{NO}_3)_2$	99.999%
Cs^+	CsNO_3	AR

Table S2. Different experiment conditions for the preparation of the HTC-CN and its sorption capacity and selectivity (S_U) toward uranium after oximation.^{a, b, c}

Number	$V_{\text{acrylonitrile}}$ (mL)	$V_{\text{H}_2\text{O}}$ (mL)	Temperature (°C)	Time (h)	q_e (mmol g ⁻¹)	S_U (%)
1	15	40	160	12	1.04	41.6
2	10	50	160	24	1.03	39.8
3	5	60	160	36	0.98	40.6
4	10	60	180	12	1.01	41.2
5	5	40	180	24	0.98	40.2
6	15	50	180	36	0.99	40.6
7	5	50	200	12	1.03	40.4
8	15	60	200	24	0.96	41.5
9	10	40	200	36	0.97	41.4

^a. The volume of acrylonitrile was kept fixed (10 mL) throughout all experiments;

^b. Oximation condition of HTC-CN: reflux at 115 °C for 6 h in ethanol aqueous solution in the presence of Na₂CO₃, pH = 8.0;

^c. Sorption conditions: $c_0 = 0.5 \text{ mmol L}^{-1}$ for all cations, pH = 4.5, $t = 120 \text{ min}$, $V = 25 \text{ mL}$, $T = 298.15 \text{ K}$, and $w = 10 \text{ mg}$.

Table S3. The oximation reaction conditions for the preparation of HTC-AO and its sorption capacity and selectivity (S_U) toward uranium.^{a, b}

Reaction condition			q_e (mmol g ⁻¹)	S_U (%)
Temperature (°C)	Time (h)	pH		
25	6	8.0	0.80	38.9
80	6	8.0	0.84	47.1
115	6	8.0	0.82	44.4
Time (h)	Temperature (°C)	pH		
3	80	8.0	1.17	54.2
6	80	8.0	0.95	48.2
18	80	8.0	0.97	46.7
pH	Temperature (°C)	Time (h)		
6.0	80	3	1.42	54.7
7.0	80	3	1.56	61.9
8.0	80	3	1.56	64.0
9.0	80	3	1.28	53.6

^a. The synthesis condition of HTC-CN: hydrothermal carbonization under 180 °C for 24 h,

$V_{\text{glyoxal}} = 10$ mL, $V_{\text{acrylonitrile}} = 10$ mL, $V_{\text{H}_2\text{O}} = 50$ mL;

^b. Sorption conditions: $c_0 = 0.5$ mmol L⁻¹ for all cations, pH = 4.5, $t = 120$ min, $V = 25$ mL, $T = 298.15$ K, and $w = 10$ mg.

Table S4. N₂ adsorption parameters for HTC-gly, HTC-CN and HTC-AO.

Sample	Surface area S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
HTC-gly	32.17	0.08	3.34
HTC-CN	11.98	0.05	1.31
HTC-AO	7.64	0.01	2.86

Table S5. The kinetic parameters for the U(VI) sorption onto HTC-AO.

q_e (mmol g ⁻¹)	Pseudo-first-order		
1.21	k_1 (min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
	0.354	0.253	0.9758
	Pseudo-second-order		
	k_2 (g mg ⁻¹ min ⁻¹)	$q_{e,cal}$ (mmol g ⁻¹)	R^2
	7.04	1.19	0.9969
	Intraparticle diffusion		
	k_{int} (mmol g ⁻¹ min ^{-0.5})	C (mmol g ⁻¹)	R^2
	0.0425	1.08	0.9964

Table S6. Thermodynamic parameters for the U(VI) sorption onto HTC-AO.

ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)				
		298.15 K	308.15 K	318.15 K	328.15 K	338.15 K
10.10	112.6	-23.48	-24.60	-25.73	-26.86	-27.98