Supporting Information

Polyamidoxime-based colloidal particles with 3D network for synergistic uranium extraction from seawater

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Experimental

Adsorption in uranium-spiked seawater.

$UO_2(NO_3)_2 \cdot 6H_2O$ (2.1311g) was dissolved in the concentrated nitric acid (20 mL) and then diluted to 1 L by deionized water to prepare a stock solution with a uranium concentration of 1000 mg/L. The stock solution was added into seawater to prepare uranium-spiked seawater with an initial uranium concentration varied from 1 to 15 mg/L. The colloidal particles (5 mg in dry weight) were added into the uranium-spiked seawater (500 mL) and then oscillated in a shaker at 25 ℃ (if not specified) for a desired period. The residual uranium concentration in uranium-spiked seawater after adsorption was determined to deduce uptake capacity (mg-U/g) according to eq1.

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where C_0 , C_e were the initial and residual concentration (mg/L), respectively, V was solution volume (mL) and m was the mass of the absorbent (mg).

Adsorption in simulated seawater.

Simulated seawater was prepared by dissolving extra salts in seawater. The salts were $UO_2(NO_3)_2 \cdot 6H_2O$, NH_4VO_3, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$, respectively. The concentration of extra metal cations (U, V, Fe, Co, Ni, Cu, Zn) was about 100 times of that in real seawater. Note that uranium concentration was about 330 μg/L in the simulated seawater. Adsorption was performed in the simulated seawater (500 mL) under shaking at 25 ℃ for 48 h. The concentration of extra metal cations before and after adsorption was analyzed by ICP-MS to deduce uptake capacity (eq1) and distribution coefficient (eq2).

$$K_d = \frac{(C_0 - C_e)V}{C_e m} \quad (2)$$

Adsorption in real seawater.

Real seawater was prepared by dissolving baysalt (3.5 kg) in water (100 L), followed by filtration to remove impurities. The uranium concentration in real seawater was about 3.3 μg/L. The colloidal particles were sealed in a nylon mesh and then immersed in 4 L seawater under stirring. The seawater was changed every two days. After a desired period, colloidal particles were taken out for digestion in a mixed solution of nitric acid and hydrogen peroxide. The uranium concentration in the digestion solution was determined by ICP-MS for the calculation of uptake capacity.

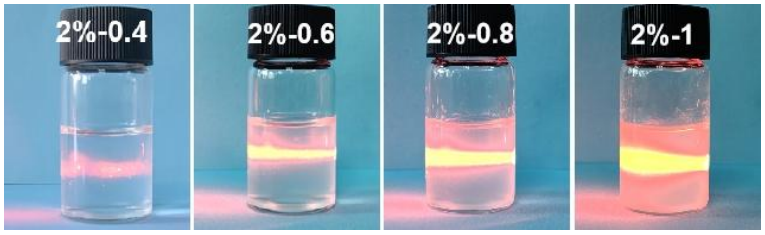

Figure S1 Optical photographs showing strong Tyndall effect of colloidal particles converted in the 2% NaOH aqueous solutions with various NH_2OH/AN molar ratio.

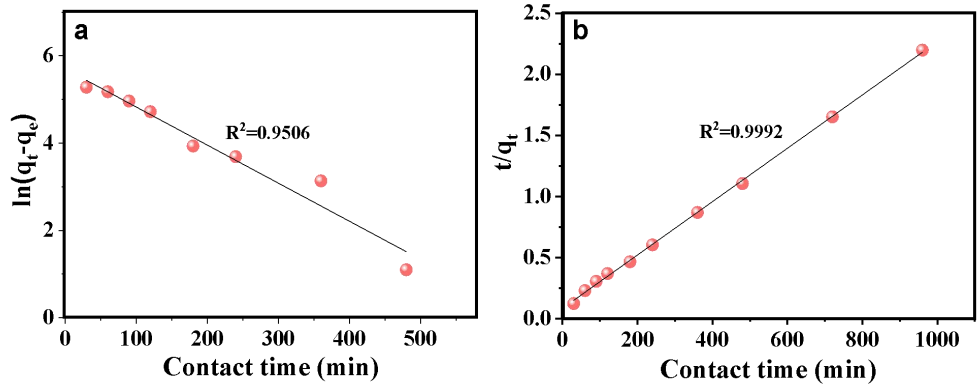

Figure S2 Adsorption kinetics fitted by (a) pseudo-first-order and (b) pseudo-second-order model, respectively.

Pseudo-first-order model.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

Pseudo-second-order model.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (4)$$

where t, q_t and q_e are contact time (min), adsorption capacity (mg-U/g) at a contact time and adsorption capacity (mg-U/g) at equilibrium, respectively. k_1 (1/min) and k_2 (g/mg/min) are the rate constant of pseudo-first-order model and pseudo-second-order model, respectively.

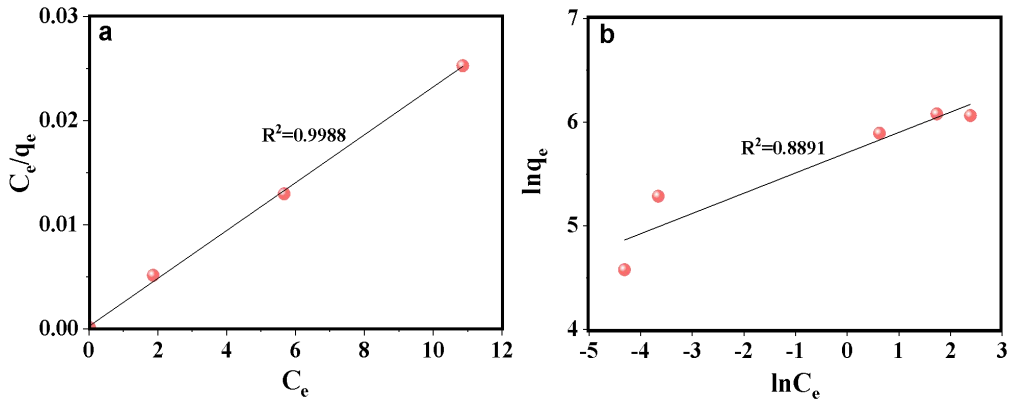

Figure S3 Adsorption isotherm fitted by (a) Langmuir and (b) Freundlich model, respectively.

Langmuir model.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (5)$$

where q_e (mg-U/g) and C_e (mg/L) are adsorption capacity and uranium concentration after equilibrium, respectively. Q_m (mg-U/g) is maximum adsorption capacity and *b* (L/mg) is a constant that is related to adsorption energy.

Freundlich model.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (6)$$

where K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

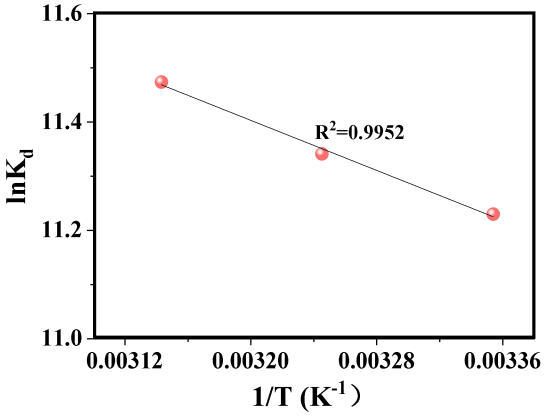

Figure S4 Plot of $\ln K_d$ versus 1/T

Calculation of thermodynamic parameters.

$$\ln K_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (7)$$

where T (K) is temperature and R (8.314 J/mol/K) is gas constant.

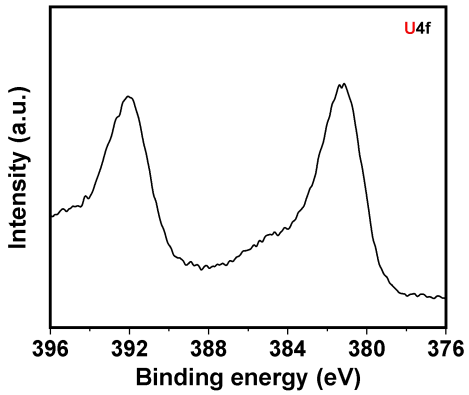

Figure S5 High-resolution XPS U4f spectrum of 2%-1 colloidal particles after adsorption in uranium-spiked seawater.

Table S1 Thermodynamic parameters and Gibbs free energy deduced from temperature-dependent uranium uptake.

ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})	ΔG (kJ·mol^{-1})		
33.88	207	298.15K	308.15K	318.15K
		-27.84	-29.91	-31.98

Calculation of Gibbs free energy (ΔG).

$$\Delta G = \Delta H^o - T\Delta S^o \qquad (8)$$