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Supporting Information

Speeding up the selective extraction of uranium through in-situ formed nano-pockets

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Contents

Experimental section

Preparation of ECP gels

To begin with, DAB (3 mmol, 642.36 mg) was dissolved in 10 mL DMSO, HCCP (2 mmol, 695.32 mg) was dissolved in 5 mL DMSO, and then the solvent containing DAB was slowly added dropwise to HCCP, stirred magnetically for 30 minutes under the protection of nitrogen gas at room temperature, and then heated at 125°Cfor 30 minutes. After the reaction was completed, the gel was cooled to room temperature, washed three times with ether and methanol, and then freeze-dried for 48 h to obtain electron-rich ECP gels.

Experimental section

Equilibrium adsorption test.

Uranium sorption experiments were carried out using a stock solution (The concentration of all uranium solutions involved in this experiment was calculated in terms of the U element). The samples were collected and filtered immediately through a 0.22 μm filter. Then the solutions were diluted to the suitable concentration and measured by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), the following adsorption experiments were conducted at pH 6.0 in this work. And all the adsorption examinations were carried out in duplicate. The amount of uranium uptake by ECP gels were calculated using the Equation as follows.

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

where V is the volume solution of uranium (L); m is the mass of adsorbent (g); C_0 and C_e are the initial and equilibrium concentrations of uranium (mg L^{-1}) respectively.

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

where K_d is a thermodynamic equilibrium constant.

The linear forms of Langmuir, Freundlich isotherm models were adopted for the adsorption isotherm studies.

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \quad (3)$$

$$Inq_e = InK_F + \frac{1}{n} InC_e \quad (4)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations, q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_m is the maximum monolayer coverage capacity, K_L (L mg^{-1}) is the Langmuir constant that describes the affinity between the adsorbate and adsorbent, K_F ((mg g^{-1}) / (mg $L^{-1})^{1/n}$) and 1/n are Freundlich constants associated with adsorption capacity and adsorption intensity (heterogeneity factor), respectively.

pH value effect:

The experimental conditions of pH value influence were the same as above, particularly, pH value ranging from 3 to 9. 0.1 M HCl and 0.1 M NaOH solutions were used to adjust the pH value of the uranium solution.

Competitive adsorption:

To determine the competitiveness of the ECP gels to marine metal ions, 10 metal ions, including UO_2^{2+}, VO^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Cd^{2+} and Mn^{2+}, were added into natural seawater to the concentration of 100 times of these metal ions in natural seawater[[1]]. The other main ions, including Na^+, Mg^{2+}, Ca^{2+}, and K^+, were maintained at their original concentrations in natural seawater. Subsequently, ECP gels were added to 1L of the above-prepared solution. After oscillating adsorption at 25 ℃ for 24 hours, the concentration of each metal in the solution was determined by ICP-MS.

Selective adsorption:

To accurately compare the selection of the other metal ions against uranium, 50 mL 10 mg L^{-1} uranyl ions in deionized water mixed with different competing metal ions (10 mg L^{-1}). For each test, ECP gels were added to the solution and the adsorption capacity to uranium was determined by ICP-OES after being adsorbed for 1 h at 25 °C with moderate shaking (Table S6). The adsorption selectivity was calculated using:

$$Selectivity = \frac{U_{EHP}}{U_{aq}} / \frac{M_{EHP}}{M_{aq}} \quad (5)$$

where U_{ECP} (mg g^{-1}) is the concentration of uranium in adsorbent at equilibrium, and U_{aq} (mg g^{-1}) is the concentration of uranium in ion-spiked deionized water at equilibrium. M_{ECP} (mg g^{-1}) is the concentration of metals in adsorbent at equilibrium and M_{aq} (mg g^{-1}) is the concentration of metals in ion-spiked deionized water at equilibrium.

Desorption and regeneration studies:

The desorption experiment was implemented by immersing adsorbents in 0.5 M HNO_3. Specifically, 0.1 g L^{-1} adsorbent was added to 16 mg L^{-1} uranium solution at 25℃ to prepare uranium adsorbent material. The regenerated sample was washed with deionized water (DI) to remove the remaining 0.5 M HNO_3 solution until pH=7, and used adsorbents were collected by filtration and evaporation, then reused in next cycle.

Computation methods:

All simulations were calculated by the first principles to perfom alldensity functional theory (DFT) within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) fomulation in the CASTEP code.[2] All the geometry opptimizations were perfomed by the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The kinetic cut-off energy of the plane wave basis set with 550 eV and the 1 × 1 × 1 Monkhorst-Pack k-point sampling for a structure.[3] The convergence criteria for the total energy and forces were set as 10^{-5} eV and 0.01 eV $Å^{-1}$. The vacuum spacing in a direction perpendicular to the plane of the structure is 20 Å.

Supporting Figures

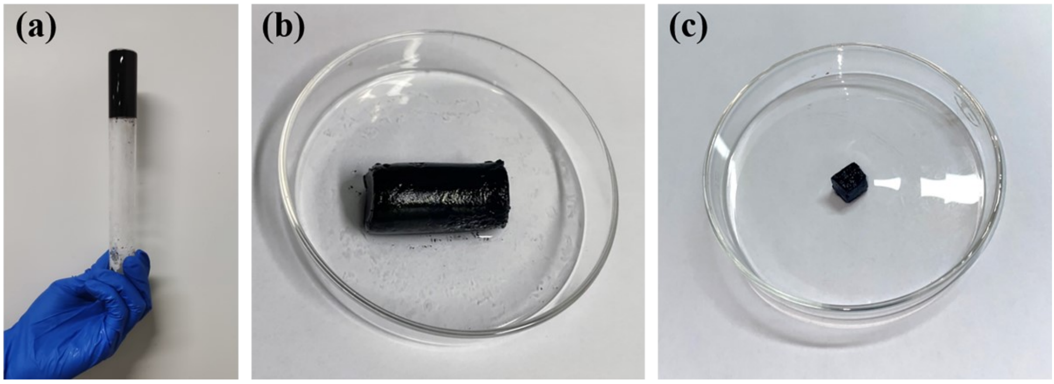

Figure S1. Photographs of ECP material. **(a)** The reaction flask (upside down) after the experiment showing the formation of a monolithic ECP gels; **(b)** The monolithic gels transferred to a petri dish; **(c)** Monolith after solvent washing.

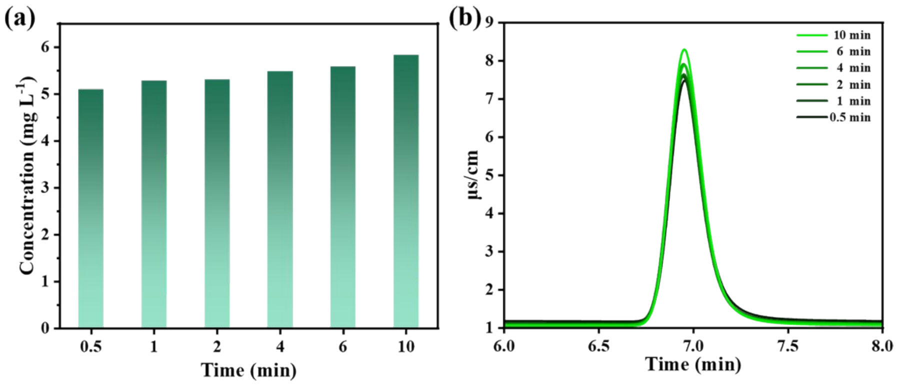

Figure S2. **(a)** 5 mg ECP gels were immersed in 100 mL of deionized water, and the chloride ion concentration in deionized water was measured by ion chromatography with time. **(b)** Different conductivity in deionized water under different soaking time conditions.

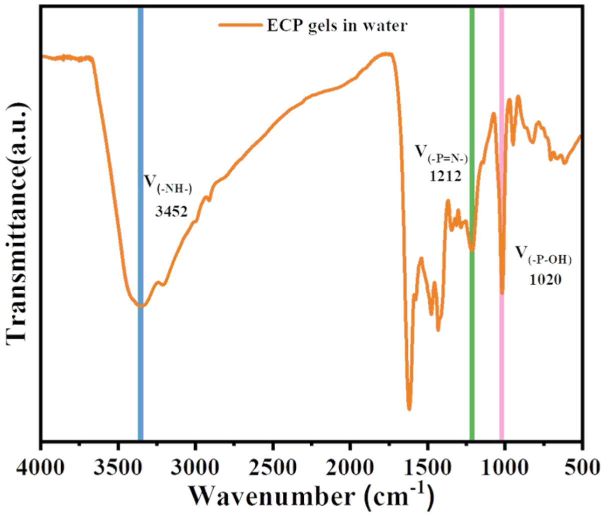

Figure S3. FT-IR spectra of ECP gels after in-situ water activated.

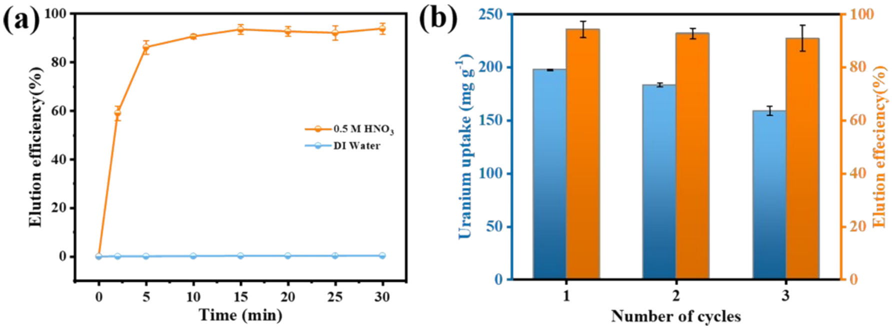

Figure S4. The uranium adsorption capacities and recovery rate of elution in three adsorption–desorption. **(a)** Elution efficiency of uranium loaded ECP gels in HNO_3 (0.5 M) eluent; elution in deionized water was performed as control. **(b)** Recyclability test.

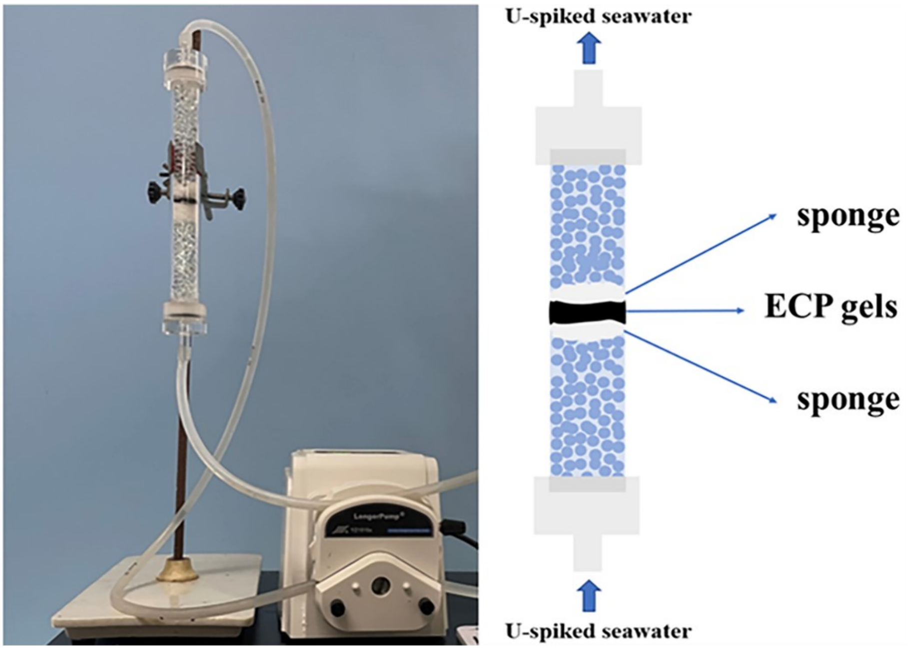

Figure S5. Installation of uranyl adsorption equipment from U-spiked seawater and seawater.

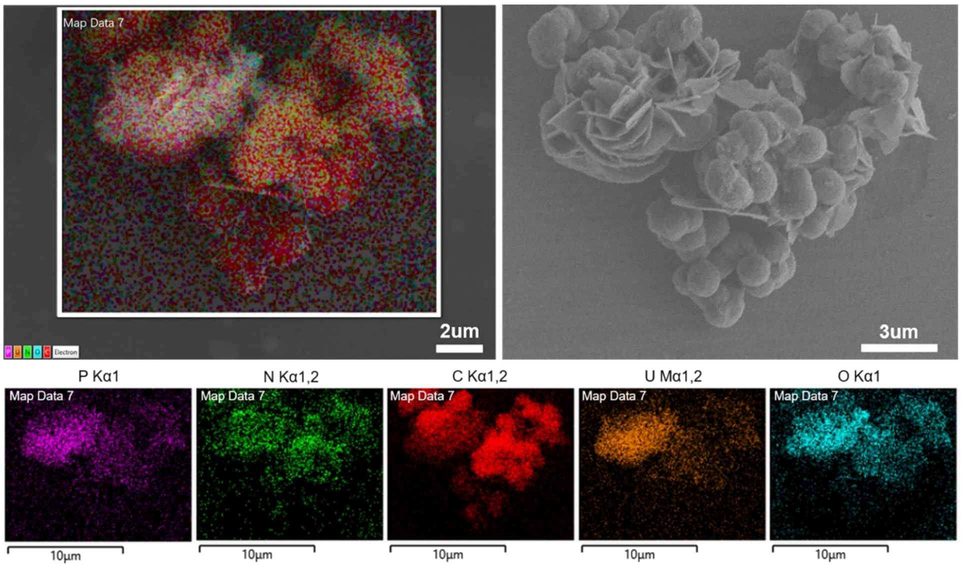

Figure S6. EDS elemental mapping of P, N, C, U, O for the surface of ECP-U.

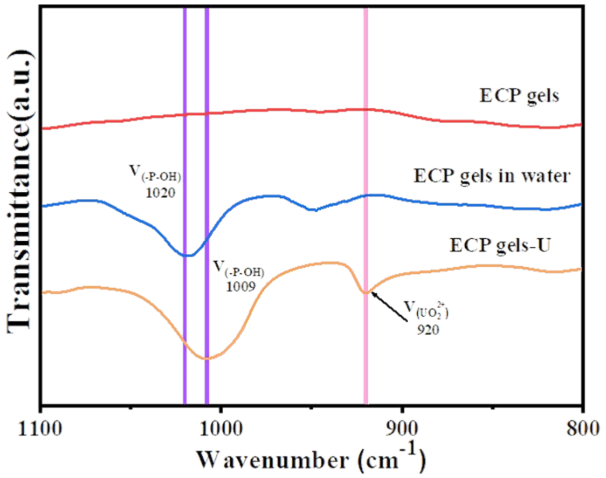

Figure S7. The FT-IR spectra of ECP gels and ECP gels-U in the 700 -1700 cm^{-1} range.

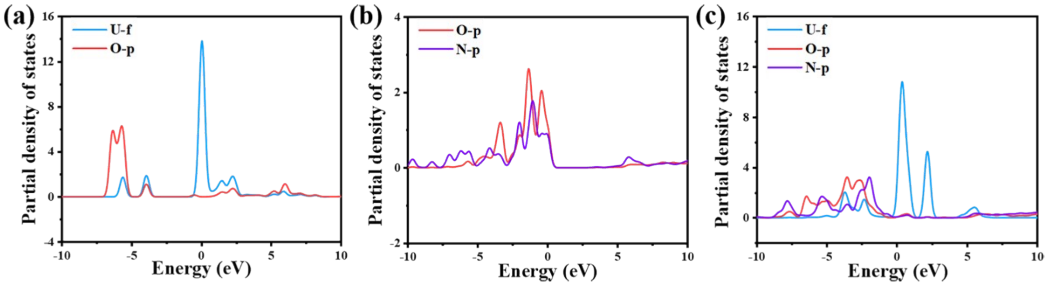

Figure S8. The partial density of states in (**a**) uranium, (**b**) ECP gels and (**c**) ECP gels-U.

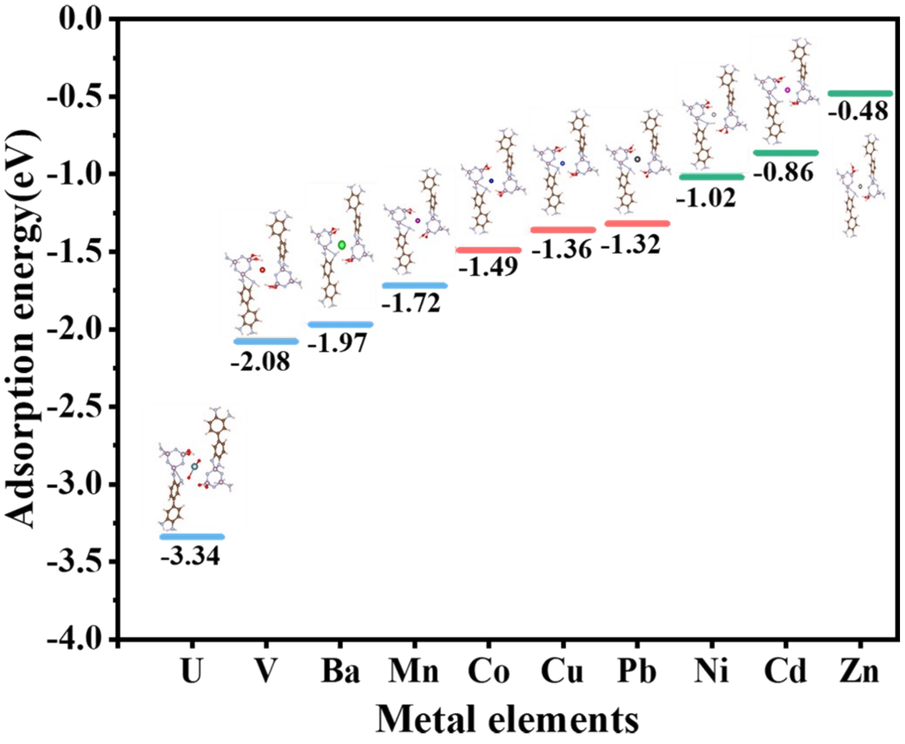

Figure S9. Plots of adsorption energy of ECP gels captured UO_2^{2+} and other metal ions.

Supporting Tables

Table S1. Comparison of adsorption capacity of some recently reported adsorbents for uranium adsorption in aqueous medium.

S.N.	Adsorbent	Equilibrium time (min)	C_0 (mg L^{-1})	pH	Q_e (reach equilibrium) (mg g^{-1})	V_{ads} (mg g^{-1} min-^{1})	reference
1	IRMOFs-1-OH	20	100	2.5	70	3.50	[4]
2	UIO-66-2COOH	100	100	4	150	1.50	[5]
3	PHCP-2	5	60	7	252	50.40	[6]
4	**EHP**	**2**	**32**	**6**	**406.02**	**203.01**	**Present study**
5	NPS-GLCs	50	20	5	294	5.88	[7]
6	PAF-1-$NH(CH_2)_2AO$	10	1	6	385	38.50	[8]
7	COF-TpDb-AO	10	9.25	6	394	39.40	[9]
8	NENP-1	60	500	7	489	8.15	[10]
9	GDC	100	50	6	642	6.43	[11]
10	h-$MnPO_4$	60	100	4	751	12.52	[12]

Table S2. The thermodynamic parameters for adsorption of U(VI) onto ECP gels.

T(k)	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (L g^{-1})	n	R^2
298.15	970.22	0.006	0.998	1065.86	0.08	0.997
308.15	1175.19	0.007	0.999	1182.91	0.10	0.982
318.15	1247.62	0.006	0.999	1331.60	0.09	0.997

Table S3. Concentrations of uranium and co-existing metals in 100 times concentrated seawater.

Element	Con.in nature sea water/ppb	Con.in 100 × natural sea water/ppb	Ions
U	3.32	332	$UO_2(CO_3)_3^{4-}$
			$UO_2(CO_3)_2^{2-}$
V	1.37	137	VO^{3-}
			$VO_2(OH)_3^{2-}$
Ba	2.71	271	Ba^{2+}
Ni	0.64	64	Ni^{2+}
Cd	0.13	13	Cd^{2+}
Co	0.055	5.5	Co^{2+}
Pb	0.121	12.1	Pb^{2+}
Zn	4.06	406	Zn^{2+}
Cu	2.6	260	Cu^{2+}
Mn	1.52	152	Mn^{2+}

Table S4. Concentration of metal ions used in determining the competition with uranyl.

	U Con. After adsorption/ppm		M Con. After adsorption/ppm		R_U	R_M	Selectivity
U-V	3.107	3.025	4.887	4.562	22.615	11.166	2.03
U-Ba	0.304	0.290	8.226	7.875	326.700	2.421	134.91
U-Ni	0.344	0.265	9.969	9.955	317.861	0.037	8426.79
U-Cd	0.090	0.093	9.922	9.903	1078.230	0.088	12249.92
U-Co	0.303	0.333	9.959	9.838	304.135	0.101	2989.25
U-Pb	0.090	0.093	9.823	9.903	1078.230	0.138	7786.85
U-Zn	0.020	0.006	9.863	9.953	7467.874	0.092	80928.08
U-Cu	0.080	0.030	9.689	9.654	1795.316	0.339	5292.86
U-Mn	0.226	0.273	9.314	9.368	389.504	0.704	552.64

Table S5. Fitting results for EXAFS analysis of uranium bound by ECP gels.

path	N	σ^2 (Å^2)	R (Å)	ΔE_0(eV)	R-factor
U-O	2.1±0.4	0.0025±0.005	1.79±0.03	8.62	0.0154
U-O	1.8±0.2	0.0234±0.037	2.36±0.30		
U-N	2.0±1.2	0.0080±0.007	2.47±0.05		

Supporting Reference

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