

*Electronic Supplementary Information for*

**Graphene Oxide Based Dopamine Mussel-like Cross-linked Polyethylene Imine  
Nanocomposite Coating with Enhanced Hexavalent Uranium Adsorption**

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### SI.1 Kinetics and isotherms study

**Table S1.** Different DA/PEI mass ratios and the corresponding adsorption capacity (pH=5, Co=200 mg g<sup>-1</sup>).

Dopamine/PEI mass ratios	Adsorption Capacity (mg g <sup>-1</sup> )
2:0	318.5
2:1	361.2
2:2	398.8
1:2	376.6
0:2	325.6

In the study of adsorption kinetics, the pseudo-first-order, pseudo-second-order and Weber-Morris (W-M) models were employed to interpret the mechanism controlling the sorption process. The linear form of the three models can be expressed by the following Eqs. S1-S3:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{S1})$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (\text{S2})$$

$$q_e = K_{ip} \sqrt{t} + C \quad (\text{S3})$$

where  $q_t$  and  $q_e$  (mg g<sup>-1</sup>) are the capacity of U(VI) at time  $t$  (min) and at equilibrium,  $K_{ip}$  is the internal diffusion constant, respectively, and  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are the respective rate constants,  $C$  is a constant of material boundary layer (mg g<sup>-1</sup>) and  $t$  (h) is the reaction time.

**Table S2** Kinetic parameter for adsorption of U (VI)

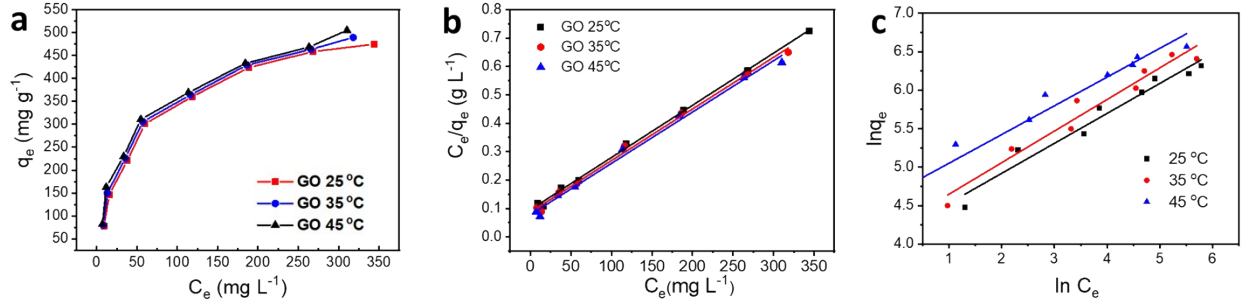
Kinetics model	U(VI) initial concentration	Materials	$K$	$q_e^{\text{exp}}$	$q_e^{\text{cal}}$	$R^2$
Pseudo-first order	210 mg g <sup>-1</sup>	GO	0.0256	279	85	0.71044
		GO-pDA	0.019	314	39.37	0.82778
		GO-pDA-PEI	0.027	416	59.97	0.67724
Pseudo-second order	210 mg g <sup>-1</sup>	GO	2.7x10 <sup>6</sup>	279	317	0.99917
		GO-pDA	0.0015	314	335.6	0.99989
		GO-pDA-PEI	0.0018	416	421.9	0.99982

**Table S3.** Morris-Weber model parameter for adsorption of U (VI)

Materials	$K^1_{ip}$	$K^2_{ip}$	$C^1$	$C^2$
GO	73.4	2.08	22.8	270.9
GO-pDA	12.2	1.94	252.4	304.05
GO-pDA-PEI	41.3	0.14	194.48	410.25

**Table S4** Isotherm parameter of GO, GO-pDA and GO-pDA-PEI for U(VI) adsorption

Materials	$T$ (K)	Langmuir isotherm			Freundlich isotherm		
		$q_o$ (mg g <sup>-1</sup> )	$b$ (L mg <sup>-1</sup> )	$R^2$	$K$ (L mg <sup>-1</sup> )	$n$	$R^2$
GO	298	534	0.1823	0.99887	36.23	0.36	0.92893
	308	549	0.2769	0.99839	40.86	0.41	0.93282
	318	552	0.3635	0.99271	47.20	0.47	0.92684
GO-pDA	298	717	1.37	0.98551	198.1	0.23	0.72233
	308	680.8	1.39	0.98027	157.3	0.28	0.90795
	318	606.8	1.40	0.97625	127.9	0.31	0.82320
GO-pDA-PEI	298	734.0	1.39	0.990	203.53	0.23	0.62621
	308	707.4	1.38	0.982	82.88	0.39	0.85613
	318	677.8	1.48	0.976	64.07	0.41	0.84625



**Fig. S1.** Isotherm model a), Langmuir model b) and c) Freundlich model for GO.

In order to probe the maximum adsorption capacity and the progress of adsorption, the adsorption isotherms were studied. The adsorption of U (VI) on the GO-pDA and GO-pDA-PEI composites increased with increasing the temperature and the Langmuir and Freundlich models were applied to simulate the experimental data.

$$C_e/q_e = 1/b \cdot q_m + C_e/q_m \quad (S4)$$

$$\ln q_e = \ln k + 1/n \ln C_e \quad (S5)$$

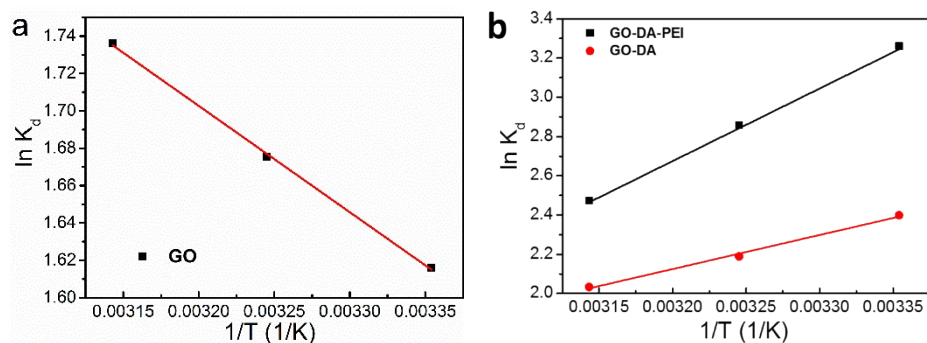
where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrated U (VI) concentration,  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of U (VI) adsorbed on the adsorbents capacity at equilibrium.  $K$  ( $\text{L mg}^{-1}$ ) is a Langmuir constant related to the energy of the adsorbent and  $q_m$  ( $\text{mg g}^{-1}$ ) is the saturation capacity at complete monolayer coverage.

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (S6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (S7)$$

$$K_d = \frac{q_e}{C_e} = \frac{(C_o - C_e)}{C_e} \cdot \frac{V}{m} \quad (S8)$$

Where  $K_d$  ( $\text{mL g}^{-1}$ ) is the distribution coefficient of U(VI),  $T$  (K) is the Kelvin temperature and  $R=8.314$   $\text{J mol}^{-1} \text{K}^{-1}$ .



**Fig. S2.** The influence of temperature on the U(VI) sorption on the a) GO and b) GO-pDA and GO-pDA-PEI relationship curve between  $\ln K_d$  and  $1/T$  (1/K).

**Table S5.** The thermodynamic parameters of GO, GO-pDA and GO-pDA-PEI for U(VI) adsorption

material	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )		
			298.15K	308.15K	318.15K
GO	21.13	29.29	-8.71	-9.04	-9.29
GO-pDA	-14.42	-28.43	-5.94	-5.66	-5.38
GO-pDA-PEI	-30.75	-76.15	-8.05	-7.28	-6.52

## SI.2 Adsorption-desorption experiments of GO-pDA-PEI adsorbents

### SI.2.1 U(VI) desorption experiments

The recyclability and reuse of adsorbents play an important role in the extraction of U(VI) from seawater. The eluent agents of NaCl, citric acid, HCl, NaHCO<sub>3</sub>, and NaOH were first investigated for desorption of U(VI). The results from Table S6 demonstrate that citric acid is the best eluent agent for reuse and recyclability of GO-pDA adsorbents. In the typical experiment, 20 mg adsorbent with U(VI) ions was added into 50 mL eluent solution, which included 0.1 M NaCl, 0.1 M citric acid, 0.1 M HNO<sub>3</sub>, 0.1 M NaHCO<sub>3</sub> and 0.1 M NaCl, respectively. The flasks were stirred for a specified time at room temperature, and then the solid phase was separated from the solution by centrifuge. The results were analysed with IRIS Intrepid II XPS instrument to obtain the concentrations of U (VI) ions. The elution rate of U (VI) ions was calculated.

**Table S6.** The elution efficiency of different eluents

Eluent	elution efficiency (%)	elution efficiency (%)
	GO-pDA	GO-pDA-PEI
0.1 M Citric acid	33.5	43.5
0.1M NaOH	58.5	65.6
0.1 M HNO <sub>3</sub>	48.8	51.3
0.1 M NaCl	75.3	80.5
0.1 M NaHCO <sub>3</sub>	49.2	55.2

In regard to the above findings, we examined the effects of different concentrations of citric acid for adsorption-desorption of U(VI) onto GO-pDA-PEI. The results, given in Table S7, indicate that the change in eluent rate responds smoothly to increasing the concentration of NaCl, especially when the NaCl concentrations are above 0.8 M. Taking into account these factors and cost issues, 0.8 M NaCl was used for the next step, which was the regeneration of GO-pDA-PEI adsorbents for U(VI).

**Table S7** The elution efficiency of different concentrations of citric acid

Eluent (NaCl)	elution efficiency (%)	elution efficiency (%)
	GO-pDA	GO-pDA-PEI
0.04 M	53.5	67.2
0.1 M	75.3	80.5
0.4 M	81.2	88.4
0.8 M	86.7	91.6
1 M	88.2	92.1

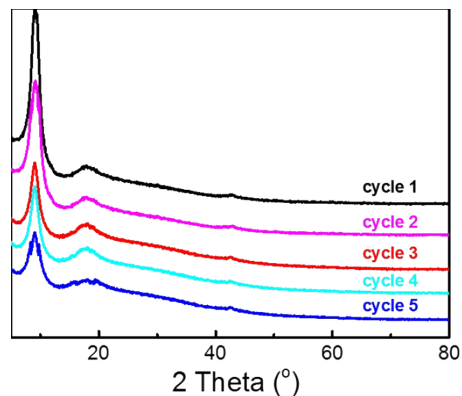


Fig. S3. The XRD of GO-pDA-PEI composites after 5 cycles.

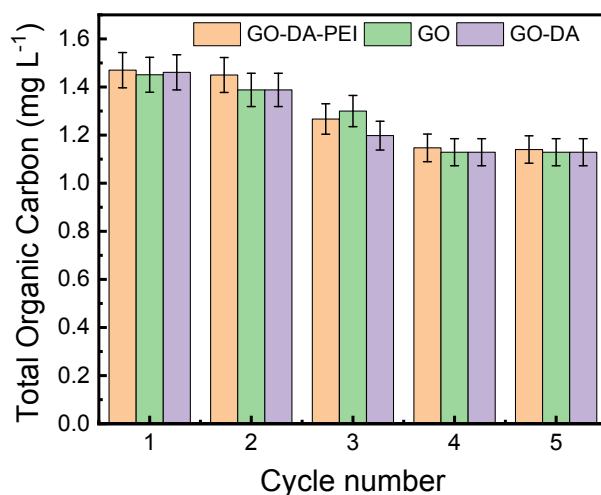


Fig. S4. Total Organic Carbon in the solution after each adsorption cycle. The initial adsorption dose was 100 mg L<sup>-1</sup>.

### SI.2.2 U (VI) absorption-desorption cycle experiments

In a typical experiment, 20 mg sorbent was added into 50 mL U (VI) solution and stirred for 6 h at room temperature. The solid phase was separated from the solution by centrifuge. Then, the adsorbent was dried in a vacuum drying oven for 24 h. The dried adsorbent was placed in 50 mL eluent solution (0.8 M NaCl) for 6 h. After elution, the GO-pDA-PEI composites were washed with abundant deionized water to remove residual H<sup>+</sup> and UO<sub>2</sub><sup>2+</sup> until UO<sub>2</sub><sup>2+</sup> cannot be detected in the aqueous solutions. The GO-pDA-PEI composites were regenerated by drying at 80 °C for 24 h and then reused. Eventually, the elution efficiency of U (VI) ions was calculated. This experiment operation was repeated for five times.

### SI. 3 Co-existing ions and simulating seawater experiments

#### SI. 3.1 Effects of co-existing ions

The selectivity coefficient ( $S_U$ ) for U(VI) is defined as a specific term to describe the potency and degree of selectivity of the adsorbents as follows:

$$S_U = \frac{K_d^U}{K_d^M} \quad (\text{S9})$$

where  $K_d^U$  and  $K_d^M$  are the distribution ratio of the U(VI) ion and other competing ions in sorbent and solution from equation S6, respectively.

**Table S8.** The selectivity coefficients ( $S_{U/M}$ ) of U(VI) for different metal ions in water.

Material	Cu	Ba	Ni	Mg	Ca
GO $S_{U/M}$	24.2	159.1	114.3	11.86	130.3
GO-pDA $S_{U/M}$	27.5	32.8	321.1	129.4	223.6
GO-pDA-PEI $S_{U/M}$	246.6	184.6	36719.6	39979.1	25572.2

#### SI.3.2 Effect of simulating seawater solution

##### Preparation of simulating seawater solution

33 g sea salt were added to 1000 mL deionized water which was fully dissolved by ultrasound. The obtained sea salt solution was used as a solvent. Uranium solution was added to prepare the simulated seawater of different uranium concentrations ( $3.35 \mu\text{g L}^{-1}$ ,  $5.86 \mu\text{g L}^{-1}$ ,  $9.52 \mu\text{g L}^{-1}$ ,  $16.8 \mu\text{g L}^{-1}$ ,  $50.5 \mu\text{g L}^{-1}$  and  $98.1 \mu\text{g L}^{-1}$ ).

The sorption procedure was as follows: GO-pDA-PEI was added into the simulated seawater of different concentrations ( $3.35\text{-}98.1 \text{ ppb}$ ) and the solid/liquid ratio was  $0.5 \text{ mg mL}^{-1}$ , which was shaken for 24 h to reach the absorption equilibrium at  $25 \text{ }^\circ\text{C}$ .

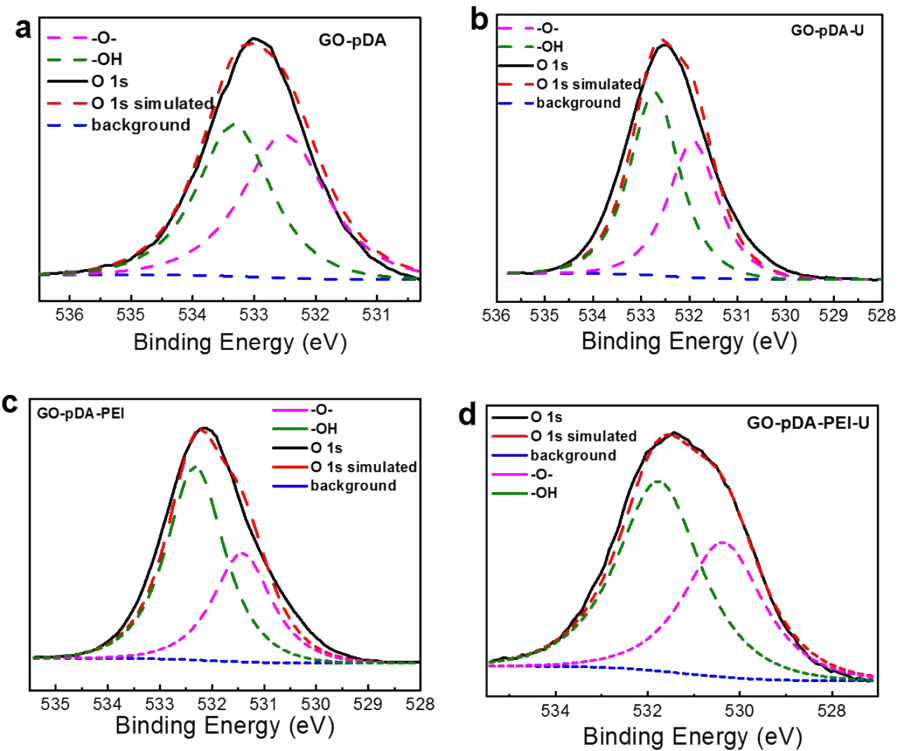


**Table S9** pH value of different U(VI) initial concentrations in simulated seawater.

Concentration of U(VI) ( $\mu\text{g L}^{-1}$ )	3.35	5.86	9.52	16.8	50.5	98.1
pH	8.26	8.27	8.28	8.28	8.29	8.29

**Table S10.** The concentrations of partially competitive ions in simulated seawater. V=20 mL, T=298 K, m=0.01 g.

$C_o$ ( $\mu\text{g L}^{-1}$ )			$C_o$ ( $\text{mg L}^{-1}$ )	
Ba	Cu	Ni	Mg	Ca
86.12	35.3	11.8	193.1	62.21



**Fig. S5.** O 1s spectra of (a) GO-pDA, (b) GO-pDA-U, (c) GO-pDA-PEI, (d) GO-pDA-PEI-U.

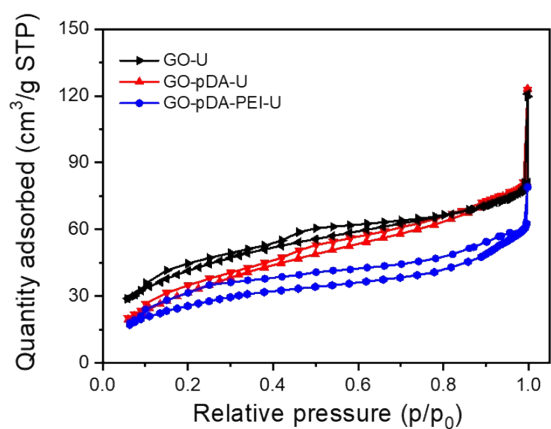


Fig. S6. N<sub>2</sub> adsorption-desorption isotherms of GO, GO-pDA and GO-pDA-PEI composites after adsorption.

Table S11. Surface area of GO, GO-pDA and GO-pDA-PEI before and after adsorption U(VI).

Samples	S <sub>BET</sub> (m <sup>2</sup> /g)	
	before	after
GO	963.53	803.55
GO-pDA	768.83	629.01
GO-pDA-PEI	598.92	508.19