

Bovine serum albumin-coated graphene oxide (GO) for effective adsorption of uranium (VI) from aqueous solutions

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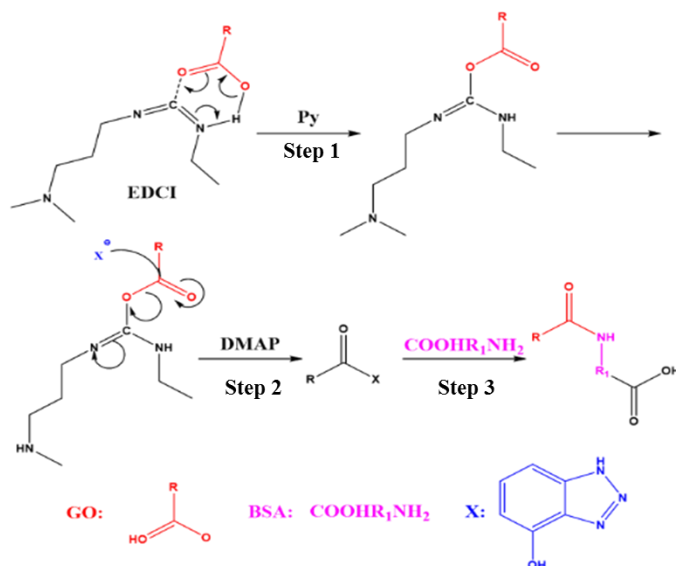
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SI.1 Characterization

The structure of the material was measured by a transmission electron microscope (TEM) from FEI Tecnai G2 S-Twin, SEM and FTIR from the SP100. X-ray diffraction analyzer (XRD) was performed on a Rigaku D-max-IIIB diffractometer with CuK α irradiation ($K\alpha = 1.54178 \text{ \AA}$). The BSA-GO composites were calculated using the Bruker of atomic force microscopy (AFM). The adsorption experiment measurement was carried out with WGJ-III Trace Uranium Analyzer. XPS analyzer was conducted using an AXIS ULTRA DLD spectrometer from Japan, which

include in a monochromatized Al K α X-ray source (1486.6 eV photons) at a constant residence time (250 ms) and a pass energy (40 eV).

SI.2 The synthesis lines and mechanism of the GO-BSA composites



Scheme S1. The proposed mechanism of the GO-BSA composites

SI.3 Adsorption studies on GO-BSA composites.

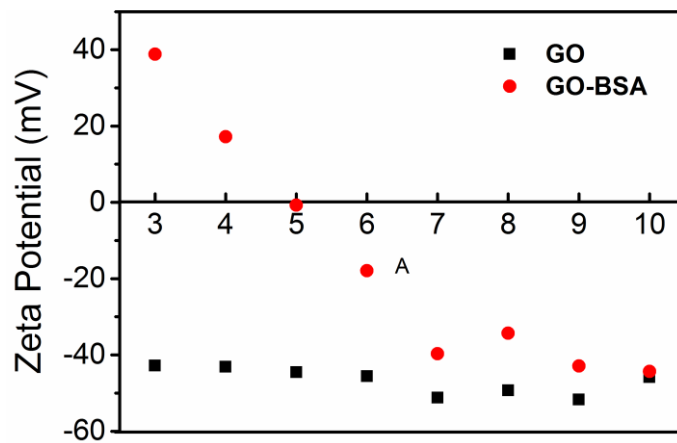


Fig. S1 ζ -potential of GO and GO-BSA at different pH values

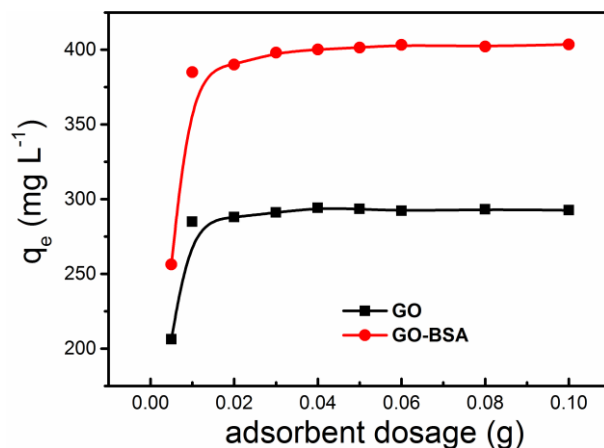


Fig. S2 Effect of adsorbent dosage on adsorption capacities of GO and GO-BSA, pH = 6.00; T = 25 °C; V = 20 mL.

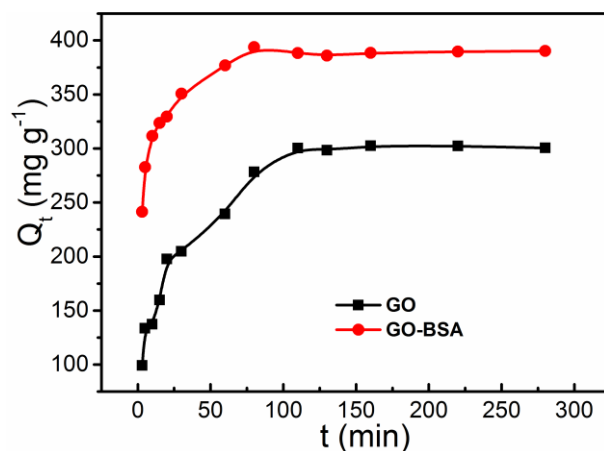


Fig. S3 Effect of contact time of U(VI) adsorption on GO and GO-BSA composites, pH= 6.0; T = 25 °C; amount of adsorbent 0.01 g and $C_0 = 200 \text{ mg L}^{-1}$.

SI.4 Adsorption kinetics and adsorption isotherms on GO-BSA composites

In order to get more information about sorption process, the pseudo-first-order kinetic model, pseudo-second-order kinetic and Weber-Morris (W-M) model were studied¹. The following equation holds true in the pseudo-first-order kinetic model

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (\text{S1})$$

Where k_1 is the rate constant of pseudo-first-order adsorption, Q_e and Q_t (mg g^{-1}) are the amount of U(VI) adsorbed capacity at equilibrium and at time (t), respectively.

The pseudo-second order kinetic model is shown as the following:

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

Where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is a constant of pseudo-second-order adsorption, Q_t (mg g^{-1}) is the amount of U(VI) ions the amount of U(VI) adsorbed capacity at time t (h), Q_e (mg g^{-1}) is the sorption amount at equilibrium and t (h) is the reaction time.

The Weber-Morris (W-M) models is shown as the following:

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

Where k_{ip} is a constant of Intramolecular diffusion, Q_e (mg g^{-1}) is the amount of U(VI) ions at equilibrium and t (h) is the reaction time., C is a constant of material boundary layer (mg g^{-1}) and t (h) is the reaction time.

Table S1 Kinetic parameter for adsorption of U(VI), pH= 6.0; T = 25 °C

Materials	Pseudo-second order kinetics model			Pseudo-first order kinetics model			
	$Q_{e,\text{exp}}$	R^2	k_2	$Q_{e2,\text{cal}}$	k_1	$Q_{e1,\text{cal}}$	R^2
GO-BSA	391	0.9998	6.08×10^7	393.15	0.016	71.70	0.7881
GO	301	0.9975	2.79×10^6	317.50	0.023	2.71	0.8063

Meanwhile, in order to get more information about sorption progress, the Langmuir and Freundlich equations model were studied¹. The Langmuir equation is supposed that the surface

and bulk phases of homogeneous sorbents delete it has been extensively used to describe the monolayer sorption process, which is expressed as follows:

$$C_e/Q_e = 1/b \cdot Q_m + C_e/Q_m \quad (S4)$$

Where C_e (mg g^{-1}) is the solute equilibrium concentration, Q_e (mg g^{-1}) is the amount of solution adsorbed per unit mass of the adsorbent, Q_m is the maximum adsorption capacity (mg g^{-1}), b is Langmuir constant. According to Eq. (S4), fitting a straight line is obtained and presented in Fig. 5. The values of Q_m and b were calculated from the slope and the intercept, and were given in Table S2.

The Freundlich equation has been used for heterogeneous surfaces and multilayer adsorption. It is expressed as follows³:

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

Where k (L g^{-1}) is the Freundlich sorption coefficient, $1/n$ is an indicator of isotherm nonlinearity corresponding to the sorption intensity at a particular temperature. The linear dependency of the Freundlich model of U(VI) sorption is shown in Fig. 5. They are determined from the intercept and slope of the linear plot of $\ln Q_e$ vs. $\ln C_e$.

The Temkin equation has been used for the interaction between the adsorbent and the adsorbate. It is expressed as follows:

$$Q_e = A \ln K_T + A \ln C_e \quad (S6)$$

Where k (L g^{-1}) is the Temkin coefficient, A is the maximum binding energy of the equilibrium binding constant. C_e (mg g^{-1}) is the solute equilibrium concentration, Q_e (mg g^{-1}) is the amount of solution adsorbed per unit mass of the adsorbent. The linear dependency of the Temkin model of

U(VI) sorption is shown in Fig. S4. They are determined from the intercept and slope of the linear plot of Q_e vs. $\ln C_e$. According to the R^2 value, the Temkin Model was applicable to the experimental data of GO, not appropriate to the GO-BSA composites.

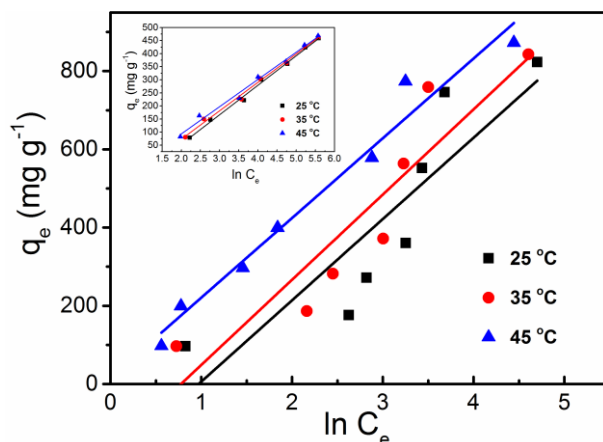


Fig. S4 Temkin model for the removal of U(VI) on GO (inset) and GO-BSA composites, pH= 6.00; T= 25 °C; amount of adsorbent 0.01 g; C_o = 200 mg L⁻¹ and t= 80 min.

Table S2. Isotherm Models and values of R^2 for GO and GO-BSA composites

Materials	T(K)	Langmuir isotherm			Freundlich isotherm		
		Q_m (mg·g ⁻¹)	b (L·mg ⁻¹)	R^2	K (L·g ⁻¹)	n	R^2
GO-BSA	298.15	389	2.46	0.9979	51.52	1.606	0.9099
	308.15	398	2.65	0.9986	61.29	1.611	0.8428
	318.15	419	2.78	0.9997	119.34	1.933	0.8644
GO	298.15	301	3.28	0.9960	33.12	2.021	0.9327
	308.15	306	3.68	0.9949	38.48	2.131	0.9284
	318.15	311	4.13	0.9936	45.33	2.269	0.9166

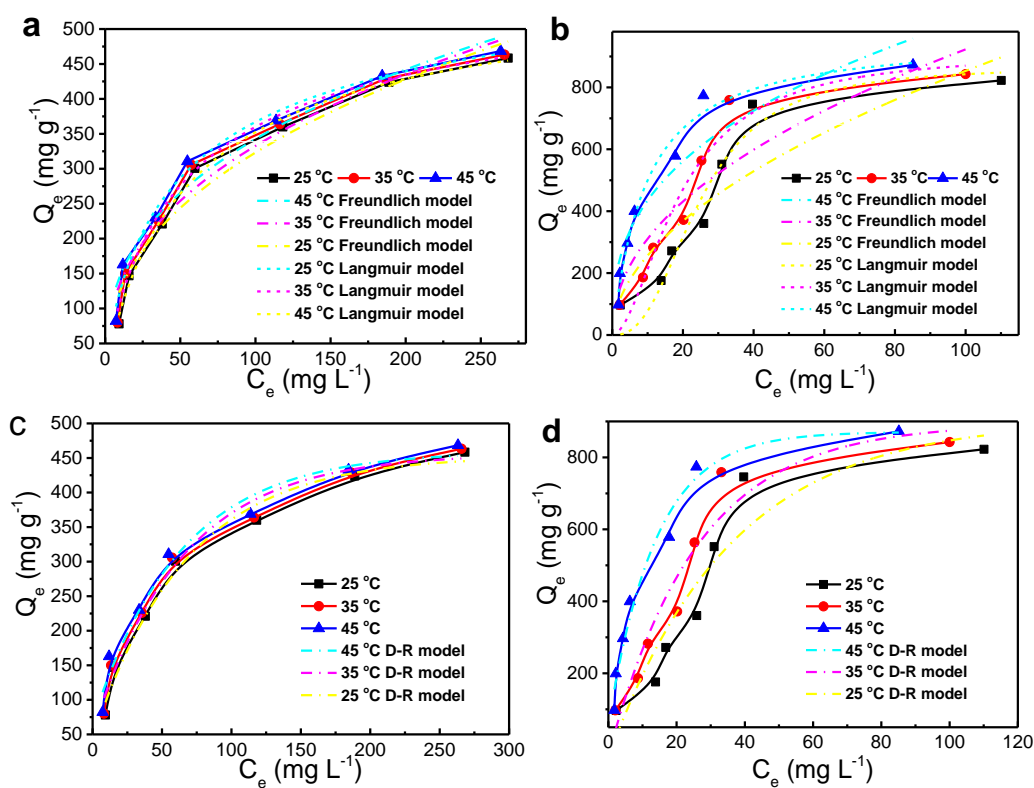
Materials	T(K)	Tempkin Model		
		K_T	A	R^2
GO-BSA	298.15	1.04	2.03	0.7282
	308.15	1.06	2.07	0.8226
	318.15	1.09	2.17	0.9668
GO	298.15	2.19	1.12	0.9946
	308.15	3.06	1.14	0.9932
	318.15	3.79	1.15	0.9889

For the comparison of the linear isotherm data with non-linear isotherm, this non-linear isotherm was fitted and shown in the Fig. S5 and Table S3. From the Fig. S5, we can observed that the GO and GO-BSA were appropriate to the Langmuir model rather than the Freundlich model and Temkin model. Meanwhile, we also calculated the parameters, the results are shown in the table S3

Table S3. Isotherm Models and values of R^2 for GO and GO-BSA composites

Materials	T(K)	Langmuir isotherm			Freundlich isotherm		
		Q_m	b	R^2	K	n	R^2
		($\text{mg}\cdot\text{g}^{-1}$)	($\text{L}\cdot\text{mg}^{-1}$)		($\text{L}\cdot\text{g}^{-1}$)		
GO-BSA	298.15	566	2.75	0.9745	77	1.823	0.8719
	308.15	614	2.95	0.9756	104	2.015	0.8104
	318.15	662	3.27	0.9809	186	2.612	0.7816
GO	298.15	470	3.68	0.9919	49.87	0.037	0.9584
	308.15	488	3.88	0.998	55.68	0.388	0.9586
	318.15	515	4.06	0.9908	63.08	0.406	0.9572

Materials	T(K)	D-R model		Temkin model		
		Q_m ($\text{mg} \cdot \text{g}^{-1}$)	R^2	K_T	A	R^2
GO-BSA	298.15	616	0.8429	1.28	1.83	0.7854
	308.15	693	0.9032	1.52	2.18	0.8389
	318.15	703	0.9658	1.64	2.38	0.9629
GO	298.15	452	0.9805	2.21	1.05	0.9946
	308.15	455	0.9752	3.12	1.12	0.9932
	318.15	587	0.9661	3.49	1.16	0.9889



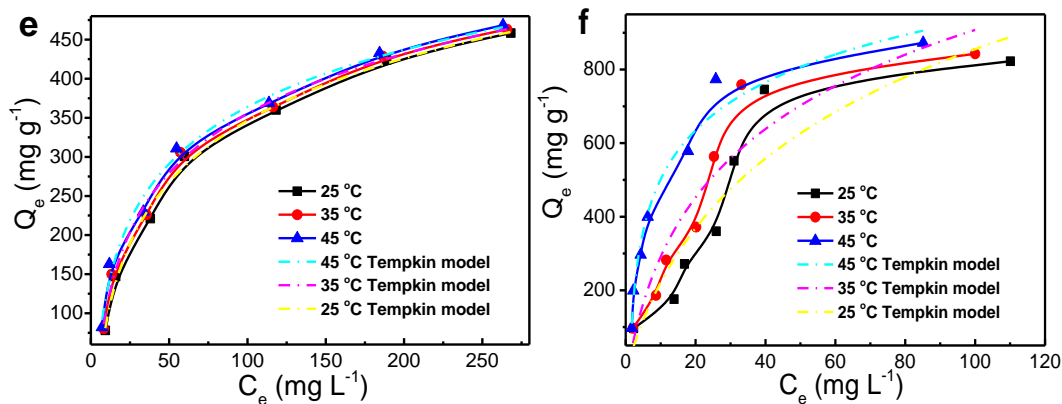


Fig. S5 Freundlich model, Langmuir model, D-R model and Temkin model for the removal of U(VI) on GO (a, c, e) and GO-BSA (b, d, f) composites, pH= 6.00; T= 25 °C; amount of adsorbent 0.01 g; $C_o = 200 \text{ mg L}^{-1}$ and $t = 80 \text{ min}$.

SI.5 Calculations for thermodynamic parameters

The thermodynamic parameters of U(VI) adsorption expounded that the adsorption capacity of GO-BSA composites show a rising trend with the change of temperature, indicating the adsorption behavior is endothermic. These formula was used to calculate the thermodynamic data³

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (\text{S7})$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{S8})$$

$$K_d = Q_e / C_e = (C_o - C_e) V / C_e m \quad (\text{S9})$$

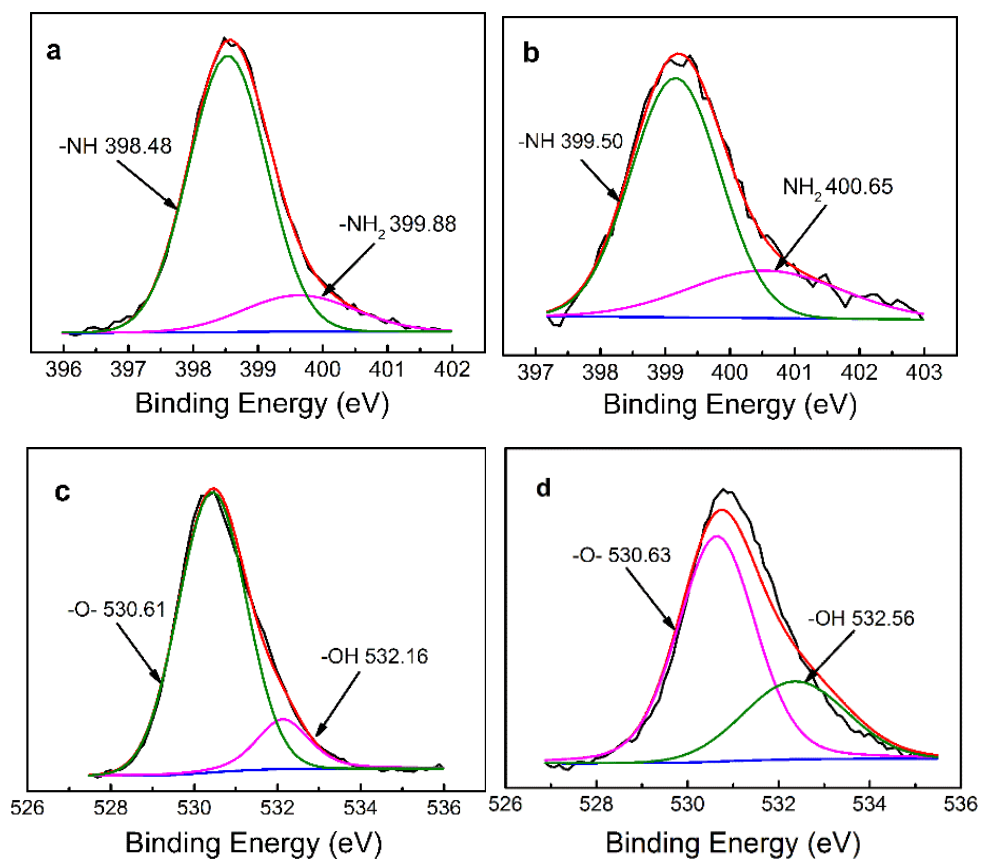
Where K_d (mL g^{-1}) is the distribution coefficient of U(VI), T (K) is the Kelvin temperature and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The function of ΔH° (standard enthalpy change) and ΔS° (standard entropy change) were counted by the Fig. 6. ΔG° (standard Gibbs energy) can be calculated using Eq.: (S7-S9). Table S4 shown the values of thermodynamic for the adsorption of U(VI) under the three temperatures, which also implied the adsorption process of U(VI) is endothermic. The

value of ΔG° illustrated that the adsorption process of GO-BSA composites were feasible and spontaneous.

Table S4. The thermodynamic parameters for U(VI) adsorption

Materials	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
GO-BSA	21.84	91.9	298.15K	308.15K	318.15K
			-5.5600	-6.2324	-7.3980
GO	5.24	29.29	298.15K	308.15K	318.15K
			-3.4928	-3.7857	-4.078

SL.6 Analysis for XPS



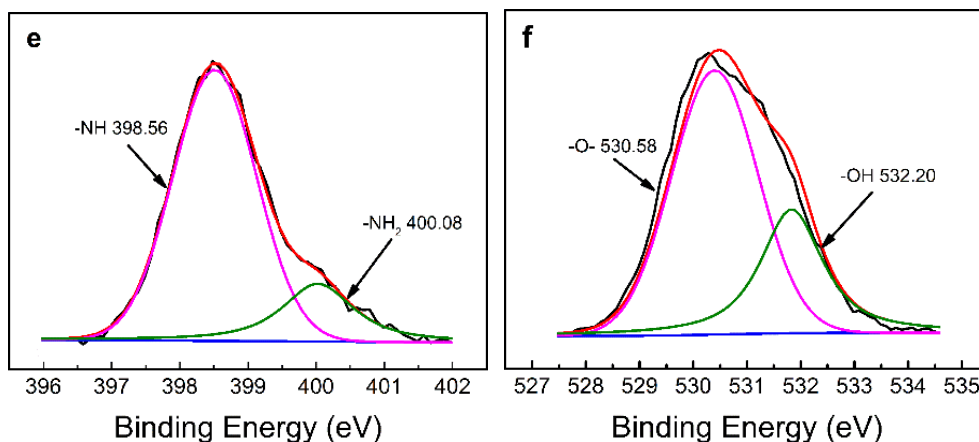


Fig. S6 The fitting peaks of GO-BSA, GO-BSA-U and Desorption-GO-BSA, (a): N 1s of GO-BSA; (b): N 1s of GO-BSA-U; (c): O 1s of GO-BSA; (d): O 1s of GO-BSA-U, (e): N 1s of Desorption-GO-BSA, and (f): O 1s of Desorption-GO-BSA ¹⁻³

SI.7 Desorption data of U(VI) on GO-BSA composites.

SI.7.1 U(VI) desorption experiments

In a typical experiment, 20 mg of sorbent with U(VI) ions was added into 50 mL eluent solution, which included in 0.1 M HCl, 0.1 M NaHCO₃, 0.1 M NaOH and H₂O, respectively. The flasks were stirred for specified time (t, min) at room temperature, and then the solid phase was separated from the solution by centrifuge. These results were analyzed with WGJ-III Trace Uranium Analyzer to obtain the concentrations of U(VI) ions. The elution rate of U(VI) ions was calculated.

Table S5. The elution efficiency upon different elution solution.

Eluent	Elution efficiency (%)
H ₂ O	7.52
HCl	80.13
NaHCO ₃	69.86
NaOH	51.21

SI.7.2 U(VI) adsorption-desorption cycle experiments

In a typical experiment, 20 mg of sorbent was added into 50 mL of U(VI) solution and stirred for 6 h at room temperature. The solid phase was separated from the solution by centrifuge. Then, the sorbent was dried in the vacuum oven for 24 h. The dried sorbent was placed in the 50 mL eluent solution (0.5 M HCl) for the 6 h. After elution, the GO-BSA composites were washed with abundant deionized water to remove residual H⁺ and UO₂²⁺ until cannot be detected in the aqueous solutions. The GO-BSA composites were regenerated by drying in vacuum oven for 24 h and then reused. Eventually the elution efficiency of U(VI) ions was calculated. Repeat this experiment operation for five times.

SI.7.3 adsorption-desorption of FTIR

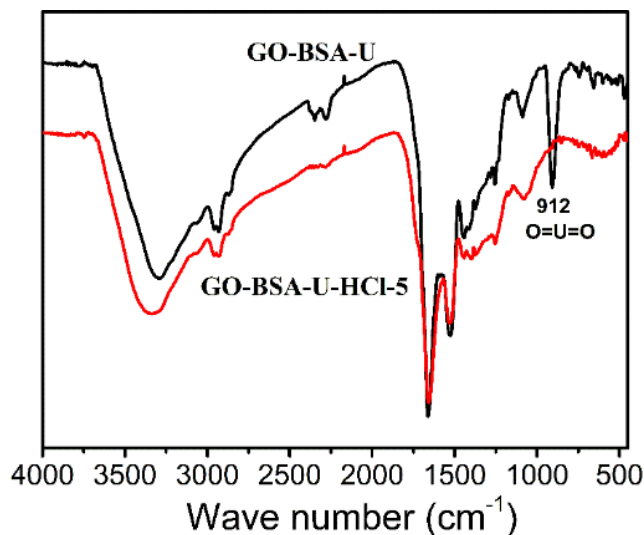


Fig. S7. FTIR of GO-BSA composites absorption for U(VI) and adsorption-desorption five times for U(VI)

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