Supporting information

# A novel U(VI)-imprinted Graphitic Carbon Nitride

## Composites for the selective and efficient removal of U(VI)

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## **Batch adsorption experiments**

To evaluate the adsorption properties of the composite sorbent, we investigated the effect of environmental conditions such as the pH, ionic strength, contact time, temperature, initial concentration, selectivity and recyclability on the adsorption of U(VI). In this experiment, the pH was adjusted by drops of 0.5 M HNO<sub>3</sub> and 0.5 M NaOH. A total of 10 mg of composite sorbent was added into 20 mL of U solution with continuous oscillation at 25 °C overnight. After adsorption, the mixture was filtered through filter paper to obtain supernatant and the supernatant U(VI) concentration was determined by ICP-AES (IRIS Intrepid II XSP instrument). The sorption capacity  $Q_e$  and the removal efficiency *R* of U(VI) was calculated using the following equation:

$$Q_e = (C_0 - C_e)V/m \tag{S1}$$

$$R = (C_0 - C_e)/C_0 \times 100\%$$
(S2)

where  $C_0 \,(\text{mg L}^{-1})$  and  $C_e \,(\text{mg L}^{-1})$  are the initial U(VI) concentration and the residual U(VI) concentration in solution, respectively. V(L) is the volume of the U(VI) solution, and  $m \,(g)$  is the weight of the composite sorbent.

2.5 Adsorption Tests in Simulated Seawater

To confirm the adsorption property at seawater conditions, we prepared simulated seawater solutions with different concentrations. Typically, 17 mg of  $(UO_2(NO_3)_2 \cdot 6H_2O)$ , 193 mg of NaHCO<sub>3</sub> and 25.6 g of NaCl were dissolved in deionized water. After that, the solution was diluted to different concentration (3 ug L<sup>-1</sup>, 5 ug L<sup>-1</sup>, 10 ug L<sup>-1</sup>, 20 ug L<sup>-1</sup>, 50 ug L<sup>-1</sup>, 100 ug L<sup>-1</sup>, and 500 ug L<sup>-1</sup>). Then, 10 mg adsorbent was added into 20 mL simulated seawater solution in water bath at 25 °C for 24 h. After adsorption, the supernatant solution was collected by filtration through a filter paper and the U(VI) concentration was analyzed by ICP-MS (X Series<sup>II</sup> instrument).

The preparation of competing ions experiments

In the part of competing ions experiments, the preparation process is presented as follows: the molar ratio of  $UO_2^{2+}$  and metal ions is 1:1. The initial concentration of  $UO_2^{2+}$  is 100ppm, m/V=0.5 g L<sup>-1</sup>, T=25 °C. The corresponding concentration of  $UO_2^{2+}$ , Na<sup>+</sup>, Ba<sup>2+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>, Sr<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, are listed in the Table S8.

#### Characterization

### materials characteristics

Structural and compositional characteristics of  $g-C_3N_4$ ,  $R-g-C_3N_4$ , IIP- $g-C_3N_4/\beta$ -CD, NIP- $g-C_3N_4/\beta$ -CD were observed by scanning electron microscopy (SEM, JEOL JSM-6480A), transmission electron microscope (TEM, Tecnai G220S-Twin), X-ray diffraction (XRD) analysis, Fourier-transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). The XRD (Rigaku TTR-III) was performed to explained the Crystal structure of the composite sorbents. The FT-IR spectra was conducted to show the structural composition or the chemical functional groups scanned by a standard KBr pellet technique. The XPS (ESCALAB 250Xi) was determined to analyze the presence of oxygenated functional groups, nitrogen

functional groups the oxidation state of the composite sorbents. The specific surface area and pore volume of the sam- were measured by Brunauer–Emmett–Teller (BET) at 77K (BK 122T-B). The concentration of uranium was detected using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) with with a X SeriesII instrument solution.

Pseudo-first-order model:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{S3}$$

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(S4)

The intra-particle diffusion model:

$$q_t = k_p t^{1/2} + C \tag{S5}$$

where qe (mg g<sup>-1</sup>) is equilibrium adsorption capacity, qt (mg g<sup>-1</sup>) is the adsorption capacity at time t (min);  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are the pseudo-first-order and pseudo-second-order rate constant, respectively.

Langmuir isotherm equation:

$$\frac{c_e}{q_e} = \frac{1}{q_{max}b} + \frac{c_e}{q_{max}}$$
(S6)

Freundlich isotherm equation:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \tag{S7}$$

where  $q_e$  and  $q_{max}$  are the experimental adsorption capacity and maximum adsorption capacity, mg g<sup>-1</sup>, respectively; *b* in Langmuir equation and  $K_F$ , *n* in Freundlich equation represent the constant.

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$
(S8)  

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
(S9)

Where *Kd*, *R* and *T* represent the distribution coefficient (mL  $g^{-1}$ ), the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and the absolute temperature (*K*), respectively.



Fig. S1 EDS analysis of g-C<sub>3</sub>N<sub>4</sub> and R-g-C<sub>3</sub>N<sub>4</sub>



Fig. S2 C 1s for IIP-g-C\_3N\_4/\beta-CD and IIP-g-C\_3N\_4/\beta-CD-U

Table S1. BET surface area and pore volume of  $g-C_3N_4$ ,  $R-g-C_3N_4$  nanosheets, IIP-g-

$C_3N_4/\beta$ -CD	and NIP-	$g-C_3N_4/$	′β <b>-</b> CD.
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Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
g-C <sub>3</sub> N <sub>4</sub>	21.42	0.0705
R-g-C <sub>3</sub> N <sub>4</sub>	45.12	0.2314
IIP-g- $C_3N_4/\beta$ -CD	34.94	0.1601
$NIP$ -g- $C_3N_4/\beta$ - $CD$	40.59	0.1747

**Table S2.** Thermodynamic parameters for the adsorption of uranium (VI) onto g- $C_3N_4$ , R-g- $C_3N_4$ , IIP-g- $C_3N_4/\beta$ -CD and NIP-g- $C_3N_4/\beta$ -CD.

Sample	T (°C)	$\Delta G (kJ/mol)$	$\Delta H (kJ/mol)$	$\Delta S (J/(mol \cdot K))$
IIPs	25	-18.25		
	35	-19.41	15.57	113.51
	45	-20.52		
NIPs	25	-17.34		
	35	-18.26	11.56	96.93
	45	-19.28		

**Table S3.** Parameters of the intraparticle di  $\square$  usion model of uranium (VI) adsorption

on g-C <sub>3</sub> N <sub>4</sub> , R-	g-C <sub>3</sub> N <sub>4</sub> , III	$P-g-C_3N_4/\beta-C$	D and NIP	-g-C <sub>3</sub> N <sub>4</sub> /β-CD
Sample	$k_{p1}$	$R_1^2$	k <sub>p2</sub>	$R_2^2$
IIPs	22.20	0.94958	1.77	0.84791
NIPs	19.89	0.94226	1.91	0.81695

Table S4. Pseudo-first-order and pseudo-second-order constants and values of R2 for

IIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD and NIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD.

T(V)	Pse	udo-first-ord	er	Pseudo-s	second-order	
I(K)	$K_1(min^{-1})$	$q_e(mg g^{-1})$	R <sup>2</sup>	$K_2(g mg^{-1} min^{-1})$	$q_e(mg g^{-1})$	R <sup>2</sup>
IIP	0.00451	390.2544	0.96239	0.00002	423.8272	0.98479
NIP	0.00408	369.7617	0.95983	0.00001	404.7781	0.96589

**Table S5.** Isotherm constants and values of  $R^2$  for IIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD.

T(K)	Lang	muir isotherm	Freund	ich isothe	rm	
IIP	$q_m (mg \cdot g^{-1})$	b (L·mg <sup>-1</sup> )	$\mathbb{R}^2$	$K(L \cdot g^{-1})$	n	R <sup>2</sup>
298	859.666	0.03	0.936	129.611	3.213	0.916
308	1001.021	0.03	0.966	156.127	3.238	0.905
318	1076.781	0.04	0.957	198.229	3.467	0.899

T(K)	Langr	Freundi	ich isothe	rm		
NIP	$q_m (mg \cdot g^{-1})$	$b (L \cdot mg^{-1})$	$\mathbb{R}^2$	$K(L \cdot g^{-1})$	n	$\mathbb{R}^2$
298	734.407	0.02	0.984	79.283	2.890	0.910
308	779.657	0.02	0.978	94.169	2.994	0.920
318	856.768	0.02	0.986	121.992	3.182	0.888

Table S6. Isotherm constants and values of  $R^2$  for NIP-g-C\_3N\_4/\beta-CD.

**Table S7** The maximum adsorption capacity of different adsorbents for uranium (VI).

Adsorbents	Q <sub>max</sub>	m/V	Conditions	Ref.
	(mg g <sup>-1</sup> )	(g L <sup>-1</sup> )		
g-C <sub>3</sub> N <sub>4</sub> @Ni-Mg-Al-LDH	99.7	0.5	T = 25 °C, pH=5.0	7
Fe3O4@ g-C <sub>3</sub> N <sub>4</sub>	352.1	0.3	T = 25 °C, pH=10.0	8
<i>l</i> -C <sub>3</sub> N <sub>4</sub> /PDA/PEI <sub>3</sub>	60.51	0.5	T = 25 °C, pH=5.0	9
β-CD@Al(OH) <sub>3</sub>	63.29	1	T = 30 °C, pH=6.0	10
MWCNTs/β-CD	100.27	0.5	T = 25 °C, pH=7.0	11
U-CMC-SAL	180	1	T = 30 °C, pH=5.0	12
GO/SiO <sub>2</sub> -IIP	17.89	0.5	T = 25 °C, pH=4.0	13
Ion-Imprinted PPNF	133.3	0.1	T = 25 °C, pH=8.0	14
$IID \sim C N / \theta C D$	850 66	0.5	$T = 25 \ ^{\circ}C \ mU = 6 \ 0$	This
ш <b>г-g-С</b> 3№4/р-СD	039.00	0.3	1 – 23 С, рп–6.0	work

 Table S8 The concentrations of the competing cations.

cations	$UO_2^{2+}$	Na <sup>+</sup>	Ba <sup>2+</sup>	Ni <sup>2+</sup>	Ca <sup>2+</sup>	Co <sup>2+</sup>	Sr <sup>2+</sup>	$K^+$	$Mg^{2+}$	Pb <sup>2+</sup>
C <sub>0</sub>	100	35.7	109.8	122.2	68.9	122.3	88.9	42.5	62.2	139.2
(mg g <sup>-1</sup> )										



**Figure. S3** (a) Effect of coexisting anions on the extraction of U(VI) by IIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD and NIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD. T=25 °C, m/V = 0.5 g L<sup>-1</sup>, C<sub>0</sub>[U(VI)] = 200 mg L<sup>-1</sup>.

Table S9. Elution efficiency of different concentrations of HNO<sub>3</sub>.

Desorption agents	Elution efficiency (%)
0.1 M HNO <sub>3</sub>	95.01
0.1 M EDTA-2Na	40.80
0.1 M NaHCO <sub>3</sub>	62.17
0.1 M NaOH	4.39
0.1 M CA	29.81



Fig. S4 The (a) FT-IR and (b) XRD patterns of IIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD before and after 5

adsorption-desorption cycles.



Fig. S5 XRD patterns of IIP-g-C<sub>3</sub>N<sub>4</sub>/ $\beta$ -CD before and after adsorption uranium (VI).