

Electronic Supplementary Information (ESI) for *PCCP*.

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## **Theoretical and experimental investigations of enhanced uranium(VI) adsorption by nitrogen doping strategy**

Yanqing Guo,<sup>a</sup> Meng Xia,<sup>a</sup> Kexin Shao,<sup>a</sup> Guangming Xu,<sup>a</sup> Wei Cheng,<sup>b</sup> Zhaorong Shang,<sup>c</sup> Hao Peng,<sup>c</sup>  
Yanguo Teng<sup>a</sup> and Junfeng Dou<sup>\*a</sup>

*a.* College of Water Sciences, Beijing Normal University, Beijing 100875, China.

*b.* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201,  
China.

*c.* Nuclear and Radiation Safety Center, Ministry of Ecology and Environment, Beijing 100082, China.

E-mail: doujf@bnu.edu.cn

## **1. Preparation of PAO-rGO**

### **1.1 Preparation of GO by modified Hummer's method**

To prepare GO we used modified Hummer's method.<sup>1</sup> In short, graphite flakes (5.0 g) were added in the mixture of concentrated H<sub>2</sub>SO<sub>4</sub> (120 mL) and NaNO<sub>3</sub> (3.0 g) and then KMnO<sub>4</sub> (20 g) was added in an ice bath. After the reaction, the mixture was cooled and added H<sub>2</sub>O<sub>2</sub> (37 wt%). The obtained mixture was centrifuged and washed 3-5 times with ultrapure water, HCl and ethanol, respectively. The GO was obtained after freeze-drying for several days.

### **1.2 Preparation of PAO-rGO by situ polymerization method**

To prepare PAO-rGO we used situ polymerization method.<sup>2</sup> Briefly, 2.0 ml acrylonitrile monomer was dispersed in 600 ml ultrapure water, 0.4 g GO were added into the solution and the mixture was stirred overnight. Then, the mixture was heated to 50 °C, followed by adding 200 ml of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> aqueous solution (0.1 M) and reacted for 3 h. After the reaction, the suspensions were centrifuged and rinsed several times with 5:1 methanol/water solution and ultrapure. The obtained composites were dispersed in 200 mL previously prepared NH<sub>2</sub>OH solution and then reacted in a 70 °C bath for 3 h. The PAO-rGO was obtained after freeze-drying for several days.

## **2. Synthesis of PAO-N-rGO**

### **2.1 Preparation of N-rGO by the hydrothermal method<sup>3</sup>**

The GO (50 mg) was thoroughly dispersed in ultrapure water (50 mL) by ultrasonication. Then, urea (0.20 g) was added into the prepared GO solution, and the mixture was stirred at 300 rpm for 30 min. After urea was completely dissolved, the solution was transferred to a reaction vessel. Then the reaction vessel was heated to 170 °C and kept for 3 h. After the reaction, the obtained black composites were washed several times with ultrapure water. Finally, the N-rGO was obtained after freeze-drying for several days.

### **2.2 Preparation of PAO-N-rGO by situ polymerization method**

We prepared PAO-N-rGO with the same method as PAO-rGO preparation and the only difference is the replacement of GO by N-rGO.

### 3. XPS Study

**Table S1** The total elemental content of C, N and O in GO, rGO, N-rGO, PAO-rGO and PAO-N-rGO samples.

species	C (at.%)	N (at.%)	O (at.%)
GO	66.82	-	33.17
rGO	84.08	-	15.91
N-rGO	78.56	9.34	12.09
PAO-rGO	79.25	5.72	15.02
PAO-N-rGO	69.24	11.02	19.73

**Table S2** C1s XPS spectral parameters.

Sample	Peak	C=C/C-C	C-O/C-N	C=O	O=C-OH
GO	Position (eV)	284.83	286.72	287.15	288.81
	Area (%)	43.94	28.18	22.73	5.14
rGO	Position (eV)	284.81	285.98	287.80	289.78
	Area( %)	58.77	20.49	17.34	3.39
N-rGO	Position (eV)	284.78	285.87	287.61	289.27
	Area( %)	61.45	14.41	22.31	1.82
PAO-rGO	Position (eV)	284.79	285.83	287.61	289.32
	Area (%)	59.84	16.18	11.16	12.81
PAO-N-rGO	Position (eV)	284.83	286.09	287.72	289.43
	Area(%)	58.66	18.06	13.23	10.04

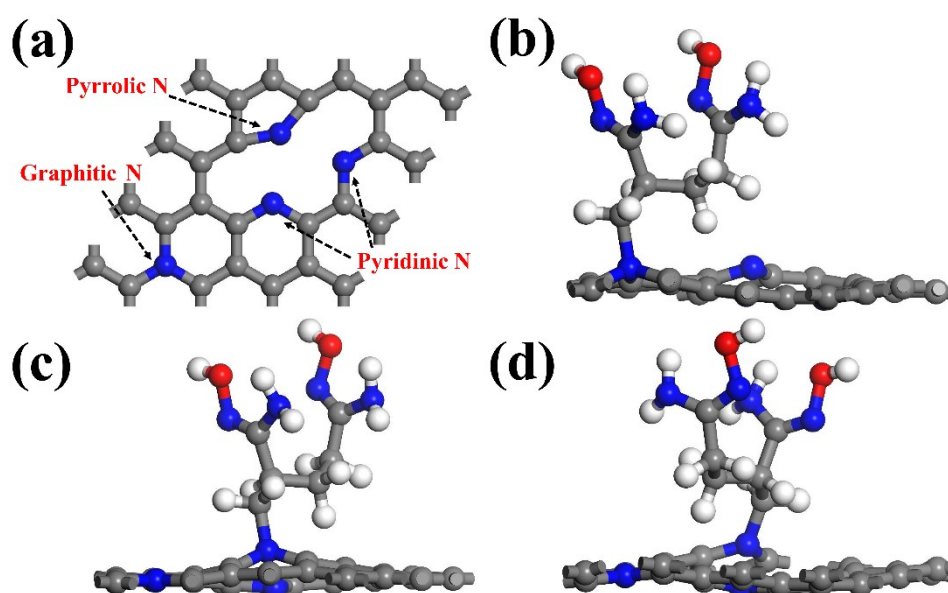
**Table S3** N1s XPS spectral parameters.

Sample	Peak	Pyridinic N	Pyrrolic N	Graphitic N	H <sub>2</sub> N-C=NOH
N-rGO	Position (eV)	398.30	399.57	400.81	-
	Area (%)	6.86	77.24	15.89	-
PAO-rGO	Position (eV)	-	-	-	399.84

	Area(%)	-	-	-	99.98
PAO-N-rGO	Position (eV)	398.32	399.29	400.68	399.85
	Area(%)	6.19	34.02	9.51	50.27

#### 4. Binding sites study

To determine the binding sites of poly(amidoxime) on nitrogen-doped reduced graphene oxide, three types of N atoms were considered. The constructed PAO-N-rGO model included PAO-N<sub>1</sub>-rGO, PAO-N<sub>2</sub>-rGO and PAO-N<sub>3</sub>-rGO, corresponding to graphitic N, pyridinic N and pyrrolic N, respectively.



**Fig. S1** (a) Three types of N doping in N-rGO. The side view of geometric models for (b) PAO-N<sub>1</sub>-rGO, (c) PAO-N<sub>2</sub>-rGO and (d) PAO-N<sub>3</sub>-rGO.

#### 5. Speciation distribution of U(VI)

According to the thermodynamic calculation of Visual MINTEQ 3.1, the U(VI) species distribution in the pH range of 3–10 was displayed in the Fig. S2. The concentration of U(VI) was 200 mg/L.

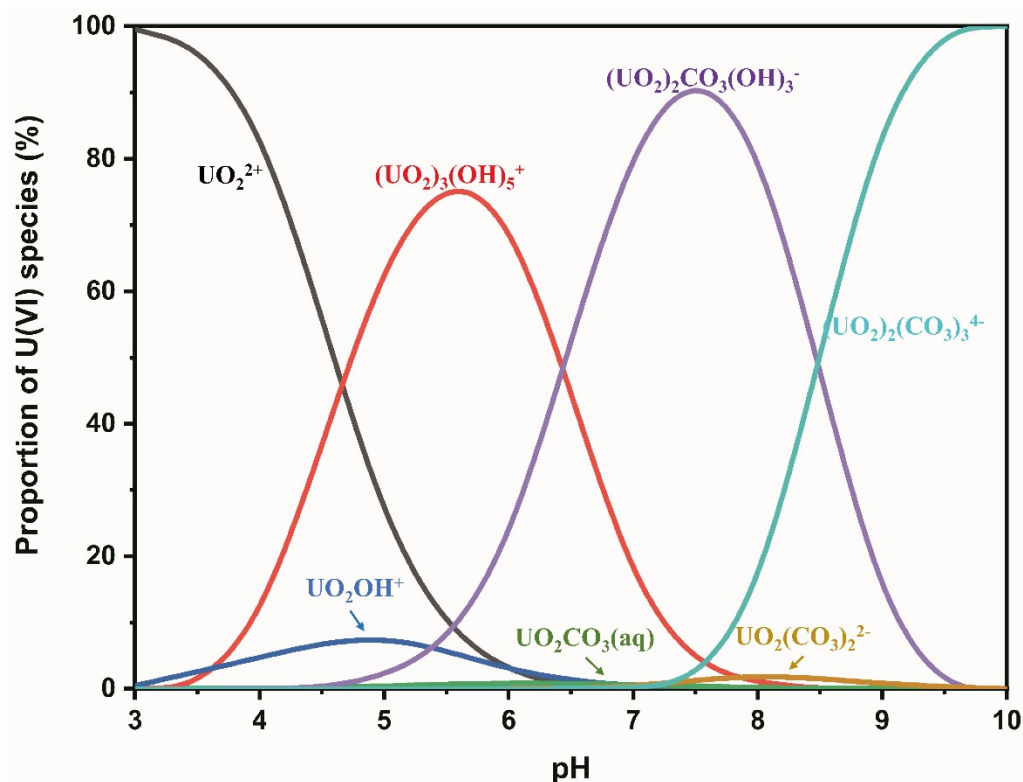


Fig. S2 U(VI) speciation as a function of pH ( $C(U(VI)) = 200 \text{ mg/L}$ ).

## 6. Effect of competing metal ions

Table S4 The initial concentrations of the competing metal ions.

Metal ions	U(VI)	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Al <sup>3+</sup>	Cu <sup>2+</sup>
$C_0 \text{ (mg}\cdot\text{L}^{-1}\text{)}$	200.0	33.7	20.4	19.3	32.8	22.7	53.3

Table S5 The removal rate (%) of the competing metal ions.

Adsorbents	U(VI)	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Al <sup>3+</sup>	Cu <sup>2+</sup>
PAO-rGO	83.7	30.7	5.4	54.3	34.6	98.3	72.0
PAO-N-rGO	99.3	32.9	5.1	62.9	33.5	98.4	65.1

The selectivity coefficient ( $S_U$ ) is defined as a specific term to describe the degree of selectivity for U(VI) of the adsorbents<sup>4</sup>. The  $S_U$  was calculated as:

$$S_U = \frac{k_U}{k_M} \quad (\text{S1})$$

where  $k_U$  and  $k_M$  are the distribution ratio of the U(VI) ion and other competing metal ions in adsorbents and solution, respectively.

Table S6 The selectivity coefficients ( $S_U$ ) of U(VI) for competing metal ions.

Adsorbents	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Al <sup>3+</sup>	Cu <sup>2+</sup>
PAO-rGO	5.1	40.1	19.0	63.5	1.7	1.4
PAO-N-rGO	7.1	49.2	43.5	391.8	6.6	2.9

### 7. Comparison of adsorption capacities

To obtain the adsorption capacity of adsorbents, the experimental data were fitted with Langmuir and Freundlich isotherm models. The equations of Langmuir and Freundlich isotherm models are as follows:

$$q_e = \frac{k_l q_{max} C_e}{1 + k_l C_e} \quad (S2)$$

$$q_e = k_f C_e^{\frac{1}{n}} \quad (S3)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) are the amount of U(VI) adsorbed at equilibrium and the equilibrium concentration of U(VI) in solution.  $q_{max}$  (mg g<sup>-1</sup>) is the maximum adsorption capacity,  $k_l$  (L mg<sup>-1</sup>) and  $k_f$  (mg<sup>1-(1/n)</sup> L<sup>1/n</sup> g<sup>-1</sup>) are the Langmuir and Freundlich equilibrium constants, respectively.  $1/n$  is the empirical adsorption intensity of the Freundlich model. The parameters including  $k_l$ ,  $k_f$ ,  $q_{max}$ ,  $1/n$  and  $R^2$  are given in Table S7.

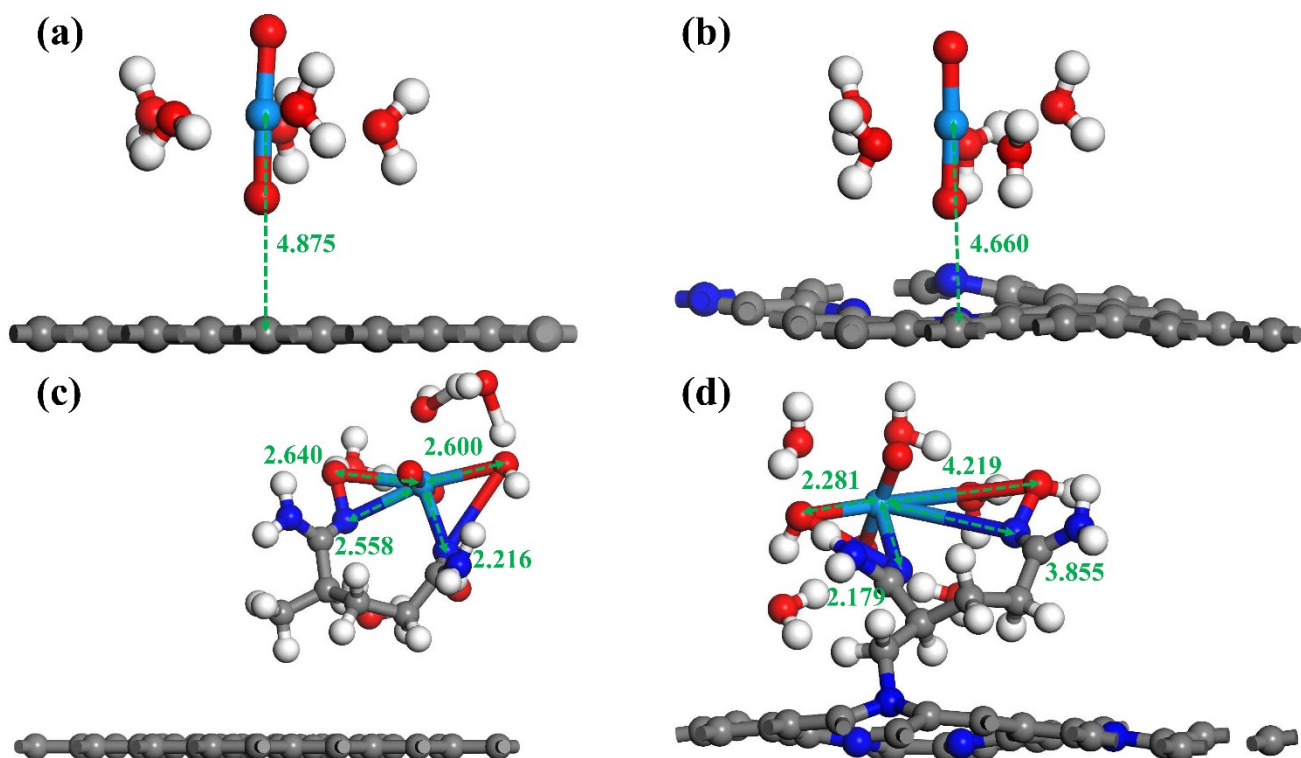
Table S7 Parameters for Langmuir and Freundlich isotherm models.

	Langmuir model			Freundlich model		
	$q_{max}$ (mg g <sup>-1</sup> )	$k_l$ (L mg <sup>-1</sup> )	$R^2$	$k_f$ (mg <sup>1-(1/n)</sup> L <sup>1/n</sup> g <sup>-1</sup> )	$1/n$	$R^2$
PAO-rGO	1500.26	0.0485	0.9996	142.5295	0.485	0.9553

PAO-N-rGO	1545.95	0.0395	0.9468	213.7719	0.382	0.9982
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## 8. Adsorption energy calculation

To calculate the adsorption energy of  $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$  on rGO, N-rGO, PAO-rGO and PAO-N-rGO, the corresponding geometric models were constructed and displayed in the Fig. S3.



**Fig. S3** The geometric models of (a) U/rGO, (b) U/N-rGO, (c) U/PAO-rGO and (d) U/PAO-N-rGO. The bond length is in Å.

## References

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