Supporting Information (SI) on

Mutual effect of U(VI) and Sr(II) with graphene oxides: Evidence from EXAFS and theoretical calculations

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Characterization. GOs were characterized by using scanning electron microscopy (SEM, FEI-JSM 6320F), transmission electron microscopy (TEM, JEM-2010), Infrared spectroscopy (IR, PerkinElmer Spectrum 100), X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250), Raman spectroscopy (LabRam HR), and potentiometric acid-base titration (Mettler Toledo DL50). IR spectra were collected in the range of 4000-400 cm⁻¹ in pressed KBr pellets (Aldrich, 99 %, analytical reagent) at room temperature. The XPS spectra of sample before and after radionuclide sorption were conducted at 10 kV and 5 mA under 10-8 Pa residual pressure. The energies were corrected using the C 1s peak at 284.6 eV as a reference, and the peaks were fitted using the XPSPEAK software (version 4.1). The Raman analysis was conducted with excitation at 514.5 nm for only 10 s by Ar⁺ laser to avoid overheating of the GOs films. The titration experiment was conducted with 0.15 g/L GOs in 0.001 mol/L NaClO₄ solutions at $T = 303 \pm 1$ K. The samples were purged with $N_{2(g)}$ for 2 h to exclude atmospheric CO₂ (g). The initial pH of suspension was adjusted to pH 3.0 by adding 0.01 mol/L HClO₄ with vigorous stirring for 1 h, and then the suspension was slowly titrated to pH 11.0 with 0.05 mol/L NaOH at a variable increment (0.008 up to 0.15 mL). The data sets of pH versus net consumption of H⁺ or OH⁻ were used to obtain intrinsic acidity constants.

SEM and TEM images in Figure S1A and S1B show that as-synthesized GOs display multilayer nanosheets with high-density and random orientations, which is consistent with previous reports.¹⁻² IR spectrum of GOs (Figure S1C) exhibits the abundance of oxygen-containing groups, such as C-O band at 1056 and 1227 cm⁻¹, C=O stretching

vibration at 1723 cm⁻¹, and OH stretching vibration at 3461 cm⁻¹ from GOs or adsorbed water.³ The peak at 1631 cm⁻¹ is assigned to C=C bond for the skeletal vibrations of non oxidized graphitic domains.³ Figure S1D shows the high resolution of C 1s XPS spectrum of GOs. The C 1s spectrum can be fitted by C-C/C-H at 284.6 eV, C-OH/ C-O-C at 286.4 eV, C=O/O-C-O at 288.0 eV, and O-C=O at 289.0 eV,⁴ further demonstrating the presence of variety of oxygen-containing groups in GOs. Fitting results reveal the content of -OH/ C-O-C groups (36.7 wt%) is higher than that of O-C=O groups (2.5 wt%), suggesting the predominance of –OH and C-O-C groups in GOs. The Raman spectrum of GOs (Figure S1E) displays a D-band at ~1350 cm⁻¹ and a G-band at ~ 1600 cm⁻¹, which can be attributed to the disordered sp³-hybridized carbon resulting from oxygen-containing groups and the sp²-hybridized carbon resulting from graphitic structure, respectively. The result of potentiometric acid-base titration is shown in Figure S1F. The pH_{PZC} (point of zero charge) and surface site density of GOs is calculated to be ~ 4.5 and 29.08 sites \cdot nm⁻², respectively. Detailed calculation on the concentration of surface active sites can be found in our previous work.1



Figure S1: characterization of GOs, A: SEM image; B: TEM image; C: IR spectrum;D: C 1s XPS spectrum; E: Raman spectrum; F: potentiometric acid-base titration.

Batch Sorption Experiment. Batch sorption experiment was conducted with 0.15 g/L GOs and 0.15 mmol/L radionuclide solution at $T = 303 \pm 1$ K in the presence of 0.001 mol/L NaClO₄ solutions. The pH value was adjusted to be in the range 3.0-10.0 by adding a negligible volume of 1.0-0.01 mol/L NaOH and HClO₄. The sorption isotherms were investigated at pH 5.0 with radionuclide concentration ranging from 0.1 to 0.6 mmol/L. The effect of ionic strength on the sorption of U(VI) and Sr(II) to

GOs was conducted in the presence of 0.001 and 0.01 mol/L NaClO₄ solutions. The effect of Na₂CO₃ concentration on radionuclide sorption was examined in 0.1 mol/L Na₂CO₃ solutions as background electrolyte. Briefly, the bulk suspensions of GOs and NaClO₄ were pre-equilibrated for 24 h in closed polycarbonate tubes. Then the radionuclide stock solution was gradually spiked into the bulk suspensions which was then sealed and continuously stirred under $N_2(g)$ conditions. Competitive sorption of U(VI) and Sr(II) on GOs was conducted in a binary U+Sr system with equivalent concentrations of each radionuclide. The suspensions were centrifuged at $8000 \times g$ for 30 min after 48 h to ensure equilibrium, and then filtered through a 0.45 µm nylon membrane filter. To eliminate the effect of metal sorption on polycarbonate tube walls, the control experiments without adsorbents were carried out under the same experimental conditions. The radioactivity of ⁹⁰Sr(II) in solutions was analyzed by liquid scintillation counting using a Packard 3100 TR/AB liquid scintillation analyzer (Perkin-Elmer) with a scintillation cocktail (ULTIMA GOLD AB, Packard). The concentrations of ²³⁸U(VI) were determined by a kinetic phosphorescence analyzer (KPA-11, Richland, USA). All experimental data were the average of triplicate determinations and the relative errors were within \pm 5%. The percentages and capacities of metal ion sorption on GOs (sorption (%) and Q (mmol/g), respectively) were determined according to Eqns. (S1) and (S2), respectively.

Sorption (%) = $(C_0 - C_e) / C_0 \times 100\%$ (S1)

$$Q(\text{mmol/g}) = V \times (C_0 - C_e) / m$$
 (S2)

where C_0 (mmol/L) and C_e (mmol/L) are the initial metal concentrations and the

aqueous metal concentration after the sorption equilibrium, respectively. m (g) and V (mL) represent the mass of GOs and the volume of the suspension, respectively.

Distribution of U(VI) and Sr(II) Species. Figure S2 shows the distribution of U(VI) and Sr(II) species varied with pH and Na₂CO₃ concentrations calculated by Visual MINEQL+3.0. U(VI) thermodynamic data were taken from the Nuclear Energy Agency (NEA) database.⁶



Figure S2. The distribution of radionuclide species in aqueous solution in the absence of 1 mmol/L Na₂CO₃, A: U(VI) and C: Sr(II), and in the presence of 1 mmol/L Na₂CO₃, B: U(VI) and D: Sr(II); $C_{0 \text{ U(VI)}} = 0.15 \text{ mmol/L}$, $C_{0 \text{ Sr(II)}} = 0.15 \text{ mmol/L}$, $T = 303 \pm 1 \text{ K}$, I = 0.001 mol/L NaClO₄.

Effect of Na₂CO₃. CO_3^{2-} is common in groundwater and can greatly influence uranium sorption on mineral surface.⁵ Thus, the impact of CO_3^{2-} on the competitive

sorption of U(VI) and Sr(II) to GOs was studied. Figure S3 shows the effect of pH on the sorption of U(VI) and Sr(II) by GOs in single-metal and binary U+Sr systems in the presence or absence of 1 mmol/L Na₂CO₃. Na₂CO₃ exhibited an inhibition effect on U(VI) sorption to GOs only at higher pH (pH > 7.0) (Figure S3A), whereas this inhibition effect was not observed for Sr(II) sorption(Figure S3B). The strong inhibition of U(VI) sorption could result from the formation of a U(VI)-carbonate species, which were more stable in aqueous solutions and were not favourable for sorption reaction.⁵ The distribution of U(VI) species in the presence of 1 mmol/L Na₂CO₃ is shown in Figure S3. It can be observed that the concentration of the U(VI)hydroxyl species was significantly decreased with increasing pH, whereas more U(VI)carbonate species (e.g., $UO_2CO_3(aq)$, $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ species) were observed. Thus, the decreased U(VI) sorption at pH > 7.0 can be attributed to the formation of negatively charged U(VI)-carbonate species. However, Even in the presence of Na₂CO₃, the sorption of U(VI) on GOs was little affected by the coexistent Sr(II) in U+Sr system, suggesting the higher affinity of U(VI) to GOs.



Figure S3. Effect of pH on the individual sorption of U(VI) (A) and Sr(II) (B) in the absence and presence of 1 mmol/L Na₂CO₃, $C_0 _{U(VI)} = 0.15 \text{ mmol/L}$, $C_0 _{Sr(II)} = 0.15 \text{ mmol/L}$, $T = 303 \pm 1 \text{ K}$, m/V = 0.15 g/L, I = 0.001 mol/L NaClO₄.

Sorption Kinetics. The individual and competitive sorption of U(VI) and Sr(II) on GOs as a function of contact time and radionuclide concentrations are shown in Figure S4. The sorption process was rapid for U(VI) and Sr(II) in single- and binary-metal systems, and the equilibrium could be reached within 0.5 h. The open and flat structure of GOs guarantees the sufficient exposure of surface active sites, which may contribute to the rapid sorption rate for U(VI) and Sr(II) on GOs. The short equilibrium time for the two radionuclides on GOs indicates that GOs can serve as the promising materials in continuous waste water treatment. The sorption amount of Sr(II) on GOs in single-Sr system (0.31 mmol/g) was higher than that in U+Sr system (0.14 mmol/g) at 0.1 mmol/L radionuclides, while the opposite result (0.43 and 0.58 mmol/g for single-Sr and U+Sr system, respectively) was observed at an initial radionuclide concentration of 0.3 mmol/L. The results are consistent with our sorption isotherms results.



Figure S4. Sorption kinetics of U(VI) (A) and Sr(II) (B) with initial radionuclide concentrations of 0.1 and 0.3 mmol/L, respectively, in single-metal and U+Sr systems, pH = 5.0, $T = 303 \pm 1$ K, m/V = 0.15 g/L, I = 0.001 mol/L NaClO₄.

Precipitation of U(VI). The control experiment (no GOs was added), relative to U(VI) sorption isotherms, was conducted at the same experimental conditions. The result showec that decreased U(VI) concentration in solution started to occur above an initial U(VI) concentration of 0.2 mmol/L at pH 5.0 and I = 0.001 mol/L, and gradual prevailed with increasing U(VI) concentration (Figure S5A). This trend was consistent with the formation of schoepite calculated by thermodynamically modeling. However, no obvious feature of U(VI) precipitate was detected by EXAFS technology (data not shown) at 0.5 mM U(VI), which might be attributed to formation of colloid U(VI) prior to precipitation or low abundance of U(VI) precipitate. According to the decreased kinetics of U(VI) in solution, the decrease process occurred fast within 10 min (Figure S5B). The decrease of U(VI) was only observed at $C_{o U(VI)} = 0.3$ mmol/L, but not at $C_{o U(VI)} = 0.1$ mmol/L.



Figure S5: A: the percentage of U(VI) decrease in solution at different concentration of U(VI), pH = 5.0, $T = 303 \pm 1$ K, I = 0.001 mol/L, t = 24 h, solid line: thermodynamic modeling of schoepite performed by Visual MINEQL+3.0. B: the decrease of different concentration of U(VI) as a function of time, pH = 5.0, T = 303K, I = 0.001 mol/L.

Langmuir Model. The Langmuir model which assumes monolayer sorption was used to fit the individual and competitive sorption isotherms of U(VI), Sr(II) and Co(II) in single- and binary-metal systems.⁷ Its linear form can be expressed as Eqn. (S3):

$$C_{\rm e}/Q = 1/(b \times Q_{\rm max}) + C_{\rm e}/Q_{\rm max}$$
(S3)

where Q_{max} (mg/g) is the maximum adsorption capacity of adsorbent at complete monolayer coverage. *b* (L/mg) is a Langmuir constant, which is related to the free energy of sorption. Fitting results are shown in Figure 2 in the text, and calculated parameters are listed in Table S1. The fitting results reveal that the individual sorption of U(VI) and Sr(II) on GOs could be well fitted by Langmuir model with $R^2 > 0.97$. In binary-metal system, Langmuir could give a well fit for the sorption of U(VI) in the presence of Sr(II), while the sorption of Sr(II) failed to be fitted by the model in the presence of U(VI).

Species	U(VI)		Sr(II)	
System	Single-U	U+Sr	Single-Sr	U+Sr
Q _{max} (mmol/g)	1.82	1.70	0.55	
b (L/mmol)	46.77	39.98	21.75	
R^2	0.97	0.98	0.98	

 Table S1 Langmuir constants for the individual and competitive sorption of U(VI)

 and Sr(II) on GOs in single-metal and binary-metal systems.

Sorption isotherms of Sr(II) onto schoepite

The synthesized schoepite was used for Sr(II) sorption at 0.001 and 0.01 mol/L NaClO₄.



Figure S6 Sorption isotherms of Sr(II) on schoepite at 0.001 and 0.01 mol/L NaClO₄,

$$pH = 5.0, m/V = 0.15 g/L, T = 303 K.$$



Figure S7 Effect of ionic strength on the sorption of Sr(II) onto GOs in binary U+Sr system, pH = 5.0, m/V = 0.15 g/L, $C_{0 \text{ U(VI)}} = 0.5 \text{ mmol/L}$, $C_{0 \text{ Sr(II)}} = 0.5 \text{ mmol/L}$, T =

Preparation of schoepite EXAFS Samples. EXAFS spectra were collected from samples of U(VI) or Sr(II) adsorbed on GOs in single-metal and binary U+Sr systems with initial metal concentrations of 0.1 and 0.5 mmmol/L. All samples were prepared under $T = 303 \pm 1$ K in the glove box (< 1 ppm CO₂). The GOs and NaClO₄ (0.001 mol/L ionic strength) were weighted into 250 mL flask bottles and then Milli-Q water (boiled then bubbled with N_{2(g)}) was pre-equilibrated for 24 h. The CO₂-free UO₂(NO₃)₂ or Sr(NO₃)₂ solution were dropwise added under vigorous stirring to obtain an initial concentration of 0.1 and 0.5 mmol/L for single-metal system (m/V = 0.15 g/L). For U+Sr system, the concentration of UO₂(NO₃)₂ or Sr(NO₃)₂, equimolar in the mixed solutions, was also 0.1 and 0.5 mmol/L. The mixed suspensions were adjusted to pH 5.0 by using neglected volume 0.01-1.0 mol/L HClO₄ or NaOH solution. Samples were then gently agitated on a shaker for 2 days. The solid phase was separated from liquid phase by centrifuging it at 8000 × g for 30 min and then

through 0.22-µm membrane filters. The wet pastes of U(VI)- or Sr(II)-bearing GOs were mounted in Teflon sample holders with Kapton tape.

Schoepite was synthesized according to the method of Riba et al.⁸. 1 mol/L NaOH was slowly added to 0.5 mol/L UO₂(NO₃)₂ solutions under a nitrogen atmosphere. After aging for 12 d, the yellow precipitate was washed with Milli-Q water, and then sonicated for 20 min. After that the products were collected by centrifuging at 8000 \times *g* for 20 min, and dried at 60 °C for 24 h. As-prepared schoepite was confirmed by XRD technique.

Sample	Shell	CN ^a	R (Å) ^b	$\sigma^2(m \AA^2)$ °
UO ₂ ²⁺ (aq)	U-O _{ax}	2.0 (6)	1.80 (7)	0.002
	U-O _{eq}	5.3 (3)	2.53 (6)	0.003
Schoepite ^d	U-O _{ax}	2.0 (5)	1.78 (2)	0.003
	U-O _{eq1}	2.0 (3)	2.29 (1)	0.003
	U-O _{eq2}	3.0 (4)	2.46 (3)	0.005
	U-U	0.5 (1)	3.80 (2)	0.007
	U-U	2.0 (3)	4.05 (5)	0.007
	U-U	2.5 (5)	4.30 (2)	0.001
GOs-U-0.1mM	U-O _{ax}	1.9 (4)	1.78 (5)	0.002
	U-O _{eq}	4.5 (7)	2.51 (6)	0.004
	U-C	1.8 (3)	3.30(1)	0.007
GOs-U-0.5mM	U-O _{ax}	2.0 (4)	1.78 (5)	0.002
	U-O _{eq}	3.9 (3)	2.45 (6)	0.004
	U-C	1.5 (3)	2.90 (1)	0.007
	U-U	0.5 (6)	3.94 (5)	0.009
GOs-(U+Sr)-0.1mM	U-O _{ax}	1.8 (4)	1.78 (5)	0.002
	U-O _{eq}	4.3 (5)	2.49 (7)	0.006
	U-C	1.1 (3)	3.10 (4)	0.008
GOs-(U+Sr)-0.5mM	U-O _{ax}	2.0 (4)	1.78 (5)	0.004
	U-O _{eq}	3.8 (5)	2.46 (6)	0.006
	U-C	1.2 (3)	2.98 (1)	0.004
	U-U	0.6 (6)	3.96 (5)	0.009

Table S2 EXAFS results of reference sample and U(VI) sorption samples at $L_{\rm III}\text{-}Edge,$

 $T = 303 \pm 1$ K, I = 0.001 mol/L NaClO₄

^a *CN*, coordination numbers of neighbors; ^b *R*, the bond distance; ^c σ^2 , the Debye-Waller factor; ^d is from the reference⁹

Sample	Shell	CN ^a	<i>R</i> (Å) ^b	$\sigma^2(m \AA^2)$ c
Sr ²⁺ (aq)	Sr-O	9.5 (3)	2.64(5)	0.007
GOs-Sr-0.1mM	Sr-O	9.0 (6)	2.59 (3)	0.004
GOs-Sr-0.5mM	Sr-O	8.9 (5)	2.62 (7)	0.008
GOs-(U+Sr)-0.1mM	Sr-O	8.5 (6)	2.56 (7)	0.006
	Sr-C	3.8 (9)	3.41 (4)	0.01
GOs-(U+Sr)-0.5mM	Sr-O	8.7 (5)	2.61 (7)	0.007

Table S3 EXAFS results of reference sample and Sr(II) sorption samples at K-Edge, $T = 303 \pm 1$ K. I = 0.001 mol/L NaClO₄.

DFT calculation. Based on the experimental condition and results, the deprotonated GO modified by a hydroxyl group on the surface (see Figure S8) was used to simulate the structures and evaluate the binding ability. U(VI) ion prefers five-coordination $[(UO_2)(H_2O)_5]^{2+}$, whereas Sr(II) ion easily forms nine-coordination $[Sr(H_2O)_9]^{2+}$ in the aqueous phase, so we selected the two complexes $[(UO_2)(H_2O)_5]^{2+}$ and $[Sr(H_2O)_9]^{2+}$ as the reactants, respectively, as provided in Figure S8. All structures were optimized using the hybrid exchange-correlation function B3LYPmethod.¹⁰⁻¹¹ The quasi-relativistic small-core pseudo-potential ECP60MWB and associated ECP60MWB valence basis sets were used to describe for U atom.¹² The small-core pseudo-potential ECP28MWB and associated ECP28MWB valence basis sets were applied for Sr atom, 13 and the 6-31G(d) basis set was used for the other light atoms H, C and O. To model the experimental condition, solvation model based on density (SMD model)¹⁴ were performed to take into solvent effect in the aqueous phase (water, $\varepsilon = 78.3553$). Moreover, the inner and outer coordination geometries of the U(VI) and Sr(II) complexes were performed at the B3LYP/6-31G(d) level of theory, respectively. The Gibbs free energies, including the thermal contribution were obtained at the same level of theory. All calculations were carried out with the Gaussian 09 program.¹⁵



Figure S8 The model of GO, structures and bond distances (Å) of $[(UO_2)(H_2O)_5]^{2+}$



Figure S9 Optimized structures (bond distances (Å) and binding energy (BE,

kcal/mol)) of the GOs-U(VI) complexes; four outer coordination complexes: ex-

 $UO_2(H_2O)_5/GO-1$, ex- $UO_2(H_2O)_5/GO-2$, ex- $UO_2(H_2O)_5/GO-3$ and ex- $UO_2(H_2O)_5/GO-3$ and ex- $UO_2(H_2O)_5/GO-4$; two inner coordination complexes: in- $UO_2(H_2O)_4/GO-1$ and in- $UO_2(H_2O)_4/GO-2$; H, C, O and U atoms are represented by white, green, red and pink spheres, respectively.



Figure S10 Optimized structures (bond distances (Å) and binding energy (BE, kcal/mol)) of the GO-Sr(II) complexes; five outer coordination complexes: ex-Sr(H₂O)₉/GO-1, ex-Sr(H₂O)₉/GO-2, ex-Sr(H₂O)₉/GO-3, ex-Sr(H₂O)₉/GO-4 and ex-Sr(H₂O)₉/GO-5; one inner coordination complex: in-Sr(H₂O)₉/GO-1; H, C, O and Sr atoms are represented by white, green, red and brown spheres, respectively.



Figure S11. The total DOS of (A) inner coordination complexes $(in-UO_2(H_2O)_4/GO, in-Sr(H_2O)_9/GO)$ and (B) outer coordination complexes $(ex-UO_2(H_2O)_5/GO, ex-Sr(H_2O)_9/GO)$.

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