A facile method for preparing three‑dimensional graphene nanoribbons aerogel for uranium(VI) and thorium(IV) adsorption

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Abstract

An three-dimensional (3D) porous structure graphene oxide nanoribbons (GONRs) aerogel has been prepared via hydrothermal method to overcome the challenges of solid–liquid separation for powdered carbon-based nanomaterials. GONRs aerogel showed low density, good mechanical strength and easy separation from water. Uranium(VI) and thorium(IV) adsorption by GONRs aerogel was investigated by batch experiments, demonstrating their strongly pH-dependent, spontaneous and endothermic adsorption processes. GONRs aerogel exhibited the maximum U(VI)- and Th(IV)-uptake capacity (430.6 and 380.4 mg g⁻¹, respectively) due to its large specific area (597.4 m² g⁻¹) and abundant oxygen-containing groups. This work suggests that GONRs aerogel has great potential for treatment of uranium and thorium-containing effluents.

Keywords Adsorption \cdot U(VI) \cdot Th(IV) \cdot Three dimension \cdot Graphene nanoribbons aerogel

Introduction

Uranium and thorium are important nuclear fuel and often used to generate electricity. However, uranium and thorium are dangerous in terms of radioactivity and chemical toxicity, which may cause the negative effect on living organism upon entry into living body [[1](#page-8-0)]. The nuclear fuel cycles including the front-end and back-end are main sources of uranium and thorium-containing wastewater [\[2](#page-8-1)]. Therefore, it is indispensable to treat uranium and thorium from the contaminated sites for environmental conservation, human well-being and nuclear energy sustainability. Currently, there are several conventional methods for treating uranium and thorium in wastewater, such as ion exchange, solvent extraction, electrochemical, membrane separation and adsorption [\[3](#page-8-2)]. Among of above methods, adsorption has been widely used for the treatment of uranium and thorium in wastewater owing to its economy and universality [[4,](#page-8-3) [5\]](#page-8-4). Up to now, various adsorbents for uranium and thorium adsorption have

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² School of Nuclear Science and Engineering, East China University of Technology, Nanchang 330013, Jiangxi, China been reported, such as clay minerals [[6\]](#page-8-5), silica materials [\[7](#page-8-6)], polymers [\[8](#page-8-7)], carbon family materials [[9,](#page-8-8) [10\]](#page-8-9)and biological adsorbents [\[11](#page-8-10)].

Carbon family materials, especially carbon-based nanomaterials such as carbon nanotubes (CNTs) and graphene, are being employed for uranium and thorium uptake because of their good radiation resistance, excellent mechanical and thermal stability. In recent years, graphene nanoribbons (GNRs), a novel quasi-one-dimensional carbon-based nanomaterials, have attracted much attention. GNRs are strips of graphene with nanometer widths and possess many excellent properties that are diferent from other carbon-based nanomaterials [\[12\]](#page-8-11). Compared to the common graphene, GNRs have excellent fexibility and adjustability, are more suitable materials for structural purposes, which have been extensively employed in numerous research felds like sensing, catalysis, electrochemistry and adsorption [[13,](#page-8-12) [14\]](#page-8-13). Our group has long been interested in developing GNRs-based adsorbents and reported on the frst application of graphene oxide nanoribbons (GONRs) for wastewater treatment [[15,](#page-8-14) [16](#page-8-15)]. Especially, several GONRs and their composites were prepared in our laboratory for the capture of Th(IV) [[17–](#page-8-16)[19](#page-8-17)]. However, due to the difficulty of solid–liquid separation after adsorption and the risk of possible secondary pollution to the environment, these powdered carbon-based nanomaterials are still limited in practical applications. In order to compensate for the above drawbacks, magnetic separation

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technology is widely used to realize rapid and efective separation for magnetic particles. Recently, interests in magnetic carbon-based nanomaterials have exploded and their signifcant potentials have been demonstrated for the treatment of radioactive wastewater [\[20](#page-8-18), [21\]](#page-8-19). Unfortunately, the most signifcant shortcoming of magnetic carbon-based nanomaterials is instability in air, acids or bases, thus degrading their performance [\[22](#page-8-20)].Therefore, it is of crucial importance to explore new type of carbon-based nanomaterials composites with easy separation of solid–liquid and strong acid–alkali resistance.

Three-dimensional (3D) carbon-based nanomaterials have porous network structure, large specifc surface area and good mechanical stability, which makes it promising as one of the most popular adsorption materials in the future [[23–](#page-8-21)[25\]](#page-8-22). Carbon nanomaterials aerogels, especially graphene aerogels, have been demonstrated numerous applications in radioactive wastewater felds [\[26](#page-8-23), [27](#page-8-24)].For example, He et al. [\[28\]](#page-8-25). synthesized 3D porous network graphene oxide (GO) hydrogels with good mechanical stability for U(VI) adsorption, and found that the maximum adsorption capacity at pH 4.0 could reach 134.23 mg·g⁻¹. Zhao et al. [[26\]](#page-8-23). prepared an ultra-light graphene aerogel (GA) by a simple hydrothermal method, and the GA had a high adsorption capacity for U(VI) (238.67 mg·g⁻¹at pH 4.0). Moreover, in order to further improve selectivity, self-assembled $CA-PO₄$ was fabricated for U(VI) adsorption and revealed high selectivity of 66.8% at pH 5.5. Up to now, most carbon nanomaterials aerogels as adsorbents were prepared using CNTs and graphene as matrix materials, but little research focused on assembling GNRs into aerogels for radionuclides adsorption. In fact, 3D porous GNRs aerogel has been widely applied in the feld of material science, environment and energy due to their superior physical and chemical characteristics [\[29,](#page-9-0) [30\]](#page-9-1).

Herein, we have synthesized 3D porous GONRs aerogel derived from unzipping of CNTs by a simple hydrothermal method for U(VI) and Th(IV) adsorption. Various techniques were employed to characterize the physical and chemical properties of GONRs aerogel. Adsorption isotherms, kinetics and thermodynamics of U(VI) and Th(IV) on GONRs aerogel were comprehensively evaluated by batch experiments.

Experimental

Materials

The raw material of CNTs was purchased from China XFNano Material Technology Company. All the analyticalgrade reagents used in this experiment, such as hydrogen peroxide (H_2O_2) , nitric acid (HNO_3) , potassium permanganate ($KMnO₄$), sodium hydroxide (NaOH), sulfuric acid $(H₂SO₄)$ and ethanol, were procured from Sinopharm Chemical Regent Co., Ltd. (China).

Synthesis of GONRs aerogel

The synthetic procedure of GONRs was referenced by previous work [[16](#page-8-15)]. The fabrication process of GONRs aerogel by hydrothermal method has been put into efect in our laboratory as described in the following steps (Scheme [1](#page-1-0)). Typically, 0.25 g of the above GONRs was weighed and dispersed through sonication into 15 mL of deionized water. Then the obtained homogeneous solution was transferred into the sealed tefon-lined stainless steel vessel (20 mL) and heated at 180 °C for 24 h. After the reaction kettle was cooled to room temperature, the black and cylindrical solid was taken out and cleaned repeatedly with ethanol and deionized water to prepare GONRs hydrogel. Subsequently, the as-prepared hydrogel was frozen at −20 °C and completely lyophilized at −55 °C for 24 h to obtain a black and cylindrical GONRs aerogel (GONRs-A). The resultant aerogel with a density of 6.2 mg⋅cm⁻³ could stand stably on top of a bristlegrass without breaking it, demonstrating its ultralight property [[31,](#page-9-2) [32\]](#page-9-3).The cylindrical GONRs aerogel could support several coins and bear more than 1000 times of itself own weight without deforming, further proving its good mechanical strength.

Scheme 1 Schematic illustration of the fabrication of GONRs aerogel and its resultant properties

Characterization

X-ray power difractions (XRD) patterns were measured on a D8 advance difractometer with Cu Kα radiation. A Hitachi S-4800 scanning electron microscope (SEM) was applied to obtain the morphological images. Thermal behavior was conducted on a Q50 model thermogravimetric analyzer (TGA) by heating each sample from 20 to 800 °C under nitrogen atmosphere. PerkinElmer 100 spectrometer was used to obtain The Brunauer–Emmett–Teller (BET) surface area was determined by a Micromeritics Tristar instrument. Fourier transformed infrared (FT-IR) spectra were acquired using PerkinElmer 100 spectrometer. X-ray photoelectron spectroscopy (XPS, Thermofsher Escalab 250Xi) was used to identify the chemical composition of samples. The Zeta potential values were determined by a Particle Metrix fowing current potential analyzer (Microtrac, America).

Batch adsorption experiments

Typically, GONRs aerogel (10 mg) was weighted into 50 mL of U(VI) or Th(IV) solution with a given concentration and pH . Negligible $HNO₃$ and NaOH were dropwise added to adjust the pH of solution. The mixture was kept agitating for indicated periods in a thermostatic oscillator at a certain temperature. Thereafter, the supernate was directly taken out and the concentrations of U(VI) and Th(IV) were detected by Optima 8000 model ICP-OES. Detailed description of the adsorption capacity q_e (mg g⁻¹) can be found in our previous work [\[19](#page-8-17)].

Results and discussion

Characterizations

Figure [1a](#page-2-0)–c exhibited morphological structures of CNTs, GONRs and GONRs aerogel by SEM. The original CNTs with hollow structure were curved and entangled (Fig. [1a](#page-2-0)), whose diameters and lengths were 10–50 nm and about a few micrometer, respectively. GONRs preserved the one-dimensional nanostructure of CNTs with widths of 30–100 nm and length extending to a few micrometer range (Fig. [1](#page-2-0)b). GONRs aerogel was assembled into 3D porous and interconnected network by randomly interleaved GONRs based on partially overlapping π - π interactions (Fig. [1c](#page-2-0)), forming micro- and nanoscale combined hierarchical structure [\[29](#page-9-0)].

To further investigate the structural evolution, XRD of GONRs and GONRs aerogel were performed with the results shown in Fig. [2](#page-3-0)a. GONRs exhibited a strong diffraction peak at $2\theta = 10.0^{\circ}$, specifying the (001) refection plane and d-spacing of 8.6 Å, of typical graphene oxide [[33\]](#page-9-4). For GONRs aerogel, the (001) peak disappeared and another dominate difraction peak at 26.0° (d-spacing of 3.46 Å) could be observed. The interplanar spacing signifcantly decreased, indicating the formation of the network of GONRs aerogel by π - π interaction [\[34](#page-9-5)].

The changes of functional groups in GONRs and GONRs aerogel were analyzed by FT-IR and the results are shown in Fig. [2](#page-3-0)b. Both GONRs and GONRs aerogel exhibited eight characteristic bands: the band at 3440 cm−1 belonged to the -OH vibrations; the C-H bonds were visible at 2920 cm^{-1} and 2850 cm⁻¹; the band at 1580 cm⁻¹ may be related to graphite structure of CNTs; the band at 1384 cm−1 was associated with the disordered structure of carbon nanomaterials [[35\]](#page-9-6); three peaks at 1050 cm⁻¹, 1220 cm⁻¹ and 1714 cm⁻¹ were corresponded to the C–O–C, C–O and C=O stretching vibrations [[36\]](#page-9-7), respectively, refecting the abundance of oxygen-containing groups on two adsorbents. Compared to GONRs, the peak intensities of GONRs aerogel at 1714 cm^{-1} and 1050 cm^{-1} improved tremendously, which implies more oxygen-containing groups formed in GONRs aerogel.

Figure [2c](#page-3-0) showed the TGA curves of GONRs and GONRs aerogel. The TGA curves of two samples consisted of three main stages. In the frst stage, a slow mass loss below 150 °C could be ascribed to water dehydration. The second stage was from 150 to 500 °C, the prominent mass losses were present for the oxygen-containing groups decomposition [[37\]](#page-9-8), at which GONRs and GONRs aerogel presented the

Fig. 1 SEM images of CNTs (**a**), GONRs (**b**) and GONRs aerogel (**c**)

Fig. 2 a XRD patterns, **b** FT-IR, **c** TG curves and **d** N_2 sorption isotherms of GONRs and GONRs aerogel

mass losses of approximately 17.6% and 28.8%, respectively. This indicated that GONRs aerogel possessed more abundant oxygen-containing groups than GONRs, which was consistent to FT-IR results. Up to 500 °C, the weight loss tended to become relatively slow, which was attributed to the burning of carbon atoms. The TGA curve of GONRs aerogel revealed a signifcant amount of the oxygen-containing groups and good thermal stability.

Figure [2d](#page-3-0) presented $N₂$ adsorption–desorption isotherms of two samples. The calculated BET specifc surface areas of the as-synthesized GONRs and GONRs aerogel were 83.8 and 597.4 m^2 g^{-1} , respectively. After hydrothermal treatment, the BET specifc surface area increased signifcantly due to the formation of 3D porous network [[26](#page-8-23), [28](#page-8-25)]. Based on BJH method, the average pore diameter of GONRs aerogel was calculated to be 34.4 nm, which confrmed the mesoporous structure, thus facilitating the adsorption process.

As illustrated in Fig. [3a](#page-4-0), two peaks centering at 284.6 eV $(C 1 s)$ and 532.5 eV $(O 1 s)$ were found in the XPS survey

spectra of two adsorbents [\[37](#page-9-8)], confrming the presence of oxygen-containing groups. The high-resolution C 1 s spectra in Fig. [3](#page-4-0)b showed fve peaks at 284.1, 285.1, 286.4 eV, 287.2 and 288.8 eV, respectively, which could be assigned to the sp²-hybridized graphite-like carbon atoms $(C=C)$, the $sp³$ -hybridized carbon atoms (C–C), hydroxyl groups $(-C-OH)$, carbonyl groups $(C=O)$ and carboxyl groups (–COO–). Moreover, It can be seen that GONRs aerogel had more oxygen-containing functional groups than GONRs aerogel. Together with previous FT-IR results, XPS analyses indicated that oxygen-containing functional groups were dramatically introduced during hydrothermal treatment.

Efect of initial solution pH

The influences of solution pH on $U(VI)$ and $Th(IV)$ removal by aerogel were shown in Fig. [4](#page-4-1)a. In this study, the pH was kept lower than 4.5 to prevent the hydrolysis of uranyl and thorium ions [[38\]](#page-9-9).The adsorption capacity of U(VI) and Th(IV) by GONRs aerogel increased

Fig. 3 a XPS survey spectra and **b** High resolution spectra of C 1 s for GONRs and GONRs aerogel

Fig. 4 a Effect of pH on U(VI) and Th(IV) adsorption by GONRs aerogel ($C_0 = 60$ mg·L^{−1} for U(VI) and 30 mg·L^{−1} for Th(IV), $w = 10$ mg *t*=240 min, *T*=298 K and *V*=50 mL). **b** Zeta potential value of GONRs aerogel with variation of pH

with the increasement of pH. At lower pH value, the active sites were taken up by more H^+ or H_3O^+ , consequently declining the adsorption capacity of UO_2^{2+} or $Th⁴⁺$ by GONRs aerogel due to the competition effect. As pH increased, U(VI) and Th(IV) gradually transformed into hydrated species, thereby favoring the adsorption of U(VI) and Th(IV) by GONRs aerogel. Moreover, the surface charges of aerogel can affect the adsorption of U(VI) and Th(IV), and the point of zero charge of GONRs aerogel was tested to be 3.6 (Fig. [4](#page-4-1)b). GONRs aerogel had a negative zeta potential value when $pH > 3.6$, thus promoting the binding of uranyl and thorium ions with negative charges [[38\]](#page-9-9).

Adsorption kinetics

Figure [5](#page-5-0)a presented the relationship of U(VI) and Th(IV) adsorption capacities changing with contact time. Clearly, the adsorption rates of $U(VI)$ and $Th(IV)$ by GONRs aerogel were quite rapid in the first 10 min, and then gradually slowed down before reaching equilibrium within 60 min. The kinetic data were correlated with three kinetic model [[2,](#page-8-1) [27\]](#page-8-24), i.e. the pseudo-first order model, pseudo-second order model and the intra-particle diffusion model, to describe the kinetic characteristics of U(VI) and Th(IV) on GONRs aerogel. The corresponding fitting parameters were given in Table [1.](#page-5-1) The adsorption of GONRs aerogel

Fig. 5 **a** Effect of contact time on U(VI) and Th(IV) adsorption by GONRs aerogel and adsorption kinetic plots of pseudo-frst-order and pseudo-second-order models (pH=4.5 and C_0 =60 mg·L⁻¹ for U(VI),

pH=3.0 and C_0 =30 mg·L⁻¹ for Th(IV), $w=10$ mg, $t=240$ min, $T=298$ K, and $V=50$ mL). **b** the fitting plots of intra-particle diffusion model

175

150

125

100

 \mathbf{I} **Th** ▲

```
a_{k_1} in min<sup>-1</sup>;
{}^{b}k_{2} in g·mg<sup>-1</sup>·min<sup>-1</sup>;
{}^{\text{c}}k_{\text{int}} in mg·g<sup>-1</sup>·min<sup>-0.5</sup>
```
for two actinides was portrayed better by pseudo-secondorder with a higher correlation coefficient (Fig. [5a](#page-5-0)). The computed adsorption capacities (167.3 and 67.7 mg g^{-1} for U(VI) and Th(IV)) from pseudo-second-order model were also much closer to the experimental values (53.5 and 64.5 mg g^{-1} for U(VI) and Th(IV)). These results suggest that the rate-controlling step of U(VI) and Th(IV) on GONRs aerogel may be chemisorption [\[27\]](#page-8-24).

Moreover, the simulation of intra-particle diffusion (Fig. [5](#page-5-0)b) showed three divided linear segments and the intra-particle diffusion rate constants accorded with the order of $k_{\text{int1}} > k_{\text{int2}} > k_{\text{int3}}$. A rapid uptake occurred at the first stage because of the binding of $U(VI)$ and $Th(IV)$ by the outer chemical sites, then the uptake rate became slower at the second stage with the entry of ions into GONRs aerogel, and finally the adsorption reached saturation at the third stage. Hence, it could be concluded that not only chemical reaction but also mass transport jointly contributed to the adsorption of U(VI) and Th(IV) by GONRs aerogel.

Adsorption isotherms

Figure [6a](#page-6-0) exhibited the effect of changing metal ions concentrations on U(VI) and Th(IV) adsorption by GONRs aerogel. Obviously, as the initial concentrations of U(VI) and Th(IV) increased, the adsorption capacity of U(VI) and Th(IV) by GONRs aerogel progressively increased, finally the saturation was attained under higher concentration. To further clarify the adsorption behavior, the adsorption isotherms were investigated based on Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models [[3](#page-8-2)]. The fitting curves of these models were shown in Fig. [6](#page-6-0) and the calculated data of different isotherm models were listed in Table [2](#page-6-1). It was noted that the isotherms were more suitable for Langmuir isotherm model with a higher correlation coefficient, demonstrating that a monolayer coverage was formed on solid–liquid interface [[38](#page-9-9)]. Also, The q_m of U(VI) and Th(IV) by GONRs aerogel from Langmuir model were computed to be 430.6 and 380.4 mg g^{-1} , respectively. Moreover, the experimental

results were also in good agreement with the D-R isotherm model (Fig. [6](#page-6-0)b). The value of mean free energy (E_{DR}) can be related to the aosorption mechanism [\[39](#page-9-10)]. The calculated E_{DR} values of U(VI) and Th(IV) adsorption on GONRs aerogel were 9.068 and 8.562 kJ mol⁻¹, respectively, demonstrating a chemisorption mechanism.

Adsorption thermodynamics

The relationship of U(VI) and Th(IV) adsorption capacities changing with temperature on was presented in Fig. [7](#page-6-2)a. The increases of adsorption capacities for U(VI) and Th(IV) were observed as temperature raised, suggesting that high temperature promoted the adsorption processes. To learn more about the adsorption thermodynamics, three crucial

Fig. 6 **a** Effect of the initial uranium and thorium concentration on adsorption by GONRs aerogel, and adsorption isothermal plots of Langmuir and Freundlich models (pH=4.5 for U(VI) and 3.0 for Th(IV), $w=10$ mg, $t=240$ min, $T=298$ K and $V=50$ mL). **b**

Best-ft plots of D-R model for U(VI) and Th(IV) adsorption on GONRs aerogel ($pH=4.5$ for U(VI) and 3.0 for Th(IV), $w=10$ mg, *t*=240 min, *T*=298 K, and *V*=50 mL)

600 65

Table 2 Isotherm parameters for adsorption of U(VI) and Th(IV) on GONRs aerogel

	Langmuir isotherm ^a			Freundlich isotherm ^b			$D-R$ isotherm ^c			
	K_{I}	$q_{\rm m}$	R^2	$K_{\scriptscriptstyle{\rm E}}$	\boldsymbol{n}	R^2	q_{DR}	β \times 10 ⁻³	$E_{\rm DR}$	\mathbb{R}^2
U(VI)	0.022	441.7	0.980	39.627	2.615	0.879	1.327	6.08	9.068	0.920
Th(IV)	0.020	380.4	0.963	25.573	2.024	0.886	1.571	6.82	8.562	0.899

^a K_L in L·mg⁻¹, q_m in mg·g⁻¹;

 b K_F in mg·g⁻¹, *n* in (L·mg⁻¹)^{1/n};

^c q_{DR} in mmol•g⁻¹; $\beta \times 10^{-3}$ in mol²⋅kJ⁻²; E_{DR} in kJ²⋅mol⁻²

Fig. 7 **a** Effect of temperature on U(VI) and Th(IV) adsorption by GONRs aerogel (pH=4.5 and C_0 =60 mg·L⁻¹ for U(VI), pH=3.0 and C_0 =30 mg·L⁻¹ for Th(IV), w =10 mg, t =240 min, T =298 K,

and $V=50$ mL). **b** Linear relationship between $\ln K_d$ and $1/T$ for U(VI) and Th(IV) adsorption on GONRs aerogel

thermodynamics parameters containing Δ*H*, Δ*S* and Δ*G*, were analyzed by Eqs. [1–](#page-7-0)[2.](#page-7-1)

$$
\ln K_d = \frac{\Delta s^{\circ}}{R} - \frac{\Delta H^{\circ}}{\text{RT}} \tag{1}
$$

$$
\Delta G^{\circ} = \Delta H^{\circ} - T\Delta s^{\circ} \tag{2}
$$

The values of Δ*H* and Δ*S* were obtained from the slope and intercept of the linear relationship of $\ln K_d$ versus T^{-1} (Fig. [7](#page-6-2)b). The corresponding values of Δ*G* were presented in Table [3.](#page-7-2) The calculated parameters for Δ*H* and Δ*S* were positive, indicative of the endothermic adsorption processes and the increasing randomness with the rise of temperature. Moreover, Δ*G* was calculated to be negative, revealing that U(VI) and Th(IV) adsorption by GONRs aerogel were thermodynamically feasible and spontaneous.

Comparison of adsorption capacity

Undoubtedly, adsorption capacity is a crucial parameter for adsorbents. Therefore, the maximum adsorption capacities of U(VI) and Th(IV) on various carbon nanomaterials-based adsorbents were compared to further evaluate the adsorption performance of GONRs aerogel, as shown in Table [4](#page-7-3). Obviously, the U(VI) and Th(IV) adsorption capacity of GONRs aerogel outperformed all other previously reported pristine CNTs and graphene-based adsorbents. However, comparing the adsorption capacities of other functionalized carbon nanomaterials, the unfunctionalized GONRs aerogel exhibited the lower adsorption capacity. Even so, GONRs aerogel still has some noteworthy advantages over the other carbon nanomaterials-based adsorbents, such as 3D porous architecture, large specifc surface area, good durability and easy solid–liquid separation, which makes it very promising for U(VI) and Th(IV) adsorption.

Conclusions

In conclusion, 3D porous network structure GONRs aerogel was successfully assembled for uranium(VI) and thorium(IV) adsorption. The obtained aerogel with low density, good mechanical strength and large specifc surface area exhibited good adsorption performance, and the maximum U(VI)- and Th(IV)- capacity of GONRs aerogel for U(VI) and Th(IV) was 430.6 and 380.4 mg g^{-1} , respectively, much more than most of the reported carbon nanomaterials. Chemisorption played a crucial role in U(VI) and Th(IV) adsorption on abundant oxygen-containing groups GONRs aerogel. The characteristics of easy separation from water and outstanding adsorption efficiency make GONRs aerogel attractive for U(VI) and Th(IV) capture.

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