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Electronic Supporting Information

Highly Efficient Uranium Adsorption by Salicylaldoxime/Polydopamine Graphene Oxide Nanocomposites

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1. Supplementary Figures

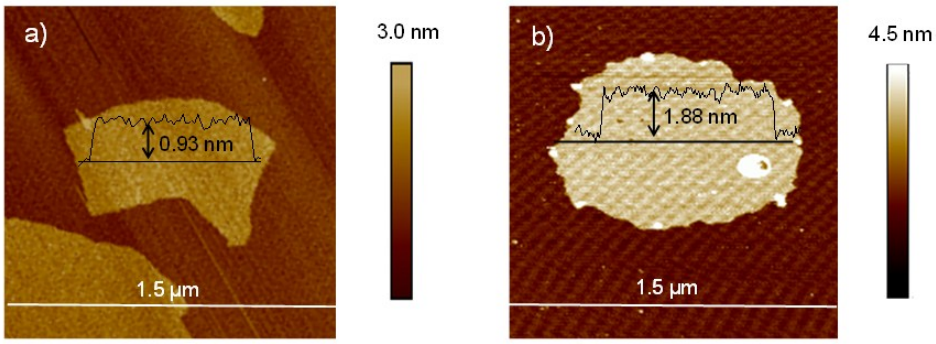

Fig. S1 AFM images showing the thickness of the GO (a) and RGO-PDA/oxime (b).

AFM analyses (Fig. 3c) showed that the RGO-PDA/oxime had a relatively smooth surface, which further demonstrated that the DA and oxime were deposited uniformly on the GO surface. Moreover, after the deposition, the samples still maintained a thin layer with an average thickness of 1.88 nm (As a contrast, the average thickness of the GO was 0.93 nm, as shown in Fig. S1a).

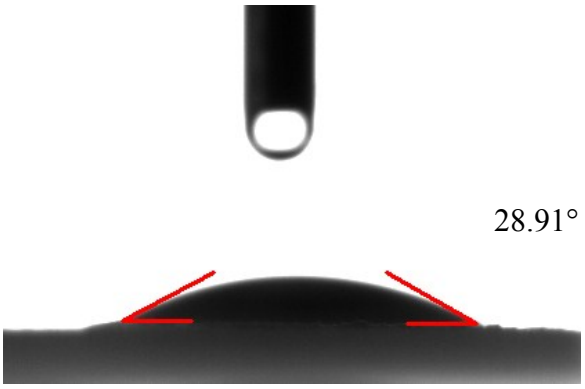

Fig. S2 Contact angle image of the RGO-PDA/oxime.

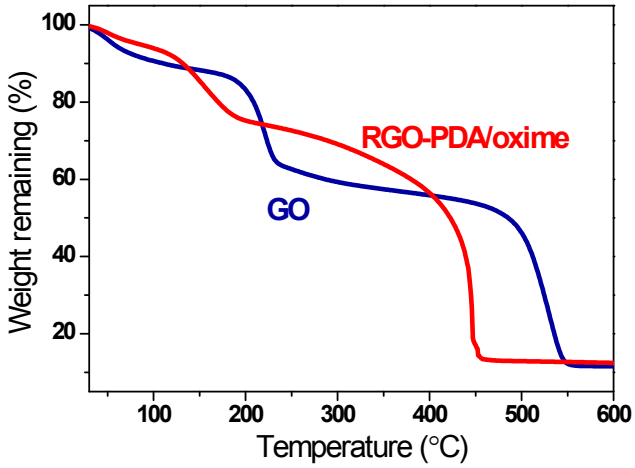

Fig. S3 TGA curves for GO, RGO-PDA/oxime at a heating rate of 10 °C/min in air.

Thermogravimetric analysis (TGA) was performed to quantify the PDA/oxime content in the RGO-PDA/oxime composites. As shown in Fig. S3, the TGA curve of GO indicated three major mass losses, the first two mass losses (before 240 °C) were because of pyrolysis of epoxide, carbonyl, hydroxyl, and phenyl groups in GO, the last one (after 450 °C) could be contributed to the decomposition of carbon lattice of GO.[1] Compared with that of GO, an additional mass loss between 200 and 400 °C appeared in the TGA curve of RGO-PDA/oxime; meanwhile, previous studies showed that the major mass losses of PDA and salicylaldoxime existed in this temperature range due to the thermal degradation of their main chains;[2, 3] to avoid the influence of GO, this mass loss was considered to be mainly caused by the decomposition of PDA and salicylaldoxime. Therefore, the content of PDA/oxime in the RGO-PDA/oxime composites was determined by its weight loss at 200 and 400 °C, which was about 20 wt%.

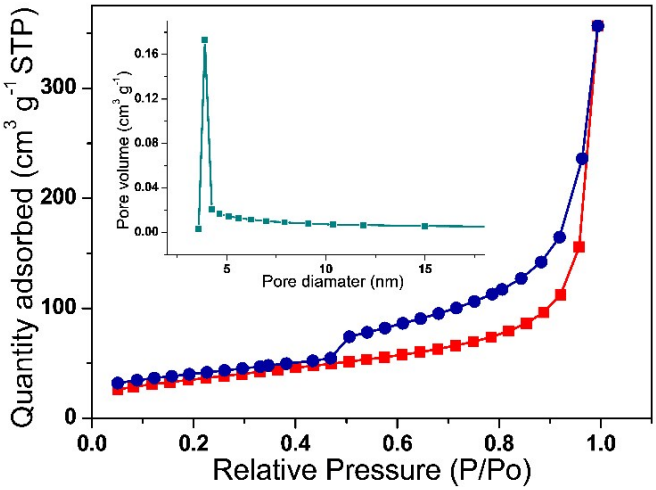

Fig. S4 Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of the RGO-PDA/oxime.

Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to determine the specific surface area and intra porosity. As shown in Fig. S4, the results indicated that the surface area and pore volume of the RGO-PDA/oxime composites were 127.28 cm^2 g^{-1} and 0.56 cm^3 g^{-1}, respectively; moreover, the curves showed typical IV isotherms with an H3-type hysteresis loop (P/P_0 > 0.4), demonstrating the existence of mesopores in sample. The inset revealed that the pore size distribution of RGO-PDA/oxime was about 3.90 nm. The higher specific surface area and the presence of multiple pores of RGO-PDA/oxime would promote the uranium adsorption.

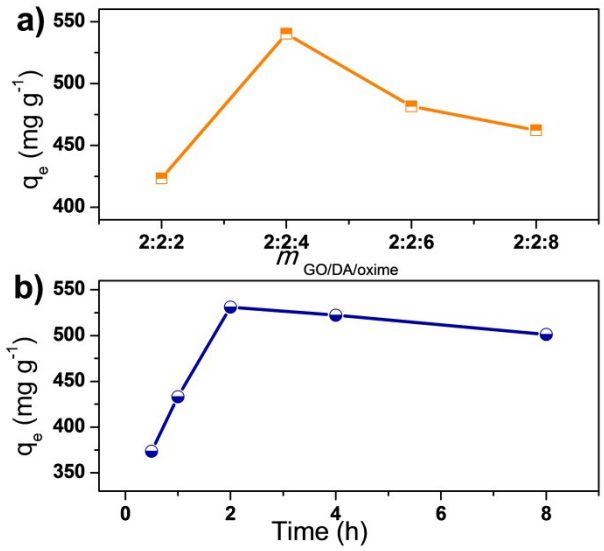

Fig. S5 Adsorption capability of the RGO-PDA/oxime prepared by different additional amounts of oxime (a) and different DA polymerization times (b).

Salicylaldoxime was immobilized onto the GO surface via the self-polymerization of DA to coordinate UO_2^{2+} by the =N–O- groups. Here, DA and oxime played key roles (surface modification and uranium adsorption, respectively) on the adsorption performance of the RGO-PDA/oxime. Meanwhile, it is reported that the polymerization degree and functional group contents of polydopamine (PDA) can be controlled conveniently by the polymerization time.[4,5] Thus, in the optimization experiment, the effects of addition amount of oxime and polymerization time of DA on the performance of the prepared RGO-PDA/oxime were evaluated, respectively.

To evaluate the effects of the addition amount of oxime on the performance of the fabricated adsorbent, we maintained the mass of GO and DA, and DA polymerization time (2 hours) constant, respectively, and set the addition amounts of oxime at 40 mg, 80 mg, 120 mg and 160 mg, i.e., the mass ratios of GO, DA and oxime ($m_{GO/DA/oxime}$) were 2:2:2, 2:2:4, 2:2:6 and 2:2:8, respectively. As shown in Fig. S5a, increasing the amount of oxime to some extent resulted in a marked increase in the adsorption capability of the prepared RGO-PDA/oxime. However, this increase was reversed when the addition amount of oxime was larger than 80 mg ($m_{GO/DA/oxime}$ was 2:2:4). These results indicated that 80 mg ($m_{GO/DA/oxime}$ was 2:2:4) was optimal in the synthesis of RGO-PDA/oxime for good absorption capability of the adsorbents. Too much oxime negatively affected the adsorption capability, presumably because the presence of a large amount of salicylaldoxime suppressed the aggregation of PDA on the GO surface, owing to the strong noncovalent interactions between the two in the bulk solution.

To evaluate the effects of DA polymerization time on the performance of the prepared absorbent, we maintained the addition amounts of GO, DA and oxime constant ($m_{GO/DA/oxime}$ was 2:2:4), and set the DA polymerization time at 0.5 h, 1 h, 2 h, 4 h and 8 h. The equilibrium absorption amount of the RGO-PDA/oxime prepared by these polymerization times was determined. As shown in Fig. S6b, the adsorption capability was increased significantly in the polymerization time from 0.5 h to 2 h. For a polymerization time of 2 h, an adsorption capability of 531 mg/g was observed. However, further increases in the polymerization time could not continue to promote the adsorption amount (even lowered the adsorption amount). There are some potential explanations for these results. On one hand, for the short polymerization time (0.5 h-2 h), the increased function contents in the polymerization time[5] resulted in more oxime molecules were immobilized on the GO surface, and achieved a better uranium adsorption capability. On the other hand, for the overlong polymerization time, the percentage of functional groups remained almost unchanged, and larger particles were deposited on the polymer surface owing to the polymerization of DA,[5, 6] resulting in a negative effect on the immobilization of oxime molecules, thus lowered the adsorption capability.

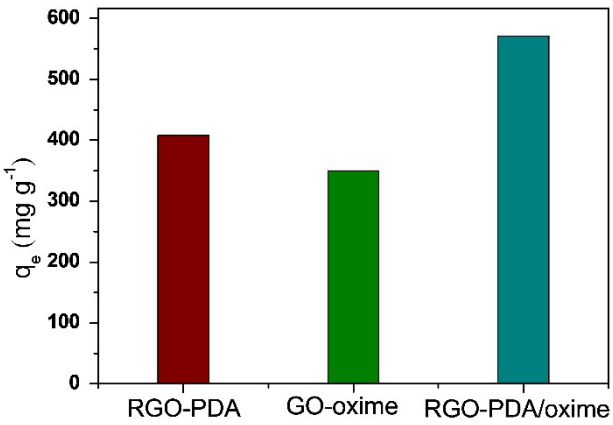

Fig. S6 The comparison of the adsorption amounts of the RGO-PDA, GO-oxime and RGO-PDA/oxime. The initial concentration of the uranium was 8 ppm.

In this work, we report a one-step process for the convenient and rapid synthesis of the RGO-PDA/oxime composites via the polymerization of dopamine and simultaneous deposition of oxime. Herein, PDA was used as a surface modification material to immobilize salicylaldoxime as much as possible on the sample surface via the electrostatic interaction, hydrogen bonding and π-π stacking; salicylaldoxime was used as a uranium adsorption molecule to chelate the UO^{2+} by its oxime groups (moreover, the oxime preferred to distribute on the upper surface of the samples due to the electrostatic repulsion between GO and salicylaldoxime). The synergy of surface modification of PDA with uranium adsorption of oxime molecules endowed the RGO-PDA/oxime with excellent uranium adsorption capability. In addition, the effects of the DA and oxime on the adsorption capability of the samples were evaluated, the results showed that the adsorption amount of the RGO-PDA/oxime (571 mg g^{-1}) was much higher than those (350 mg g^{-1} for GO-oxime; 408 mg g^{-1} for RGO-PDA) of the RGO-PDA and GO-oxime, respectively (as shown in Fig. S6).

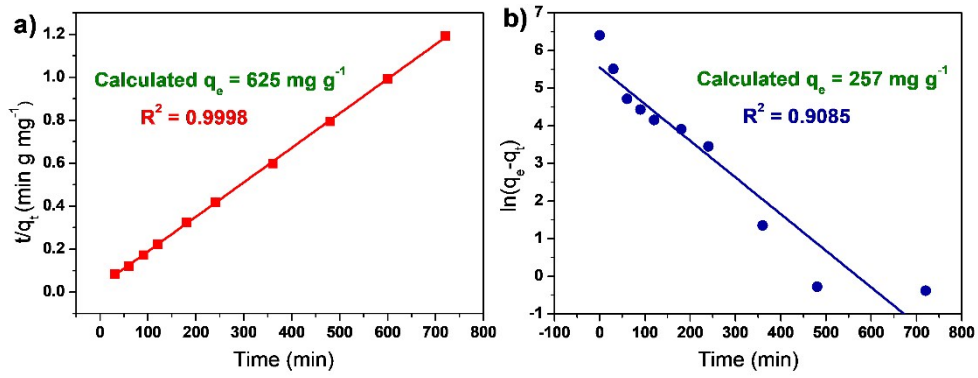

Fig. S7 Pseudo-second-order (a) and Pseudo-first-order (b) kinetics models of the uranium adsorption on the RGO-PDA/oxime surface.

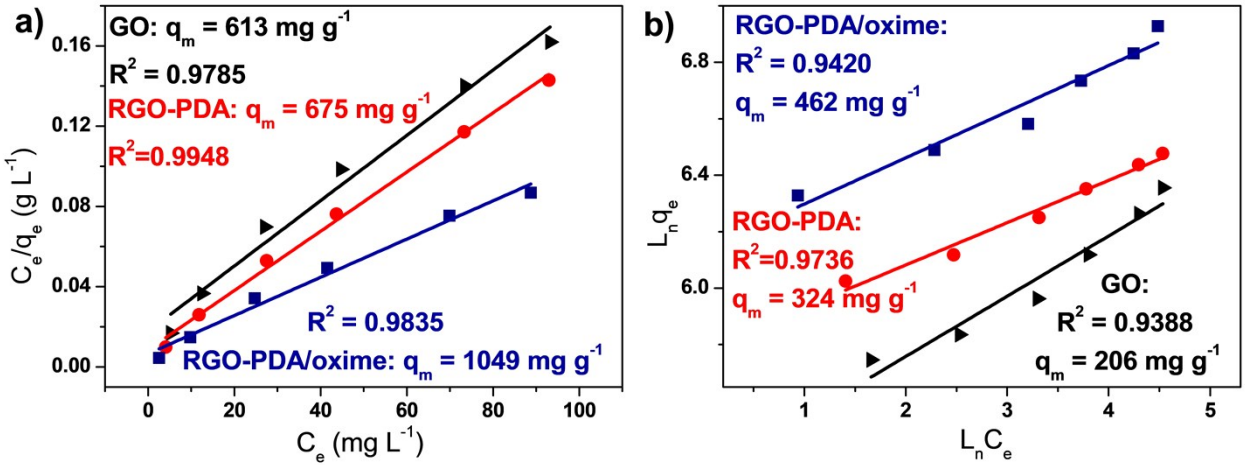

Fig. S8 Langmuir (a) and Freundlich (b) adsorption models for the RGO-PDA/oxime, RGO-PDA and GO, respectively.

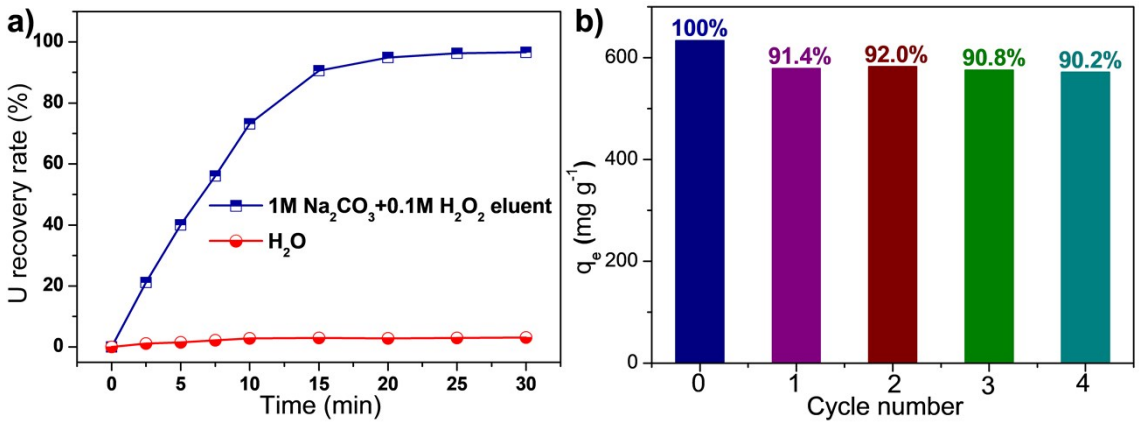

Fig. S9 (a) Rates of uranium elution from the RGO-PDA/oxime with 1M Na_2CO_3+0.1M H_2O_2, elution in H_2O was performed for comparison; (b) Recyclability of the RGO-PDA/oxime absorbent.

2. Supplementary Tables

Table S1. Kinetic parameters of uranium adsorbed on RGO-PDA/oxime.

Pseudo-first-order			Pseudo-second-order		
K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2(g (mg min)$^{-1}$)	q_e (mg g^{-1})	R^2
9.74E-03	257	0.9085	2.56E-06	625	0.9998

Table S2. Isotherm constants for uranium adsorption on RGO-PDA/oxime, RGO-PDA and GO respectively.

	Langmuir isotherm			Freundlich isotherm		
Samples	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1})	n	R^2
RGO-PDA/oxime	1049	0.1458	0.9835	462	0.1635	0.9420
RGO-PDA	675	0.1729	0.9948	324	0.1499	0.9736
GO	613	0.0920	0.9785	206	0.2134	0.9388

Notes and references

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