

## Supporting Information

### Graphene Oxide Covalently Functionalized with 5-Methyl-1,3,4-thiadiazol-2-amine for pH-Sensitive Ga<sup>3+</sup> Recovery in Aqueous Solutions

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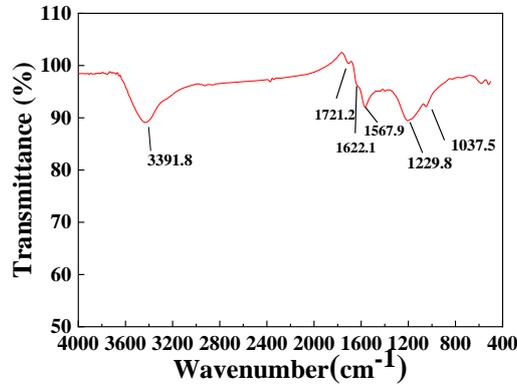
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#### 1. Reagents and materials

Potassium permanganate (KMnO<sub>4</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 85 wt.%) were bought from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China); Hydrochloric acid (HCl, 37 wt.%), sodium hydroxide (NaOH; AR, 97 wt.%), and concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 wt.%) were purchased from Chengdu Cologne Chemical Co. Ltd. (Chengdu, China); Flake graphite (80-90.5 wt.%) was supplied by Qingdao Braide Graphite Co., Ltd (Qingdao, China); 5-methyl-1,3,4-thiadiazol-2-amine (MTA, C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>S, 99 wt.%) , acetic acid (CH<sub>3</sub>COOH, 99.5 wt.%) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China); Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30.0 wt.%) was bought from Shanghai Wokai Biotechnology Co., Ltd. (Shanghai, China); Indium(III) chloride (InCl<sub>3</sub>, 99.99%), scandium(III) nitrate hydrate (Sc(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O; 99.9 wt.%) and gallium(III) nitrate hydrate (Ga(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O; 99.99 wt.%) were bought from Shanghai Run-Biotech Co., Ltd. (Shanghai, China); All chemicals were of analytical grade and used without further purification. Ultrapure water with a resistivity of 18.2 MΩ cm<sup>-1</sup> was produced from a Millipore Milli-Q water purification system (Millipore Trading Co., Ltd.; Shanghai, China).

## 2. FT-IR spectra of GO

As shown in **Figure S1**, the peaks at 3391.8 and 1721.2  $\text{cm}^{-1}$  can be attributed to the stretching vibrations of the hydroxyl ( $-\text{OH}$ ) and  $\text{C}=\text{O}$  groups of GO, respectively. In addition, the peak at 1622.1  $\text{cm}^{-1}$  can be assigned to the  $\text{C}=\text{O}$  stretching vibrations of carboxyl groups, and the peak at 1567.9 corresponds to the aromatic skeletal vibrations, while the peaks at 1229.8 and 1037.5  $\text{cm}^{-1}$  belong to the  $\text{C}-\text{O}$  and  $\text{C}-\text{C}$  stretching vibrations, respectively.



**Figure S1** FT-IR spectra of GO.

## 3. Adsorption kinetic models

The linear pseudo-first-order rate and the linear pseudo-second-order rate equation are used to simulate the adsorption kinetics (**Equations (S1) and (S2)**):

$$\text{Linear pseudo-first-order model: } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (\text{S1})$$

$$\text{Nonlinear pseudo-first-order model: } q_t = q_e (1 - e^{-k_1 t}) \quad (\text{S2})$$

$$\text{Linear pseudo-second-order model: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{S3})$$

$$\text{Nonlinear pseudo-second-order model: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (\text{S4})$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the amounts of  $\text{Ga}^{3+}$  adsorbed by GO-MTA

composite at equilibrium state and at contact time  $t$  (min), respectively;  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) are the specific adsorption rate constant of the pseudo-first-order model and the pseudo-second-order model, respectively.

#### 4. Adsorption isothermal models

The linear/nonlinear Langmuir isothermal model and the linear/nonlinear Freundlich isothermal model are used to simulate the adsorption isotherms (**Equations (S5)–(S8)**):

$$\text{Linear Langmuir isothermal model: } \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m k_L} \quad (\text{S5})$$

$$\text{Nonlinear Langmuir isothermal model: } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (\text{S6})$$

$$\text{Linear Freundlich isothermal model: } \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (\text{S7})$$

$$\text{Nonlinear Freundlich isothermal model: } q_e = k_F C_e^{\frac{1}{n}} \quad (\text{S8})$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of  $\text{Ga}^{3+}$ ;  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of  $\text{Ga}^{3+}$  adsorbed by GO-MTA composite at equilibrium state;  $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer adsorption capacity;  $k_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir equilibrium constant; The two Freundlich constants,  $n$  represents the relative advantage of adsorption process,  $k_F$  ( $\text{mg L}^{1/n} \text{g}^{-1} \text{mg}^{-1/n}$ ) is defined as adsorption or distribution coefficient which corresponds to the amount of  $\text{Ga}^{3+}$  adsorbed on GO-MTA composite at unit equilibrium concentration. The slope  $1/n$  ranging between 0 and 1 could be used as a measure of adsorption intensity or surface heterogeneity, and a value close to zero suggests a more heterogeneous surface.

#### 5. Adsorption thermodynamics

The change in the enthalpy ( $\Delta H^\circ$ ,  $\text{kJ mol}^{-1}$ ), the change in the entropy ( $\Delta S^\circ$ ,  $\text{J K}^{-1}$ )

mol<sup>-1</sup>) and the change in the Gibbs free energy ( $\Delta G^\circ$ , kJ mol<sup>-1</sup>) can be calculated by

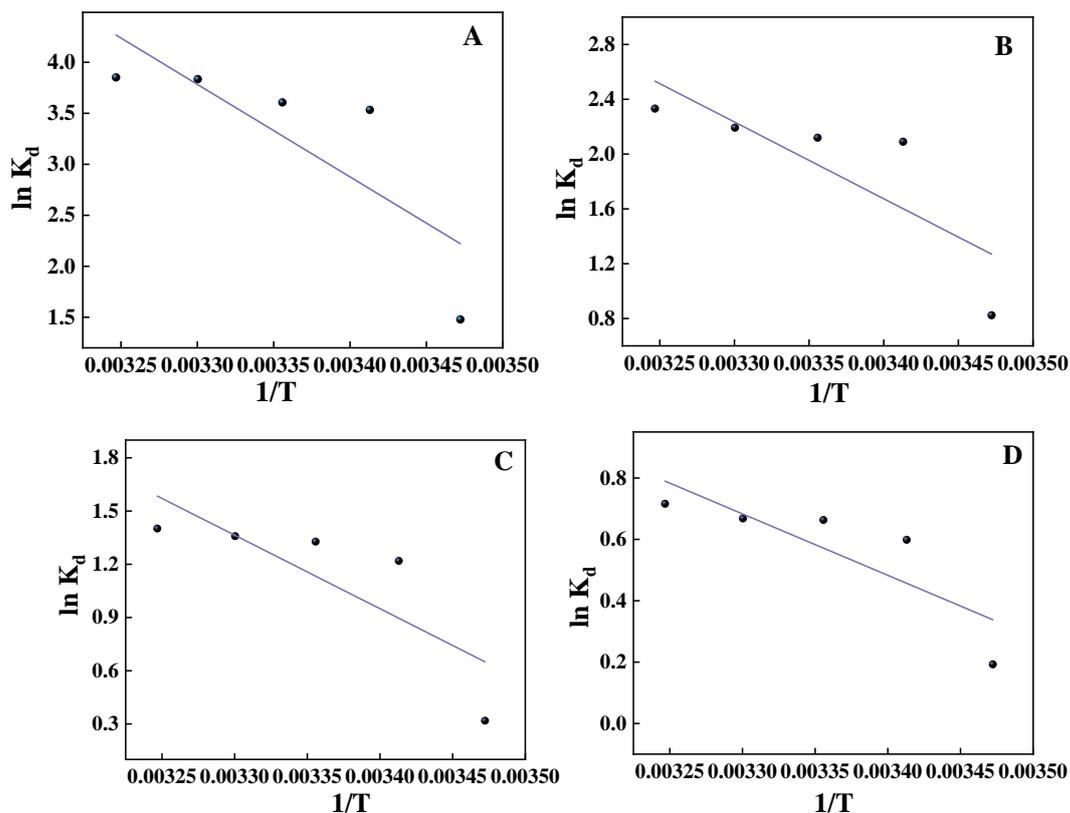
**Equations (S9)–(S11).**

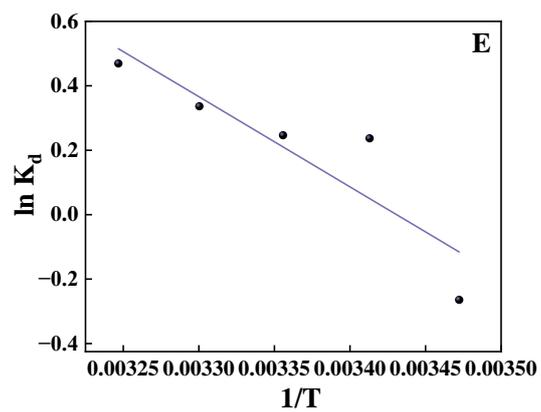
$$k_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (\text{S9})$$

$$\ln k_d = \frac{-\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (\text{S10})$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{S11})$$

where  $k_d$  (L mg<sup>-1</sup>) represents the thermodynamic equilibrium constant;  $V$  (L) and  $m$  (g) are defined as the volume of Ga<sup>3+</sup> solution and the mass of GO-MTA composite, respectively;  $T$  (K) represents the absolute temperature;  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) represents the ideal gas constant.





**Figure S2** Experimental data and the fitted curve of  $\ln k_d$  versus  $1/T$  calculated from Van't Hoff plots of GO-MTA composite for  $\text{Ga}^{3+}$  with different concentration: (A)  $10 \text{ mg L}^{-1}$ ; (B)  $20 \text{ mg L}^{-1}$ ; (C)  $30 \text{ mg L}^{-1}$ ; (D)  $40 \text{ mg L}^{-1}$ ; (E)  $50 \text{ mg L}^{-1}$ .

**Table S1** Adsorption thermodynamic parameters of GO-MTA composite for Ga<sup>3+</sup>.

$C_0$ (mg L <sup>-1</sup> )	$T$ (K)	$\Delta G^\ominus$ (kJ mol <sup>-1</sup> )	$R^2$	$\Delta H^\ominus$ (kJ mol <sup>-1</sup> )	$\Delta S^\ominus$ (J mol <sup>-1</sup> K <sup>-1</sup> )
10	288	-5.318	0.646	75.45	280.43
	293	-6.721			
	298	-8.123			
	303	-9.525			
	308	-10.927			
20	288	-3.040	0.658	46.57	172.24
	293	-3.040			
	298	-4.762			
	303	-5.623			
	308	-6.485			
30	288	-1.557	0.656	34.45	125.03
	293	-2.182			
	298	-2.808			
	303	-3.433			
	308	-4.058			
40	288	-0.809	0.698	16.66	60.66
	293	-1.113			
	298	-1.416			
	303	-1.719			
	308	-2.023			
50	288	0.277	0.802	23.27	79.82
	293	-0.122			
	298	-0.521			
	303	-0.920			
	308	-1.319			