

## Supporting Information

### **Effective and sustainable Cs<sup>+</sup> remediation via exchangeable sodium-ion sites in graphene oxide fibers**

Heehyeon Lee,<sup>ab†</sup> Kyungeun Lee,<sup>c†</sup> Sang Ouk Kim,<sup>\*c</sup> Jae-Seung Lee,<sup>\*b</sup> and Youngtak Oh<sup>\*a</sup>

<sup>a</sup> Center for Environment, Health, and Welfare Research, Korea Institute of Science and Technology (KIST), Seoul 02792, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Korea University, Seoul 02841, Republic of Korea

<sup>c</sup> Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

† These authors contributed equally to this work.

\*Corresponding authors:

Sang Ouk Kim: [sangouk.kim@kaist.ac.kr](mailto:sangouk.kim@kaist.ac.kr)

Jae-Seung Lee: [jslee79@korea.ac.kr](mailto:jslee79@korea.ac.kr)

Youngtak Oh: [ytoh@kist.re.kr](mailto:ytoh@kist.re.kr)

## Experimental

### Graphene oxide synthesis and analysis

Graphene oxide was prepared using a modified Hummers' method. First, 1 g of graphite and 1.7 g of  $\text{NaNO}_3$  were added to 60 ml of sulfuric acid in a round-bottom flask. The mixture was stirred for 30 min; then, 5 g of  $\text{KMnO}_4$  was added to the mixture for 30 min while stirring in an ice bath. Next, the temperature was controlled at  $35^\circ\text{C}$  for 1 day with stirring. 100 ml of deionized (DI) water was added to solution drop wise, and the solution was continuously stirred for 12 h. A 30 ml solution of  $\text{H}_2\text{O}_2$  was added to the mixture for 30 min in the ice bath.

The oxidation product was filtered with 1 L of HCl 5%. The filtered solution was centrifuged three times at a speed of 100 rpm for 30 min. The precipitation was collected in a dialysis tube, and dialysis is conducted 10 times for acquiring high-purity graphene oxide liquid crystal (GO LC). The GO dispersion solution was characterized via atomic force microscopy (AFM) using XE-100 (Park system, Korea). The GO solution was casted on a silicon wafer after dilution for 2000 times. The resulting AFM image of the doped GO LC shows a single layer of  $\sim 1.2\text{-nm}$  thickness.

### Na-functionalized graphene oxide fiber synthesis

GO was obtained using a modified Hummers' method. A 5-ml syringe was filled with 1.5 ml of the GO solution and connected to polytetrafluoroethylene (PTFE) tubing of 0.5-mm diameter. It was then spun into 100 ml of 2 wt% NaOH solution (ethanol:water = 1:1 v/v) at a rate of 0.4 ml/min. Lip of tubing is placed 2.5 cm away from the center of the coagulation bath rotating at 140 rpm. The doped GO at 20 mg/ml was spun in this rotating coagulation bath, and the fibers were left for 30 min to allow  $\text{Na}^+$  ion to sufficiently penetrate into the fibers. After coagulation for 30 min, the GO hydrogel fiber was washed with 50 ml of 50% ethanol solution and immersed in 100 ml of 50% ethanol solution for 5 min to remove excess  $\text{Na}^+$  ions. Next, the fiber is rolled up on a Teflon bobbin. After complete drying for 24 h at room temperature, the fiber was heat treated in a  $6^\circ\text{C}$  vacuum oven for 3 h to increase its stability. A Cs-removal experiment was then conducted to evaluate the performance of the fiber as an absorbent.

### Fibril Na-GO structure characterizations

Raman spectra were obtained using an inVia Raman Microscope (Renishaw, UK) with an excitation wavelength of 532 nm. Cross-sectional SEM images of Na-GO fibers were obtained using the Hitachi S-4800. Elemental analysis was conducted using a Philips XL 30 EDS unit. Chemical analysis was

performed via XPS (K-alpha, Thermo VG Scientific) and data fitting was processed using the Thermo Scientific™ Advantage software. Raman spectra were measured using the ARAMIS system with a 514-nm laser source.

#### Cs ion remediation experiment and detection

A 100-ml cesium chloride (CsCl) aqueous solution was prepared. The Na-GO fiber was added to the 100ppm CsCl solution and stirred at 250 rpm for a period of time (30 – 120 min).

The concentration of Cs ions and other ions can now be determined via inductively coupled plasma mass spectrometry (ICP-MS) (iCAP RQ, Thermo Scientific, USA). Next, 0.015 ml of HNO<sub>3</sub> was added to sample solution for acidification. After the solution was diluted 100 times with DI, its concentration was detected. The Cs adsorption capacity of the Na-GO fiber can be calculated using the following equation:

$$Q_e = \frac{V(C_i - C_f)}{m},$$

where  $C_i$  and  $C_f$  are the initial and final Cs concentrations, respectively;  $V$  is the volume of the Cs ion solution; and  $m$  is the weight of the GO hydrogel fiber used in the Cs ion remediation experiment.

#### PH control experiment

The CsCl solution was adjusted at the pH of 2, 4, 6, 8, 10 by addition of either 1M HCl or 1M NaOH. The adsorbent was immersed and stirred in the solution at 250 rpm for 2 hours.

#### Ion remediation experiment and detection

The salts of NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> as monovalent and divalent ion source were used to confirm the remediation capacity of other ions on the adsorbent. Each aqueous solution were prepared at the concentration of 100ppm. After 2 hours of remediation, the ions were detected via inductively coupled plasma atomic emission spectrometer (ICP-AES) (OPTIMA 8300, Perkin-Elmer, USA).

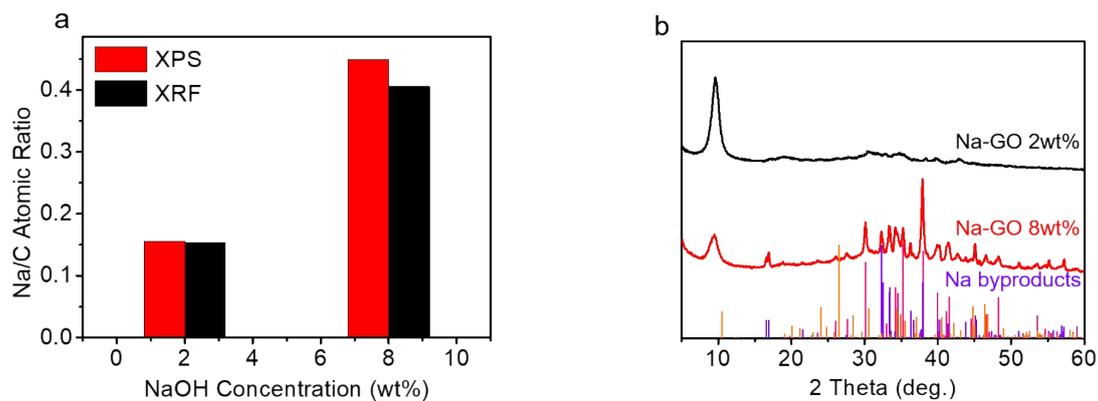
#### Co-existing ion experiment

The NaCl and CsCl were added for aqueous solution at the initial concentration ratios of 1 : 0, 0.6 : 0.4, 0.5 : 0.5, 0.3 : 0.7, 0.2 : 0.1, 0.1 : 0.9 (Na<sup>+</sup> : Cs<sup>+</sup>). In every solution, the Cs ion remediation experiment were done for 2 hours.

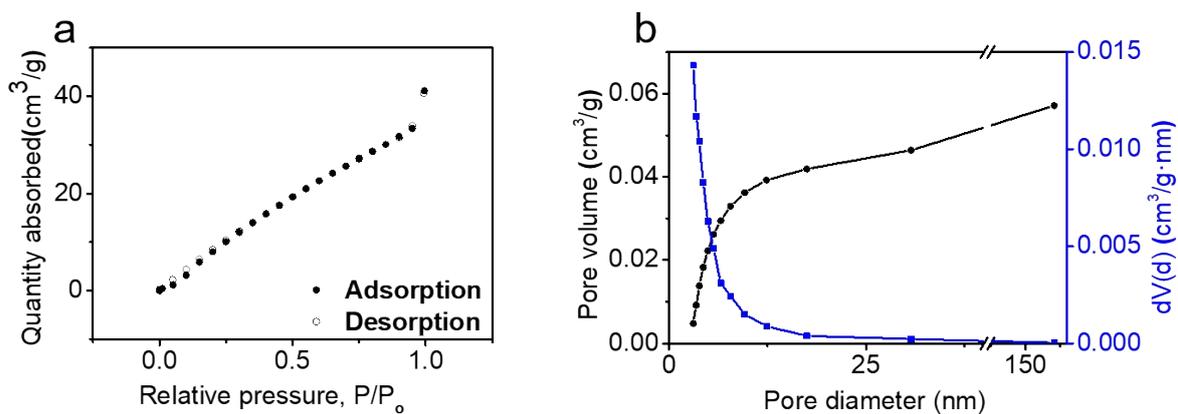
#### Volumetric isotherm measurement

The N<sub>2</sub> adsorption–desorption isotherm was obtained using a surface area analyzer (Autosorb-iQ-MP, Quantachrome, USA). The graph obtained was interpreted using the Brunauer–Emmett–Teller (BET) surface area method and the Barrett–Joyner–Halenda (BJH) pore size distribution method.

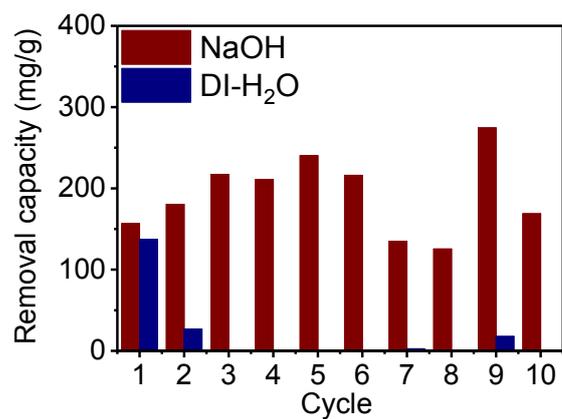
## Supporting Figure and Table



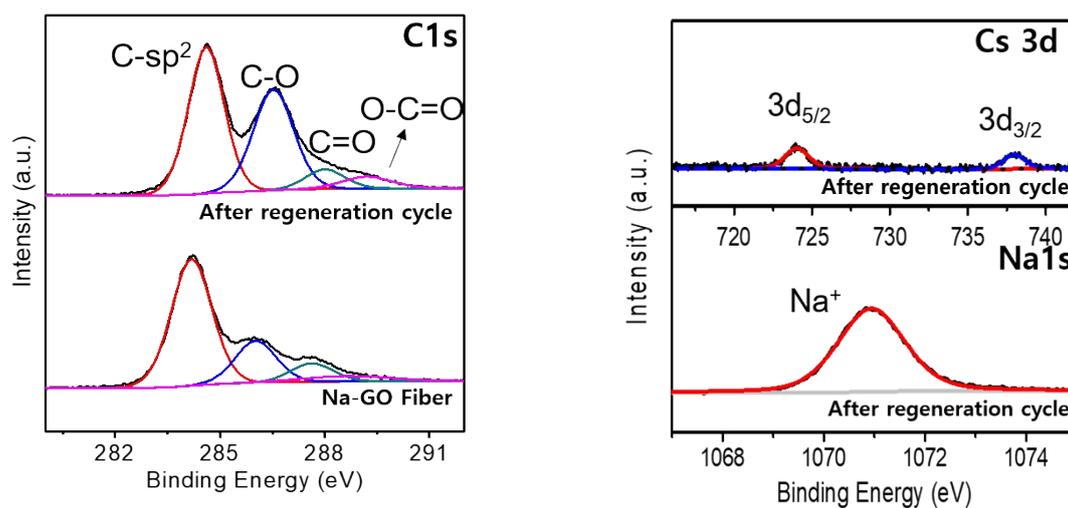
**Fig. S1.** (a) Na/C atomic ratio of Na-GO fiber obtained with different coagulation concentration. (b) XRD result of Na-GO fiber obtained with 2 wt% (black) and 8 wt% (red) NaOH coagulation bath.



**Fig. S2.** Surface Area Analysis of Na-GO fiber (a) N<sub>2</sub> isotherm (b) BJH method plot of Na-GO fiber.



**Fig. S3.** Regeneration testing (with glass container) of Na-GO using NaOH and deionized water (DI-H<sub>2</sub>O) regeneration agent.



**Fig. S4.** Graphene oxide structure (a) XPS C1s analysis of pristine Na-GO and regenerated Na-GO (b) Cs 3d, Na1s of regenerated Na-GO.

**Table S1.** Selected benchmark materials and Na-GO Cs<sup>+</sup> remediation adsorbents

	$Q_e$ mg·g <sup>-1</sup>	$C_i$ ppm	$K_d$ mL·g <sup>-1</sup>	pH	t (eq.) h
PB+CNT <sup>a</sup>	144.7	400	$3.62 \times 10^3$	4–10	3 (~2.5)
PB-GO hydrogel beads <sup>b</sup>	154.5–164.5	665	$2.78 \times 10^3$	7	10–15
GO-membrane on CaF <sub>2</sub>	~148.0	87.3		4	0.5–32
CMC-g-PAM/MMT <sup>c</sup>	265.9	150–350	-	7–10	2
PAN-KNiCF <sup>d</sup>	110.3	20–240	$\alpha 1.46 \times 10^5$	-	24
NiFeCF <sup>e</sup>	180.5	100	-	5.8	1
Nano mordenite	$\alpha 37.3$	100	-	-	2(1~)
nFe/Cu-Z <sup>f</sup>	$\alpha 77.51$	1–1000	$\alpha 3.90 \times 10^3$	6	0.5–2
<b>Na-GO fiber</b>	220	100	$2.51 \times 10^3$	2-10	0.5

$Q_e$  = equilibrium adsorption capacity.  $C_i$  = initial Cs<sup>+</sup> concentration.  $C_f$  = final concentration. E = removal efficiency. t (eq.) = adsorption time (equilibrium time) <sup>a</sup> Prussian blue impregnated carbon nanotube. <sup>b</sup> PVA-alginate-encapsulated PB-GO hydrogel beads. <sup>c</sup> Carboxymethylcellulose-g-poly(acrylamide)/montmorillonite. <sup>d</sup> PAN-based potassium nickel hexacyanoferrate(II) composite spheres. <sup>e</sup> Ni-Fe-hexacyanoferrate. <sup>f</sup> Nano-Fe/Cu-zeolite  $\alpha$  values calculated by the Langmuir isotherm model.