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Electronic Supplementary Information for *Environmental Science: Nano*

Concurrent enhancement of structure stability and adsorption capacity of freeze-dried graphene oxide aerogel via the removal of oxidation debris nanoparticles on nanosheets

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Preparation of Graphene Oxide. Graphene Oxide (GO) was synthesized from natural Graphite flake (325 mesh, 99.8%, Alfa Aesar) by a modified Hummers Method. Generally, the graphite powder (30 g) was added into an 80 °C solution of concentrated H_2SO_4 (120 mL) which contained $K_2S_2O_8$ (24.99 g) and P_2O_5 (24.99 g), then kept at 80 °C for 4.5 h. After that, the mixture was collected and rinsed with deionized water until the pH became neutral, dried in the oven overnight at 60 °C, as pre-oxidized graphite obtained. The pre-oxidized graphite powder (30 g) and $NaNO_3$ (15 g) were put into cold (0 °C) concentrated H_2SO_4 (690 mL) in an ice bath, and $KMnO_4$ (90 g) was slowly added slowly added with continuously stirring to keep the temperature below 4 °C. Then the mixture was stirred at 35 °C for 2 h, after which deionized water (1380 mL) and 30% H_2O_2 solution (25 mL), so as to obtain graphite oxide. The resultant bright yellow mixture was rinsed by 10% HCl solution (10.8 L) to remove residual SO_4^- (checked by 0.01 mol/L $BaCl_2$) and metal ions, followed by centrifugation at 8000 rpm, then the solid phase was redispersed in deionized water and peeled by ultrasonication for 30 min at the power of 250 W. The centrifugation and ultrasonication were recycled for 3 times, then the solution was subjected to dialysis to remove the acid and other impurities.

Kinetics models

Pseudo first-order equation is:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (1)$$

the pseudo second-order equation is:

where t is the time, h; q_e is the adsorption capacity coefficient at equilibrium time, mg/g; q_t is the amount adsorbed per unit weight at time t, mg/g; k_1 is the equilibrium rate constant of pseudo first-order adsorption process, h^{-1}.

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \quad (2)$$

Where t is the time, h; q_e is the adsorption capacity coefficient at equilibrium time, mg/g; q_t is the amount adsorbed per unit weight at time t, mg/g; k is the equilibrium rate constant of pseudo second-order adsorption, mg $g^{-1}h^{-1}$.

Isotherm models

The following expression describes the Langmuir equation:

$$q_e = q_m C_e/(K_L + C_e) \quad (3)$$

Where q_e is the equilibrium-sorbed concentration, mg/g; C_e is the equilibrium solution phase concentration, mg/L; K_L is the Langmuir constant, L/g; q_m is the maximum adsorption capacity of the adsorbent, mg/g.

The following expression describes the Freundlich equation:

$$q_e = K_f C_e^{\ N}$$

Where K_f is the Freundlich affinity coefficient, $(mg/L)(mg/L)^N$; N is the exponential coefficient.

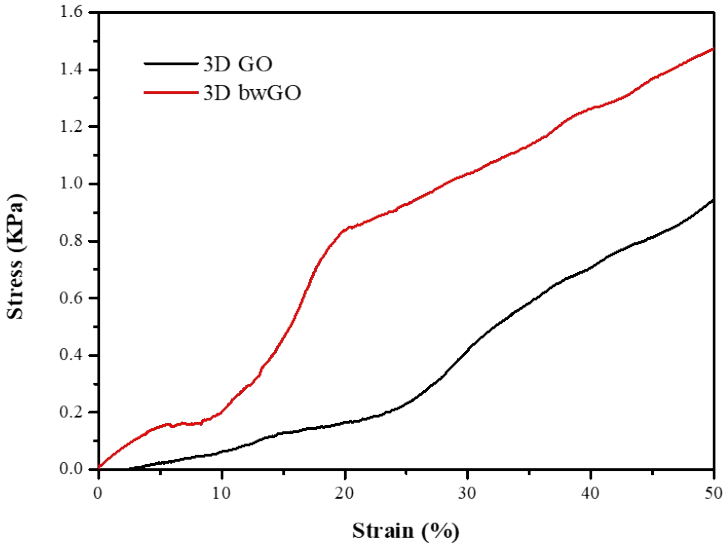

Figure S1. Compressive stress-strain curve of 3D GO and 3D bwGO.

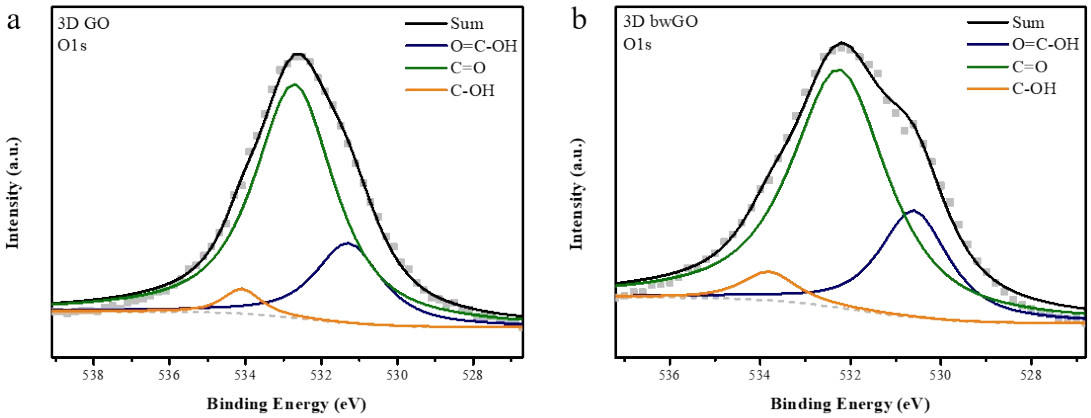

Figure S2. XPS O 1s spectra of 3D GO (a) and 3D bwGO (b).

Table S1. Distribution of C1s species of 3D GO and 3D bwGO derived from XPS data

	species	3D GO	3D bwGO
C1s	C=C	45.55%	55.43%
	C-C	9.81%	6.66%
	C-O	27.19%	19.36%
	C=O	15.21%	11.58%
	O-C=O	2.24%	6.97%
O1s	O=C-OH	21.29%	23.37%
	C=O	74.97%	71.72%
	C-OH	3.73%	4.91%
C/O		1.59	2.03

Table S2. The weight loss of 3D GO and the GP aerogels at different temperature stage

sample	20-105 °C	105-400 °C	400-810°C
3D GO	18.95%	27.06%	24.04%
3D bwGO	18.47%	19.37%	25.57%

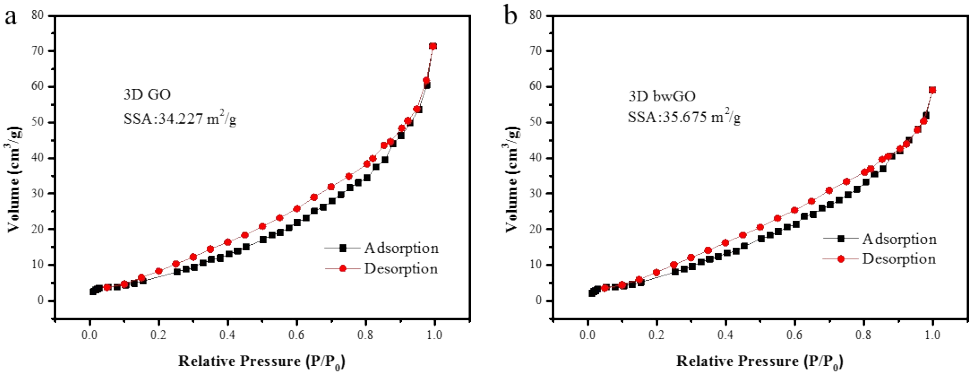

Figure S3. Nitrogen adsorption/desorption isotherms of 3D GO (a) and 3D bwGO (b).

Table S3. Regression parameters of kinetic model for DEP adsorption on 3D GO and 3D bwGO

	Pseudo first-order			Pseudo second-order		
	q(mg/g)	k_1(1/h)	R^2	q(mg/g)	k_2(g/(mg·h))	R^2
3D GO	4.043	0.129	0.843	4.120	0.096	0.849
3D bwGO	20.541	0.012	0.872	22.692	7.50512E-4	0.934

Table S4. Langmuir and Freundlich regression parameters of DEP adsorption onto 3D GO and 3D bwGO

	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_f($mg^{1-n}\cdot L^n$/g)	N	R^2
3D GO	29.073	0.049	0.889	1.301	0.912	0.882
3D bwGO	114.180	0.126	0.968	17.826	0.542	0.992

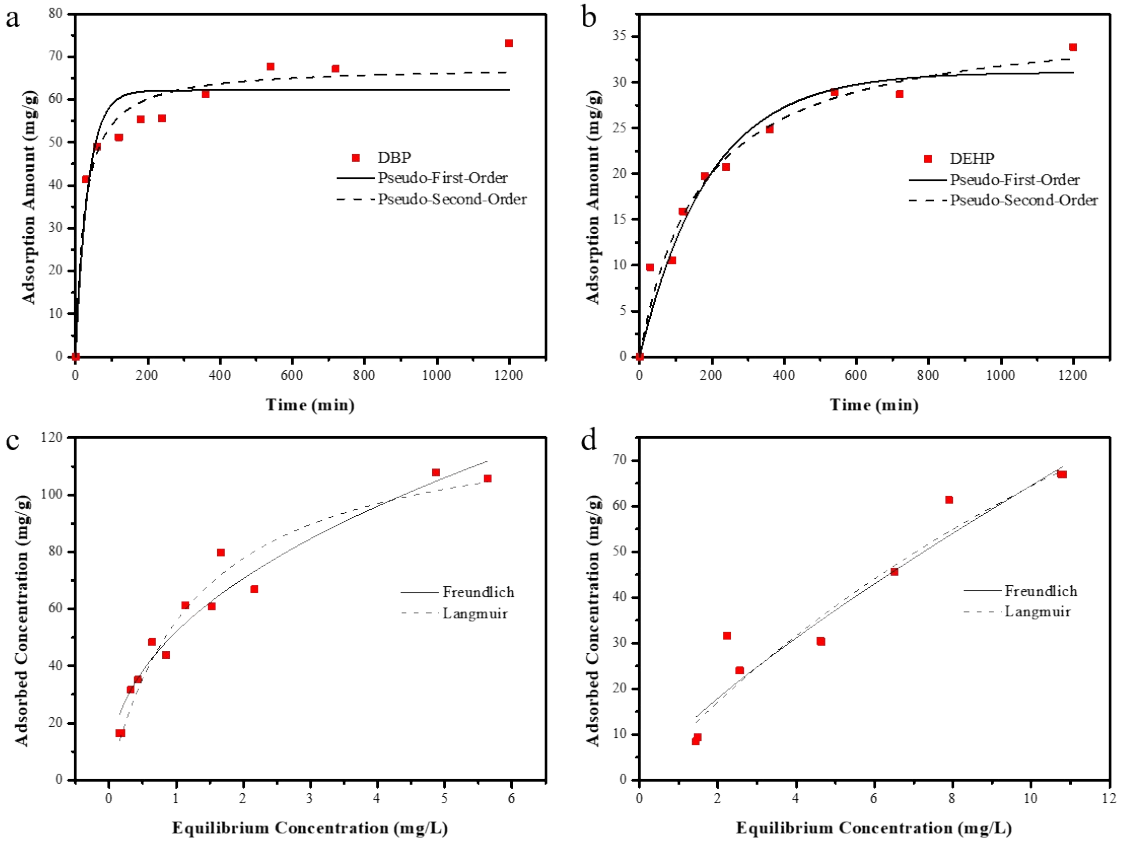

Figure S4. Adsorption kinetics of 3D bwGO for DBP (a) and DEHP (b); Adsorption isotherms of 3D bwGO for DBP (c) and DEHP (d).

Table S5. Regression parameters of kinetic model of DBP adsorption and DEHP onto 3D bwGO

	Pseudo first-order			Pseudo second-order		
	q(mg/g)	k_1(1/h)	R^2	q(mg/g)	k_2(g/(mg·h))	R^2
DBP	62.15	0.029	0.890	67.74	5.85E-4	0.954
DEHP	31.11	0.0052	0.946	37.20	1.58E-4	0.967

Table S6. Langmuir and Freundlich regression parameters of DBP and DEHP adsorption onto 3D bwGO

	Langmuir			Freundlich		
	Q_0 (mg/g)	b (L/mg)	R^2	K_f($mg^{1-n}\cdot L^n$/g)	N	R^2
DBP	128.831	0.762	0.947	52.022	0.442	0.946
DEHP	207.934	0.0449	0.921	10.358	0.795	0.919

Table S7. Comparison of adsorption capacities of 3D GO and 3D bwGO for DEP with other adsorbents.

Adsorbent	T (K)	Adsorption capacity (mg/g) [a]	Reference
α-cyclodextrin-linked chitosan bead	298	32	[1]
Single-walled carbon nanotube	298	142	[2]
Multi-walled carbon nanotubes	RT	25	[3]
Graphene oxide functionalized magnetic nanoparticles	RT	8.71	[4]
Pinewood biochar	298	21.50	[5]
Reduced graphene oxide	298	127.21	[6]
3D GO	298	29.07	This work
3D bwGO	298	114.2	This work

[a] The adsorption capacity of 3D GO, 3D bwGO and other adsorbents toward diethyl phthalate (DEP) are calculated from Langmuir fitting of isotherm data.

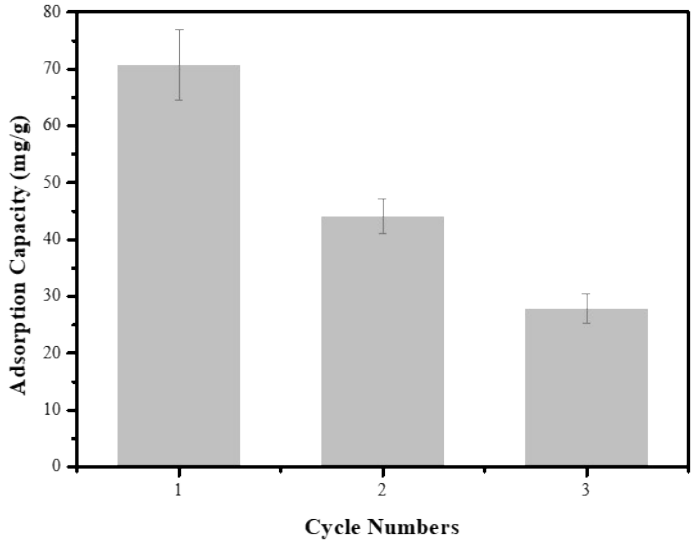

Figure S5. Reusability of 3D bwGO for DEP adsorption. The adsorption reusability of 3D bwGO for DEP is carried out with an initial concentration of 11 mg/L. The solid-to-water ratio was 2.8-2.9 mg per 50 mL. After each cycle, 3D bwGO is regenated with 10 mL methanol for 10 min.

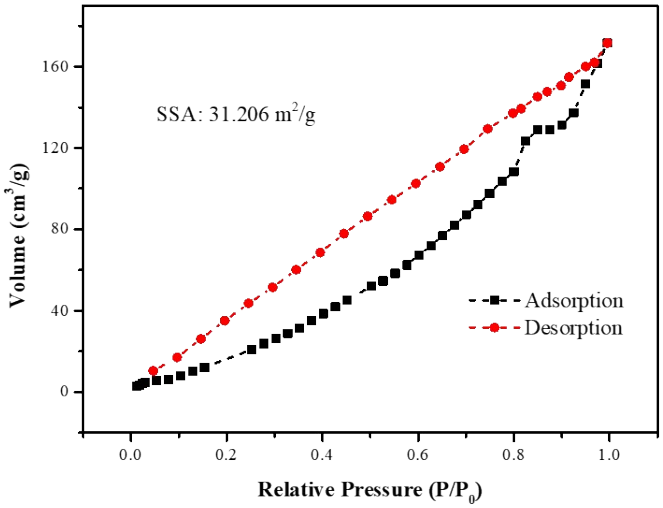

Figure S6. Nitrogen adsorption/desorption isotherms of 3D bwGO recycled from three adsorption cycles. Note that 3D bwGO was freezed again for lyophilization.

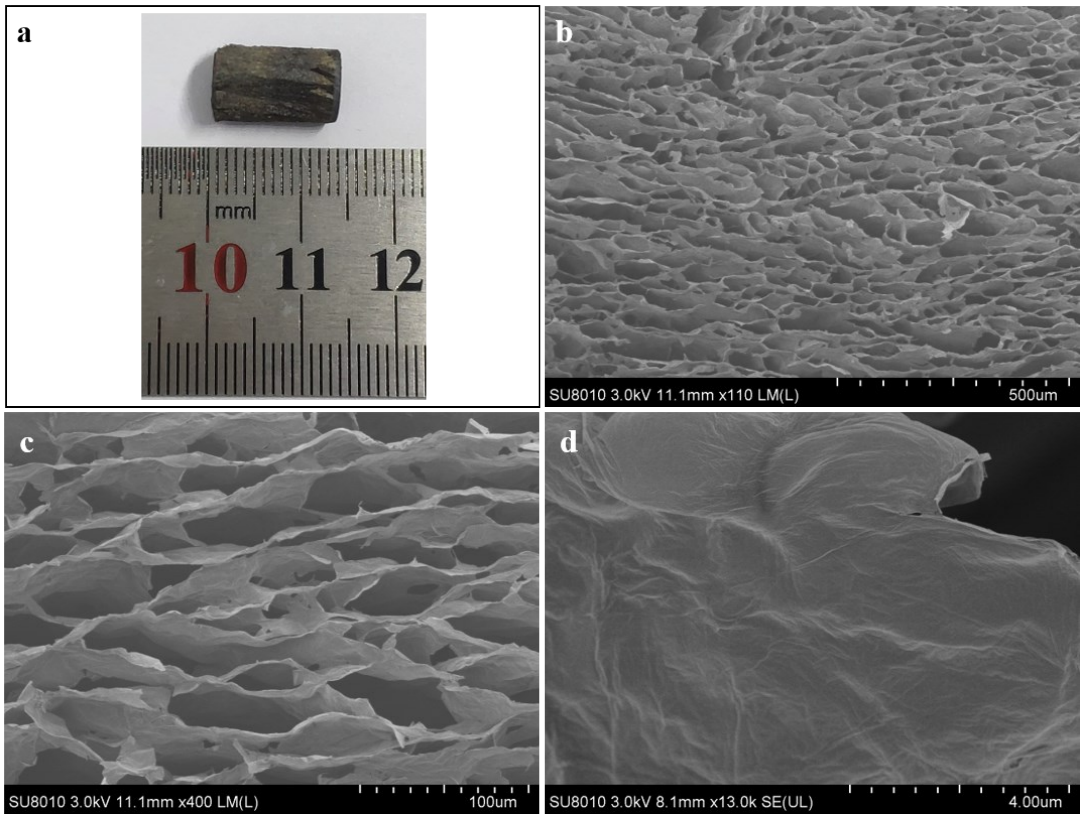

Figure S7. Optical image (a) and SEM images (b, c and d) of 3D bwGO recycled from three adsorption cycles. Note that 3D bwGO was freezed again for lyophilization.

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