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Size Effects of Graphene Oxide Nanosheets for Construction of Three-Dimensional Graphene-Based Macrostructures as Adsorbents

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Supporting Information consists of 17 pages, including this one.

There are 7 Tables and 4 Figures.

Materials and Characterization. SGO was synthesized from natural Graphite flake (325 mesh, 99.8%, Alfa Aesar) by a modified Hummers Method. Generally, the graphite powder (10 μm, 10 g) was added into an 80 ºC solution of concentrated H_2SO_4 (40 mL) which contained $K_2S_2O_8$ (8.33 g) and P_2O_5 (8.33 g), then kept at 80 ºC 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 ºC, as preoxidized graphite obtained. The preoxidized graphite powder (10 g) and $NaNO_3$ (5 g) were put into cold (0 ºC) concentrated H_2SO_4 (230 mL) in an ice bath, and $KMnO_4$ (30 g) was slowly added with continuously stirring to keep the temperature below 4 ºC. Then the mixture was stirred at 35 ºC for 2 h, after which deionized water (460 mL) was gradually added, producing much heat. The mixture was further stirred for 15 min at 98 ºC to increase the oxidation level, the reaction was terminated by adding deionized water (460 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 (3.6 L) to remove the residual SO_4^{2-} (checked by 0.01mol/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 250W. The centrifugation and ultrasonication were recycled for 3 times, then the solution was subjected to dialysis to remove the acid and other impurities.

Atomic force microscopy (AFM) images of graphene or graphene oxide on a freshly cleaved mica surface were taken using a Nanoscope III in tapping mode with a NSC14/no Al probe (Dimension icon, Veeco). After sonication for 5 minutes, a droplet of graphene dispersion (or graphene oxide dispersion) ~0.01 mg/mL was cast onto a freshly cleaved mica

surface. The sample was kept at room temperature overnight to let the water evaporate. The FTIR spectra were recorded in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1} using a Bruker Vector 22 FTIR spectrometer.

Characterization of 3D GBM. The surface morphologies of 3D GBM were characterized through KYKY-3200 scanning electron microscopy (SEM). The Brunauer-Emmett-Teller (BET) nitrogen specific surface areas and pore volume were determined by nitrogen adsorption-desorption at -196ºC with a NOVA-2000E surface area and pore volume analyzer. Raman spectra were obtained with a LabRamHRUV Raman spectrometer (JDbin-yvon, FR); the laser excitationwas provided by an Ar+ laser at a wavelength of 514 nm. The XPS experiments were performed on a VG Escalab Mark II with a resolution below 0.2 eV, and the C1s peak spectra were analyzed using XPS Peak 4.1 software. The FTIR spectra were recorded in the 4000-400 cm^{-1} region with a resolution of 4 cm^{-1} using a Bruker Vector 22 FTIR spectrometer.

The Adsorption Kinetics Experiment. Methylene blue (98%+. Acros Organics) and Cd^{2+} (98%+, Sinopharm Chemical Reagents Co. Ltd. (China)) were selected as model pollutants. The Time-dependent adsorptions of 3D GBM (3D GGO0.8, 3D GGO1, 3D GGO3, 3D GGO5, 3D GGO10, 3D BGO3, 3D BGO5, 3D BGO10, 3D SGO5, 3D SGO10, 3D rGGO3, 3D rGGO5, 3D rGGO10, 3D rBGO3, 3D rBGO5, 3D rBGO10, 3D rSGO5, 3D rSGO10) were conducted with an initial MB and Cd^{2+} concentration of 5 and 10 mg/L, respectively. The solid-to-water ratios for 3D GBM were 0.8-10 mg per 500 mL. The remaining concentrations in a series of independent samples were measured from 0 min to 2880 min for MB and Cd^{2+}. MB solution was measured using an UV/Vis spectrometer and

calculated by the absorbance at 664 nm, and Cd^{2+} was analyzed with a Perkin-Elmer Analyst 700 (PE700, USA) atomic absorption spectrometer. The removal rate (%) and specific adsorbed amount (Q) of pollutant (MB and Cd^{2+}) was calculated according to the following equation:

$$\text{Removal rate (\%)} = (C_0\text{-}C_t)/\ C_0 \times 100\% \quad (1)$$

$$Q = (C_0\text{-}C_t)\times V/m \quad (2)$$

where C_0 and C_t are the initial and specific time (t) concentrations of pollutants (mg/L); V is the volume of aqueous solution (mL); and m is the mass of the 3D GBM (mg).

The Column Experiment. Six samples of 3D GBM (e.g., 3D GGO5, 3D GGO10, 3D BGO5, 3D BGO10, 3D SGO5, 3D SGO10) were prepared and conducted as column experiment to measure the adsorption capacity of MB and Cd^{2+} . The adsorbed capacity (Q) of pollutant (MB and Cd^{2+}) was calculated according to the following equation:

$$Q = Q_1+Q_2+\ldots\ldots+Q_n \quad (3)$$

$$Q_n = (C_0\text{-}C_n)\times V/(m\times 1000) \quad (4)$$

where Q_n was the adsorption capacity of the column volume in specific number (n); C_0 is the initial concentrations of pollutants (mg/L); C_n is the effluent concentration of pollutant in specific number column volume (mg/L); V is the column volume (mL); and m is the mass of the 3D GBM (mg).

The Soaked Method (for diesel). The soaked method was applied in the 12 samples of 3D GBM (e.g., 3D GGO5, 3D GGO10, 3D BGO5, 3D BGO10, 3D SGO5, 3D SGO10 and 3D rGGO5, 3D rGGO10, 3D rBGO5, 3D rBGO10, 3D rSGO5, 3D rSGO10) to measure the absorption capacity (Q) of diesel. Q was obtained using the following equation:

$$Q = (M-M_0)/M_0 \quad (5)$$

where M_0 and M are the weights of 3D GBM before and after absorption,[24] respectively.

Kinetic Models. The pseudo first-order model can be presented as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (6)$$

Where k_1 is the rate constant of the pseudo first-order model of adsorption (1/h); Q_e and Q_t is the absorbed amount of sorbate at equilibrium and at different time (mg/g), respectively. The values of k_1 and Q_e can be determined from the slope and intercept of linear fittings of $\ln(Q_e - Q_t)$ versus t. The pseudo second-order model is given by:

$$t/Q_t = 1/k_2 Q_e^2 + t/Q_e \quad (7)$$

where k_2 is the rate constant of the pseudo second-order model of adsorption (g/(mg·h)), while Q_e and Q_t are defined the same as the parameters in the pseudo first-order model. The values of k_2 and Q_e can be determined from the slope and intercept of linear fittings of t/Q_t versus t.

Diffusion Model. To gain insight into the adsorption mechanism and rate controlling steps that affects the kinetics of adsorption, the intraparticle diffusion model is applied:

$$Q_t = k_{pi} t^{1/2} + C_i \quad (8)$$

where, k_{pi} (mg/g·min$^{1/2}$) is the intraparticle diffusion rate constant of stage i, and C_i (mg/g) is the intercept of stage i. To follow the data points, the intraparticle diffusion model can be described as a successive process of sorbate diffusion through the boundary layer and intraparticle, namely the adsorbate molecules move slowly from larger pores to micropores.[16,22,63] C_1 values give information about the thickness of the boundary layer, that is, the larger the intercept, the greater the boundary-layer effect.

Pores Semi-Quantitative Models

Single Pore Volume

$$V_{\text{single pore}}=xL^3 \quad (9)$$

where $V_{\text{single pore}}$ (cm^3) means the single pore volume in the 3D GBM, L means the side length of graphene (cm).

Porous Ratio

$$P=V_{\text{pores}}/V_{\text{total}}=1-V_{\text{virtual}}/V_{\text{3D structure}}\sim 1-V_{\text{graphene particle}}/V_{\text{3D structure}} \quad (10)$$

$$V_{\text{graphene particle}}= 1.06\ m_{\text{graphene particle}}\ (\rho_{\text{graphene particle}}\sim 1.06 g/cm^3) \quad (11)$$

where P means the porous ratio, V_{pores} (cm^3) means the pore volume in the 3D GBM, $V_{\text{3D structure}}$ (cm^3) means the volume of 3D GBM, V_{virtual} (cm^3) means the actual volume of graphene in the 3D GBM, which is equal to $V_{\text{graphene particle}}$ (cm^3) on the hypothesis of the volume of each graphene particle didn't change before and after forming the 3D GBM. $m_{\text{graphene particle}}$ (mg) means the quality of graphene particles.

Porous Amount

$$n=V_{\text{pores}}/V_{\text{single pore}}=V_{\text{3D structure}}\times P/V_{\text{single pore}} \quad (12)$$

where n means the porous amount.

Table S-1. The distribution of surface functional groups of 3D GBM derived from XPS data.

sample	C/O	C-C /C=C	C-O	C=O	O-C=O	-COOH (mmol/g)	-OH, -O- (mmol/g)
3D GGO5	2.61	0.24	0.56	0.16	0.05	2.55	30.7
3D BGO5	3.13	0.36	0.50	0.10	0.04	2.42	29.2
3D SGO5	2.84	0.48	0.39	0.11	0.02	1.20	22.0
3D rGGO5	9.50	0.69	0.14	0.09	0.07	----	9.55
3D rBGO5	8.83	0.71	0.15	0.09	0.05	----	10.5
3D rSGO5	9.78	0.69	0.15	0.10	0.05	----	10.0

Table S-2. Adsorption kinetic parameters of methylene blue (MB) onto 3D GBM.

pollutant	adsorbent	pseudo first-order model			pseudo second-order model		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/(mg·min))	R^2
MB	3D GGO10	112	0.0323	0.972	118	0.000251	0.996
	3D GGO5	156	0.0570	0.990	163	0.000268	0.992
	3D GGO3	178	0.0423	0.989	187	0.0003201	0.994
	3D GGO1	249	0.0659	0.965	261	0.000306	0.980
	3D GGO0.8	277	0.0466	0.982	291	0.000467	0.987
	3D BGO10	107	0.0321	0.981	113	0.000240	0.998
	3D BGO5	141	0.0607	0.987	147	0.000277	0.993
	3DBGO3	153	0.0331	0.988	161	0.0003457	0.996
	3D SGO10	97.1	0.0263	0.991	102	0.000230	0.998
	3D SGO5	126	0.0139	0.974	130	0.000240	0.986
	3D rGGO10	28.7	0.0585	0.987	30.0	0.0000373	0.990
	3D rGGO5	38.1	0.0587	0.991	39.8	0.0000484	0.991
	3D rGGO3	43.3	0.0126	0.977	45.3	0.0000563	0.996
	3D rBGO10	25.1	0.0446	0.970	26.5	0.0000440	0.993
	3D rBGO5	33.8	0.0401	0.956	35.5	0.0000612	0.991
	3D rBGO3	32.3	0.0155	0.987	33.7	0.0000837	0.992
	3D rSGO10	17.0	0.0282	0.968	17.7	0.0000406	0.992
	3D rSGO5	24.3	0.00391	0.917	26.2	0.0000552	0.948

Table S-3. Adsorption kinetic parameters of cadmium (Cd^{2+}) onto 3D GBM.

pollutant	adsorbent	pseudo first-order model			pseudo second-order model		
		q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/(mg·min))	R^2
Cd^{2+}	3D GGO10	61.0	0.0456	0.985	64.0	0.000102	0.996
	3D GGO5	75.3	0.0470	0.987	79.2	0.000122	0.998
	3D GGO3	82.5	0.0643	0.984	86.71	0.000132	0.988
	3D GGO1	94.7	0.0557	0.988	99.4	0.000134	0.991
	3D GGO0.8	106	0.0675	0.978	111	0.000143	0.990
	3D BGO10	55.0	0.0507	0.982	57.7	0.0000841	0.994
	3D BGO5	64.2	0.0318	0.991	67.6	0.000102	0.995
	3DBGO3	79.3	0.0336	0.987	83.2	0.000115	0.998
	3D SGO10	48.1	0.0467	0.994	50.5	0.0000785	0.994
	3D SGO5	55.4	0.0875	0.979	57.7	0.0000875	0.995
	3D rGGO10	18.1	0.0442	0.990	19.0	0.0000315	0.994
	3D rGGO5	15.8	0.0177	0.977	16.6	0.0000453	0.996
	3D rGGO3	18.1	0.0257	0.978	19.0	0.0000517	0.995
	3D rBGO10	13.7	0.0313	0.991	14.5	0.0000333	0.992
	3D rBGO5	11.8	0.0224	0.991	12.4	0.0000383	0.996
	3D rBGO3	13.1	0.0423	0.983	13.8	0.0000346	0.984
	3D rSGO10	8.62	0.0433	0.987	9.08	0.0000154	0.990
	3D rSGO5	9.74	0.0466	0.967	10.2	0.0000159	0.992

Table S-4. Diffusion model parameters of the stage 1 of MB and Cd^{2+} onto3D GBM.

samples	MB			Cd^{2+}		
	k_{p1}	C_1	R^2	k_{p1}	C_1	R^2
3D GGO10	7.96	8.07	0.903	4.85	4.03	0.914
3D BGO10	7.80	6.49	0.911	4.38	4.34	0.906
3D SGO10	7.27	2.21	0.906	3.70	4.01	0.927
3D GGO5	11.7	19.1	0.893	5.64	2.27	0.932
3D BGO5	10.7	17.9	0.917	4.86	2.28	0.915
3D SGO5	9.33	8.03	0.924	4.08	10.6	0.911

Table S-5. Adsorption capacity of methylene blue (MB) and cadmium (Cd^{2+}) onto 3D GBM column.

adsorbent	MB q_e (mg/g)	q_e (mmol/g)	Cd^{2+} q_e (mg/g)	q_e (mmol/g)
3D GGO10	164	0.512	89.3	0.794
3D GGO5	182	0.569	104	0.925
3D BGO10	137	0.428	77.8	0.692
3D BGO5	164	0.513	91.7	0.816
3D SGO10	111	0.347	60.4	0.537
3D SGO5	142	0.444	79.8	0.710

Table S-6. Absorption capacity of diesel onto 3D GBM.

adsorbent	q_e (mg/g)	adsorbent	q_e (mg/g)
3D GGO10	77.0	3D rGGO10	79.1
3D GGO5	95.0	3D rGGO5	147
3D GGO3	100	3D rGGO3	193
3D BGO10	70.0	3D rBGO10	73.4
3D BGO5	89.2	3D rBGO5	124
3D BGO3	98.4	3D rBGO3	167
3D SGO10	68.0	3D rSGO10	71.7
3D SGO5	80.9	3D rSGO5	110

Table S-7. Pore volume, pore ratio and pore amount of 3D GBM predicted theoretically.

samples	single pore volume (cm^3)	pore ratio	pore amount
3D GGO10	2.70E-08	0.991	3.67E+07
3D GGO5	2.70E-08	0.995	3.69E+07
3D GGO4	2.70E-08	0.996	3.69E+07
3D GGO3	2.70E-08	0.997	3.69E+07
3D GGO2	2.70E-08	0.998	3.70E+07
3D GGO1	2.70E-08	0.999	3.70E+07
3D GGO0.8	2.70E-08	0.999	3.70E+07
3D BGO10	1.00E-09	0.991	9.91E+08
3D BGO5	1.00E-09	0.995	9.95E+08
3D BGO4	1.00E-09	0.996	9.96E+08
3D BGO3	1.00E-09	0.997	9.97E+08
3D SGO10	3.38E-12	0.991	2.94E+11
3D SGO5	3.38E-12	0.995	2.95E+11

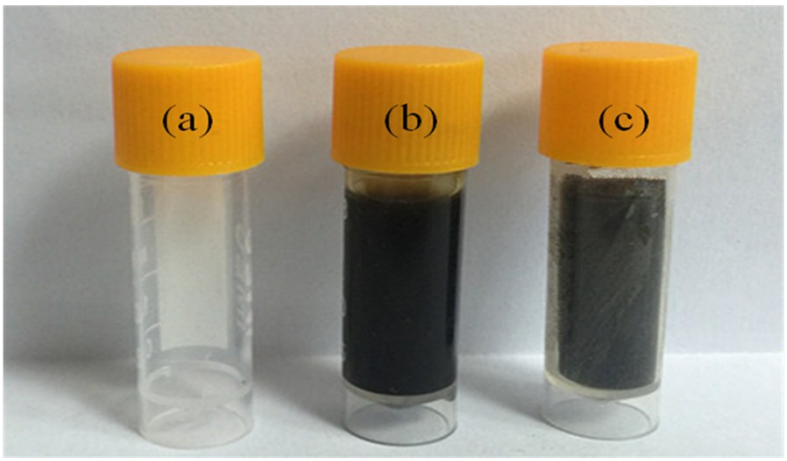

Figure S-1. The photos of (a) cryo tubes (b) GO suspension (c) GO aerogel.

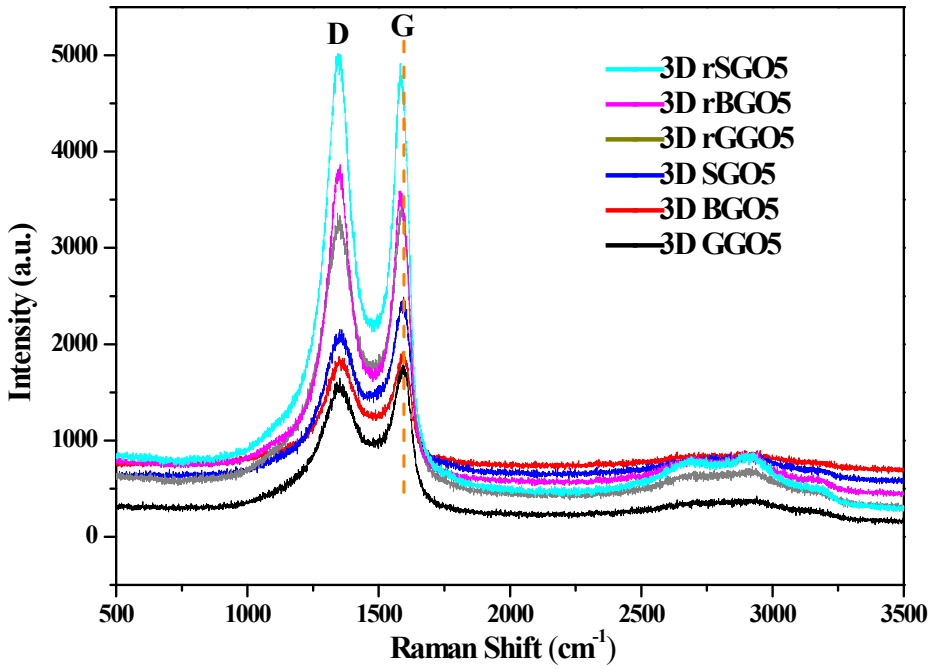

Figure S-2. Raman of 3D rSGO5, 3D rBGO5, 3D rGGO5, 3D SGO5, 3D BGO5, and 3D GGO5.

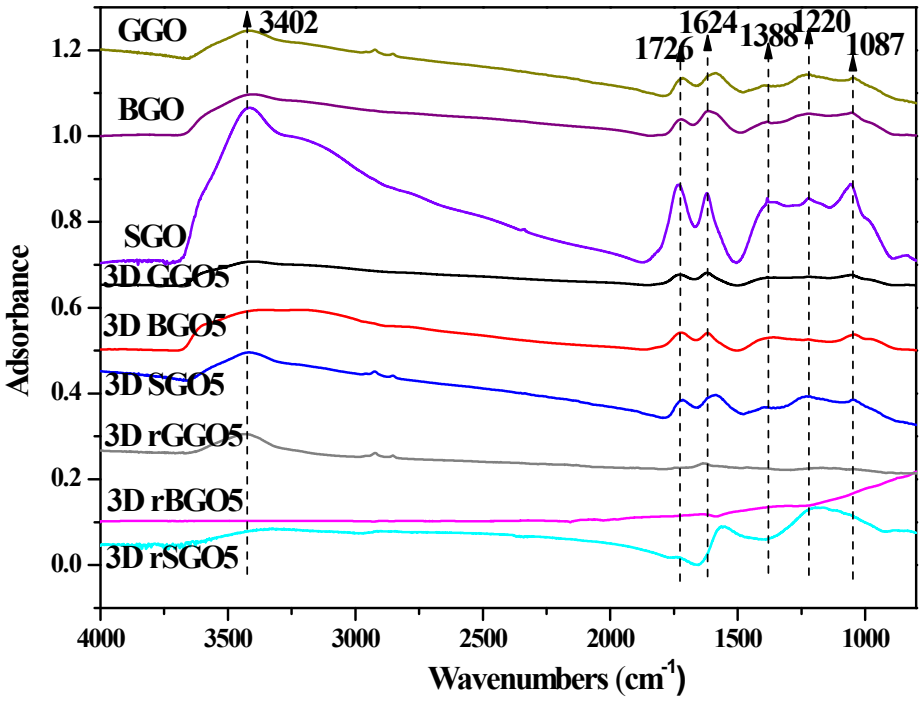

Figure S-3. FTIR of building blocks (GGO, BGO, and SGO), and the 3D GBM at the oxidized states (3D GGO5, 3D BGO5, and 3D SGO5) and at the reduced state (3D rGGO5, 3D rBGO5, and 3D rSGO5).

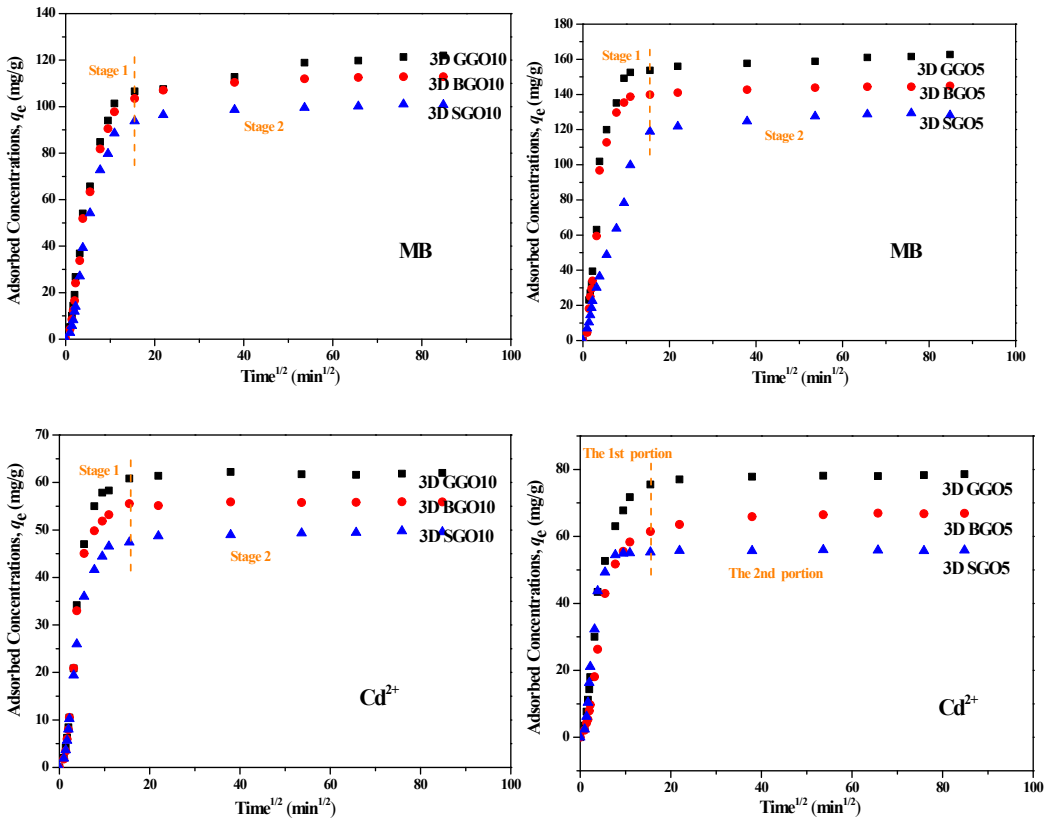

Figure S-4. MB/Cd^{2+} diffusion model onto 3D GGO10, 3D BGO10, 3D SGO10 and 3D GGO5, 3D BGO5, and 3D SGO5.