

Supporting Information

Three-Dimensional Graphene Oxide Nanostructure for Fast and Efficient Water-Soluble Dye Removal

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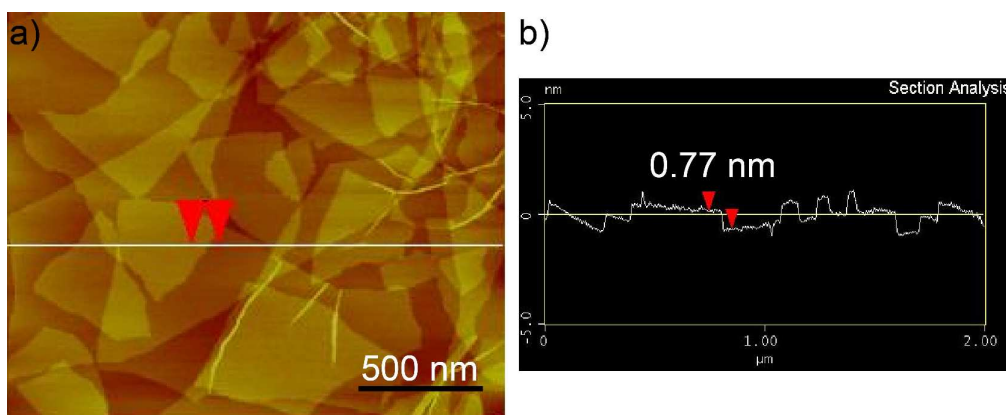


Figure S1. AFM characterization of GO sheets which were prepared by a modified Hummers' method.

The diluted aqueous GO suspension was dropped on a mica substrate (dia. 10 mm) and dried in air. Then the height and morphology of GO sheets were recorded by using AFM in a tapping mode and a 512×512 pixel resolution. The height of monolayer GO prepared by the

modified Hummers' method was 0.77 nm.

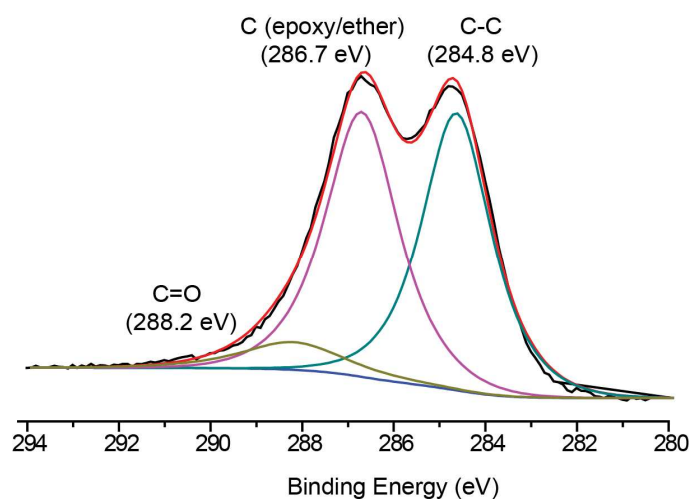


Figure S2. XPS spectra of the synthesized GO sheets.

The XPS sample was prepared by dropping the GO solution (5 mg/mL) on a silicon substrate and dried in air. The GO sheets showed two main oxygen-containing carbon peaks in the XPS data: epoxy/ether group at 286.7 eV and carbonyl group (C=O) at 288.2 eV in addition to non-oxygenated C at 284.8 eV in the C 1s XPS spectrum (Figure S2).

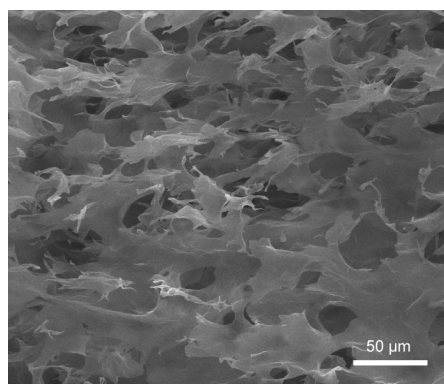


Figure S3. Low-magnification of SEM images for the inner part of the 3D GO sponge.

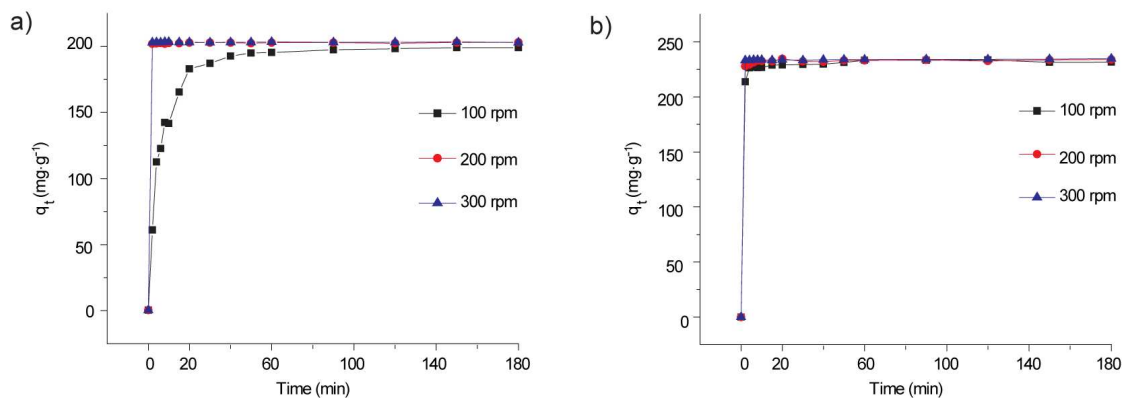


Figure S4. The effect of stirring speed on the adsorption rate of a) MB and b) MV dyes with concentration of 1.2×10^{-3} M.

Table S1. Coefficients of a pseudo first-order diffusion model for MB and MV adsorption on the GO sponge.

Pseudo first-order model of MB				
Temperature (K)	$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	k_1 (min ⁻¹)	R^2
298	389.84	11.102496	0.00951	0.39797
323	396.89	3.0124087	0.01683	0.59684
343	397.65	1.0191205	0.00485	0.03071
Pseudo first-order model of MV				
Temperature (K)	$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	k_1 (min ⁻¹)	R^2
298	385.6637365	84.9387153	0.01125	0.66257
323	402.6763275	55.8958423	0.02431	0.52632
343	467.2161569	3.568837812	-0.01006	0.08247

Theoretical Background

1. Adsorption analysis

On the basis of known dye concentration, we could calculate the average ε from Beer's law.

$$A = \varepsilon b C \quad (1)$$

A is absorbance, ε (L mg⁻¹ cm⁻¹) is the molar absorptivity, b (cm) is 1, C (mg L⁻¹) is concentration of dye samples. Then, from the recorded A , known average ε , and b we could

calculate C_t . The amount of dyes attached onto GOs was calculated according to the mass balance equation as

$$q_t = \frac{V(C_0 - C_t)}{W} \quad (2)$$

q_t is the amount of dyes absorbed on GOs (mg/g) at the fixed time intervals; C_0 and C_t are the initial and liquid-phase concentration of dyes (mg L⁻¹); V (L) is the employed dyes volume; and W (g) is the weight of used 3D GOs.

2. Kinetic analysis of adsorption

Kinetic analysis of the dye adsorption is performed at 298, 323 and 343 K with constant pH 7 at room temperature, and 300 rpm. Pseudo-first, pseudo-second order model is used. These models are commonly used to describe the adsorption kinetics on solid sorbents. Parameters of the kinetic models were taken from experimental data and linear curve-fitting procedure is used.

2.1 Pseudo first-order model

Pseudo-first-order model of Lagerergrgren is widely used in lower concentration of solute from liquid solution. The pseudo-first-order kinetic equation is written in differentiate form.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

q_t is the amount of adsorbed MB and MV on GO sponge (mg of dye/g of GO sponge) at any time t (min); q_e is the amount of adsorbed MB and MV on GO sponge at equilibrium (mg of dye/g of GO sponge). k_1 is the rate constant of pseudo-first-order adsorption(min⁻¹).

After definite intergradations, the equation becomes

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The plot of $\ln(q_e - q_t)$ versus t should give a straight line with slope $-k_1$ and intercept $\ln q_e$ if the adsorption kinetics follows pseudo first-order model. Table I and II show the correlation coefficient values for adsorption MB and MV on sponge varies from 0.03071 to

0.59684 and from 0.08247 to 0.66257, respectively. These results show that experimental data does not agree with the pseudo-first-order kinetic model.

2.2 Pseudo second-order model

The pseudo second-order model equation on adsorption equilibrium can be expressed as following

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

k_2 is the rate constant of pseudo second-order adsorption. Integrated form becomes

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

The plot of t/q versus t should give a straight line with slope $1/q_e$ and intercept $\frac{1}{k_2 q_e^2}$ if the adsorption kinetics follows pseudo second-order model.

2.3 Adsorption mechanism – Intra-particle diffusion model

Weber-Morris plot shows adsorption capacity (q_t) versus $t^{0.5}$ relation with linearity. It can be expressed by

$$q_t = k_i \sqrt{t} + C \quad (7)$$

where k_i is an intra-particle diffusion parameter ($\text{mg g}^{-1} \text{min}^{-0.5}$) and C is the intercept. If the intercept is 0, intra-particle diffusion is the only process mechanism dominant in adsorption. If it is not, it will have complex mechanism with others.

2.4 Thermodynamic analysis

From kinetic analysis, the pseudo second-order is the dominant adsorption kinetics. We estimate the activation energy and Arrhenius factor of MB and MV adsorption on GO sponge with Arrhenius equation using k_2 .

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT} \quad (8)$$

E_a is activation energy (J mol^{-1}); k_2 is the rate constant of adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$); R is the gas constant ($\text{J K}^{-1} \text{ mol}^{-1}$); T is the solution temperature (K). By plotting the experiment data, $\ln k_2$ versus $\frac{1}{T}$, we got slope $-\frac{E_a}{R}$ and intercept $\ln k_0$.

Enthalpy of activation (ΔH^\ddagger) can be derived by Eyring equation. Originally Eyring equation is derived from first-order kinetic process, but it can be used for second-order kinetic process if it is spatial symmetry.

$$\ln \left(\frac{k_2}{T} \right) = \ln \left(\frac{k_b}{h} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (9)$$

Where k_b is Boltzmann's constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$); h is Plank's constant ($6.626 \times 10^{-34} \text{ J s}$); k_2 is the rate constant of adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$); R is the gas constant ($\text{J K}^{-1} \text{ mol}^{-1}$); T is the solution temperature (K). Fig. 4f shows a plot of $\ln \left(\frac{k_2}{T} \right)$ versus $\frac{1}{T}$ with slope $-\frac{\Delta H^\ddagger}{R}$.