Supporting Information for

Ordered Self-Assembly of Amphipathic Graphene Nanosheets into Three-Dimensional Layered Architectures

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The SI file includes:

Experimental Section.

Figure S1. The immersion of net S-RGO in toluene. The fluffy S-RGO monolith was obtained from directly freeze-drying of S-RGO dispersion with very high concentration.

Figure S2. Photograph of S-RGO dispersion (5 mg mL⁻¹, without PVA) after hydrothermal process, which can't form hydrogel.

Figure S3. (a) Photograph of RGO+PVA hydrogel after hydrothermal process (GO: 5 mg mL⁻¹, the mass ratio of GO to PVA is 1:1), with a certain degree of volume shrinkage. (b) and (c) SEM images of RGO+PVA aerogel at different magnifications.

Figure S4. (a-l) SEM images of S-RGO+PVA aerogel with layered microstructures at different magnifications and viewing angles.

Figure S5. SEM image of the parallel-stitching layer surface of S-RGO+PVA aerogel and its corresponding C, O, and S elemental mapping images; EDX spectrum and the concentrations of C, O, S elements in the corresponding table.

Figure S6. Thermogravimetric analysis of S-RGO (after hydrothermal), and S-RGO+PVA aerogel.

Figure S7. Raman spectra of S-RGO (after hydrothermal), and S-RGO+PVA aerogel before and after annealing.

Figure S8. UV-vis spectra of GO, S-RGO and S-RGO+PVA aqueous dispersions.

 Table S1 Regression parameters of kinetic models for MB adsorption onto RGO+PVA

 and S-RGO+PVA aerogels.

Illustration about the samples prepared for adsorption test

Experimental Section

Synthesis of GO: GO was prepared from natural graphite powder (particle size, 80 µm) using a modified Hummers' method. Briefly, graphite (3g) was pre-oxidized using 2.5g K₂S₂O₈, 2.5g P₂O₅, and 12 mL concentrated H₂SO₄ in 80 °C for 4.5 h, then, the solid was washed using deionized (DI) water repeatedly and oven dried. The pre-oxidized graphite and 1.5g NaNO₃ were added to pre-cooled (< 4 °C) concentrated H_2SO_4 (70 mL) under vigorous stirring in an ice bath, followed by the slow addition of 9 g KMnO₄ and carried out a low temperature reaction for half an hour. After that, the reaction was carried out in a moderate temperature (35 °C, 2 h) and high temperature (after 140 mL DI water was added, 98 °C, 15 min). Additional 140 mL DI water was added to the yellow suspension, followed by the addition of 20 mL H₂O₂ (30%). The mixture was filtered and washed with 10% HCl solution until no SO_4^{2-} could be detected with BaCl₂. The resulting solid was dispersed in water via ultrasonication for 30 min and then centrifuged at 8000 rpm to obtain an aqueous dispersion of GO, and any aggregates were discarded. Finally, the GO aqueous dispersion was dialyzed for approximately 2 weeks to remove remaining salt impurities.

Synthesis of S-RGO: S-RGO was synthesized from GO via three steps: (1) prereduction, 4g NaBH₄ dissolved in 100 mL DI water was added to 500 mL GO dispersion (1 mg mL⁻¹), and the mixture was adjusted to pH of 9~10 using ammonium hydroxide and kept at 80 °C for 1h under constant stirring, then, the partially reduced GO was centrifuged and rinsed with DI water several times; (2) sulfonation, 307 mg sulfanilic acid and 120 mg sodium nitrite in 67 mL DI water were reacted with 3.4 mL 1 M HCl solution in an ice bath to form the aryl diazonium salt, which was then added to the redispersed pre-reduced GO dispersion (in 500 mL water via mild sonication) and kept in ice bath for 2 h under stirring, afterwards, the sulfonated product was centrifuged and rinsed several times again; (3) post-reduction, 25 mL hydrazine (50 w/w%) was put into the above redispersed solution and the mixture was reacted at 100 °C for 24 h equipped with reflux condensation. The final obtained sample was purified by washing with water/methanol thoroughly, followed by redispersion of the S-RGO sheets in DI water.

Preparation of S-RGO+PVA and RGO+PVA aerogels: 1 mL of PVA solution (30 or 7.5 mg mL⁻¹, MW: 75, 000~80,000) was added to a 5 mL of S-RGO or GO dispersion (6 mg mL⁻¹) and homogenized with 15 min sonication. All the samples reached to a final S-RGO (GO) concentration of 5 mg mL⁻¹, and possess S-RGO (GO) : PVA weight ratios of 1 : 1 and 4 : 1, respectively. The mixture was then carried out in a hydrothermal reaction at 180°C for 6 h to form hydrogel, which was subsequently freeze-dried to get aerogel. The resulting samples are named as S-RGO+PVA aerogel and RGO+PVA aerogel (GO is reduced in the hydrothermal process). Annealing was carried out in a tube furnace under Ar atmosphere, and the temperature was first increased to 300°C by heating rate of 5°C/min and kept 1h, then further increased to 800 °C (heating rate of 10°C/min) and stayed for 2h.

Characterization: The microstructures of the prepared S-RGO nanosheets and 3D monoliths were characterized by a field emission scanning electron microscopy equipped with an energy dispersive x-ray analysis (FE-SEM/EDAX, S4800, Hitachi), transmission-electron microscope/selected-area diffraction (TEM/SAED, Tecnai F20, FEI) and atomic

force microscope (AFM, Dimension 3100V, Veeco). Powder X-ray diffraction (XRD) profiles were obtained using an AXS D8 Advance diffractometer with Cu K α radiation. Fourier transform infrared spectra (FTIR) was recorded in the 4000-40 cm⁻¹ region by a Thermo Nicolet FTIR spectrophotometer (model 6700). Raman spectra analysis was conducted by a Renishaw inVia Reflex Raman spectrometer with excitation by a 532 nm-wavelength laser. UV-vis spectra measurement was performed on a UV/vis/NIR spectrophotometer (Lambda 950, Perkin Elmer). The specific surface area was measured by Brunauer-Emmett-Teller (BET) N₂ method using an ASAP 2020M surface area analyzer (Micromeritics), and thermogravimetric analysi was measured using a TGA/DSC simultaneous thermal analyzer (STA 449F3, Netzsch) under nitrogen atmosphere, with heating from 30 °C to 800 °C at a rate of 5 °C min⁻¹.

MB adsorption: Methylene blue (MB), one type of cationic dye, was chosen as the model molecule to test the transfer process in different channels of 3D graphene-based macrostructures (RGO+PVA and S-RGO+PVA aerogels). Time-dependent adsorptions were carried out at an initial MB concentration of 50 mg L⁻¹. At predetermined time intervals, MB concentrations were analyzed using UV/vis/NIR spectrometer and calculated by the absorbance at 664 nm. The specific adsorbed amount (q_t) of MB was calculated using Equation 1,

$$q_t = (C_o - C_t) V/m \tag{1}$$

where C_o and C_t are the initial and specific time (*t*) concentrations of MB (mg L⁻¹), respectively, *V* is the volume of aqueous solution (mL), and *m* is the mass of the added aerogels (mg).



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Illustration about the samples prepared for adsorption test

We have selected the same volume density of GO+PVA aerogel to S-RGO+PVA aerogel as far as possible. In our previous test, the effect of PVA amount on the obtained GO+PVA hydrogel was studied, as shown in Figure S9. With increase of PVA, the volume shrinkage of GO+PVA monolith gradually weakened until vanished, while for S-RGO+PVA, there were almost no volume shrinkage observed (but with low PVA, they can't gelate). Therefore, we select an appropriate PVA additive amount to avoid the difference of volume density between GO+PVA and S-RGO+PVA aerogels (both of the concentration of GO and S-RGO was 5 mg mL⁻¹), meanwhile, avoiding that the interlayer spacing were fully filled with PVA filaments.



Increase of PVA

Figure S9. The gelation of GO+PVA mixture after hydrothermal treatment with different PVA addition.

	Pseudo-first-order model ^a			Pseudo-second-order model ^b			Elovich model ^c		
Samples	$q_{\rm e} ({\rm mg \ g^{-1}})$	K_1 (h ⁻¹)	<i>R</i> ²	$q_{\rm e} ({\rm mg \ g}^{-1})$	$K_2 (\mathrm{mg \ g^{-1} \ h^{-1}})$	R^2	β (g mg ⁻¹)	$\alpha ({ m mg g}^{-1}{ m h}^{-1})$	R^2
RGO+PVA	300.52	0.0166	0.9884	381.61	4.1997×10 ⁻⁵	0.9934	0.0196	36.839	0.9011
S-	377.32	0.0106	0.9666	411.85	3.0369×10-4	0.9917	0.0152	199.64	0.9780
RGO+PVA									

Table S1. Regression parameters of kinetic models for MB adsorption on RGO+PVA and S-RGO+PVA aerogels at 50 mg L⁻¹

^{*a*} The pseudo-first-order parameters (q_e and K_1) were calculated using the logarithmic form of the equation $q_t = q_e (1-e^{(-K_1t)})$, where q_t is the amount sorbed per unit weight of sorbent at *t* time, mg g⁻¹; *t* is the time, h; q_e (mg g⁻¹) is the adsorption capacity coefficient at equilibrium time, and K_1 (h⁻¹) is the rate constant. R^2 is the regression coefficient.

^{*b*} The pseudo-second-order parameters (q_e and K_2) were calculated using the logarithmic form of the equation $q_t = K_2 q_e^2 t /(1 + K_2 q_e t)$, where q_t is the amount sorbed per unit weight of sorbent at *t* time, mg g⁻¹; *t* is the time, h; q_e (mg g⁻¹) is the adsorption capacity coefficient at equilibrium time, and K_2 (mg g⁻¹ h⁻¹) is the rate constant. R^2 is the regression coefficient.

^c The Elovich parameters (α and β) were calculated using the logarithmic form of the equation $q_t = (1/\beta)\ln(\beta\alpha) + (1/\beta)\ln(t)$, where q_t is the amount sorbed per unit weight of sorbent at *t* time, mg g⁻¹; *t* is the time, h; β (g mg⁻¹) is the desorption constant, and α (mg g⁻¹ h⁻¹) is the initial adsorption rate. R^2 is the regression coefficient.