

## Electronic Supporting Information

### Nanoscale ionic materials based on hydroxyl-functionalized graphene

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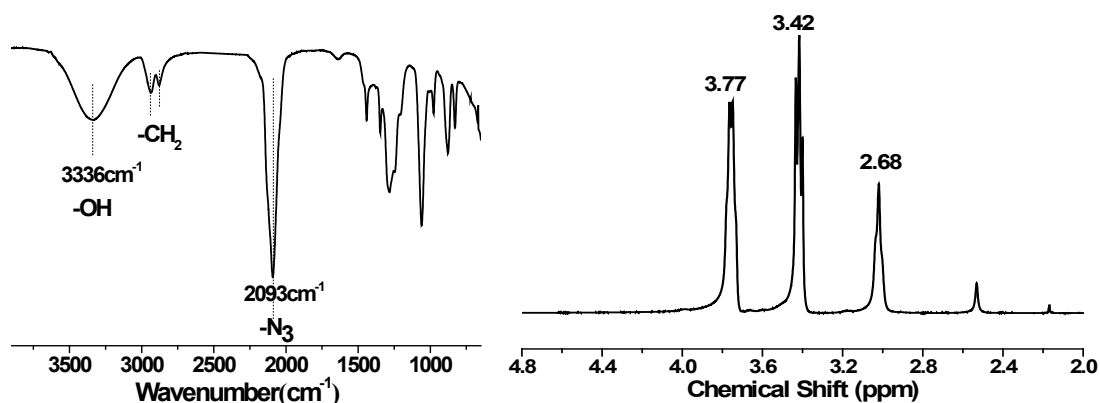
#### 1. Materials used in this study

Expandable graphite flake (GrafGuard 220-80 N) was provided by GrafTech International, USA. 3-(Trihydroxysilyl)-1-propane sulfonic acid (SIT, 40 wt% solution in water) was obtained and used as received from Gelest Inc., USA. An amino-terminated block copolymer (Jaffamine M-2070,  $M_w \approx 2,000$ ) was purchased from Huntsman Corp., USA, and used as received. Most of the solvents or reagents used in the experiment, including 2-chloroethanol, concentrated sulfuric acid ( $H_2SO_4$ ), concentrated hydrochloric acid (HCl), diethyl ether, methanol, ethanol, acetone, toluene, chloroform, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidinone (NMP) were all in the AR grade and obtained from Sinopharm Chemical Reagent Beijing Co., Ltd, China. The potassium permanganate ( $KMnO_4$ ) and sodium azide ( $NaN_3$ ) were purchased from Solarbio Biotechnology Beijing Co. The dialysis tubing used in this study (14K MWCO) was purchased from Jingke Biotechnology Co., Beijing.

#### 2. Preparation of 2-azidoethanol [S1] and hydroxyl-functionalized graphene (G-OH) [S2]

Typically, sodium azide (20 g, 0.3 mol) and 2-chloroethanol (16 g, 0.2 mol) were mixed in deionized water (80 mL), and then the aqueous solution was added to a 250 mL three-neck round-bottom flask equipped with a condenser. The mixture was kept being stirred for 96 h with its temperature maintained at 80 °C. After cooling to room temperature, the reaction mixture was fully extracted with diethyl ether (5×100 mL). The extracts were concentrated with a rotary evaporator under reduced pressure to produce colorless oil, and then further dried over anhydrous  $Na_2SO_4$  overnight.

As seen from Fig. S1, the appearance of peaks in FTIR spectra at  $2093\text{ cm}^{-1}$ ,  $3336\text{ cm}^{-1}$ , and  $2883 \sim 2993\text{ cm}^{-1}$  corresponds to the vibrations of  $\text{-N}_3$ ,  $\text{-OH}$  and  $\text{-CH}_2$  groups of  $\text{N}_3\text{CH}_2\text{CH}_2\text{OH}$ , respectively. Moreover, the  $^1\text{H}$  NMR peaks at 3.77, 3.42 and 2.68 ppm can be assigned to the three types of hydrogen atoms in  $\text{N}_3\text{CH}_2\text{CH}_2\text{OH}$ , and the ratio of peak areas is about 2 : 2 : 1. The obtained results suggest that 2-azidoethanol has been successfully prepared.



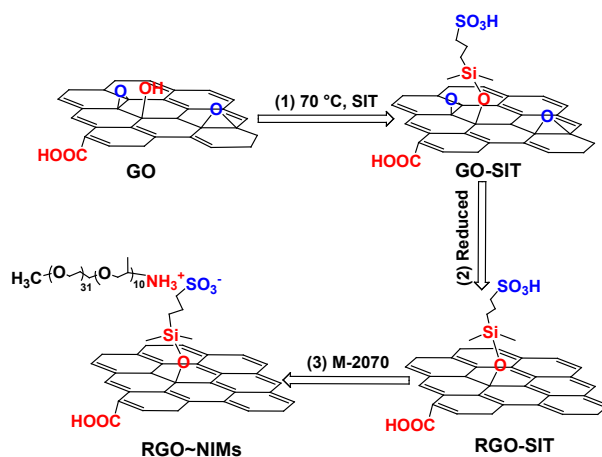
**Fig. S1.** FTIR (left) and  $^1\text{H}$  NMR (right) spectra of as-prepared 2-azidoethanol.

The graphite oxide (0.5 g) was mixed with NMP (200 mL), and the mixture was treated with an ultrasonic bath (100 W, 40 kHz) for 2 h. After that, the mixture was transfer to a 500 mL three-necked flask fitted with a condenser. The mixture was bubbled with high purity  $\text{N}_2$  for 30 minutes to expel the air inside the flask. The as-prepared 2-azidoethanol (10 g) was then injected into the mixture. The reaction mixture was heated up and kept at  $160\text{ }^\circ\text{C}$  in  $\text{N}_2$  atmosphere for 18 h under vigorous stirring. After the reaction, the mixture was naturally cooled to room temperature. The product G-OH was collected by repeated high-speed centrifugation and washing with acetone.

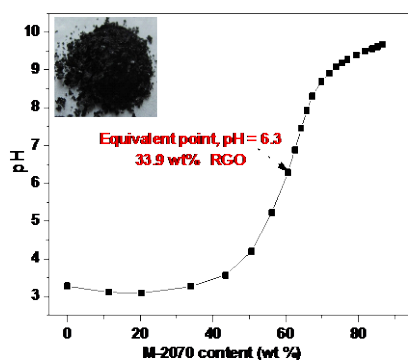
### 3. Preparation of reduced graphene oxide (RGO)-based NIMs (RGO~NIMs)

As shown in Scheme S1, the RGO~NIMs were prepared using a three-step reaction, which was very similar to that adopted for the preparation of G-OH~NIMs. Graphite oxide powder (300 mg) was dispersed in deionized water (200 mL) with the aid of ultrasonic treating for 1 h. The pH value of the dispersion was adjusted to *ca.* 10 through the addition of several drops of 10 wt% NaOH aqueous solution, and the

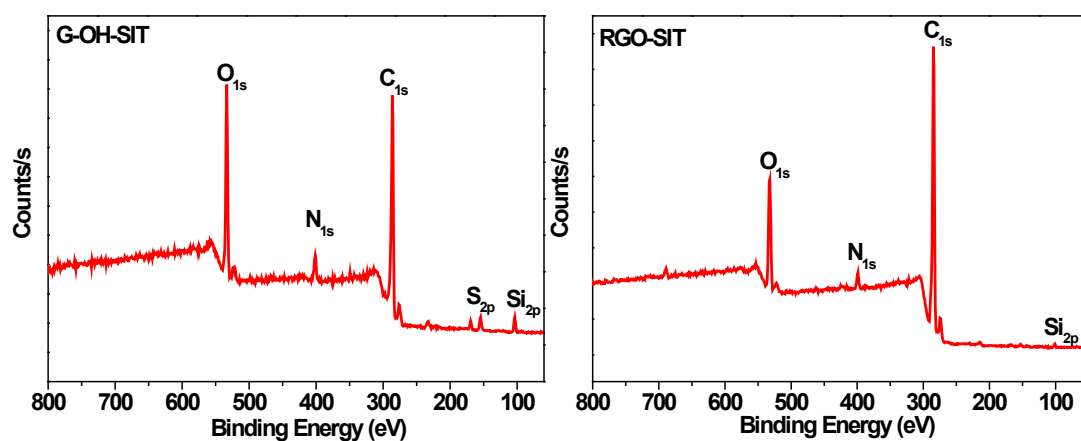
dispersion was ultrasonicated for another 1 h. The 40 wt% SIT solution (2 mL) was diluted with 20 mL deionized water. The diluted SIT solution was dropwise added to GO/H<sub>2</sub>O suspension while stirring vigorously. The silylation reaction between GO and SIT was carried out for 24 h at the temperature of 70 °C. Then the obtained aqueous solution of product (GO-SIT) was dialyzed for 48 h to remove the excess silane coupling agent. The obtained GO-SIT in the aqueous solution was chemically reduced with hydrazine hydrate at 80 °C for 12 h to obtain the reduced GO (RGO)-SIT. During the reduction process, mainly the epoxy groups on the surface of GO were eliminated [S3]. After the chemical reduction, the solution of RGO-SIT was also run through an ion-exchange column to fully protonate the sulfonate groups grafted on the surface of RGO. Finally, the RGO~NIMs could be obtained by using the acid–base reaction between RGO-SIT and M-2070. The composition of final products could also be adjusted by stopping the titration at different pH points.



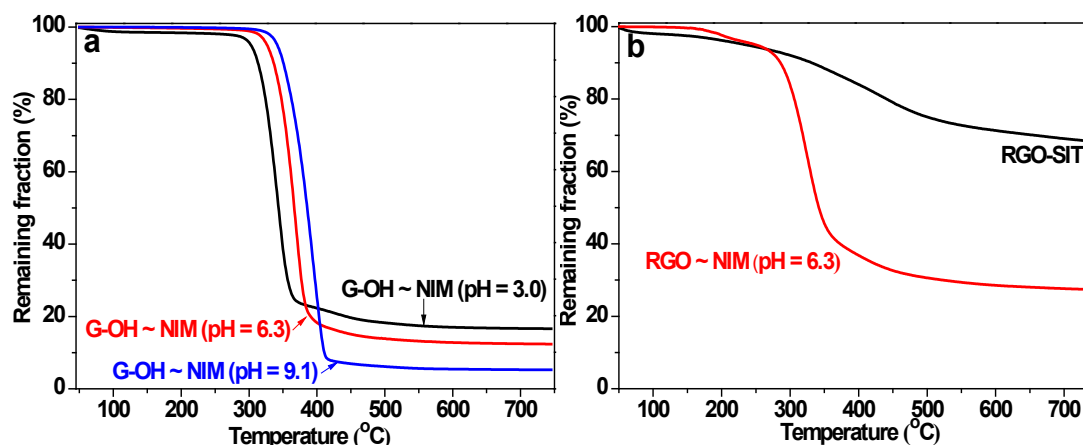
**Scheme S1.** Schematic for synthesis of RGO~NIMs: (1) Silylation reaction between GO and SIT; (2) Chemical reduction of GO-SIT with hydrazine hydrate; (3) Acid–base reaction between RGO-SIT and amino-terminal block copolymer M-2070.



**Fig. S2.** Titration curve for the acid–base reaction between RGO-SIT and M-2070 (Inset: the digital photograph that shows the black solid appearance of RGO~NIM obtained by stopping the titration at the equivalence point, pH = 6.3).



**Fig. S3.** XPS general spectra of G-OH-SIT (left) and RGO-SIT (right). The relative content of Si element in G-OH-SIT is higher than that in RGO-SIT as seen from the spectra. The atomic ratios of Si/C in G-OH-SIT and RGO-SIT are approximately 1/27 and 1/100, respectively. Since one azide compound contains two carbon atoms and one SIT contains three carbon atoms, the grafting density is 1 SIT per 22 and 97 graphene carbon atoms of G-OH and RGO, respectively.



**Fig. S4.** A series of TGA curves of NIMs based on (a) G-OH, and (b) RGO in the temperature range from 50 to 750 °C at a heating rate of 10 °C min<sup>-1</sup> under the nitrogen atmosphere.

#### 4. The calculation of the compositions for G-OH~NIMs and RGO~NIMs based on TGA measurement results

The G-OH~NIM (pH = 6.3) has a thermal residue fraction of 12.3 wt% up to the temperature of 750 °C (see Fig. 3 in the main text), which is totally the leftover from the thermal decomposition of G-OH-SIT. In the same temperature range, the thermal residue fraction of G-OH-SIT is 62.2 wt%. So the mass fraction of M-2070 is 80.2 wt%

$(1 - \frac{12.3\%}{62.2\%})$ , and the fraction of G-OH-SIT is 19.8 wt% in G-OH~NIM (pH = 6.3).

Moreover, SIT and M-2070, which involve in the acid–base reaction to form G-OH~NIM, are in the molar ratio of 1 : 1 at the equivalence point. Taking into account the molecular weight of SIT and M-2070 (i.e. 202 and 1975, respectively), we can obtain the relative content of SIT, which is 8.2 wt%. Thus, the weight percent of G-OH for G-OH~NIM (pH = 6.3) can be easily obtained, and it is 11.6 wt%.

The mass fractions of M-2070 for the other two G-OH~NIMs (pH = 3.0 and pH = 9.1) can be calculated similarly by considering their final thermal residual fractions relative to that of G-OH-SIT. Besides, we have gotten the composition of G-OH-SIT (G-OH : SIT = 11.6 : 8.2 wt%), so we can further acquire the detail compositions of G-OH~NIMs (pH = 3.0 and pH = 9.1).

The relative weight concentration of each component in RGO~NIM (pH = 6.3) can be calculated by using the analogous method as described above. The obtained

compositions for the investigated G-OH~NIMs and RGO~NIMs are listed in Table S1.

**Table S1.** Detailed compositions for the prepared NIMs based on G-OH and RGO obtained from TGA measurement results

Samples	Thermal residue fraction /wt% <sup>a</sup>	Mass fraction of each component			Grafting density of SIT <sup>b</sup>
		Graphene/%	SIT/%	M-2070/%	
G-OH-SIT	62.2	58.4 (G-OH)	41.6	—	1 SIT/21 graphene C
G-OH~NIM (pH = 3.0)	16.6	15.6 (G-OH)	11.4	73.0	—
G-OH~NIM (pH = 6.3)	12.3	11.6 (G-OH)	8.2	80.2	—
G-OH~NIM (pH = 9.1)	5.2	4.9 (G-OH)	3.6	91.5	—
RGO-SIT	68.2	85.0 (RGO)	15.0	—	1 SIT/94 graphene C
RGO ~ NIM (pH = 6.3)	27.3	33.9 (RGO)	6.1	60.0	—

<sup>a</sup> The data were read from TGA curves (Figs. 3 & S4);

$$^b n = \frac{W_{\text{graphene}}}{m_{\text{graphene}}} \bigg/ \frac{W_{\text{SIT}}}{m_{\text{SIT}}}, \text{ where } n \text{ is the grafting density of SIT; } W_{\text{graphene}} \text{ and } W_{\text{SIT}} \text{ are weight percent}$$

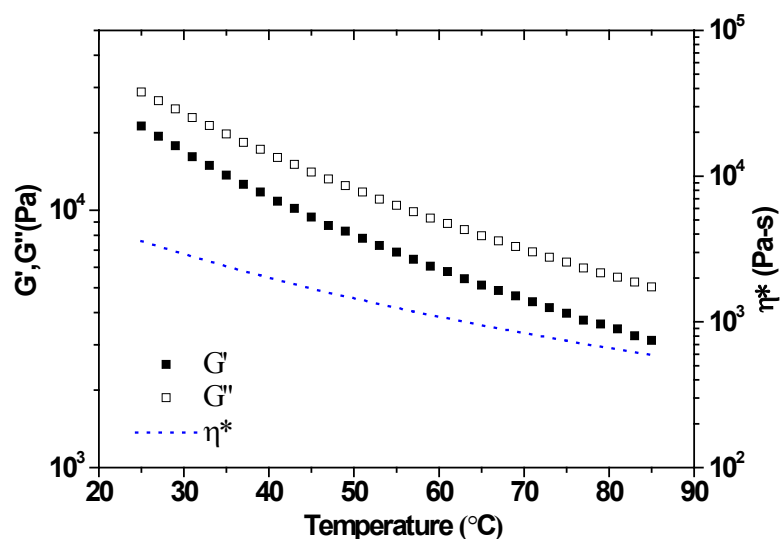
of the graphene and SIT in silanated graphene (RGO-SIT or G-OH-SIT);  $m_{\text{graphene}}$  and  $m_{\text{SIT}}$  are the molar mass of carbon and SIT.

## 5. The influence of temperature on the rheological properties of G-OH~NIM

**(pH = 6.3)**

We carried out the tests to investigate the influence of temperature on the rheological properties of G-OH~NIM (pH = 6.3). The moduli vs. temperature curves were recorded in the temperature sweep mode at fixed angular frequency of 10 rad s<sup>-1</sup> and strain amplitude of 0.1%. The investigated temperature range was 25–85 °C with temperature step of 2 °C and equilibration time of 30 s at each temperature point. The tested result is depicted in Fig. S5.

As expected,  $G''$  and  $G'$  decrease with the increasing of temperature, and  $G''$  is higher than  $G'$  in the investigated temperature range as the separation between them increases with the temperature increasing, which indicates the enhanced fluidity of G-OH~NIM (pH = 6.3) at higher temperatures.



**Fig. S5.** Dynamic elastic ( $G'$ ), viscous ( $G''$ ) moduli, and complex viscosity ( $\eta^*$ ) as a function of temperature for G-OH~NIM (pH = 6.3, 11.6 wt%).

**Table S2.** The Hansen's solubility parameters ( $\delta_p + \delta_h$ ) of all tested solvents [S4]

Solvent	Toluene	CHCl <sub>3</sub>	THF	Acetone	DMF	DMSO	Ethanol	Methanol	Water
$\delta_p + \delta_h$ (MPa <sup>-1/2</sup> )	3.4	8.8	13.7	17.4	25.0	26.6	28.2	34.6	58.3

$\delta_p$  is the polarity cohesion parameter;  $\delta_h$  is the hydrogen-bonding cohesion parameter.

### References for ESI

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