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 ($5\times100$ 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 cm\(^{-1}\), 3336 cm\(^{-1}\), and 2883 ~ 2993 cm\(^{-1}\) corresponds to the vibrations of -N\(_3\), -OH and -CH\(_2\) groups of N\(_3\)CH\(_2\)CH\(_2\)OH, respectively. Moreover, the \(^1\)H NMR peaks at 3.77, 3.42 and 2.68 ppm can be assigned to the three types of hydrogen atoms in N\(_3\)CH\(_2\)CH\(_2\)OH, and the ratio of peak areas is about 2 : 2 : 1. The obtained results suggest that 2-azidoethanol has been successfully prepared.

![FTIR and 1H NMR Spectra](image)

**Fig. S1.** FTIR (left) and \(^1\)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 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 °C in 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/H₂O 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⁻¹ 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

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

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

b \( n = \frac{W_{\text{graphene}}}{m_{\text{graphene}}} \times \frac{W_{\text{SIT}}}{m_{\text{SIT}}} \), where \( n \) is the grafting density of SIT; \( W_{\text{graphene}} \) and \( W_{\text{SIT}} \) 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

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(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\(^{-1}\) 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.

![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%).](image)

**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]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Toluene</th>
<th>CHCl(_3)</th>
<th>THF</th>
<th>Acetone</th>
<th>DMF</th>
<th>DMSO</th>
<th>Ethanol</th>
<th>Methanol</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta_p + \delta_h) (MPa(^{-1/2}))</td>
<td>3.4</td>
<td>8.8</td>
<td>13.7</td>
<td>17.4</td>
<td>25.0</td>
<td>26.6</td>
<td>28.2</td>
<td>34.6</td>
<td>58.3</td>
</tr>
</tbody>
</table>

\(\delta_p\) is the polarity cohesion parameter; \(\delta_h\) is the hydrogen-bonding cohesion parameter.
References for ESI


