

## Supplementary Information

### Phase Transfer and Dispersion of Reduced Graphene Oxide

#### Nanosheets Using Cluster Suprasurfactants

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#### Materials:

H<sub>4</sub>[SiW<sub>12</sub>O<sub>40</sub>] (POM-4), Dimethyldioctadecylammonium bromide (DODA·Br, 99%) and graphite powder were commercial products from Sigma-Aldrich and used as received. K<sub>5</sub>[BW<sub>12</sub>O<sub>40</sub>] (POM-5), K<sub>6</sub>[CoW<sub>12</sub>O<sub>40</sub>] (POM-6), K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>] (POM-7), K<sub>8</sub>[SiW<sub>11</sub>O<sub>39</sub>] (POM-8), K<sub>8</sub>H[BW<sub>11</sub>O<sub>39</sub>] (POM-9) and Na<sub>10</sub>[SiW<sub>9</sub>O<sub>34</sub>] (POM-10) were freshly prepared according to the previous procedures in the literatures.<sup>[1-6]</sup>

#### Measurements:

Elemental analysis (C, H, N) was performed on a Flash EA1112 from ThermoQuest Italia S.P.A. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer with a monochromic X-ray source (Al K $\alpha$  line, 1486.6 eV) and the charging shift was corrected by the binding energy of C(1s) at 284.6 eV. Dynamic light scattering (DLS) and Zeta potential data were collected on a Zetasizer Nano-ZS (Malvern Instruments). FTIR spectra were carried out on a Bruker Vertex 80V FTIR spectrometer equipped with a DTGS detector (64 scans) with a resolution of 1 cm<sup>-1</sup> on a KBr pellet. The UV-vis-NIR absorption spectra were recorded by a Varian CARY 50 Probe spectrometer in 10 mm quartz cuvettes. Transmission electron microscopy (TEM) was conducted on a JEOL JEM 2010 electron microscope under an accelerating voltage of 200 kV and energy-dispersive X-ray (EDX) spectrum was collected on a FEI Tecnai F20 microscope operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected on a Japan Rigaku SmartLab X-ray diffractometer (D/max rA, using Cu K $\alpha$ 1 radiation at 1.542 Å). Atomic force microscopy (AFM) images were taken with a Nanoscope IIIa AFM Multimode (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was

operated in the tapping mode with an optical readout using Si cantilevers. AFM sample of GO was prepared by a dip coating method. Typically, a mica was dipped into a GO suspension ( $0.2 \text{ mg mL}^{-1}$ ) and then slowly withdrawn from the solution at a constant speed of  $1 \text{ mm min}^{-1}$ , allowing for the deposition of a large amount of GO sheets on the substrate surface. AFM sample of RGO was prepared by spin coating on HOPG substrate. Thermal gravimetric analysis (TGA) measurement was performed on a STA 449 C (NATZSCH) under flowing air with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

#### **Preparation of graphene oxide (GO):**

Graphene oxide (GO) nanosheets were prepared by vigorous oxidation and exfoliation of the graphite powder following our published procedure,<sup>[7]</sup> then sonication (100 W) and centrifugation for cutting. In a typical experiment, the as-prepared GO suspension ( $1 \text{ mg mL}^{-1}$ ) was under sonication for 2 h accompanying with stirring, and then centrifugation with 12000 rpm for 10 min. The collecting supernatant was concentrated to  $2 \text{ mg mL}^{-1}$  and under centrifugation with 6000 rpm for 10 min to collect the supernatant, then further centrifugation with 12000 rpm for 1 h to collect the flocculent precipitate. At last evaporated it at  $60 \text{ }^\circ\text{C}$  with ethanol for 3 times to remove the residual water and then dried it in vacuum oven at  $60 \text{ }^\circ\text{C}$  for 48 h. The pH value of obtained GO suspension is about 5.

#### **Preparation of reduced GO (RGO):**

In a typical procedure, GO (5 mg) and water (100 mL) were loaded in a 250-mL round-bottom flask, then under sonication (100 W) for 15 min, yielding a yellow-brown dispersion. Hydrazine hydrate ( $50 \text{ } \mu\text{L}$ , 85%) was then added and the solution heated in an oil bath at  $95 \text{ }^\circ\text{C}$  under a water-cooled condenser for 1 h over which the reduced GO gradually became black. The excess hydrazine was removed by reacting with oxygen at  $50 \text{ }^\circ\text{C}$ . During the whole process, almost no precipitate was observed. The pH value of as-prepared RGO suspension is *ca.* 7.

#### **Synthesis of SEPs:**

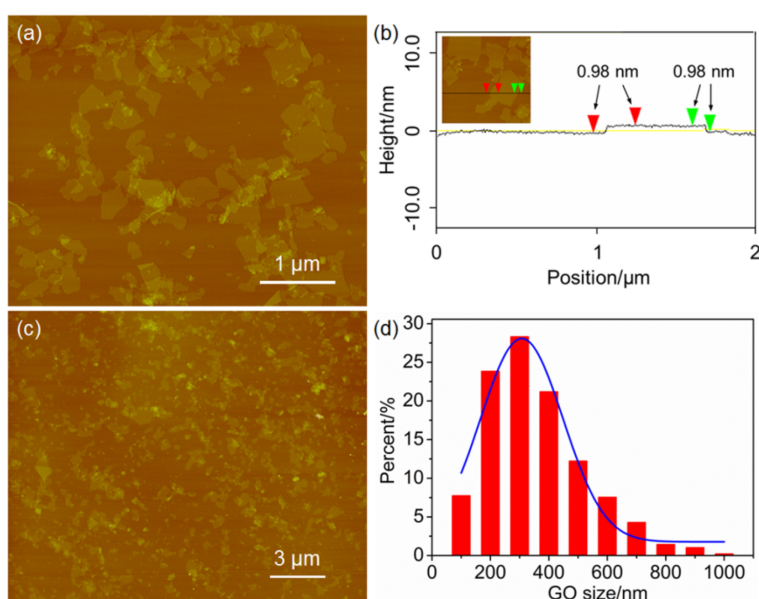
SEPs were synthesized according to the previously reported procedures,<sup>[8,9]</sup> exemplified by SEP-4. POM-4 was dissolved in aqueous solution, and then a chloroform solution of DODA·Br was added with stirring. The initial molar ratio of DODA·Br to POM-4 was controlled at 3.8:1. The organic phase was separated, and  $(\text{DODA})_4[\text{SiW}_{12}\text{O}_{40}]$  (SEP-4) was obtained by evaporating the chloroform to dryness. Next, the sample was further dried under vacuum until its weight remained constant. Following similar procedures,  $(\text{DODA})_5[\text{BW}_{12}\text{O}_{40}]$  (SEP-5),  $(\text{DODA})_6[\text{CoW}_{12}\text{O}_{40}]$  (SEP-6),  $(\text{DODA})_7[\text{PW}_{11}\text{O}_{39}]$  (SEP-7),  $(\text{DODA})_8[\text{SiW}_{11}\text{O}_{39}]$  (SEP-8),  $(\text{DODA})_9[\text{BW}_{11}\text{O}_{39}]$  (SEP-9) and  $(\text{DODA})_{10}[\text{SiW}_9\text{O}_{34}]$  (SEP-10) were prepared. For SEP-4, Anal. Calc.: C 35.95, H 6.35, N 1.10; Found: C 36.15, H 6.28, N 1.09. For SEP-5, Anal. Calc.: C 40.67, H 7.18, N 1.25; Found: C 40.69, H 7.04, N 1.17. For SEP-6, Anal. Calc.: C 44.08, H 7.79, N 1.35; Found: C 43.96, H 7.55, N 1.25. For SEP-7, Anal. Calc.: C 48.89, H 8.64, N 1.50; Found: C 48.68, H 8.51, N 1.49. For SEP-8, Anal. Calc.: C 51.55, H 9.11, N 1.58; Found: C 51.30, H 9.22, N 1.63. For

SEP-9, Anal. Calc.: C 53.93, H 9.53, N 1.66; Found: C 53.84, H 9.36, N 1.51. For SEP-10, Anal. Calc.: C 58.99, H 10.42, N 1.81; Found: C 58.67, H 10.45, N 1.87. FTIR spectra (Figure S5) showed that the characteristic peaks of POMs appeared in SEPs, confirming the structures of POMs maintained in SEPs.

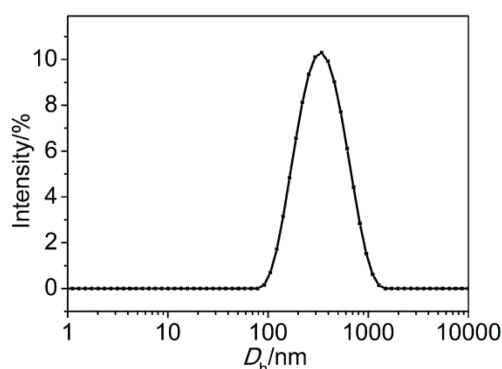
**Calculation of maximum amount SEP adsorbed by RGO:**

According to the literatures, the theoretical specific surface area of graphene is  $2360 \text{ m}^2 \text{ g}^{-1}$  [10] and the condensed molecular area of SEP-4 calculated from surface pressure-area isotherm result is  $3.05 \text{ nm}^2$ . [11] Based on these values, the maximum amount ( $n_0$ ) of SEP-4 which can be adsorbed by 1 mg RGO can be estimated by applying the following formula:

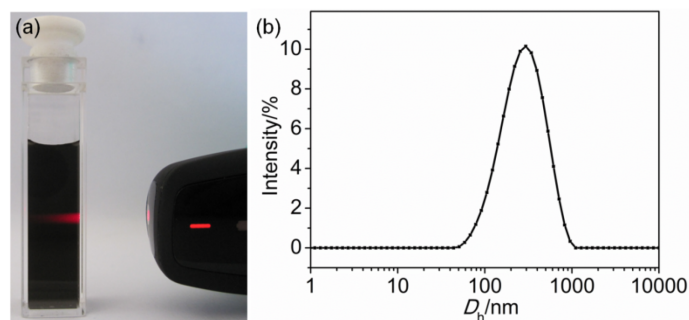
$$n_0 = \frac{2360 \times 1 \times 10^{-3}}{3.05 \times 10^{-18} \times 6.02 \times 10^{23}} = 1.3 \times 10^{-6} \text{ mol}$$



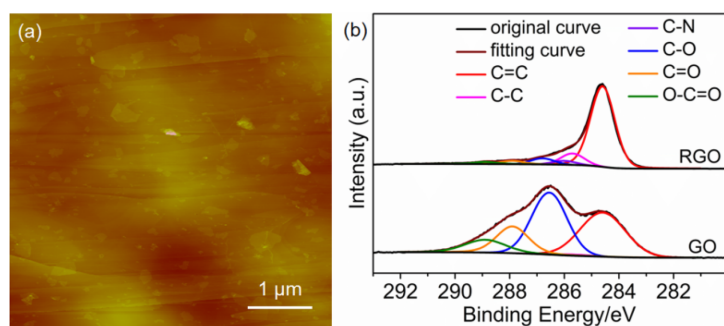
**Fig. S1** (a) and (c) AFM images, (b) height profile of AFM image (inset) and (d) histogram and Gaussian fit curve in size of GO nanosheets on mica substrate.



**Fig. S2** DLS diagram of GO aqueous solution.



**Fig. S3** (a) Photograph of Tyndall scattering observation and (b) DLS diagram of the as-prepared RGO aqueous solution.

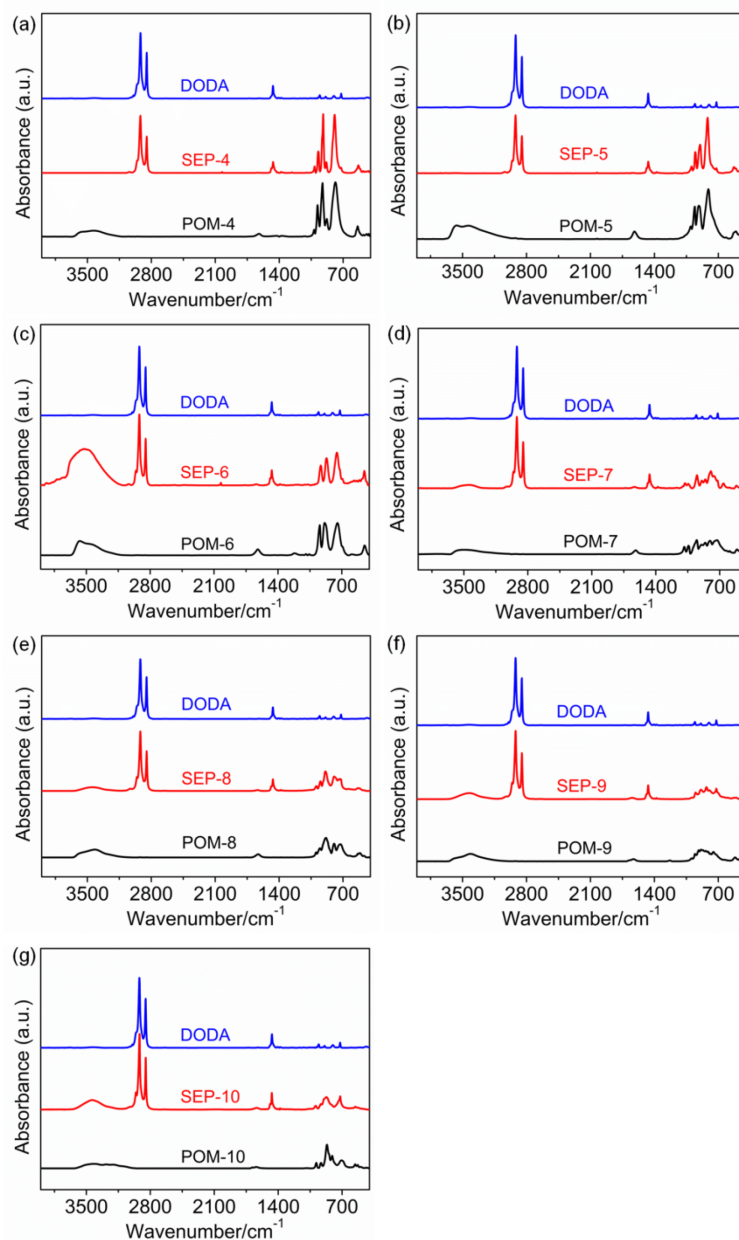


**Fig. S4** (a) AFM image of RGO nanosheets on HOPG substrate. (b) XPS spectra of GO and RGO.

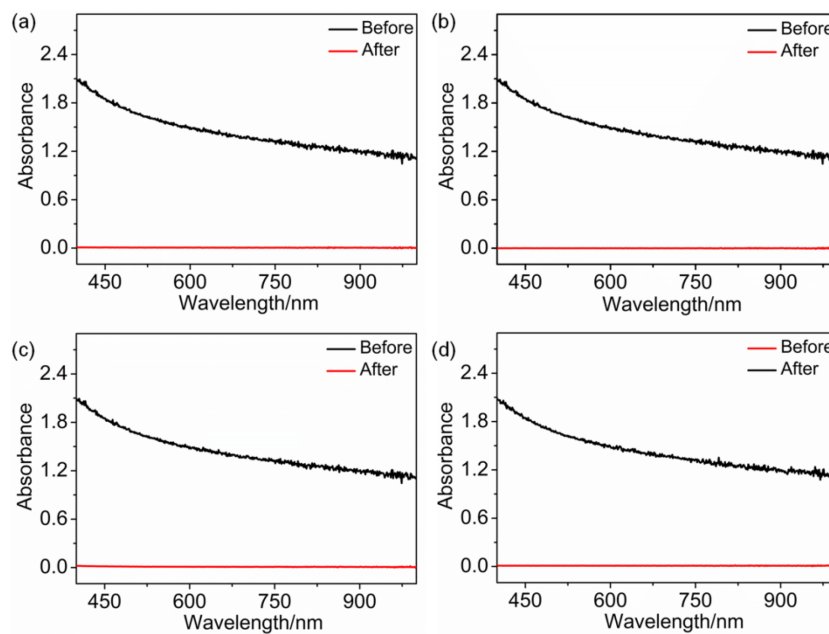
**Table S1** Summary of the content of six types of carbon with different chemical states in GO and RGO.

	C=C	C-C	C-N	C-O	C=O	O-C=O
<i>E/eV</i>	284.6	285.7	286.0	286.8	287.9	288.9
GO/%	34.7	0.8	0	38.0	16.6	9.9
RGO/%	75.5	9.8	3.3	5.2	3.4	2.8

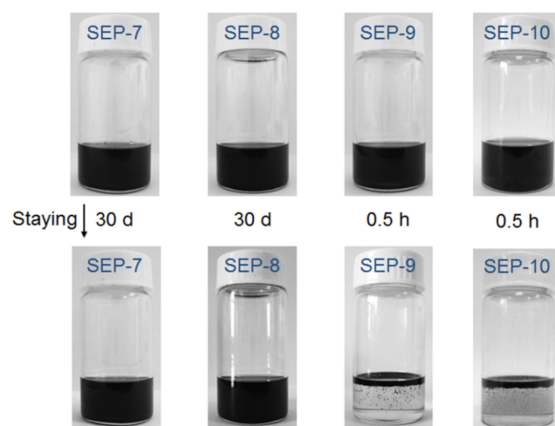




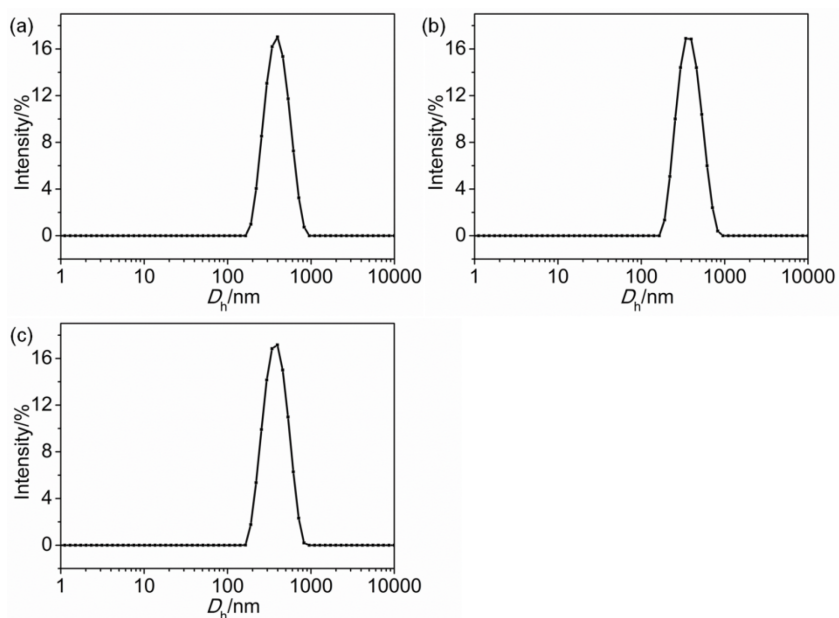
**Fig. S5** FTIR spectra of DODA (blue), POMs (black) and SEPs (red) in KBr pellets: (a) POM-4 and SEP-4; (b) POM-5 and SEP-5; (c) POM-6 and SEP-6; (d) POM-7 and SEP-7; (e) POM-8 and SEP-8; (f) POM-9 and SEP-9; (g) POM-10 and SEP-10.



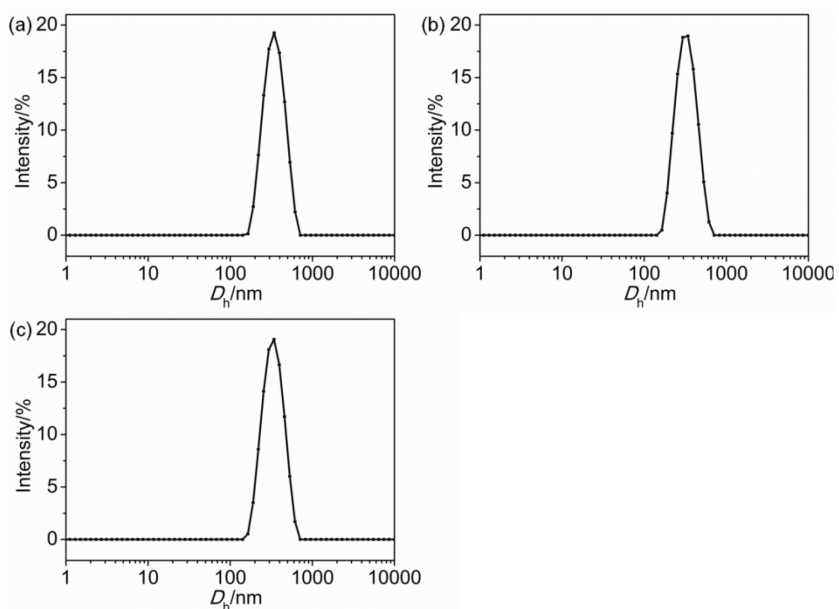
**Fig. S6** UV-vis-NIR absorption spectra of the water phase before (black) and after (red) phase transfer of RGO by SEPs: (a) SEP-7; (b) SEP-8; (c) SEP-9; (d) SEP-10.



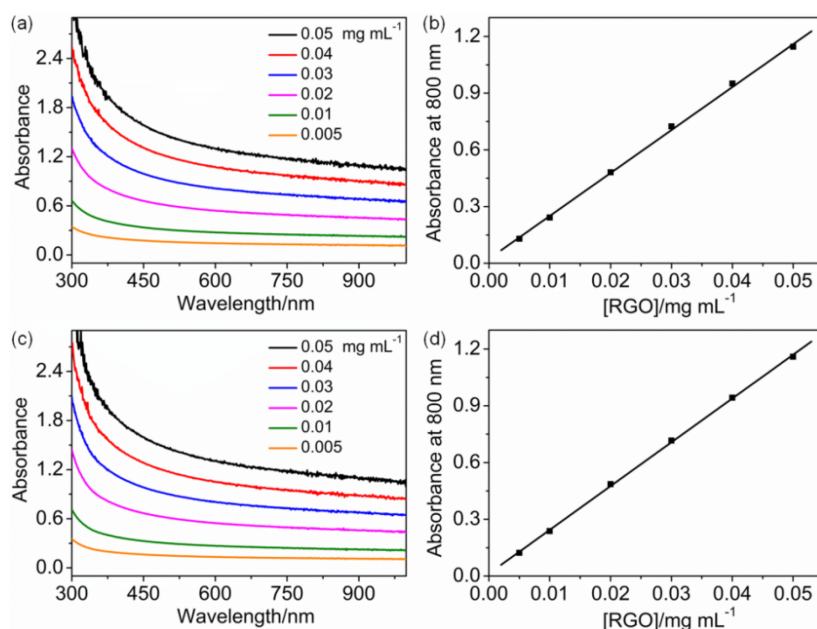
**Fig. S7** Photographs of the chloroform phases after phase transfer of RGO by SEP-7, SEP-8, SEP-9 and SEP-10 before and after staying for 30 d, 30 d, 0.5 h and 0.5 h, respectively.



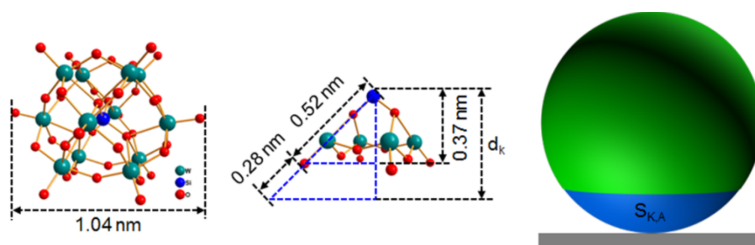
**Fig. S8** DLS diagrams of the obtained chloroform solutions of SEP-7/RGO nanocomposite after staying for different time: (a) 0 d; (b) 1 d; (c) 2 d.



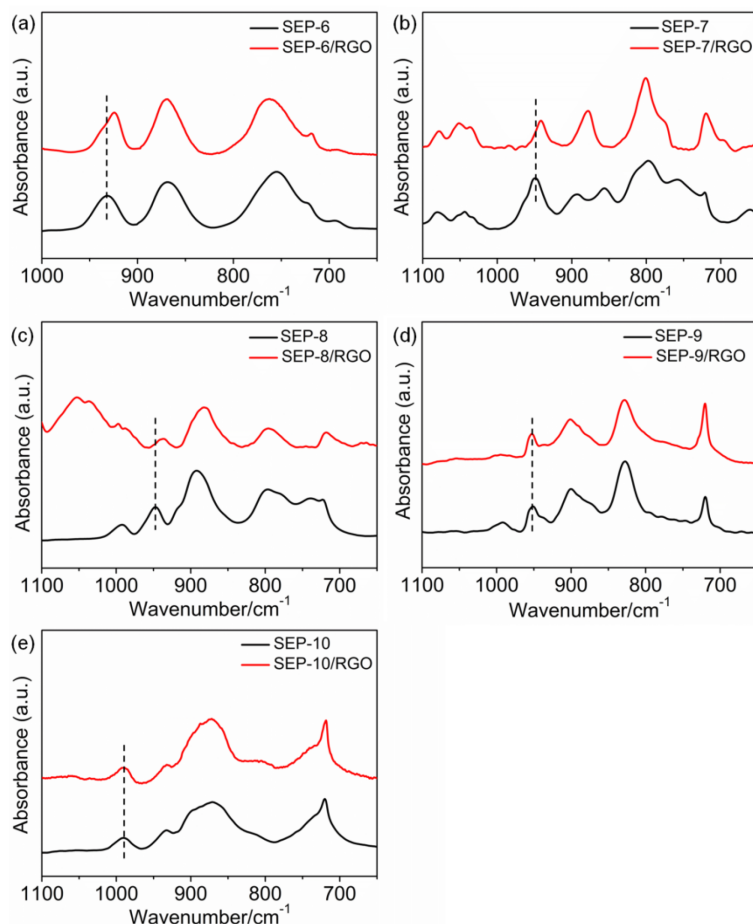
**Fig. S9** DLS diagrams of the obtained chloroform solutions of SEP-8/RGO nanocomposite after staying for different time: (a) 0 d; (b) 1 d; (c) 2 d.



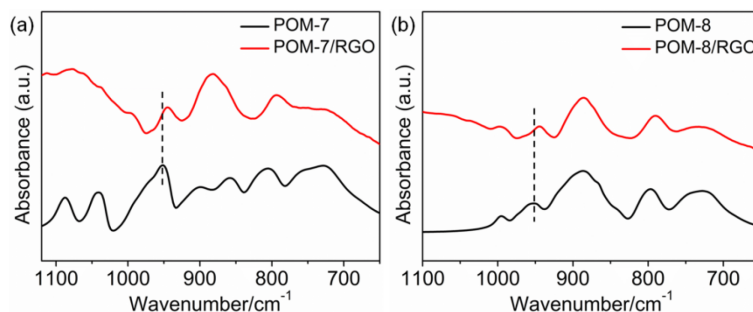
**Fig. S10** UV-vis-NIR absorption spectra of (a) SEP-7/RGO nanocomposite and (c) SEP-8/RGO nanocomposite varying with the concentration of RGO from 0.005 to 0.05 mg mL<sup>-1</sup> in chloroform. Plots of absorbance at 800 nm against [RGO]: (b) SEP-7/RGO nanocomposite and (d) SEP-8/RGO nanocomposite.



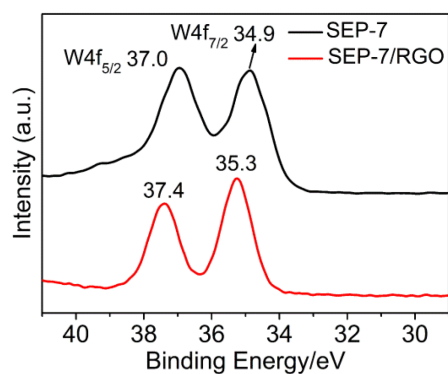
**Fig. S11** The calculation of the POM-RGO interacting area  $S_{K,A}$  (four terminal oxygen atoms perpendicular to the S4 orientation adsorbed on RGO<sup>[12]</sup>),  $S_{K,A} = 2\pi R(R - d_k) = 1.16 \text{ nm}^2$ . The radius of the sphere:  $R = 0.52 + 0.28 = 0.80 \text{ nm}$ ; the distance from sphere center to the cross section of ball crown:  $d_k = 0.37 \times 0.80 / 0.52 = 0.57 \text{ nm}$ ; 0.52 nm: the radius of the POM; 0.28 nm: van der Waals radius; 0.37 nm: the distance from sphere center to the plane formed by the adsorbed four terminal oxygen atoms.



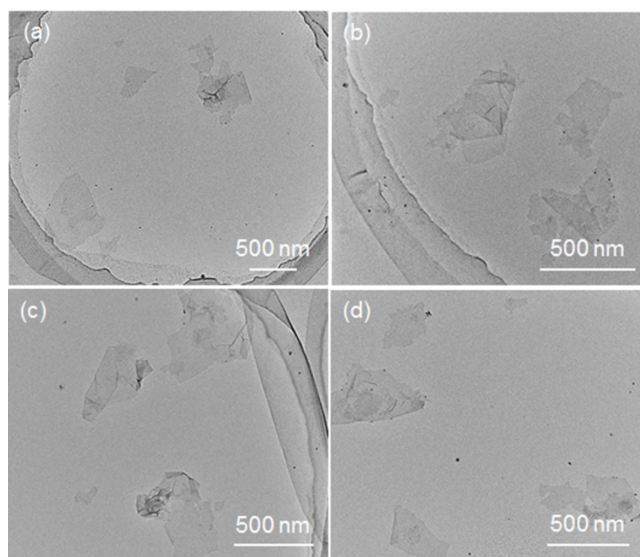
**Fig. S12** FTIR spectra of (a) pure SEP-6 (black) and SEP-6/RGO nanocomposite (red); (b) pure SEP-7 (black) and SEP-7/RGO nanocomposite (red); (c) pure SEP-8 (black) and SEP-8/RGO nanocomposite (red); (d) pure SEP-9 (black) and SEP-9/RGO nanocomposite (red); (e) pure SEP-10 (black) and SEP-10/RGO nanocomposite (red). The  $\nu_{as}(W=O_d)$  vibration band of SEP-6 appears at  $931\text{ cm}^{-1}$ , while it shifts to  $924\text{ cm}^{-1}$  for SEP-6/RGO nanocomposite, confirming an electron transfer interaction between POM-6 clusters and RGO nanosheets.



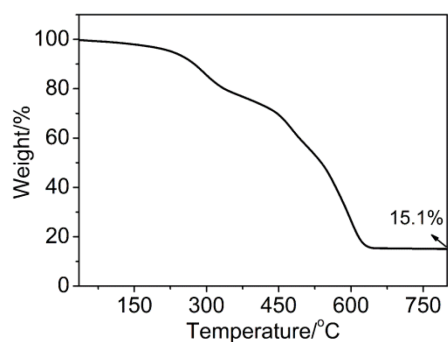
**Fig. S13** FTIR spectra of (a) pure POM-7 (black) and POM-7/RGO nanocomposite (red); (b) pure POM-8 (black) and POM-8/RGO nanocomposite (red). The  $\nu_{as}(W=O_d)$  vibration bands of POM-7 and POM-8 appear at  $954$  and  $952\text{ cm}^{-1}$ , while they shift to  $945$  and  $944\text{ cm}^{-1}$  for POM-7/RGO and POM-8/RGO nanocomposites, respectively, indicating the electron transfer interactions between POM clusters and RGO nanosheets.



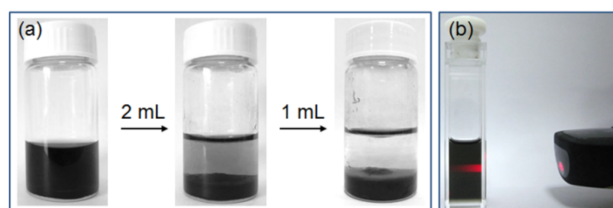
**Fig. S14** W(4f) XPS spectra of the pure SEP-7 (black) and SEP-7/RGO nanocomposite (red).



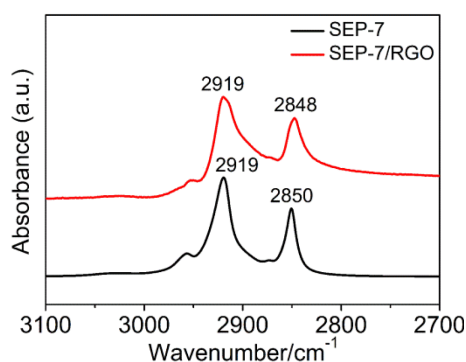
**Fig. S15** (a), (b), (c) and (d) HRTEM images of the SEP-7/RGO nanocomposite.



**Fig. S16** TGA curve of the SEP-7/RGO nanocomposite, which was separated under centrifugation, after adding the same volume of hexane in chloroform where SEP-7 is still soluble. Assuming that the RGO has decomposed completely and all the inorganic residuals are  $\text{WO}_3$  and  $\text{P}_2\text{O}_5$ , the calculated weight percentage of SEP-7 in the nanocomposite is 37.6%.



**Fig. S17** (a) Photographs of RGO (0.35 mg, 7 mL H<sub>2</sub>O) after adding different volume of SEP-7 chloroform solution with concentration of 0.1 mg mL<sup>-1</sup>: 0 mL (left); 2 mL (middle); 3 mL (right). (b) Photograph of Tyndall scattering observation of the chloroform solution of the right bottle in a. The critical value of SEP-7 for phase transfer of RGO is estimated to be  $1.3 \times 10^{-7}$  mol mg<sup>-1</sup>.



**Fig. S18** FTIR spectra of pure SEP-7 (black) and SEP-7/RGO nanocomposite (red).

Reference:

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