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PAPER

Nanoscale liquid-like graphene@Fe₃O₄ hybrid with excellent amphiphilicity and electronic conductivity

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Abstract : A nanoscale liquid-like graphene@Fe₃O₄ hybrid was firstly obtained by using sulfuric acid terminated organosilanes as corona and polyether amine as canopy. The microstructures, rheological property, solubility, magnetic property and electronic conductivity of the hybrid had been extensively characterized by various analytical techniques. The hybrid is a superparamagnetism material with specific magnetization of 0.39 emu/g, which is a Newtonian fluid with liquid-like behavior at room temperature. At the same time, the hybrid shows excellent amphiphilicity and electronic conductivity. Those unique properties of the hybrid make it very promising for producing super capacitors, batteries and nanocomposites. In addition, it can act as a special ferrofluid and can be used as a kind of graphene lubricant. Most importantly, the successful preparation of liquid-like graphene@Fe₃O₄ hybrid may provide new insight and assist the efficient preparation of other kinds of liquid-like nanocrystal graphene hybrid, such as graphene@SiO₂ and graphene-POSS, which also can be used in the fabrication of graphene based nanocomposites.

Introduction

Graphene, a newly discovered two-dimensional carbon nanomaterial, not only possesses a stable structure but also exhibits high specific surface area and excellent electronic conductivity.¹⁻⁴ These properties make graphene very promising for producing resonators, catalyst supports, electronic devices, super capacitors, batteries, solar cell, nanocomposites etc.⁵⁻⁷ Moreover, researchers have grown different inorganic nanocrystals on the surface of graphene,⁸⁻¹³ yielding nanocrystal-functionalized graphene, which processes not only the individual property of graphene and nanocrystals, but also additional function derived from the synergy between them.¹⁴⁻¹⁸ As such, nanocrystal-functionalized graphene have been widely used in the areas of super capacitors and many others.

Magnetic nanoparticles, which have many applications in environmental, electronic, and biological process,¹⁹⁻²¹ are one of such nanocrystals due to their excellent magnetic properties. Among them, Fe₃O₄ NPs have been paid much attention for their good biocompatibility and low toxicity. The functionalization of graphene with Fe₃O₄ NPs hold immense potential in polymer composites because of their large saturation magnetization.²² For this purpose, one needs to disperse the graphene uniformly in solvent and polymer matrix. However, it is one of the major challenges for the application of graphene or nanocrystal-functionlized graphene.²³

A promising and facile way is developed in this paper by grafting short oligomer onto the surface of the nanocrystal graphene oxide. We can get liquid-like nanocrystal graphene hybrid in the absent of solvent, which has good dispersion in solvent and polymer matrix. To date, there are several works reported in the field of liquid-like functionalized nanoscale materials, such as silicon dioxide,^{24,25} gold,^{26,27} sepiolite,²⁸ metal oxides, sulfides^{24,29} and nonocarbons.³⁰ These materials are liquid-like at room temperature or slightly above ambient temperature, thus making them different from the conventionally functionalized nanoparticles, which are generally solid-like in the absence of solvent and do not undergo a microscopic solid-to-liquid transition below 150°C.³¹ Similarly, Tang also prepared graphene nanofluid that could flow at room temperature.³² However, liquid-like graphene fluid utilizing GO@Fe₃O₄ as a core is not attempted so far. The nanoscale liquid-like graphene@Fe₃O₄ hybrid possesses both broad solubility and amphiphilic characteristics, which are especially important in the fabrication of graphene@Fe₃O₄ based composites, as well as a super-paramagnetism material. In addition, the nanoscale liquid-like graphene@Fe₃O₄ hybrid may have a great potential industrial applications including CO₂ capture.³³

In this work, we prepare a liquid-like graphene@Fe₃O₄ hybrid by attaching organosilances SIT8378.3 and Jeffamine M-2070 onto the surface of graphene@Fe₃O₄. The amount of graphene@Fe₃O₄ nanoparticles is up to 13.78wt%. In addition, the particular hybrid material is engineered to single homogeneous phase and exhibits liquid-like behavior at room temperature without solvent. Moreover, the nanoscale liquid-like

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graphene@Fe₃O₄ hybrid is a super paramagnetism material and can act as a special ferrofluid. Most importantly, the fluid behavior and excellent amphiphicity may extend their potential application in the fabrication of graphene based nanocomposites.

5 Experimental Section

Materials

Graphite powder (< 20um) was purchased from Xiamen Knano-Tech Port Co. Ltd., which was produced through mechanical exfoliation. The reagents used for the oxidation of graphite, including concentrated sulfuric acid (H₂SO₄), hydrochloric acid (HCl), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), and 30wt% of hydrogen peroxide (H₂O₂) were all analytically pure and used without further purification. Methanol (99.5%), ethanol (99.7%), acetone ammonia (NH₄OH, 25% aqueous solution), and tetrahydrofuran were purchased as analytical grade reagents from Fuchen Chemical Ind. Ltd. FeCl₃ 6H₂O (wt% >99.0%) and FeCl₂ 4H₂O (wt% >99.7%) were obtained from Tianjing Organics. Deionized water was made in lab. 3-(Trihydroxysilyl)-1-propanesulphonic acid 30-35% in water (SIT 8378.3, (CH₃)₃Si(CH₂)₃HSO₃) was from Gelest Inc. Jeffamine M-2070 (CH₃-(OCH₂CH₂)₃₁-(OCH₂CH₂-CH₃)₁₀-NH₂) was from Huntsman.

Synthesis of GO@Fe₃O₄ Hybrid

To begin with, FeCl₂ 4H₂O and FeCl₃ 6H₂O with a molecule ratio of 1:1.75 were dissolved completely in deionized water. Subsequently, the brown GO suspension (1mg/mL) was obtained by exfoliating 100mg of GO flakes in 100mL of distilled water with the assistance of sonication. The as-prepared GO suspension was added under continuous stirring in nitrogen atmosphere. After 45min, ammonia(5%) was dropwise added into the solution and reacted for 30min. Then the black precipitate in the solution was collected by removing the supernatant and washed with distilled water several times. Finally, the wet precipitate was freeze-dried for 24h to obtain GO@Fe₃O₄ hybrid.

35 Preparation of nanoscale liquid-like graphene@Fe₃O₄ hybrid

Firstly 300mg GO@Fe₃O₄ hybrid was exfoliated in 100mL deionized water under sonication to yield a GO@Fe₃O₄ aqueous suspension. Then 3g SIT8378.3 water solution was dropwise added into the solution and stirred for 20min. Next the NaOH solution (1mol/L) was added until the pH was 6. After that the solution was reacted at room temperature for 24 h. In order to remove the residual SIT8378.3, the product was dialyzed by dialysis tube (Spectra/Por RC Biotech Membrane, 3500 MWCO, 16 mm flat width) for 48h, while the water was changed every 8h. A cation exchange system (Dowex HCR-W2, Sigma-Aldrich) was employed to remove Na⁺ ion from the functionalized graphene@Fe₃O₄ suspension and to protonate the sulfonate group. Finally, polymer chains were grafted onto the functionalized graphene@Fe₃O₄ nanoparticles by dropwise adding 10 wt% Jeffamine M-2070 solution to neutralized all the sulfonate groups of the linker. The final product was the nanoscale liquid-like graphene@Fe₃O₄ hybrid, and the hybrid was dried under vacuum at 50°C prior to testing.

Characterization

X-ray diffraction (XRD) analysis was carried out on a Scintag D/MAX-3C using Cu K α radiation ($\lambda=1.54056\text{\AA}$). The instruments were operated at 36 kV and 20 mA current. The measured 2 θ ranged from 10° to 80° for the XRD measurement and the scan step was 0.02. Transmission electron microscope (TEM) images were obtained at an accelerating voltage of 120 kV with the JEM-2100 instrument. The sample was prepared by placing a few drops of the graphene@Fe₃O₄ hybrid water dispersion onto a copper grid and evaporated the solvent prior to observation. Atomic force microscopy (AFM) was carried out on an Innova (Veeco, USA) operated in a tapping mode. The sample for AFM measurement was prepared by dispersing in water and then drop casting on silicon surface. The silicon was dried at ambient conditions and examined. The structure of the nanoscale liquid-like graphene@Fe₃O₄ hybrid was investigated by Fourier transform-infrared (FTIR) spectrometer analysis (WQF-310, Beijing Second Optical Instruments Factory) with KBr pellets. The UV-vis absorption spectra were measured with a Shimadzu UV1800 spectrometer. X-ray Photoelectron Spectroscopy(XPS) curve and image were obtained with the Kratos Axis Ultra DLD instrument after a few nanoparticles or hybrid were placed on a conductive blanket. The wide scan ranged from 0eV to 800eV. Raman spectra were recorded on an ALMEGAD dispersive Raman spectrometer, equipped with a He-Ne ion laser (532nm) as the excitation source. Thermogravimetric analysis (TGA) measurements were taken under N₂ flow with heating rate of 10°C/min by using TGAQ50 TA instrument. Differential scanning calorimetry (DSC) traces were collected using a Q1000 TA instrument at heating rate of 10°C/min. The samples were first heated to 100°C at the rate of 10°C/min, then cooled to -80°C. Rheological measurements were tested at 25°C on an ARG2 using a cone and plate geometry with a 40 mm diameter plate and 2° cone angle. Magnetic study was performed by a vibrating sample magnetometer (VSM, Riken Denshi, BHV-525). Then the Digital conductivity meter (DDS-307) was used to estimate the electrical conductivity of the nanoscale liquid-like graphene @Fe₃O₄ hybrid.

Results and discussion

Characterizations of nanoscale liquid-like graphene@Fe₃O₄ hybrid

As we all know, GO is always used as a direct starting material to fabricate graphene-based hybrids, because it possesses abundant oxygen groups and can steadily suspended in water and organic solvents. Here, the nanoscale liquid-like graphene@Fe₃O₄ hybrid is prepared by chemical deposition of iron ions onto GO sheets and then chemical reduction. A schematic for the preparation of nanoscale liquid-like graphene@Fe₃O₄ hybrid is illustrated in Fig. 1. At the same time, the nanoscale liquid-like graphene@Fe₃O₄ hybrid exhibits liquid-like behavior in the absence of solvents at room temperature (Fig. 1).

TEM was employed to reveal the morphology of nanoscale liquid-like graphene@Fe₃O₄ hybrid. Compared with GO (Fig. 2a), the GO@Fe₃O₄ (Fig. 2b) is decorated homogenously with numerous Fe₃O₄ clusters on the surface. In addition, it can be observed that in the nanoscale liquid-like graphene@Fe₃O₄ hybrid, the Fe₃O₄ NPs were attached onto the graphene (Fig. 2c and Fig. 2d). However, it seems that the process of preparation of

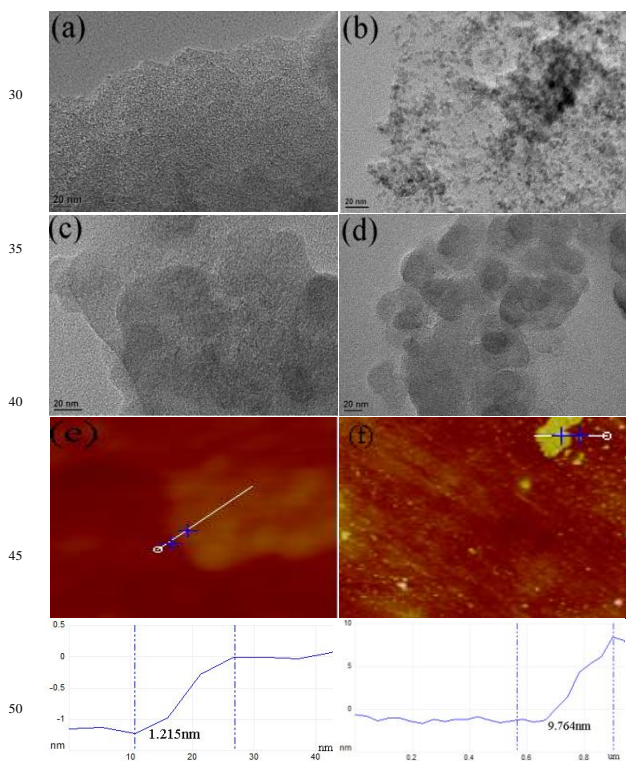
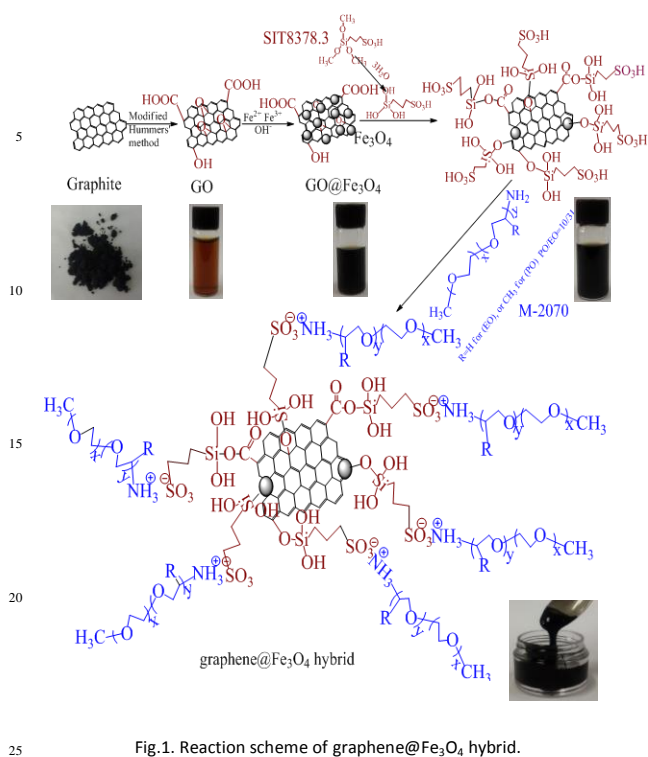


Fig. 2. TEM images of (a) GO, (b) GO@Fe₃O₄, (c and d) graphene@ Fe₃O₄ hybrid; AFM images of (e) GO, (f) graphene@Fe₃O₄ hybrid.

nanoscale liquid-like graphene@Fe₃O₄ hybrid has passive influence on the surface coating layer of Fe₃O₄. The height profile of the coating layer has been obtained from AFM studies. Figs.

2e and 2f shows the typical images and height profiles of GO, as well as the nanoscale liquid-like graphene@Fe₃O₄ hybrid. A thickness of 9.764nm is identified in the nanoscale liquid-like graphene@Fe₃O₄ hybrid, which is thicker than that of GO nanosheet (Fig. 2e).

The crystalline structure of GO and the Fe₃O₄ NPs on GO were characterized by XRD diffraction. As shown in Fig. 3, the diffraction peak at $2\theta=11.4^\circ$ corresponds to the (002) reflection of GO.³⁴ Compared with GO, the characteristic diffraction peaks of Fe₃O₄ NPs are present in the obtained GO@Fe₃O₄ hybrid, which can be assigned in the (111), (220), (311), (222), (400), (422), (511) and (440) planes according to JCPDS no.19-0629. It suggests that the Fe₃O₄ NPs is attached onto GO successfully. Besides, the characteristic diffraction peak (002) of GO still exists in GO@Fe₃O₄ hybrid. This indicates that GO is not completely destroyed in the preparation of GO@Fe₃O₄ hybrid.

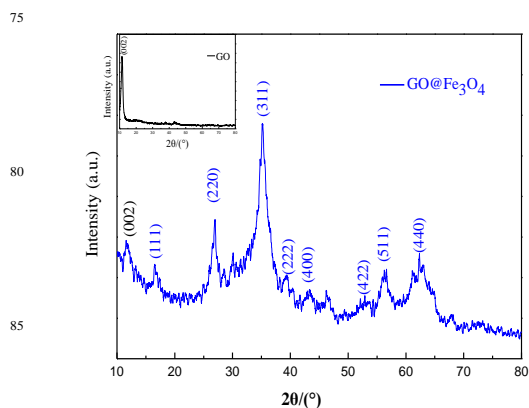


Fig. 3. XRD patterns of GO and GO@Fe₃O₄.

The synthesis and groups on surface of the nanoscale liquid-like graphene@Fe₃O₄ hybrid was monitored by FTIR and UV-vis. As expected, the FTIR spectrum of graphene oxide shows the presence of hydroxyl (3400 cm⁻¹), epoxy (1177 cm⁻¹), and carbonyl (1729 cm⁻¹) groups. The intensities of these IR peaks decreases significantly after chemical deposition of iron ions onto GO sheets. In addition, the absorption peak of Fe-O bond vibration at 560cm⁻¹ confirms that Fe₃O₄ has been attached onto the surface of GO. As for the liquid-like graphene@Fe₃O₄ hybrid, there is an absorption peak of -Si-O- at 950 cm⁻¹, which indicates that SIT8378.3 has been attached onto the surface of GO@Fe₃O₄ hybrid. Meanwhile, the absorption peak at 1107 cm⁻¹ is assigned to the asymmetric stretching vibration of -CH₂-O-CH₂-, suggesting that M-2070 has also been decorated. The UV-vis absorption of GO showed typical bands at 232nm, corresponding to $\pi \rightarrow \pi^*$ transition of aromatic C-C bonds, and a shoulder at ~300nm, which can be attributed to $n \rightarrow \pi^*$ transitions of C=O bonds.³⁵ The characteristic UV-vis absorption peaks of Fe₃O₄ with no absorption and no visible peak can be detected within this region in the curve of GO@Fe₃O₄ hybrid, suggesting that the restoration of electronic conjugation occurs in the basal plane of graphene upon reduction.³⁶ Meanwhile, the characteristic peaks of GO at 232nm also appear in the UV-vis spectrum of liquid-like graphene@Fe₃O₄ hybrid with strong absorption at 225nm. The shift of the peak from 232 to 225 nm is due to the introduction of M-2070, which leads to the increase in sterically hinderer. As a

result, the degree of conjugation reduces and the molecular excitation wavelength moves to short-wave, indicating that blue shift takes place.

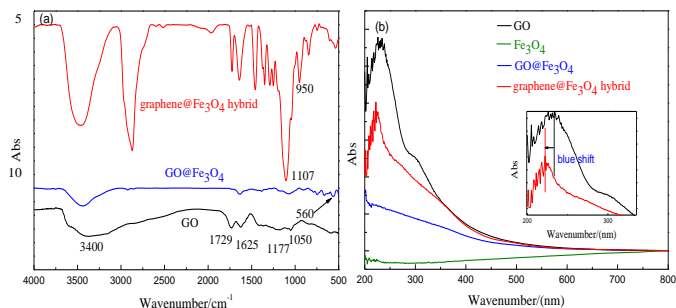


Fig. 4. (a) FTIR spectra of GO, GO@Fe₃O₄, graphene@Fe₃O₄ hybrid, (b) UV-vis spectra of GO, Fe₃O₄, GO@Fe₃O₄, graphene@Fe₃O₄ hybrid.

To gain further insights into the surface chemical changes associated with the schematic illustrated in Fig. 1, the XPS spectra were used to analysis the chemical preparation. Firstly, Figs. 5b and 5d show four kinds of carbon, corresponding to the C-C, epoxies and hydroxyl, -C=O, -COO-. However, the relative intensity of oxygen groups has a noticeable decrease relative to that of GO. Moreover, the emergence of the signals of Fe_{2p3/2} and Fe_{2p1/2} in the XPS spectrum in Figs. 5c and 5e indicates that Fe₃O₄ has grafted onto the surface of GO. Fig. 5f gives the electrical photo Fe 2p of GO@Fe₃O₄, which shows that GO is decorated homogenously with numerous Fe₃O₄ clusters on the surface. Therefore, we can conclude that Fe₃O₄ NPs is attached onto the surface of GO successfully, which is consistent with the XRD result. Compared to GO@Fe₃O₄ hybrid, the emergence of the signals of Si 2s and Si 2p in the XPS spectrum of nanoscale liquid-like graphene@Fe₃O₄ hybrid (Fig. 5g) suggests that SIT8378.3 has covalently grafted onto the surface of GO@Fe₃O₄. Fig. 5h presents the C1s spectrum of nanoscale liquid-like graphene@Fe₃O₄ hybrid, which the relative intensity of the signal can be divided into three carbon components with different binding energy, including C-C, epoxies, hydroxyl, and -COO-. Obviously, the intensity of the oxygen groups in liquid-like graphene@Fe₃O₄ hybrid has a significant increase compared with that of GO@Fe₃O₄, which is due to the introduce of M-2070. Compared to Fig. 5g, the emergence of the signals of Fe_{2p3/2} and Fe_{2p1/2} in the XPS spectrum in Figs. 5i and 5k indicates that liquid-like graphene@Fe₃O₄ hybrid is coated by the M-2070. Most importantly, the Fe₃O₄ NPs are uniformly dispersed on the surface of graphene (Fig. 5l). These evidences confirmed that the nanoscale liquid-like graphene@Fe₃O₄ hybrid has been synthesized successfully, which is consistent with the FTIR and UV results.

Raman spectra is a convenient and powerful tool to investigate the structure of carbonaceous materials. As shown in Fig. 6, a broad D band at 1350 cm⁻¹ and a G band at 1600 cm⁻¹ are displayed, which are due to activation in the first order scattering process of sp³ carbon and sp²-bonded carbon atoms in graphene sheets, respectively.³⁷ The intensity ratio of D-band and G-band I(D)/I(G) is always related to the ratio of disordered sp³

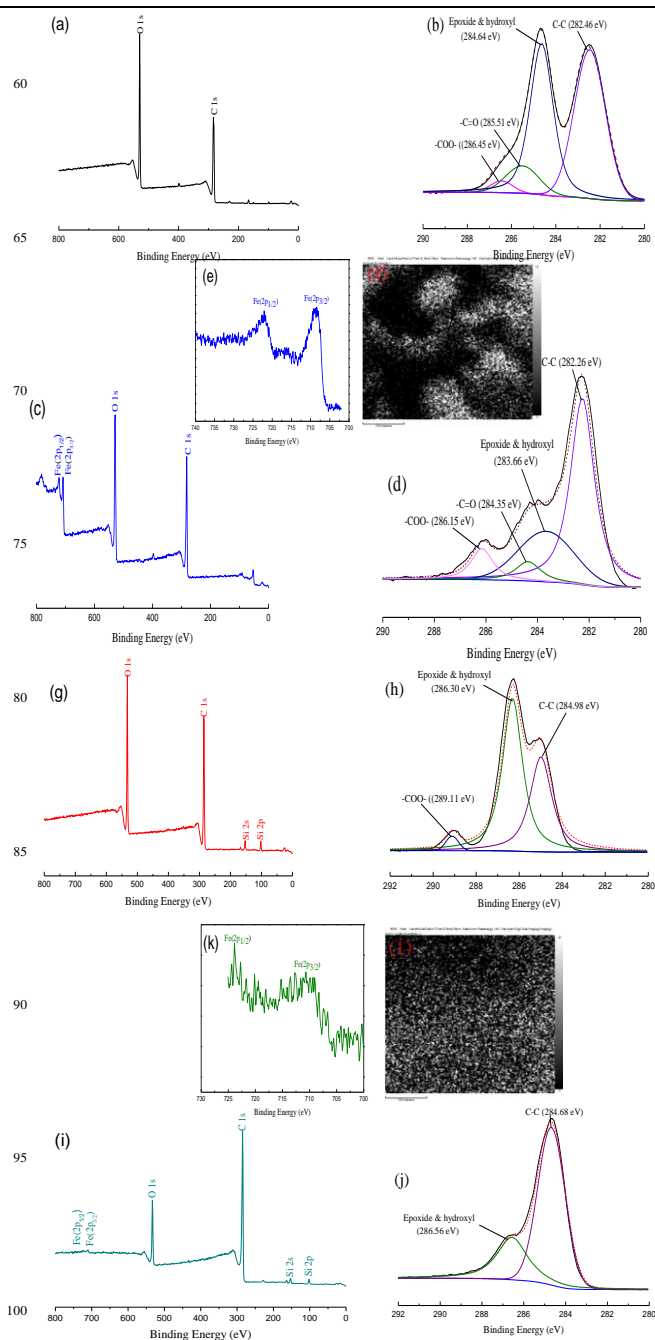


Fig. 5. XPS spectra of (a) GO, (c) GO@Fe₃O₄, (g) graphene@Fe₃O₄ hybrid and (i) Ion etching graphene@Fe₃O₄ hybrid; C 1s XPS spectra of (b) GO, (d) GO@Fe₃O₄, (h) graphene@Fe₃O₄ hybrid and (j) Ion etching graphene@Fe₃O₄ hybrid; Fe 2p spectra of (e) GO@Fe₃O₄ and (k) Ion etching graphene@Fe₃O₄ hybrid; electrical photos of Fe 2p of (f)GO@Fe₃O₄ and (l) Ion etching graphene@Fe₃O₄ hybrid.

and ordered sp² carbon domains.³⁸ The higher intensity ratio of I(D)/I(G) refers to the relative higher defect concentration.³⁹ Compared with that of GO, the I(D)/I(G) ratio of GO@Fe₃O₄ increases from 0.81 to 1.02 and the I(D)/I(G) ratio of the liquid-like graphene@Fe₃O₄ hybrid increases from 0.81 to 1.24, suggesting that the average size of sp² carbon domains decreases, which could be explained by the creation of more numerous but smaller sp² carbon domains after the reduction, as well as the presence of some unrepaired defects.^{37,40} In addition, the doping

by molecular charge transfer between M-2070 and graphene also contributed to the increase of I(D)/I(G) ratio.⁴¹ At the same time, the G band position of GO@Fe₃O₄ shifts to higher wave numbers (inset in Fig. 6), which is due to the decrease of graphene layers induced by Fe₃O₄ NPs.⁴²

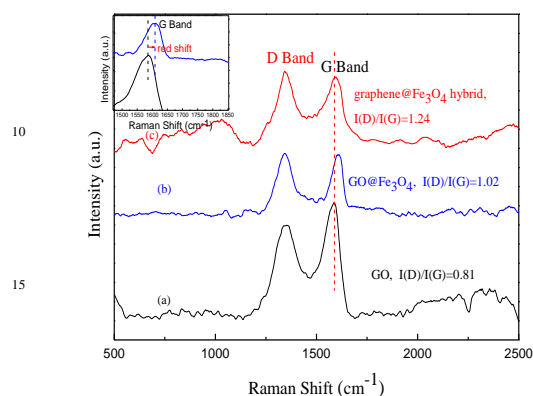


Fig. 6. Raman spectra of GO, GO@Fe₃O₄ and graphene@Fe₃O₄ hybrid.

The content of the organic canopy on the surface of liquid-like graphene@Fe₃O₄ hybrid influences the properties of hybrid material. For checking this point, the TGA was carried out to confirm the thermal stability (Fig. 7). Most oxygenic groups of GO@Fe₃O₄ hybrid are lost in the temperature range of 100–400°C. However, for M-2070, it exhibits a higher decomposition temperature, which is the range of 350–425°C, and its weight can be completely lost up to the temperature of 425°C. Most importantly, the TGA curve of liquid-like graphene@Fe₃O₄ hybrid shows that the sample does not contain any residual solvent. The weight loss above 350°C is due to the decomposition of M-2070. Therefore, we can roughly deduce that the content of inorganic component (graphene and Fe₃O₄ NPs) in this system is about 13.78wt%.

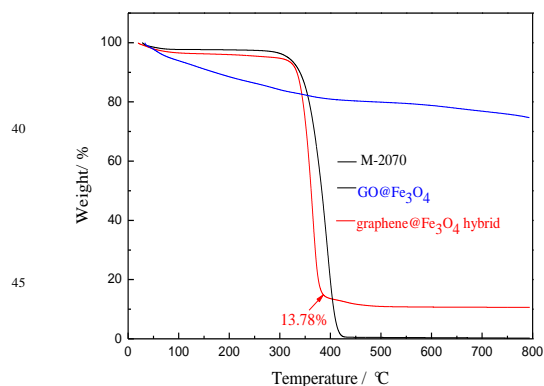


Fig. 7. TGA curves of M-2070, GO@Fe₃O₄ and the graphene@Fe₃O₄ hybrid.

DSC was used to characterize the thermal properties of the nanoscale liquid-like graphene@Fe₃O₄ hybrid (Fig. 8). DSC trace of pure M-2070 shows a large endothermic peak and a sharp and strong exothermic peak at -3.15°C and -34.70°C, respectively, which corresponds to the melting and crystallization of crystalline regions of M-2070, respectively. The fusion heat of crystalline units is 99.67 J/g. Compared to M-2070, the DSC cooling trace of

liquid-like graphene@Fe₃O₄ hybrid also shows a crystallization peak at -47.30°C, and the heating trace shows not only a melting peak but also a crystallization peak, corresponding to the T_m (-2.24°C) and T_c (-43.53°C), respectively. However, the fusion heat of liquid-like graphene@Fe₃O₄ hybrid decreases to 45.21 J/g. The relative percentage of crystallinity can be calculated according to the following formula.

$$x = \frac{\Delta H_f}{\Delta H_{f,o}} \quad (1)$$

where x is the relative crystallinity percentage of liquid-like graphene@Fe₃O₄ hybrid. $\Delta H_{f,o}$ is the heat of fusion of pure M-2070, and ΔH_f is the heat of fusion of the liquid-like graphene@Fe₃O₄ hybrid, which is related with the percentage of M-2070.³¹ The calculated result shows that the crystallinity percentage decreases from 100% of M-2070 to 45.36% of the graphene@Fe₃O₄ hybrid. All these results are probably caused by the restriction of the chain mobility of M-2070, which is due to the graphene and Fe₃O₄ NPs.^{25,43}

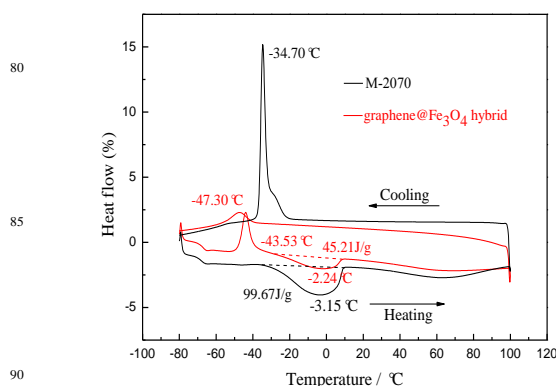


Fig. 8. DSC curves of M-2070 and the graphene@Fe₃O₄ hybrid.

Rheological property of nanoscale liquid-like graphene@Fe₃O₄ hybrid

The nanoscale liquid-like graphene@Fe₃O₄ hybrid shows a characteristic of definite liquid-like behavior (Fig. 1), which is further improved by the rheological measurements. Steady flow test result (Fig. 9) shows that the nanoscale liquid-like graphene@Fe₃O₄ hybrid exhibits Newtonian behavior, which is consistent with the work of Chen and Prasher. They reported the Newtonian behavior for EG/TiO₂⁴⁴ and propylene glycol/Al₂O₃⁴⁵ nanoparticle-based fluids.

Usually, a dynamic spectrum can be used to understand the structures and properties of material. It is well known that dynamical storage modulus G' and loss modulus G'' exhibit the relationship between the molecular motion and rheological behavior of the material.⁴⁴ G' denotes the elastic behavior of materials, which is the driving force for molecule deformation and G'' represents the consumption energy of viscous deformation.^{45,46} Because the liquid materials have permanent deformation with flowing and exhibit viscous behavior, their G'' is higher than G' .⁴⁷

Fig. 10(a) shows the storage modulus G' and the loss modulus G'' versus temperature curve. It can be seen that G' and

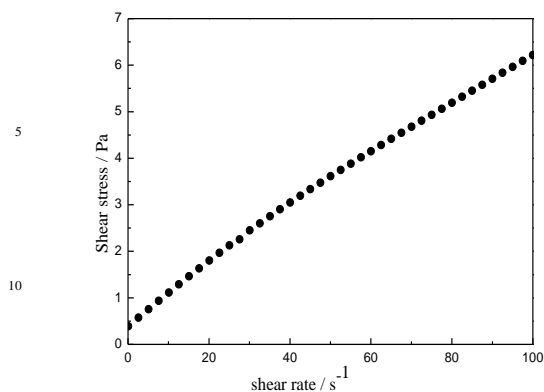


Fig. 9. Shear stress vs shear rate of the graphene@Fe₃O₄ hybrid at 25°C.

G' decreases with temperature increasing. G' is always higher than G'' from room temperature to 75°C. At the same time, Fig. 10(b) gives the relationships between G', G'' and the frequency. Both of them increase with the increase of frequency. These evidences reveal that the increase of the temperature and the decrease of the frequency have the similar effect on the movement of the molecule.²⁹ In addition, the viscosity is so low that the liquid-like graphene@Fe₃O₄ hybrid can be easily dispersed homogeneously in polymer matrix. This feature makes it possible for future application of the liquid-like graphene@Fe₃O₄ hybrid in graphene/polymer nanocomposite.

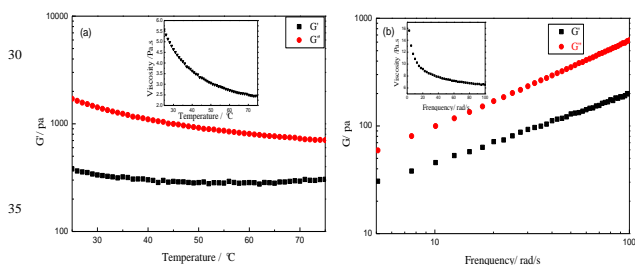


Fig. 10. (a) The modulus and viscosity of the graphene@Fe₃O₄ hybrid vs temperature at 314.25 s⁻¹; (b) The modulus and viscosity of the graphene@Fe₃O₄ hybrid vs frequency at 25°C.

Solubility of nanoscale liquid-like graphene@Fe₃O₄ hybrid

Fig. 11 shows that the solubility of the nanoscale liquid-like graphene@Fe₃O₄ hybrid in solvents at a concentration of 20 mg/mL before and after setting for 1 month. As we all know, the graphene or GO@Fe₃O₄ is insoluble in organic and inorganic solvent, such as water and ethanol. However, the nanoscale liquid-like graphene@Fe₃O₄ hybrid exhibits excellent amphiphilicity. It is almost soluble in all solvents and can disperse stably in water and organic solvents. Two reasons can account for the excellent amphiphilicity. Firstly, it is a result of the ionic nature in nanoscale liquid-like graphene@Fe₃O₄ hybrid between SIT8378.3 and M-2070.³⁹ Secondly, the M-2070 molecules impart its amphiphilicity.⁴⁸ The unique solubility of the nanoscale liquid-like graphene@Fe₃O₄ hybrid suggests promising applications in the fabrication of various GO or graphene based composite materials.³⁹

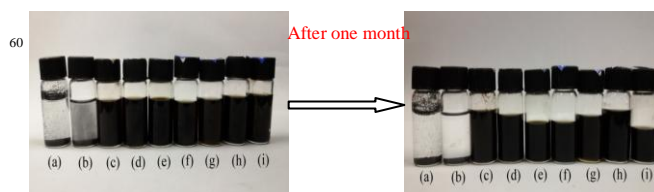


Fig. 11. photos of (a, b) GO@Fe₃O₄ and (c, d, e, f, g, h, i) graphene@Fe₃O₄ hybrid in various solvents. (a)water, (b)ethanol, (c)water, (d)ethanol, (e)acetone, (f) , (g)toluene, (h)N-N dimethylformamine, (i)chloroform.

Magnetic property of nanoscale liquid-like graphene@Fe₃O₄ hybrid

As shown in Fig.12, the magnetization was measured at room temperature in the magnetic field range from -13 to 13 kOe. Compared with that of pure Fe₃O₄, the curve of GO@Fe₃O₄ hybrid shows reversible, nonlinear characteristic with no significant coercivity after removing the applied magnetic field, implying that the GO@Fe₃O₄ is super paramagnetic. However, the magnetic saturation value (M_s) of GO@Fe₃O₄ decreases from 53.3 to 6.2 emu/g, due to the nanoscale size of Fe₃O₄ and the presence of graphene sheets.^{15,49,50} In addition, the GO@Fe₃O₄ hybrid could be easily separated under a magnet (inset in Fig.12a). Fig. 12b shows that the magnetic saturation value (M_s) of nanoscale liquid-like graphene@Fe₃O₄ hybrid, which is also a typical superparamagnetism material (inset in Fig.12b), is 0.39 emu/g. It suggests that the nanoscale liquid-like graphene@Fe₃O₄ hybrid can act as a special ferrofluid with M-2070 as a carrier and the surfactant SIT8378.3 is attached onto the surface of the graphene through covalent bond. There are electrostatic interaction between M-2070(Carrier) and SIT8378.3(surfactant).

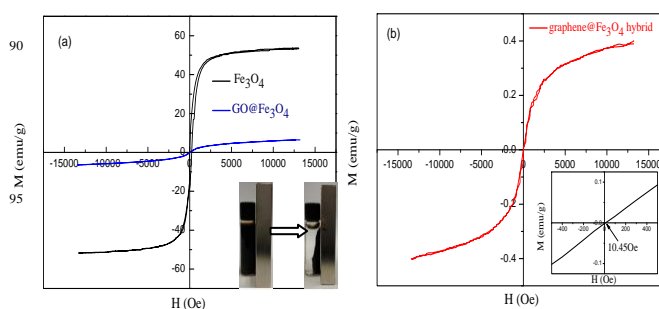


Fig. 12. (a)Magnetization hysteresis loops of Fe₃O₄ and GO@Fe₃O₄ at room temperature. The bottom inset shows the photographs of GO@Fe₃O₄ in water and their response to an external magnetic field. (b) Magnetization hysteresis loops of graphene@Fe₃O₄ hybrid.

Electrical conductivity of nanoscale liquid-like graphene@Fe₃O₄ hybrid

The conductivity of nanoscale liquid-like graphene@Fe₃O₄ hybrid in deionized water was also investigated. The relationship between the electrical conductivity and the volume fraction of the liquid-like graphene@Fe₃O₄ hybrid in water is given in Fig. 13. f is determined by the following equation.

$$f = \frac{\frac{m_n}{d_n}}{\frac{m_n}{d_n} + \frac{m_w}{d_w}} \quad (2)$$

where m_n and m_w represent the weight of nanoscale liquid-like graphene@Fe₃O₄ hybrid and water, respectively; d_n and d_w are the densities of nanoscale liquid-like graphene@Fe₃O₄ hybrid (1.285g cm⁻³) and water (1g cm⁻³). d_n is measured by drainage method.

As shown in Fig.13, the electrical conductivity slightly increases with the material volume fraction increasing. When the volume fraction is at the percolation threshold (f_c), the value of electrical conductivity increases rapidly. The effective conductivity of the system near the transition is further analyzed by the power law according to the two phase percolation theory.⁵¹

$$\sigma \propto (f_c - f)^{-s} \quad f_c > f \quad (3)$$

$$\sigma \propto (f - f_c)^t \quad f > f_c$$

where σ represents the effective conductivity of the system, s and t are the critical exponents in the insulating region and conduction region.

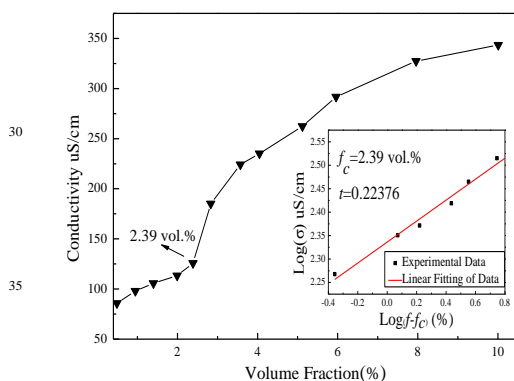


Fig. 13. Plot of the conductivity with volume fraction at room temperature. The bottom insert shows the fit of experimental data according to equ (3).

t generally reflects the dimensionality of the system with values typically around 1.3 and 2.0 for two and three dimensions, respectively. Fig.13 shows that f_c is about 2.39 vol.% and t is 0.22376 for the hybrid material in water. The low value of t reflects the decrease in system dimensionality.⁵² When the material volume fraction is less than f_c , the conductive network does not form, so the conductivity is low. When it increases up to f_c , the conductive network forms and the conductivity increased rapidly.

Conclusions

In summary, nanoscale liquid-like graphene@Fe₃O₄ hybrid was prepared by employing GO@Fe₃O₄ as a core, sulphuric acid terminated organosilanes as corona and polyether amine as canopy. The content of graphene@Fe₃O₄ is determined to reach 13.78wt% in the hybrid material, showing that it is a Newtonian

fluid with relatively low viscosity. Meanwhile, the nanoscale liquid-like graphene@Fe₃O₄ hybrid with liquid-like behavior at room temperature is a superparamagnetism material with specific magnetization of 0.39 emu/g. The percolation threshold of the electronic conductivity of the material is about 2.39 vol%. Most importantly, the nanoscale graphene@Fe₃O₄ hybrid exhibits excellent amphiphilicity, which paves the way for the fabrication of graphene-based material.

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Notes and references

- 1 A. K. Geim, A. H. MacDonald, *Phys. Today*, 2007, **60**, 35.
- 2 Y. Si, E. T. Samulski, *Nano Lett.*, 2008, **8**, 1679.
- 3 P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim and K. S. Novoselov, *Nano Lett.*, 2008, **8**, 1704.
- 4 R. Miranda, A. L. Vazquez de Parga, *Nat. Nanotechnol.*, 2009, **4**, 549.
- 5 S. C. Kim, H. Lee, H. Jeong, B. Kim, J. Kim, C. Shin, *Macromol Res.*, 2010, **18**, 1125.
- 6 X. Wang, X. Zhou, K. Yao, J. Zhang, Z. Liu, *Carbon*, 2011, **49**, 133.
- 7 S. Park, R. S. Ruoff, *Nat. Nanotechnol.*, 2009, **4**, 217.
- 8 H. L. Wang, J. T. Robinson, G. Diankov, H. J. Dai, *J. Am. Chem. Soc.*, 2010, **132**, 3270.
- 9 X. Huang, H. Li, S. Li, S. Wu, F. Boey, J. Ma, H. Zhang, *Angew. Chem.*, 2011, **123**, 12453.
- 10 X. Zhang, H. Li, X. Cui, Y. Lin, *J. Mater. Chem.*, 2010, **20**, 2801.
- 11 C. Xu, X. Wang, *Small*, 2009, **5**, 2212.
- 12 X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, H. Zhang, *Small*, 2011, **7**, 3163.
- 13 J. Liang, Y. Huang, J. Oh, M. Kozlov, D. Sui, S. Fang, R. H. Baughman, Y. Ma and Y. Chen, *Adv. Fun. Mater.*, 2011, **21**, 3778.
- 14 L. Gao, W. Ren, B. Liu, Z. Wu, C. Jiang, H. Cheng, *J. Am. Chem. Soc.*, 2009, **131**, 13934.
- 15 X. Yang, X. Zhang, Y. Ma, Y. Huang, Y. Wang, Y. Chen, *J. Mater. Chem.*, 2009, **19**, 2710.
- 16 H. Cong, J. He, Y. Lu, S. Yu, *Small*, 2010, **6**, 169.
- 17 V. Chandra, J. Park, Y. Chun, J. Lee, K.S. Kim, *ACS Nano*, 2010, **4**, 3979.
- 18 J. Su, M. Cao, L. Ren, C. Hu, *J. Phys. Chem. C*, 2011, **115**, 14469.
- 19 R. Hao, R. Xing, Z. Xu, Y. Hou, S. Gao, S. Sun, *Adv. Mater.*, 2010, **22**, 2729.
- 20 J. Lu, X. Jiao, D. Chen, W. Li, *J. Phys. Chem. C*, 2009, **113**, 4012.
- 21 H. He, C. Gao, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3201.
- 22 G. Sun, B. Dong, M. Cao, B. Wei, C. Hu, *Chem. Mater.*, 2011, **23**, 1587.
- 23 C. Chen, X. Chen, L. Xu, W. Li, *Carbon*, 2005, **43**, 1660.
- 24 A. B. Bourlinos, R. Herrera, N. Chalkias, D. D. Jiang, Q. Zhang, L. A. Archer and E. P. Giannelis, *Adv. Mater.*, 2005, **17**, 234.
- 25 R. Rodriguez, R. Herrera, A. B. Bourlinos, R. Li, A. Amassian, L. A. Archer and E. P. Giannelis, *Appl. Organomet. Chem.*, 2010, **24**, 581.
- 26 S. C. Warren, M. J. Banholzer, L. S. Slaughter, E. P. Giannelis, F. J. DiSalvo and U. B. Wiesner, *J. Am. Chem. Soc.*, 2006, **128**, 12074.
- 27 Y. Zheng, J. Zhang, L. Lan, P. Yu, R. Rodriguez, R. Herrera, D. Wang and E. P. Giannelis, *ChemPhysChem.*, 2010, **11**, 61.
- 28 Y. Zheng, J. Zhang, L. Lan and P. Yu, *Applied Surface Science.*, 2011, **257**, 6171.
- 29 A. B. Bourlinos, S. Ray Chowdhury, R. Herrera, D. D. Jiang, Q. Zhang, L. A. Archer and E. P. Giannelis, *Adv. Funct. Mater.*, 2005, **15**, 1285.
- 30 Q. Li, L. Dong, J. Fang and C. Xiong, *ACS Nano*, 2010, **4**, 5797.
- 31 J. Zhang, Y. Zheng, P. Yu, S. Mo, R. Wang, *Carbon*, 2009, **47**, 2776.

- 32 Z. Tang, L. Zhang, C. Zeng, T. Lin, B. Guo, *Soft Matter*, 2012, **8**, 9214.
- 33 K. A. Lin and A. A. Park, *Environ. Sci. Technol.*, 2011, **45**, 6633.
- 34 M. Alvand, F. Shemirani, *Microchimica Acta*, 2014, **181**, 181.
- 5 35 D. A. Skoog, F. J. Holler, T. A. Nieman, *Harcourt Brace & Company*, 1998, **Chapter**, 13.
- 36 D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.
- 37 S. Stankovich, D. Dikin, R. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon*, 2007, **45**, 1558.
- 10 38 K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'homme, I. A. Aksay, R. Car, *Nano Lett.*, 2007, **8**, 36.
- 39 C. Zeng, Z. Tang, B. Guo, L. Zhang. *Phys. Chem.*, 2012, **14**, 9838.
- 40 Y. Zhou, Q. Bao, L. A. L. Tang, Y. Zhong, K. P. Loh, *Chem. Mater.*, 2009, **21**, 2950.
- 15 41 R. Voggu, B. Das, C. S. Rout and C. N. R. Rao, *J. Phys.: Condens. Matter.*, 2008, **20**, 472204.
- 42 M. S. Dresselhaus, *Trans. R. Phil. Soc. A.*, 2008, **28**, 1863.
- 43 S. C. Warren, M. J. Banholzer, L. S. Slaughter, E. P. Giannelis, F. J. DiSalvo, U. B. Wiesner, *J. Am. Chem. Soc.*, 2006, **128**, 12074.
- 20 44 P. X. Xu, *Beijing Chemical Industry Press*, 2003. P. 3-13.
- 45 J. H. Yin, J. Y. Nie, J. S. Yang, B. J. Hua, *Acta Mater Compos Sin.*, 1992, **9**, 103.
- 46 X. Guo, Y. Zhao, P. Ning, L. K. Li, *China Plast Ind.*, 2006, **34**, 35.
- 25 47 Q. Wu, J. Wu, *Beijing: Higher Education Press*, 1994, **P**, 1.
- 48 A. B. Bourlinos, V. Georgakilas, V. Tzitzios, N. Boukos, R. Herrera and E. P. Giannelis, *Small*, 2006, **2**, 1188.
- 49 B. Jia, L. Gao, J. Sun, *Carbon*, 2007, **45**, 1476.
- 50 F. He, J. Fan, D. Ma, L. Zhang, C. Leung, H. L. Chan, *Carbon*, 2010, **48**, 3139.
- 30 51 C. W. Nan, *Prog. Mater. Sci.*, 1993, **37**, 1.
- 52 J. Zhang, Y. Zheng, L. Lan, S. Mo, P. Yu, W. Shi and R. Wang, *ACS Nano*, 2009, **3**, 2185.