

# Graphene Foam with Switchable Oil Wettability for Oil and Organic Solvents Recovery

Haiguang Zhu, Dongyun Chen,\* Najun Li, Qingfeng Xu, Hua Li, Jinghui He, and Jianmei Lu\*

One of the most pervasive environmental issues is water contaminated with oil or organic solvents; this global challenge calls for emerging materials that could effectively separate oil or organic solvents from water. Here, such a material is presented by integrating 3D porous graphene foam (GF) with a smart pH-responsive surface, showing switchable superoleophilic and superoleophobic properties in response to the medium pH. The key chemistry applied in this study is to modify the 3D porous GF with an amphiphilic copolymer containing a block of poly(2-vinylpyridine) and polyhexadecyl acrylate (P2VP-*b*-PHA), resulting in a smart GF (ss-GF) with an either superoleophilic or superoleophobic surface at different medium pH. The as-designed ss-GF can effectively absorb oil or organic solvents from the aqueous media by using its superoleophilic surface at pH of 7.0, and it can also completely release the adsorbates when the pH is switched to 3.0 (and the surface of ss-GF is therefore shifted to superoleophobic); with a continuous operation of many cycles (e.g., >10). Furthermore, the as-designed ss-GF shows superior absorption capacity for oil and organic solvent, with a high capacity of  $\approx 196$  times of the weight relative to that of the pristine ss-GF. The present work suggests encouraging applications of the ss-GF to water–oil and water–organic solvent separation.

## 1. Introduction

Problems with water are expected to grow worse with the society development. One serious environmental or water pollution is caused by the discharge of the industrial oily wastewater, the leakage of organic solvents, or the spillage of crude oil; such problems have already led to severe global ecological and survival crises, which have attracted worldwide attention from both basic and applied research.<sup>[1–4]</sup> A number of conventional methods have been applied to address this serious issue. Examples include controlled burning, and the use of dispersants, oil skimmer vessels, oil containment booms, and

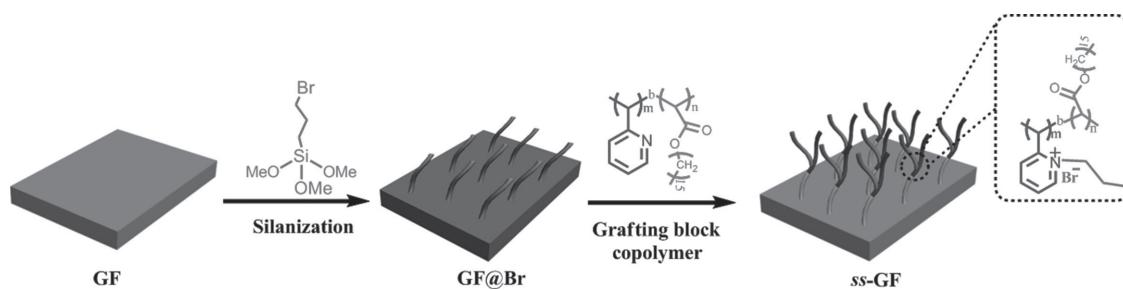
adsorbent materials.<sup>[5–7]</sup> Among these methods, the use of adsorbent materials is one most attractive approach owing to its simple process and operation that can effectively remove oil and organic solvents from the aqueous media. A variety of adsorbents have been recently developed to treat the contaminated water, including expanded graphite,<sup>[8]</sup> wool fibers,<sup>[9]</sup> activated carbon,<sup>[10]</sup> and synthetic organic polymers,<sup>[11]</sup> boron nitride (BN) nanosheets.<sup>[12,13]</sup> These materials are promising to some extents, but the practical applications of some of them are limited by their relatively low adsorption capacity and poor recyclability. In addition, potential toxicity of some adsorbents is another concern that requires the concerted efforts from the community. Therefore, the society is searching for some emerging materials that could be used to effectively separate oil or organic solvents from water, typically with a high adsorption capacity and good recyclability.

Graphene foam (GF) is one such material, which has already shown impact in the water sector due to its 3D porous structure, low density, high elasticity, and hydrophobicity.<sup>[14–19]</sup> Recently, there are several successful attempts by using GF for water–oil or water–organic solvent separation. For example, Ruoff and co-workers reported the use of a sponge-like graphene (SG) to separate oil from water,<sup>[20]</sup> showing a good adsorption capacity for oil; the adsorption capacity of SG for oil was 20–86 times of the weight of SG. In addition, the SG also showed good recyclability (up to 10 times) by heating. In another study, Gao and co-workers<sup>[21]</sup> developed a carbon aerogel with attractive features of ultralow density, super elasticity, and high adsorption capacity for oil and organic solvents. The carbon aerogel also exhibited remarkable recyclability via combustion or squeezing. However, the heating process is relatively complicated for the recycle of the adsorbent materials, especially, when the involved solvents have a high boiling point.<sup>[20]</sup> On the other hand, the squeezing method is generally restricted to those elastic adsorbent materials, while the combustion method often destroys the adsorbates; and such nonrecovery processes may limit their practical use if the adsorbates are of value.<sup>[21,22]</sup> The effective adsorption followed by the complete recovery of the oil or organic solvents from the aqueous media is of paramount interest to the society, which could be achieved by a delicate control of surface properties of adsorbent materials.<sup>[23]</sup>

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**Scheme 1.** Schematic illustration of the process to fabricate ss-GF. In the first step, GF was immersed in a 2% anhydrous toluene solution of (3-bromo-propyl)trimethoxysilane to synthesize GF@Br via silanization. In the second step, the ss-GF was produced via a quaternization between the bromoalkyl groups of GF@Br and the pyridine groups of the block copolymers.

In this context, the modification of adsorbent materials with a smart surface is appealing, since the simple operation of the external stimuli can simultaneously achieve the removal and recovery of oil from the aqueous media.<sup>[24,25]</sup> Several external stimuli could be used to trigger this adsorption and desorption process, including UV irradiation,<sup>[26]</sup> electricity,<sup>[27]</sup> heating,<sup>[28]</sup> and pH.<sup>[29]</sup> Among which, the pH-responsive method is the most attractive because this process could rapidly reverse the adsorption and desorption process by switching the surface property between hydrophobic and hydrophilic in a short period of time.<sup>[30]</sup> The use of a block amphiphilic copolymer is a good way to achieve smart pH-responsive surface.<sup>[31–33]</sup> For example, Zhang and co-workers<sup>[34]</sup> reported a promising material with switchable superoleophilicity and superoleophobicity by grafting block copolymer (P2VP-*b*-PDMS) on non-woven textiles. However, the use of costly block copolymer may limit its practical applications.

To specifically address this issue, here we report a cost-effective copolymer that can effectively create smart surface. The key strategy is to use a block copolymer (P2VP-*b*-PHA), which consists of a pH-responsive poly(2-vinylpyridine) (P2VP) and a hydrophobic/oleophilic polyhexadecyl acrylate (PHA), to modify the surface of GF, leading to the formation of smart surface GF (or ss-GF for short). The process is illustrated in Scheme 1, where the GF is grafted with a block copolymer (P2VP-*b*-PHA) via a silanization and quaternization process. The block of P2VP is pH-responsive, featuring with hydrophilic and hydrophobic properties via the protonation and deprotonation at different pH of the aqueous media. The switchable surface property can consequently control the adsorption and desorption of oil by the PHA block. Our experiments showed that the oil droplets can be easily and effectively adsorbed by the as-designed ss-GF at neutral pH, and the adsorbates can be completely desorbed and recovered at acidic pH. In addition, the ss-GF showed a high adsorption capacity for oil and organic solvents from the aqueous media, with an adsorption capacity of ≈196 times of the weight of ss-GF. Presented below are the details of this investigation.

## 2. Results and Discussion

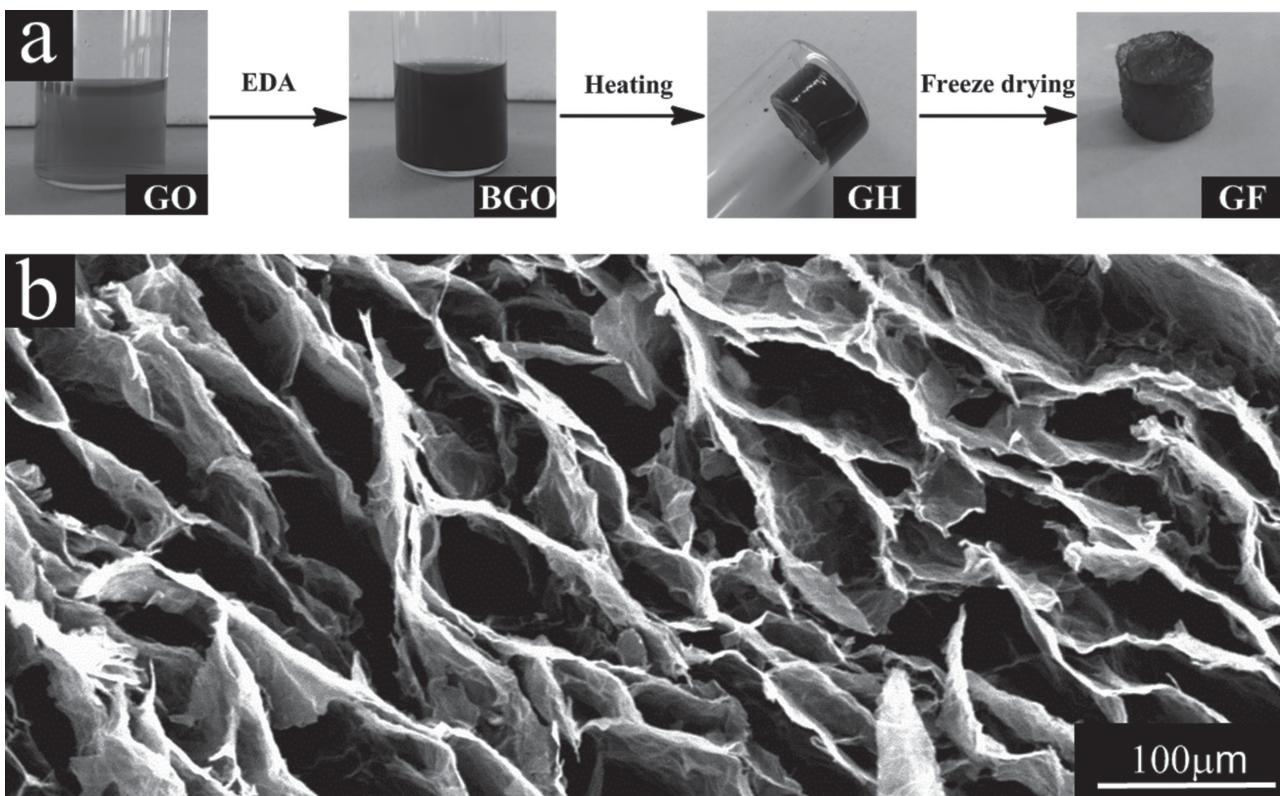
### 2.1. Preparation and Characterization of the As-Designed ss-GF

We chose GF as the substrate in this study due to its porous structure, low density, and hydrophobicity. In addition, owing to its large, rough, and hierarchical surface, GF is also an ideal

substrate for surface modification that could produce adsorbents with controllable oil and organic solvent adsorption. In general, GF is prepared by the reduction of graphene oxide (GO). There are a number of reducing agents, such as ammonium hydroxide,<sup>[35]</sup> hydrazine,<sup>[36]</sup> tea polyphenols,<sup>[37]</sup> hydrohalic acids,<sup>[38]</sup> and ascorbic acid.<sup>[39]</sup> In this study, we chose ethylenediamine (EDA) because of its dual functionalities as both reductant and crosslinker.<sup>[17]</sup> The fabrication process of GF was shown in Figure 1a. In the first step, EDA was injected into the GO solution, where the solution turned to black, leading to the assembly of graphene into a 3D graphene hydrogel (GH) after 6 h at 95 °C. The as-prepared GH was freeze-dried to remove the solvent, followed by a 60 s microwave in Ar atmosphere to produce the final GF.

After a microwave treatment, some hydrophilic functional groups (e.g., hydroxyl and carboxyl) of GF can be removed to improve its hydrophobicity.<sup>[17,40,41]</sup> The morphology of GF was characterized by scanning electron microscopy (SEM). As shown in Figure 1b, the SEM image of the as-prepared GF shows 3D porous structure consisting of a number of pores ranging from tens to hundreds of micrometers. The 3D porous and hydrophobic structures of GF are highly desirable for oil and organic solvent adsorption.<sup>[42,43]</sup>

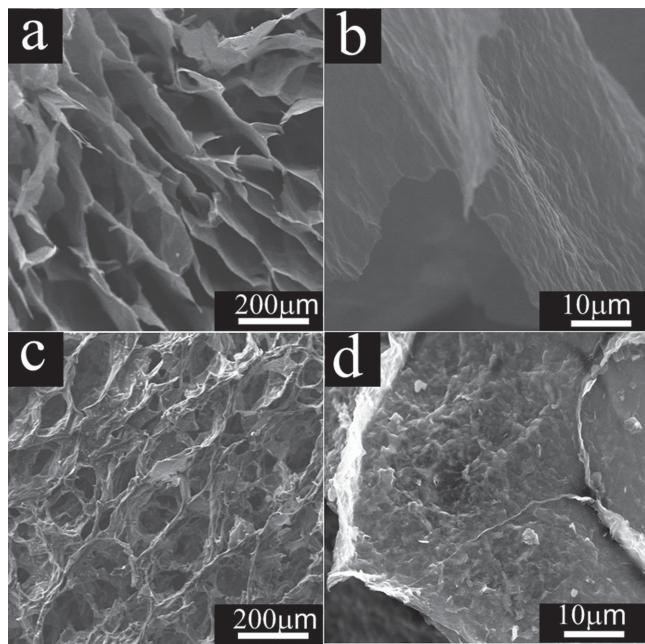
A block copolymer, P2VP-*b*-PHA, was then used to modify the GF surface with switchable oil wettability in response to the pH of the aqueous media. In particular, the P2VP was synthesized by using 2-vinyl pyridine as a monomer via a reversible addition-fragmentation chain transfer (RAFT) polymerization. The successful synthesis of P2VP was supported by the gel permeation chromatography (GPC) analysis (Table S1, Supporting Information). The P2VP was then used as a macrochain transfer agent to synthesize P2VP-*b*-PHA, where the size difference of P2VP before and after the block polymerization (from the GPC data, Table S1, Supporting Information) provides a supportive evidence for the successful grafting of PHA on the P2VP chains. The <sup>1</sup>H NMR data (Figure S1, Supporting Information) further verified the successful synthesis of the as-designed copolymer:  $\delta$  (ppm) 8.45–6.10 and 2.30–1.05 are attributed to P2VP and PHA, respectively. The final fabrication process of ss-GF was shown in Scheme 1, where the ss-GF was synthesized by grafting the block copolymer on the surface of GF via a silanization and quaternization. The surface morphologies of GF and ss-GF were characterized by SEM. As shown in Figure 2a, the GF exhibits porous structure. In addition, its SEM image (Figure 2b) also indicates that the cell structure of GF comprises of graphene sheets with smooth surface. After grafting with the block copolymer, the porous structure of



**Figure 1.** a) Photo illustration of the synthesis process of GF. b) A representative SEM image of the as-synthesized 3D porous GF.

the ss-GF is similar as that of the pristine GF (Figure 2c), implying that the basic structure was not destroyed during the surface modification. It should be noted that the surface structure of ss-GF

became rougher compared to that of the GF. The magnified SEM image of the ss-GF clearly suggests that the surface was uniformly coated with polymer (Figure 2d). Elemental analysis of GF and GF@Br was obtained from X-ray photoelectron (XPS). The comparison of Figure 3a,b suggests that (3-bromopropyl)trimethoxysilane has been successfully grafted on the surface of GF, where the signal of bromine in Figure 3b is a solid evidence. In the Fourier transform infrared (FTIR) spectra of GF and ss-GF (Figure S2, Supporting Information), three distinct peaks at 1587, 1472, and 1436 cm<sup>-1</sup> could be ascribed to the stretching vibration of C=C and C=N groups of pyridine ring, respectively, while the peak at 744 cm<sup>-1</sup> is characteristic for  $-\text{CH}_2-$  with  $n > 4$ . The FTIR data provide a supportive evidence for the successful grafting of the copolymer on the GF surface, leading to the formation of ss-GF. Thermogravimetric analysis (TGA) is a standard technique to confirm the composition of materials. Hence, it was employed to determinate the composition of ss-GF. The curves of GF and ss-GF were shown in Figure S3 (Supporting Information), indicating  $\approx 5$  wt% (3-bromopropyl) trimethoxysilane and  $\approx 35$  wt% P2VP-*b*-PHA were attached on the GF.



**Figure 2.** SEM images of a) porous structure of GF; b) wall structure of GF; c) porous structure of GF after grafting the block copolymer; and d) cell structure of GF after grafting the block copolymer.

## 2.2. Switchable Wettability of the ss-GF upon the pH Change

A number of studies have suggested that the block copolymer P2VP features with switchable wettability, which could be triggered by the protonation and deprotonation at different pH medium.<sup>[44–46]</sup> Therefore, the successful grafting of P2VP on the surface of GF may lead to the same surface property.

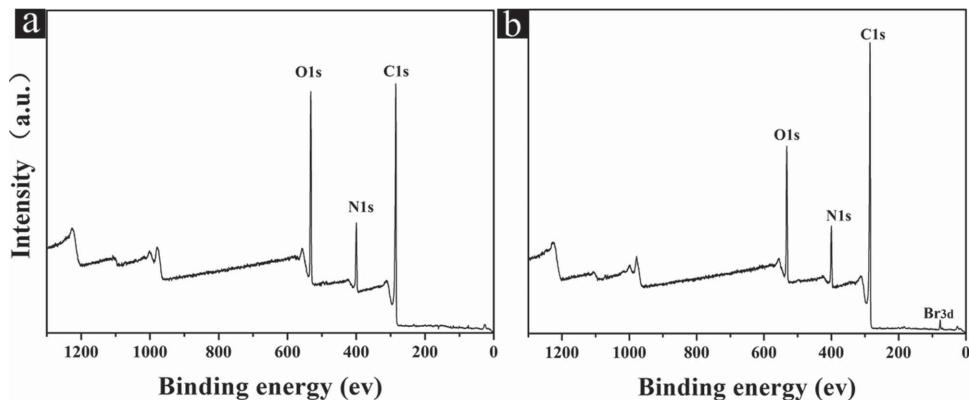


Figure 3. XPS spectra of a) GF and b) GF@Br.

To assess this, a contact angle measurement was used to characterize the surface properties of the as-fabricated ss-GF at different pH. As shown in Figure 4a, a neutral water droplet appeared as a sphere with a contact angle of 152° on the surface of ss-GF in air, which indicates the superhydrophobic surface of the as-fabricated ss-GF at pH 7.0. This surface property was not unexpected, because the P2VP is a weak polybase with a  $pK_a$  of 3.6,<sup>[47]</sup> and when touching with a neutral water droplet, P2VP is deprotonated. The deprotonated P2VP results in its collapsed conformation due to the hydrophobic effect between the deprotonated P2VP chains.<sup>[48]</sup> As a result, the hydrophobic PHA chains are exposed on the surface of ss-GF, serving as the dominant chains that can con-

trol the wettability of ss-GF. In addition, the 3D-layered structure of ss-GF could further enhance its hydrophobicity. Taken together, the as-fabricated ss-GF showed superhydrophobicity in response to neutral water. More importantly, the as-fabricated ss-GF exhibited high hydrophobic and oleophilic property after treated in severe conditions (Figure S4, Supporting Information), including heating (100 °C, 1 h), freezing (-40 °C, 1 h), and treated with DMSO (12 h), indicating its excellent stability against those harsh environments. This feature indicates that the as-fabricated ss-GF can be well used in severe conditions.

On the other hand, the ss-GF also features with superoleophilicity. As shown in Figure 4b, an oil droplet was completely

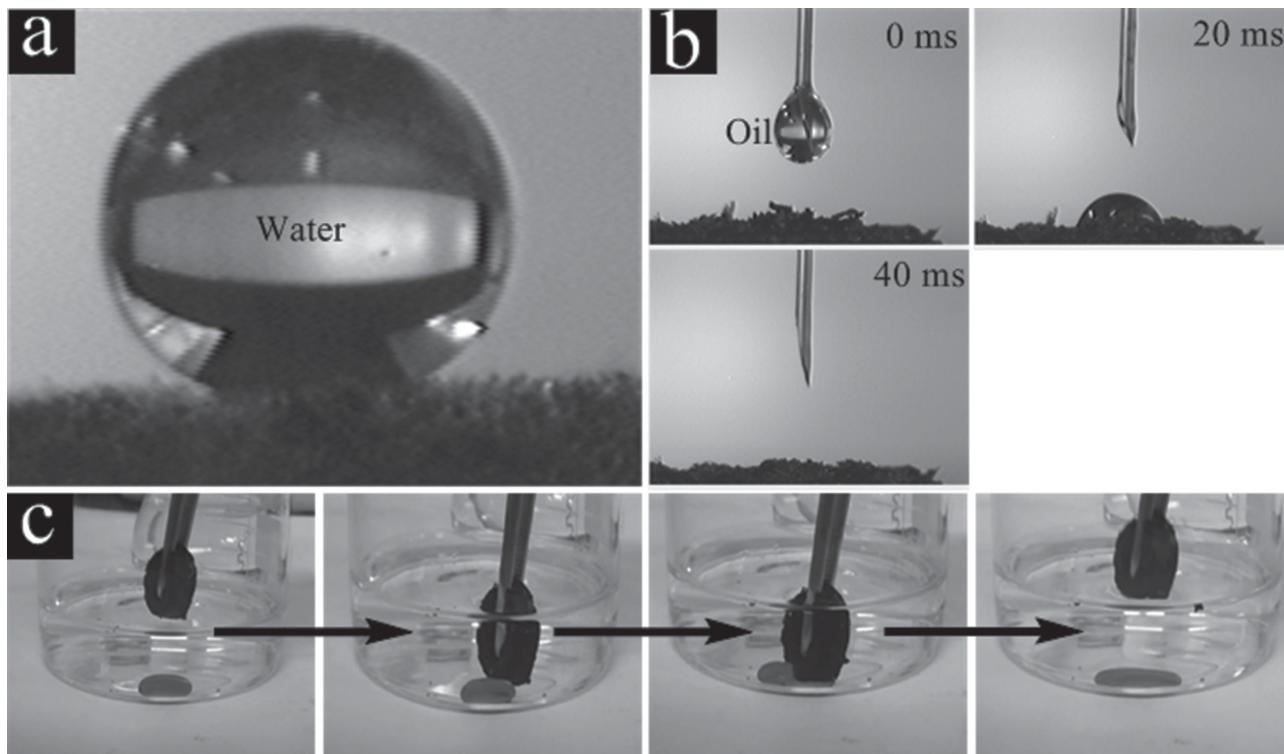
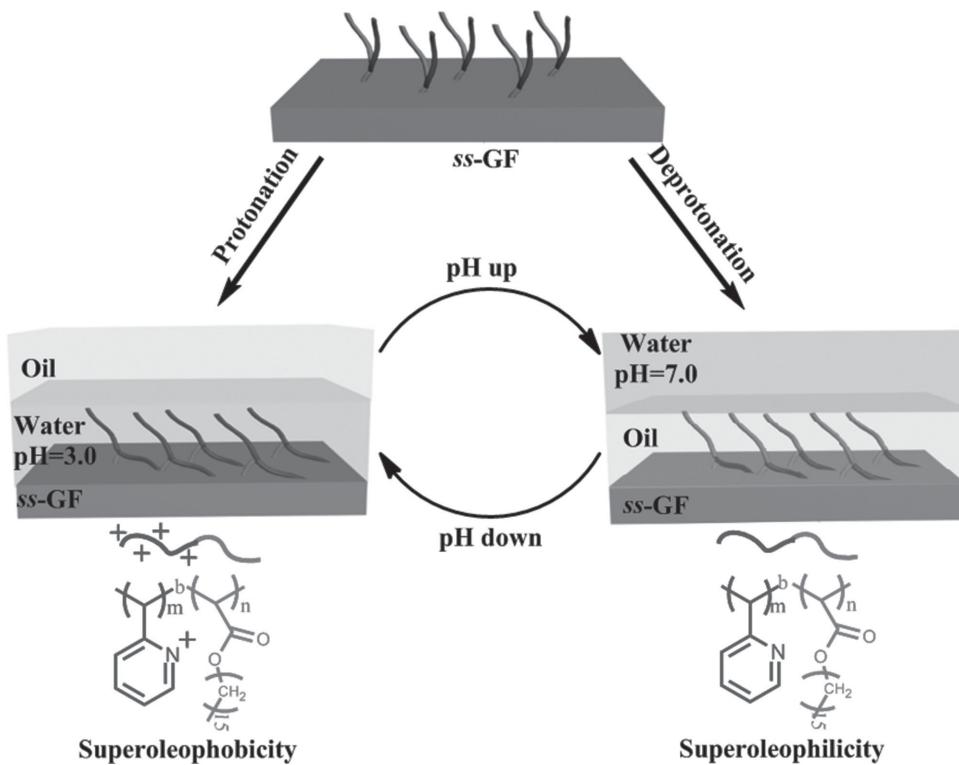


Figure 4. Contact angle measurements of the as-fabricated ss-GF. a) Neutral water droplet on the ss-GF surface with a contact angle of 152°. b) Oil droplet on the ss-GF surface, showing the oil was quickly adsorbed within 40 ms. c) Screenshots of the movie showing chloroform (stained with the Sudan red) in water at pH 3.0 was not adsorbed by the as-fabricated ss-GF.



**Scheme 2.** Schematic illustration of switchable wettability of the as-fabricated ss-GF: (left) oleophobic property of the ss-GF in water at pH 3.0; and (right) oleophilic property of the ss-GF in a neutral aqueous medium.

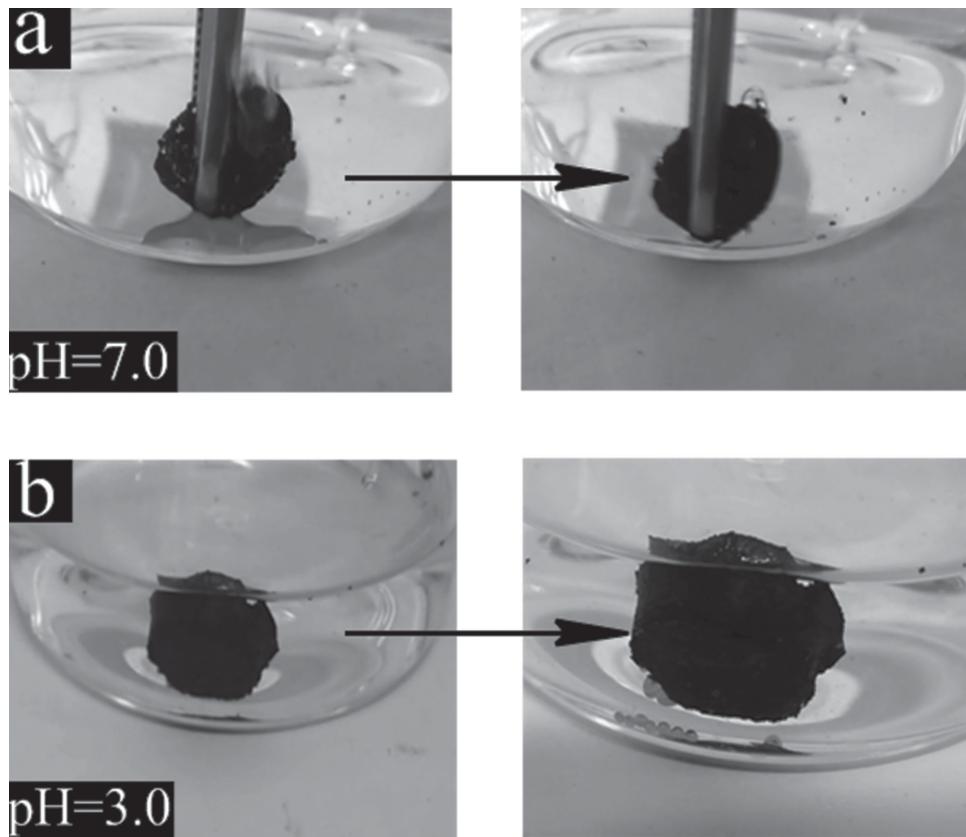
adsorbed by the as-fabricated ss-GF within 40 ms, which implies its superoleophilic surface. This surface characteristic is largely contributed from the chemical properties of the ss-GF surface, where PHA chains are exposed on the surface when the P2VP is deprotonated; and it is well known that the PHA is a hydrophobic/oleophilic material owing to its long-chain alkyl groups. The dominant PHA chains on the ss-GF surface render a superoleophilic surface in air. In addition, the 3D porous structure of ss-GF makes possible a fast oil and organic solvent adsorption. However, when the as-fabricated ss-GF was used to adsorb the chloroform droplet in the aqueous medium with a pH of 3.0, the chloroform droplet slides back and forth on the surface of ss-GF, and no obvious adsorption of chloroform was observed (Figure 4c, Movie 1), indicating the oleophobic surface of ss-GF when response to an acidic water.

The switchable oil wettability of the as-fabricated ss-GF in response to pH was contributed to the block copolymer P2VP-*b*-PHA that was grafted on the surface. The P2VP chains could switch their wettability via the protonation and deprotonation upon the pH change. In particular, as shown in Scheme 2, when the ss-GF is submerged in an aqueous medium of pH 3.0, the pyridyl groups of P2VP chains combine with H<sup>+</sup> and become protonated. The protonated P2VP leads to a stretched structure of the P2VP chains, making them expose on the surface of ss-GF owing to the electrostatic repulsion of those protonated pyridyl groups (Scheme 2, protonation process). The exterior P2VP is hydrophilic/oleophobic and the surface of ss-GF is wetted with the acidic water. As a result, the adsorption of oil by PHA could be effectively blocked, and the ss-GF exhibits oleophobicity in the acidic water.

Similarly, if the ss-GF is immersed in a neutral aqueous medium, the wettability of ss-GF can be completely reversed. As shown in Scheme 2 (deprotonation process), the P2VP chains are deprotonated and exhibit the collapsed structure due to the loss of electrostatic repulsion among the pyridyl groups.<sup>[45,46]</sup> However, the PHA chains would expose on the surface of ss-GF and could stretch into oil owing to their oleophilic/hydrophobic property, which could lead to an oleophilic/hydrophobic surface of the ss-GF. Moreover, this surface property could be further magnified with a 3D-layered structure, leading to the superoleophilic surface of the ss-GF.

### 2.3. Application of the ss-GF for Oil and Organic Solvent Adsorption and Desorption

Based on the pH-reversible conversion between oleophilicity and oleophobicity in the aqueous media, the as-designed ss-GF could be potential in water–oil or water–organic solvent separation. As a proof-of-concept, a model separation system was constructed. Firstly, the ss-GF was applied to adsorb the chloroform (stained with the Sudan red) in a neutral aqueous medium. Because of the hydrophobicity and oleophilicity of the ss-GF in the neutral aqueous medium, the chloroform was quickly adsorbed by the ss-GF (Figure 5a, Movie 2). After that, the ss-GF was put into an aqueous medium with a pH of 3.0. The P2VP chains were gradually protonated and exposed on the surface of ss-GF, leading to the wetting of the surface of ss-GF with the acidic water. The polar and protonated P2VP chains were gradually wetted by the polar acidic water, and the nonpolar



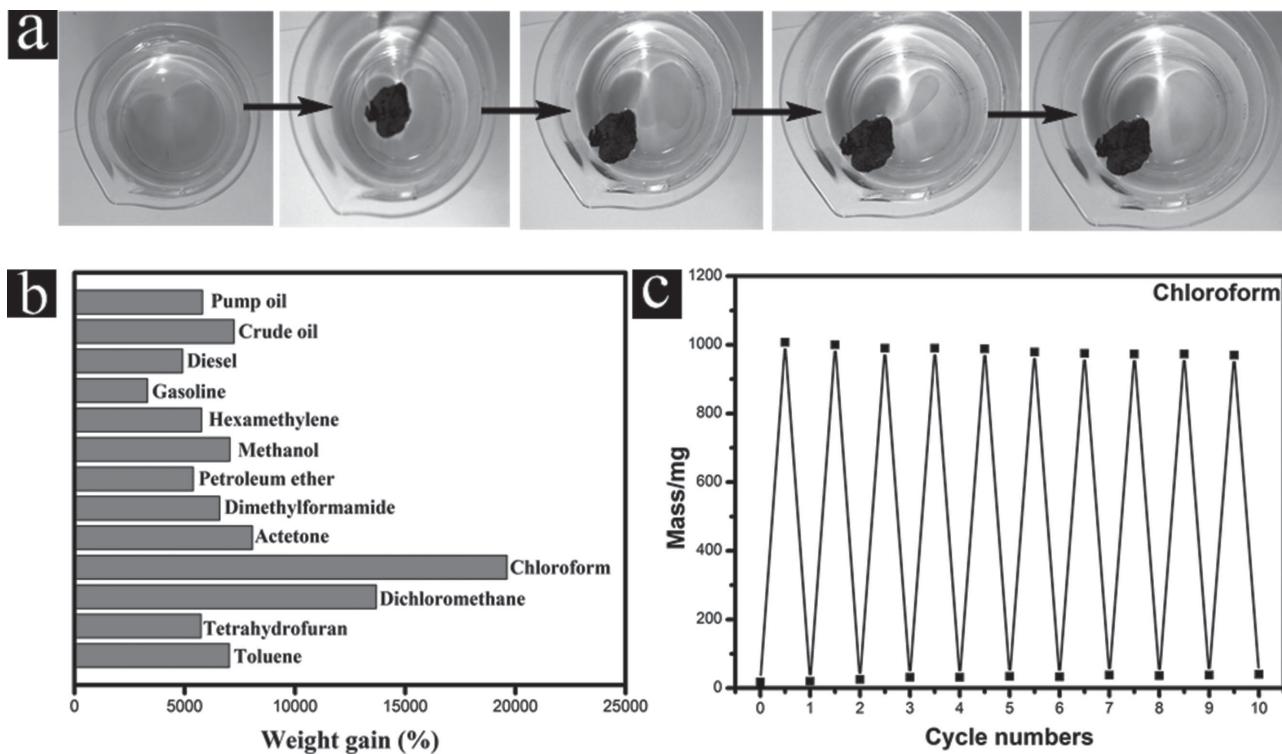
**Figure 5.** Screenshots of the movie showing the oil wettability of the ss-GF in water. a) The adsorption of chloroform (stained with the Sudan red) by the ss-GF in water of pH 7.0; and b) the desorption of chloroform by the ss-GF in water of pH 3.0.

chloroform was expelled from the ss-GF drop by drop because of the high repulsive force between the polar and nonpolar materials (Figure 5b, Movie 3). This data suggest that the ss-GF is able to adsorb and desorb the underwater organic solvents by varying the medium pH.

In addition, the as-fabricated ss-GF inherits some unique properties of GF, such as the compressible property, and a fast and high adsorption capacity. As shown in Figure S5a (Supporting Information), the as-fabricated ss-GF can bear 20 cycles compressive stress test. More importantly, the as-fabricated ss-GF remains the porous structure as original (Figure S5b, Supporting Information), indicating microscopic structure is not destroyed after the compressive tests. **Figure 6a** (screenshot of Movie 4) shows that 2 mL of toluene (stained with the Sudan red) floating on the water was completely adsorbed by the ss-GF within 21 s. More interestingly, from the video, we observed that the ss-GF could adsorb toluene even when toluene was not touching the surface of ss-GF, indicating a fast adsorption rate and excellent adsorbability of the as-fabricated ss-GF. To further assess the adsorption capacity of the ss-GF, we measured the weight gain (wt%, defined as the weight of adsorbed oil or organic solvents per unit weight of ss-GF). Some common oil and organic solvents were used as the model adsorbates. The ss-GF exhibited high adsorption capacity of these oil and organic solvents. A typical weight gain of the as-fabricated ss-GF is  $\approx$  40–196 times of its own weight (Figure 6b), which

is similar or even higher than the values reported for other adsorbents,<sup>[20,49–52]</sup> such as hydrophobic polymers (10–20 times),<sup>[49]</sup> sponge foams (20–86 times),<sup>[20]</sup> exfoliated graphite (60–90 times),<sup>[50]</sup> carbon nanotube gels (40–115 times),<sup>[51]</sup> and carbon nanotube sponges (80–180 times).<sup>[52]</sup> Although the adsorption capacity of our ss-GF is lower than some of the reported adsorbents, such as the carbon nanotube aerogel (106–312 times) and the ultraflyweight aerogel (215–913 times), the ss-GF developed in this study has an additional attractive feature, which is the pH-triggered adsorption and desorption. This merit is promising for the collection of oil and organic solvents from water.

The controllable adsorption and desorption is one salient point of our ss-GF, considering most pollutants could be useful raw materials (some are also expensive) for valuable chemicals. In addition, the recovery and reuse of the pollutants may also mitigate the waste of resources and therefore to prohibit the secondary contamination.<sup>[40]</sup> Therefore, the recyclability of the absorption process could be of value to the practical oil cleanup. The recycle experiment of the as-fabricated ss-GF was performed using the chloroform as the model adsorbate, where chloroform was adsorbed in a neutral aqueous medium and was desorbed when the medium was shifted to acidic. The ss-GF can be recovered by washing with neutral water that could remove the acidic water, followed by drying in Ar atmosphere. During the drying process, the PHA chains can spontaneously



**Figure 6.** a) Screenshots of the movie showing a 2 mL of toluene (stained with the Sudan red) was completely adsorbed by the ss-GF within 21 s. b) The adsorption capacity of the ss-GF for oil and organic solvents. c) The recyclability of ss-GF in water with a pH of 7.0 and 3.0.

expose on the surface of the ss-GF because PHA is more hydrophobic than P2VP, which could fully recover the hydrophobic/oleophilic property of the ss-GF. The results are presented in Figure 6c, where no loss in the adsorption capacity was observed even after ten cycles of experiments. This data strongly suggest that our ss-GF has good recyclability in the process of organic solvent adsorption and desorption.

### 3. Conclusion

In summary, we report a facile approach to prepare the ss-GF by grafting a block copolymer (P2VP-*b*-PHA) on the surface of GF. The as-designed ss-GF featured with a smart surface of switchable wettability for oil and organic solvents, which could be simply triggered by the medium pH. In addition, the ss-GF developed in this study has integrated the attractive features of the GF (high adsorption capacity) and the block copolymer P2VP-*b*-PHA (pH-responsive surface property). The possible synergistic effect between the GF and P2VP-*b*-PHA has rendered the ss-GF not only with high adsorption capacity and fast adsorption rates of oil and organic solvents, but also with a smart surface property that could switch the absorption and desorption of oil and organic solvents simply by varying the medium pH. Furthermore, the pH-responsive surface also makes possible good recyclability of the ss-GF under the operation of the organic solvent adsorption and desorption. The attractive features of the ss-GF are advantageous for developing promising adsorbents for sewage treatment in environmental protection.

### 4. Experimental Section

**Materials:** Graphite flakes (purity > 99.7%), potassium permanganate, sulfuric acid, sodium nitrate, H<sub>2</sub>O<sub>2</sub>(30%), EDA, 2-vinyl pyridine, hexadecyl acrylate were purchased from Sinopharm Chemical ReagentCo.,Ltd. (China). 4,4'-Azobis(4-cyanovaleic) (V-501) and azobisisobutyronitrile (AIBN) were purchased from Aladdin Chemical Co., Ltd. (China).

**Instrumentation:** SEM images of the samples were obtained from a QUANTA 450 microscope. Number-average molecular weight, weight-average molecular weight, and polydispersity index were measured by GPC using a Waters 1515 HPLC system. <sup>1</sup>H NMR was recorded on an INOVA 400 MHz NMR instrument. XPS spectra were obtained from an ESCALAB MK II X-ray photoelectron spectrometer. The contact angle measurement was carried out on a DropMeter A-200. FTIR spectra were recorded by a Nicolet 4700 FTIR spectrometer. The compression tests were performed using the CMT 0625 MTS systems. The TGA was performed using Rigaku-TD-TDA using a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere.

**Synthesis of GF:** GO was synthesized according to a previous report.<sup>[53]</sup> The GF was prepared via an EDA reduction method. In a typical synthesis, 20 μL of EDA was introduced into a 5 mL of GO solution (3 mg mL<sup>-1</sup>). The mixture was then placed into a glass vial and heated up to 95 °C for 6 h. The graphene aerogel was produced after freeze drying the sample for 48 h. The GF was obtained after a 1 min microwave of the graphene aerogel under the Ar atmosphere.

**Synthesis of RAFT Agent—4-Cyanopentanoic Acid Dithiobenzoate (CAD):** The synthesis of CAD was according to a reported procedure.<sup>[54]</sup> Firstly, benzyl chloride (6.4 g) was added to a methanolic solution of sodium methoxide (86 g, 12.5%) containing 6.4 g elemental sulfur. The mixture was then refluxed for 10 h in argon. After that, the mixture was separately extracted by diethyl ether, 0.5 M hydrochloric acid, and sodium hydroxide, resulting in a sodium dithiobenzoate solution. A potassium ferricyanide solution (250 mL, 6.5%) was then introduced (drop wise)

to the above solution under vigorous stirring. The as-obtained red precipitate was filtered, washed copiously with deionized water, and dried in vacuum (40 °C) for 12 h. Dithiobenzoyl disulfide (4.3 g) was added to the ethyl acetate (75.0 mL) solution containing 5.8 g V-501. After refluxing for 20 h, the reaction solution was concentrated in vacuum and the product was purified by column chromatography (moving phase: ethyl acetate-hexane, 1:3 by volume).

**Synthesis of P2VP-*b*-PHA:** P2VP was synthesized by the RAFT polymerization of 2-vinyl pyridine using CAD as a transfer agent (Scheme S1, Supporting Information). Briefly, 10 mg CAD and 5.0 mg V-501 were added to 5 mL of cyclohexanone solution containing 1.0 g 2-vinyl pyridine. The tube was then sealed and cycled between vacuum and nitrogen for five times. After 6 h reaction at 70 °C in oil bath, the mixture was washed with a large amount of diethyl ether. The as-obtained copolymer was dried under vacuum and stored in a glass vial for further polymerization. The pH-responsive diblock polymer P2VP-*b*-PHA was synthesized using P2VP as a macrochain transfer agent. Briefly, 0.23 g P2VP was added to a 10 mL of cyclohexanone solution containing 0.45 g HA and 10.6 mg AIBN. The tube was then sealed and cycled between vacuum and argon for three times. After 24 h reaction at 70 °C in oil bath, the mixture was washed with a large amount of ethyl ether. The as-obtained diblock polymer was dried under vacuum and stored in a glass vial.

**Synthesis of ss-GF:** GF was first immersed in a 2% anhydrous toluene solution of (3-bromopropyl)trimethoxysilane at 25 °C for 12 h to form GF@Br, followed by a thorough washing process with a large amount of toluene and ethanol to remove the unreacted (3-bromopropyl) trimethoxysilane. The as-prepared GF@Br was then dried under nitrogen. The as-obtained GF@Br was immersed in a P2VP-*b*-PHA THF solution (3 mg mL<sup>-1</sup>). The mixture was then placed in a vacuum oven at 150 °C for 12 h to enable the quaternization between the bromolalkyl and pyridine groups of the block copolymers. Finally, the mixture was washed with a large amount of THF to remove the ungrafted polymers.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] T. Dalton, D. Jin, *Mar. Pollut. Bull.* **2010**, *60*, 1939.
- [2] Y. C. Chem, C. F. Li, Q. Xu, B. A. Ole, W. G. Pichel, *Mar. Pollut. Bull.* **2011**, *62*350.
- [3] M. Lnagaki, M. Toyoda, *Spill Sci. Technol. Bull.* **2007**, *8*, 467.
- [4] J. Aurell, B. K. Gullet, *Environ. Sci. Technol.* **2010**, *44*, 9431.
- [5] A. Bayat, S. F. Aghamir, A. Moheb, G. R. Vakili-Nezhaad, *Chem. Eng. Technol.* **2005**, *28*, 1525.
- [6] M. O. Adebajo, R. L. Kloprogge, T. J. Camody, S. Kokot, *J. Porous Mater.* **2003**, *10*, 159.
- [7] V. Rajakovic, G. Aleksic, M. Rajatic, L. Rajakovic, *J. Hazard Mater.* **2007**, *143*, 494.
- [8] M. Lnagaki, M. Toyoda, K. Moriya, H. Konno, *Desalination* **2000**, *128*, 213.
- [9] T. R. Annuncidao, T. H. D. Sydenstricker, S. C. Arico, *Mar. Pollut. Bul.* **2005**, *50*, 1340.
- [10] M. A. Lillo-Ródenas, D. Cazorla-Amoró, *Carbon* **2005**, *43*, 1758.
- [11] H. B. Sonmez, F. Wudl, *Macromolecules* **2005**, *38*, 1623.
- [12] W. W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, *Nat. Commun.* **2013**, *4*, 1777.
- [13] Y. L. Yu, H. Chen, Y. Liu, V. S. J. Craig, C. Wang, L. H. Li, *Adv. Mater. Interfaces* **2014**, *1*, 1300002.
- [14] W. F. Chen, S. R. Li, C. H. Chen, L. F. Yan, *Adv. Mater.* **2011**, *23*, 5679.
- [15] Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei, H. M. Cheng, *Nat. Mater.* **2011**, *10*, 424.
- [16] Y. Xu, K. Sheng, G. Shi, *ACS Nano* **2010**, *4*, 4324.
- [17] H. Hu, Z. Zhao, W. Wan, Y. Gogotsi, J. Qiu, *Adv. Mater.* **2013**, *25*, 2219.
- [18] S. H. Lee, H. W. Kim, J. O. Hwang, R. S. Ruoff, S. O. Kim, *Angew. Chem. Int. Ed.* **2010**, *49*, 10084.
- [19] E. Singh, Z. P. Chen, F. Houshmand, N. Koratkar, *Small* **2013**, *9*, 75.
- [20] H. C. Bi, X. Xie, K. B. Yin, Y. L. Zhou, S. Wan, L. B. He, F. Xu, F. Banhart, R. S. Ruoff, *Adv. Funct. Mater.* **2012**, *22*, 4421.
- [21] H. Y. Sun, Z. Xu, C. Gao, *Adv. Mater.* **2013**, *25*, 2554.
- [22] Y. Yang, T. Zhen, T. Ngai, C. Y. Wang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 6351.
- [23] Z. X. Xue, Y. Z. Gao, N. Liu, L. Feng, L. Jiang, *J. Mater. Chem. A* **2014**, *2*, 2445.
- [24] K. S. Liu, Y. Tian, L. Jiang, *Prog. Mater. Sci.* **2013**, *58*, 503.
- [25] X. J. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 3063.
- [26] H. S. Lim, D. Kwak, D. Y. Lee, S. G. Lee, K. Cho, *J. Am. Chem. Soc.* **2007**, *129*, 4128.
- [27] B. Xin, J. Hao, *Chem. Soc. Rev.* **2010**, *39*, 769.
- [28] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angew. Chem. Int. Ed.* **2004**, *43*, 357.
- [29] Y. G. Jiang, Z. Q. Wang, X. Yu, F. Shi, H. P. Xu, W. Dehaen, *Langmuir* **2005**, *21*, 1986.
- [30] F. Xia, Y. Zhu, L. Feng, L. Jiang, *Soft Matter* **2009**, *5*, 275.
- [31] I. Luzinow, S. Minko, V. Tsukruk, *Soft Matter* **2008**, *4*, 714.
- [32] A. Blanazs, S. P. Armes, J. A. Ryan, *Macromol. Rapid Commun.* **2009**, *30*, 267.
- [33] S. Kumar, Y. L. Dory, M. Lepage, Y. Chao, *Macromolecules* **2011**, *44*, 7385.
- [34] L. B. Zhang, Z. H. Zhang, P. Wang, *NPG Asia Mater.* **2012**, *4*, 1.
- [35] L. Janowska, K. Chizari, O. Ersen, S. Zafeiratos, D. Soubane, *Nano. Res.* **2010**, *3*, 126.
- [36] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, *Carbon* **2007**, *45*, 1558.
- [37] R. J. Liao, Z. H. Tang, Y. D. Lei, B. C. Guo, *J. Phys. Chem. C* **2011**, *115*, 20740.
- [38] S. F. Pei, J. P. Zhao, J. H. Du, W. C. Ren, H. M. Cheng, *Carbon* **2010**, *48*, 4466.
- [39] J. Gao, F. Liu, Y. L. Liu, N. Ma, Z. Q. Wang, X. Zhang, *Chem. Mater.* **2010**, *22*, 2213.
- [40] Y. W. Zhu, S. Murali, M. D. Stoller, A. Velamakanni, R. D. Piner, R. S. Ruoff, *Carbon* **2010**, *48*, 2118.
- [41] H. Han, Z. B. Zhao, Q. Zhou, Y. Gogotsi, J. S. Qiu, *Carbon* **2012**, *50*, 3267.
- [42] H. C. Bi, Z. Y. Yin, X. H. Cao, X. Xie, L. Tan, X. Huang, B. Chen, F. T. Chen, Q. L. Yang, X. Y. Bu, X. H. Lu, L. T. Sun, H. Zhang, *Adv. Mater.* **2013**, *25*, 5916.

- [43] H. Hu, Z. B. Zhao, Y. Gogotsi, J. S. Qiu, *Environ. Sci. Technol. Lett.* **2014**, *1*, 214.
- [44] S. Chang, S. Singamaneni, E. Kharlampieva, S. Young, V. V. Tsukurk, *Macromolecules* **2009**, *42*, 5781.
- [45] S. J. Zhai, X. M. Song, D. Yang, W. L. Chen, J. H. Hu, G. L. Lu, X. Y. Huang, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4055.
- [46] E. J. Kim, C. J. Kang, H. Y. Beak, K. Y. Huang, D. W. Kwak, E. K. Lee, Y. J. Kang, E. L. Thomas, *Adv. Funct. Mater.* **2010**, *20*, 1728.
- [47] S. Chang, S. Singamaneni, E. Kharlampieva, S. L. Young, V. V. Tsukurk, *Macromolecules* **2009**, *42*, 5781.
- [48] T. J. Martin, S. E. Webber, P. Munk, *Macromolecules* **1996**, *29*, 6526.
- [49] A. Li, H. S. Sun, D. Z. Tan, W. J. Fan, S. H. Wen, X. J. Qing, G. X. Li, S. Y. Li, W. Q. Deng, *Energy. Environ. Sci.* **2011**, *4*, 2062.
- [50] M. Toyoda, M. Lnagaki, *Carbon* **2000**, *38*, 199.
- [51] H. W. Liang, Q. F. Guan, L. F. Chen, Z. Zhu, W. J. Zhang, S. H. Yu, *Angew. Chem. Int. Ed.* **2012**, *51*, 5101.
- [52] X. C. Gui, J. Q. Wei, K. L. Wang, A. Y. Cao, H. W. Zhu, Y. Jia, Q. K. Shu, D. H. Wu, *Adv. Mater.* **2010**, *22*, 617.
- [53] C. D. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Z. Sun, B. Alemany, J. M. Tour, *ACS Nano* **2010**, *4*, 4806.
- [54] D. Y. Chen, X. W. Xia, H. W. Gu, Q. F. Xu, J. F. Ge, Y. G. Li, N. J. Li, J. M. Lu, *J. Mater. Chem.* **2011**, *21*, 12683.