Compressible Carbon Nanotube—Graphene Hybrid Aerogels with Superhydrophobicity and Superoleophilicity for Oil Sorption

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ABSTRACT: Spilled oil represents a menace to the aquatic ecosystem and the whole environment in general and requires timely cleanup. Among all the available technologies, oil sorption has attracted the most attention because of its simplicity and high level of effectiveness. The key for the development of this technology is convenient fabrication of high-performance oil sorbents that can be used repeatedly. In this work, a fast microwave irradiation-mediated approach has been proposed for manufacturing multivall carbon nanotube (MWCNT)—graphene hybrid aerogels, in which MWCNTs are vertically anchored on the surface of cell walls of graphene aerogels. The hybrid monoliths show superhydrophobicity and superoleophilicity, a large pore volume, a large pore size, and excellent compressibility, demonstrating outstanding performance for recyclable oil sorption.

INTRODUCTION

The fast development of modern society and the modern economy with an increasing demand for energy has prompted offshore oil exploitation and transportation, which results in unexpected disasters such as oil spills.1−5 Spilled oil is a menace to the aquatic ecosystem and the whole environment in general.6,7 As such, the development of new functional materials that can remove and reclaim spilled oil is urgently required.7−16 Many materials, including inorganic minerals and natural organic and synthetic organic products, have been developed;15 the possibilities and feasibilities of their use in the recovery and/or removal of spilled oil have been tested.8,16 Nevertheless, very few can meet all the practical demands for selectivity, sorption capacity, sorption rate, and recyclability. These issues, which are mainly governed by the structures of the absorbents that exhibit superhydrophobicity and superoleophilicity,17 high porosity,18 suitable pore sizes,19,20 and reversible deformation under a high level of strain,5,8 must be addressed. Until now, fabricating sorbents with superior oil sorption performance has remained a great challenge.

A graphene aerogel (GA) represents a new form of monolithic structure, which integrates unique properties of individual graphene sheets into highly porous, macroscopic ensembles of practical importance.21,22−24 The oleophilicity and pore-rich property of GAs offer great advantages for their use as oil sorbents, which show ultrahigh oil sorption capacity much greater than those of any reported materials.26,27 However, modulation of surface properties, pore sizes, and mechanical properties, which are imperative for high-performance oil sorbents with practical applications, has not attracted enough attention to date. Using the functionalization—lyophilization—microwave approach, we reported an ultralight graphene aerogel (ULGA) with a porosity of up to 99.8%, excellent compressibility, and pore sizes ranging from several tens to hundreds of micrometers (Figure S1 of the Supporting Information), which are suitable for rapid oil sorption.28 However, its practical application still requires a superhydrophobic surface for high selectivity.

Superhydrophobicity can generally be found on hydrophobic surfaces with enhanced surface roughness because of the minimization of contact areas between the surface and water by trapped air.26,27 As such, carbon nanotubes (MWCNTs; we call them CNTs for the sake of simplicity), specifically their vertically aligned arrays, have been widely explored for the generation of superhydrophobic surfaces because of their large aspect ratio, chemical inertness, and hydrophobicity.28,29 Herein, we present an ultrafast microwave irradiation (MWI)-mediated approach to the production of CNT/GA hybrid structure, in which the cell walls of GAs are carpeted with vertical CNT forests, yielding superhydrophobicity, sorbing oils, and achieving high selectivity.

Received: January 18, 2014
Revised: February 24, 2014
Accepted: February 25, 2014
Published: February 25, 2014
MATERIALS AND METHODS

The fabrication process for CNT/GA is illustrated in Figure 1. First, a functionalized graphene aerogel (FGA) via an ethylenediamine-functionalized approach with a high porosity and large pore sizes was exposed under MWI to give rise to ULGA.25 Afterward, ULGA was coated with ferrocene by impregnating it in an acetone solution of ferrocene and drying naturally, where π–π interactions between them can drive the uniform distribution of ferrocene on ULGA.30,33 Lastly, additional MWI was involved to produce rapid in situ superheating of ULGA,25 resulting in the decomposition of ferrocene into iron particles and cyclopentadienyl, which serve as the catalyst and carbon source, respectively, for the growth of CNTs,33,34 leading to the formation of CNT/GA hybrid structure. The details of the experiments are provided in the Supporting Information.

RESULTS AND DISCUSSION

The monolithic graphene structure withstands intensive MWI as well as an impregnation and drying process (Figure 1), indicative of strong interactions between building blocks. Because of the ultralow density, the hybrid structures still exhibit a high porosity of up to 99%. Furthermore, the cellular structures are also well-maintained as shown in panels a and b of Figure 2. Both ULGA (Figure 2a) and CNT/GA (Figure 2b) exhibit large cells with sizes ranging from several tens to hundreds of micrometers (Figure S1 of the Supporting Information), which is totally different from the size distribution of most reported GAs with curved sheets randomly stacked together.21,34–37 The pore sizes in the ranges mentioned above are highly desired for rapid transport of viscous liquid, such as oils, providing the possibility of fast oil sorption.39 In contrast to the relatively smooth walls of ULGA (Figure S2 of the Supporting Information), the walls of CNT/GA are highly rugged (Figure 2b,c) because of the incorporation of CNTs. Detailed microscopic observations of wall surfaces under higher magnification show that CNTs grew almost vertically on the walls (Figure 2d) with a high density (Figure 2e). Thus, a hierarchical structure model of the cell wall can be proposed where the cell wall is carpeted by vertical CNT forests as shown in Figure 2f, whereas CNTs were mainly wrapped by graphene sheets in previously reported solution mixing processes (Figure S3 of the Supporting Information).38,39 resulting in compromised hydrophobicity. The as-grown CNTs show uniform diameters around 30–50 nm, revealed by field emission scanning electron microscopy (FESEM) (Figure 2g) and transmission electron microscopy (TEM) images (Figure 2h). The catalyst particles located at the tip of CNTs (Figure 2i and Figure S4 of the Supporting Information) indicate a “tip-growth” model.30,40 As shown in Figure S4a of the Supporting Information, the decomposition of ferrocene results in the decoration of wall surfaces with iron particles at the initial stage of MWI. Then, the iron particles move forward, leaving the CNTs behind (Figure S4b of the Supporting Information), revealing a tip-growth process, which allows directly anchoring CNTs to the surface of graphene.

Raman spectra of FGA, ULGA, and CNT/GA are compared in Figure 3. FGA with highly functionalized surfaces shows an $I_D/I_G$ ratio of 1.22, while the corresponding value for ULGA decreases to 1.14 because of the elimination of functional groups, as well as restoration of conjugated regions.25,41 Strikingly, CNT/GA exhibits a sharply decreased $I_D/I_G$ ratio as low as 0.54 and a strong two-dimensional peak, indicative of graphitic carbon coming from the dense CNT forest, in good agreement with the scanning electron microscopy (SEM) observations (Figure 2b–e). Because of the strong absorption of MWI by graphene, superheating may create a unique atmosphere for the fast growth of CNTs with fewer defects and strong bonding to graphene.30,41 The strategy developed here may inspire new possibilities for the production of high-quality CNTs.33 The content of CNTs can be easily modulated by changing the content of ferrocene in an acetone solution. As shown in Figure S5 of the Supporting Information, impregnating ULGA in solution with a ferrocene concentration of 5 mg/mL finally gives rise to 14 wt % CNTs and ~46 wt % CNTs can be produced with a 20 mg/mL solution. The variation of CNT content can also be reflected by the corresponding SEM images (Figure S6 of the Supporting Information) as the vertical CNT forests become denser with an increasing concentration of ferrocene.

Originally, ULGA demonstrates a typical carbon with the hydrophobic surface32 with a water contact angle of ~100°, as shown in Figure 3a, determined by the heteroatoms (Figure S7 of the Supporting Information) and flatness of the surfaces (Figure S2 of the Supporting Information).33 The introduction of vertical CNT forests on the surface of cell walls can result in lower heteroatom contents (Figure S7 of the Supporting Information) and create a lotuslike structure with greatly enhanced roughness, increasing the hydrophobicity.27 The introduction of 14 wt % CNTs gives rise to a contact angle of 110°, and superhydrophobicity is achieved after integration of 37 wt % CNTs. Accordingly, the sorption of water, which impairs the selectivity during the oil sorption process, decreases from 78 g·g⁻¹ for ULGA to almost zero for CNT/GA with superhydrophobicity. The spreading and permeating behavior of oils with different viscosities on superhydrophobic CNT/GA has been tested. As shown in Figure 3b, a diesel fuel droplet can fully permeate the porous structure within 0.1 s and even a highly viscous pump oil droplet (Figures S8 and S9 and Table S1 of the Supporting Information).
can be fully sucked into the pores rapidly, demonstrating the superoleophilicity of the material.\textsuperscript{2}

The compressibility test required for oil reclaim\textsuperscript{5–9} is performed on a superhydrophobic CNT/GA. The structure can survive 90\% compression and recover to its original volume after the external force is removed (Figure S10 of the Supporting Information). The hysteresis loop formed during the loading and unloading process indicates an elastomeric open cell foam (Figure 3c).\textsuperscript{25,44,45} Furthermore, the stresses remain above zero in the stress–strain curves until the strain is totally released, suggesting the rapid and timely recovery under a high level of strain, which is strongly required for the separation of sorbed oils.\textsuperscript{8,9} This full recovery under a high level of strain was also demonstrated by SEM (Figure 3d), where the largely shrunken pores during loading can be totally restored after compression is released. This performance is superior to that of most of the reported monolithic structures,\textsuperscript{15,19,21,22,27} indicating the excellent compressibility of ULGA has been well-maintained in the final product.

The sorption performance of CNT/GA on different oils has been investigated. As shown in Figure S11 of the Supporting Information, a spherical water droplet can rest on the surface of the superhydrophobic and superoleophilic CNT/GA while the oil droplet (dyed with Sudan III) immediately permeates the porous structure, allowing the fast sorption of oil. The consecutive sorption progress was reflected by a series of images, where the dyed diesel fuel with a volume similar to that of the monolith can be fully sorbed by CNT/GA within 1 s. It also can be seen in these images that most of the oil can be sucked into the pores within 0.4 s, demonstrating an ultrafast sorption rate. Figure 4b exhibits the saturated sorption capacity for several kinds of oils as well as an organic liquid, and the capacity for all

$\text{\textsuperscript{2}Environmental Science & Technology Letters}$

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\caption{SEM images of the porous structure of ULGA (a) and CNT/GA (b). (c) SEM image of rugged cell walls of CNT/GA. (d and e) SEM images of wall surfaces of CNT/GA. (f) Schematic illustration of vertical CNTs on the cell wall of ULGA. (g) FESEM image of the as-grown CNTs. (h and i) TEM images of as-grown CNTs. (j) Raman spectra of FGA, ULGA, and CNT/GA.}
\end{figure}
these pollutants is higher than 100 g·g\(^{-1}\), indicative of a high sorption capacity over a wide range of oils. The comparison in Figure 4b and Figure S12 of the Supporting Information indicates that the sorption capacities of different pollutants are highly related to their viscosity as CNT/GA can absorb more pump oil with high viscosity than ethyl acetate for its 100-fold lower viscosity. The dynamic sorption process of diesel fuel, vegetable oil, and pump oil is shown in Figure 4c, where the amount of sorbed liquid increases rapidly at the initial stage and then gradually reaches equilibrium capacities. The oil sorption performance of ULGA is similar to that of CNT/GA, as shown in Figure S13 of the Supporting Information. Both of the porous structures show BET surface areas of 20–30 m\(^2\)/g (Figure S14 of the Supporting Information), indicating the oils may be trapped in the macropores because of the capillary effect\(^{5,47}\). The kinetics can be described by a second-order model\(^{5,46}\):

\[
\frac{1}{Q - Q_t} - \frac{1}{Q} = Kt
\]

where \(Q\) indicates the saturated sorption capacity, \(Q_t\) is the amount of sorption at time \(t\), \(t\) represents the sorption time, and \(K\) is the sorption constant that is viscosity-dependent.\(^5\) Table S2 of the Supporting Information provides the fitted parameters. The results are in good agreement with the experimental data. The saturated sorption of diesel fuel (3.4 cP) can be reached within 4 s, showing a sorption constant as high as 47.6 × 10\(^{-3}\) s\(^{-1}\). Even for the highly viscous oils, such as vegetable oil (57 cP) and

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Figure 3. (a) Variation of water contact angle and water sorption capacity of samples with different CNT contents. (b) Wetting behavior of a diesel fuel droplet placed on the surface of CNT/GA. (c) Stress–strain curves of CNT/GA under different stains. (d) SEM observation of the loading and unloading of CNT/GA.

Figure 4. Sorption performance of CNT/GA. (a) Video snapshots of the diesel fuel sorption by CNT/GA. (b) Sorption capacity of CNT/GA over oils and organic solvents with different viscosities. (c) Sorption kinetics of different pollutants absorbed by CNT/GA.
pump oil (415 cP), saturated sorption can be achieved within 20 s, further indicative of a viscosity-dependent property (Figure S15 of the Supporting Information). The sorption rate is much faster than most of the reported results where hundreds to thousands of seconds is required.\textsuperscript{5,38} GAs via hydrothermal- and vitamin C-mediated reduction\textsuperscript{34,35} have also been selected as substrates for the growth of CNTs, and the corresponding hybrid structures consisting of graphene and CNTs have been used as oil sorbents (Figure S16 and Table S2 of the Supporting Information). These structures exhibit not only a much lower saturated sorption capacity but also a greatly decreased sorption rate because of a smaller pore volume as well as much smaller pore sizes.\textsuperscript{34,35}

The recyclability of CNT/GA, which is in high demand in oil cleanup applications, is exhibited in Figure 5. The sorbed oils can be easily harvested by compressing the carbon mat and mechanically extruding the sorbed oil. As shown in Figure 5a, the oil gradually squeezes out from the monolith under compression. The sorption and desorption processes of different oils are listed in Figure 5b, and the recovery percentage by compression is also viscosity-dependent; ethyl acetate with the lowest viscosity shows 90% recovery, while the most viscous pump oil exhibits a recovery of 72% for the first cycle. Figure S17 of the Supporting Information and Figure 5c show multiple sorption–desorption cycles for diesel fuel, where 70% of the saturated sorption capacity can be maintained over many cycles. Surprisingly, the recovery ratio increases to almost 100% after the second cycle. Because of the interaction between oils and the monolith, part of the volume has been occupied by oil, which cannot be regenerated by mechanical extrusion, but the remaining pores can be fully utilized in cyclic applications. Thus, the full reclaim of sorbed oils is shown after the first cycle.

In summary, a fast MWI-mediated approach has been designed to produce CNT/GA, where CNTs are vertically grown on the cell wall surfaces of the ULGA. The introduction of CNTs gives rise to superhydrophobicity and superoleophilicity. Coupled with a large pore volume, suitable pore sizes, and compressibility inherited from ULGA, the CNT/GAs demonstrate rapid oil sorption, large sorption capacity, and good recyclability. The sorption capacities and sorption rates of CNT/GAs for oils are superior to those of most superhydrophobic and superoleophilic structures. Furthermore, the sorbed oils can be easily harvested by applying mechanical extrusion, allowing recyclable usage of CNT/GAs. The synergistic effect between graphene and CNT for environment remediation has been demonstrated. This result may inspire the development of more efficient structures combining different carbon nanomaterials and producing new functionalities for a variety of applications.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

Details of experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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\section*{Notes}

The authors declare no competing financial interest.

\section*{ACKNOWLEDGMENTS}

This work was supported by the National Science Foundation of China (Grants 51072028 and 21336001). Collaboration between Drexel University and the Dalian University of Technology was supported by the Cheung Kong Scholarship.

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