ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

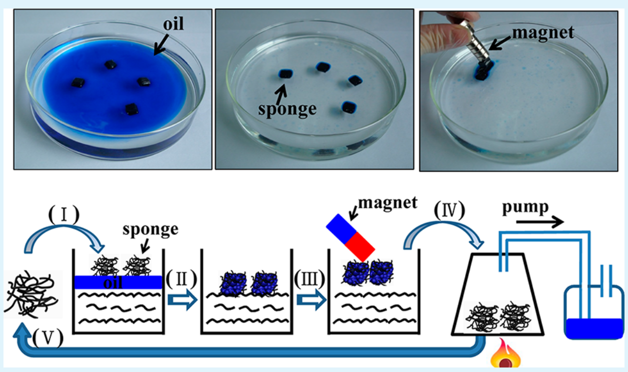
Magnetic and Highly Recyclable Macroporous Carbon Nanotubes for Spilled Oil Sorption and Separation

Xuchun Gui,*[†] Zhiping Zeng,[†] Zhiqiang Lin,[†] Qiming Gan,[†] Rong Xiang,[†] Yuan Zhu,[†] Anyuan Cao,[‡] and Zikang Tang[†,§]

[†]State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China

[‡]Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, P. R. China

[§]Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China



ABSTRACT: Development of sorbent materials with high selectivity and sorption capacity, easy collection and recyclability is demanding for spilled oil recovery. Although many sorption materials have been proposed, a systematic study on how they can be reused and possible performance degradation during regeneration remains absent. Here we report magnetic carbon nanotube sponges (Me-CNT sponge), which are porous structures consisting of interconnected CNTs with rich Fe encapsulation. The Me-CNT sponges show high mass sorption capacity for diesel oil reached 56 g/g, corresponding to a volume sorption capacity of 99%. The sponges are mechanically strong and oil can be squeezed out by compression. They can be recycled using through reclamation by magnetic force and desorption by simple heat treatment. The Me-CNT sponges maintain original structure, high capacity, and selectivity after 1000 sorption and reclamation cycles. Our results suggest that practical application of CNT macrostructures in the field of spilled oil recovery is feasible.

KEYWORDS: *carbon nanotube, spilled oil, sorption and desorption, sorption capacity, mechanical strength, recyclability*

INTRODUCTION

In recent years, frequent oil-spill accidents have caused severe ecological problems, including nearly irreversible damage to ecological systems. Various techniques have been proposed and used for spilled oil recovery, including physical sorption by porous sorbent materials, mechanical recovery by oil skimmers, in situ burning, physical diffusion (aided by dispersants), and biodegradation.[1,2] Among these existing methods, physical sorption by porous materials is probably a simple, fast, and effective technique. Therefore, much attention has been paid to developing inexpensive, practical sorbents with potential applications in spilled oil cleanup.

An ideal sorbent material working in water environment should be hydrophobic and oleophilic to render selectivity, and has a high oil sorption rate and capacity. Related to low-cost application, it is important for the sorbent to be readily reusable and that oil recovery from it is possible and straightforward. Recently, various high porosity, lightweight superhydrophobic and superoleophilic sorbents, such as carbon nanotube sponges (CNT sponges),[3,4] CNT solids,[5,6] polydimethylsiloxane (PDMS) sponges,[7] polystyrene fibers,[8] graphene aerogels, and sponges,[9−12] have been reported with a wide range of structures and sorption capacities. Among them, carbon nanomaterials such as CNTs and graphene show high sorption capacity and reusability, while also being environmentally friendly; these materials have significant advantages over traditional absorbent materials such as active carbon.[4,13−16] For example, a 3D graphene framework with ultralow density of 2.1 mg/cm^3 can take up 200 to 600 times its own weight in oil;[13] CNT sponges can be regenerated simply by squeezing or directly burning;[3] graphene oxide foams retain their original high sorption capability after more than 10 cycles.[11,17,18] High recyclability of the sorbents could reduce the cost of spill oil recovery. For these new carbon nanomaterial structures, there has been no systematic study on the regeneration and related performance degradation and recycled use has been limited to a small number of cycles.

Sorbents with high sorption capacity usually have low mechanical strength, which restricts their practical application.[13,18] For example, the high-sorption-capacity 3D graphene shows a strain of 50% under a compressive stress of only 0.3 kPa.[18] This means that the viable stack height of the sorbent after sorption is only several centimeters, making practical application difficult. Therefore, not only the sorption capacity

Received: April 23, 2013
Accepted: May 30, 2013
Published: May 30, 2013

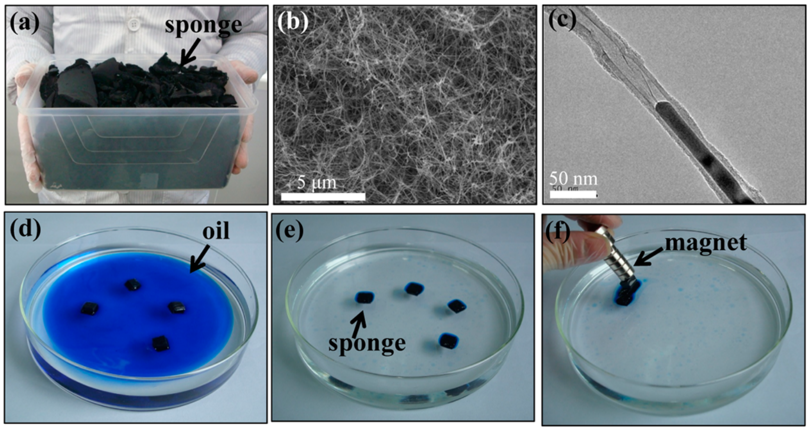


Figure 1. Removal of spilled oil from water surface by Me-CNT sponges under magnetic field. (a) Optical image of a box of sponges with volume of approximately 5 L. (b) SEM image of the porous CNT. (c) TEM image of a CNT filled with magnetic Fe nanowires. (d) Oil (dyed blue) spreading on water; four Me-CNT sponge blocks have been placed onto the oil. (e) Clean water surface after complete oil absorption by the sponges. (f) Collecting the sponges using a magnet.

but also the mechanical strength, cost, and convenience of use and reuse are also important in practice. However, only a few reports have focused simultaneously on the sorption capacity, mechanical strength, recyclability, and stability of absorbent materials in harsh environments.[3−5,13,14]

CNT macrostructures have oleophilic and hydrophobic properties, unique porous structure and large specific surface area.[19−21] They are widely used as filter films and sorbents for volatile organic compounds (VOCs) and heavy metal ions.[22−24] In our previous work, we have reported porous CNT macrostructures as sorbents for oil-spill cleanup.[3] It shows high sorption capacities and fast sorption. Here we synthesize a magnetic CNT sponge (Me-CNT sponge) by filling the CNT inner cavity with magnetic Fe nanowires, and use it as a sorbent for oil-spill recovery. The material shows nearly full volume sorption capacities and high recyclability, retaining most of its sorption performance for at least 1000 cycles. After sorption, the sponge can be collected conveniently using a magnet, and desorption can be realized by simple heat-treatment at modest temperatures (200−300 °C).

■ EXPERIMENTAL SECTION

Synthesis and Characterization of Me-CNT Sponge Sorbents. The Me-CNT sponges were fabricated by chemical vapor deposition (CVD) using ferrocene and dichlorobenzene as the precursors, as reported in our previous work.[4] In the present experiment, the concentration of ferrocene in dichlorobenzene was increased to 150 mg/mL in order to obtain more encapsulated Fe within the cavity of CNTs. The density of the Me-CNT sponges is about 15 mg/cm^3. The microstructure and morphology of CNT sponges were investigated by scanning electron microscopy (SEM, S4800). The static contact angles (CA) were measured on a Kruss DSA100 contact angle testing system at room temperature. The average CA was obtained by measuring at more than five different positions on the same sample.

Mechanical Properties of Me-CNT Sponges. Mechanical tests were carried out on an Instron 5943 equipped with 10 and 1000 N load cells. The Me-CNT sponges were cut into small blocks with sizes of about 10 × 10 × 10 mm^3. Compression rates were set at 1−5 mm/min. For the cyclic compressive testing of the sponges in oil, a cup-shaped lower stage filled with the appropriate oil and a square-head upper stage were used as the compression stages.[25] During cyclic testing, the sponge was completely immersed in the oil, and could only expand its volume from the compressed state by absorbing the surrounding oil into the pores.

Oil Sorption and Reusability of Me-CNT Sponges. The sorption experiment was similar to that in our previous work.[3] The Me-CNT sponges (about 10 × 10 × 10 mm^3) were put onto the oil. After sorption, the sponge was left to drip for 30 s and then weighed. The mass sorption capacities were calculated as $((m - m_0)/m_0)$, where m is the weight of sample after sorption and m_0 is the initial weight of the sample.

The reusability experiments were carried out by immersing the sponge in oil to complete saturation sorption and then compressing it at high strain (85%) to desorb the oil. After every 200 sorption and desorption cycles, the sample was allowed to fully adsorb oil, then left for 30 s to drip off surface oil and weighed to determine the mass sorption capacity. After that, the sample was regenerated by heat treatment at a selected temperature. After regeneration, the CA was measured and the sample was weighed before being returned to the oil for further cycling.

The sorption height experiments were performed by using a piece of Me-CNT sponge with size of 5 × 2 × 100 (width, thickness and length) mm. And one end of the sponge was immersed in oil for sorption. During sorption, the sorption height of oil in the sponge was recorded with a digital camera.

■ RESULTS AND DISCUSSION

The Me-CNT sponges, like polymer sponges, are light and porous. The sponge can be synthesized using a simple CVD system, which can be easily scaled up by using a furnace with a large reactive chamber. Figure 1a shows an optical image of a box containing approximately five liters of Me-CNT sponges. SEM shows that the sponge contains highly interconnected CNTs, which formed porous structures (Figure 1b) with pore sizes from several nanometers to a few micrometers.[3] These pores provide sufficient space for the storage of absorbed oil, and also provide capillary action which spontaneously drives the spilled oil into the pores. The TEM image shows that the inner cavity of the CNT is filled with long and continuous iron catalyst nanowires (Figure 1c). These iron nanowires are ferromagnetic, and allow the Me-CNT sponge to be attracted by conventional magnets. The saturation magnetization of the sponges is about 21.1 emu/g.

The porous Me-CNT sponges speedily take up spilled oil from the water surface. As showed in figure 1d, four samples were floated on the oil film. The oil film then shrank toward the samples. After a short time, the entire oil film was taken up by the sponges, which remained floating on the water surface (Figure 1e). The CNT sponges could then be collected easily using a magnet (Figure 1f). Some magnetic nano particles or nano powders, such as Fe_3O_4 nanoparticles, have previously been used as sorbents for oil-spill recovery, and can be collected by a magnet.[26−28] The present Me-CNT sponge, because it is in block form and has larger saturation magnetization, is even easier to collect.

Spilled oil recovery requires that spilled oil is not only very efficiently taken up and prevented from further harming the aquatic environment, but also that the technology is low-cost and eco-friendly. Recycling and reusing the sorbent is an effective way to reduce the cost. Recycling of spilled oil and regeneration of the Me-CNT sponges by heat treatment are illustrated in Figure 2. After the spilled oil had been absorbed

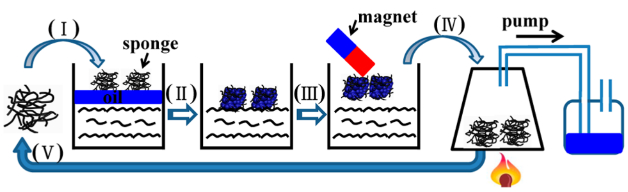


Figure 2. Schematic of the recycling of Me-CNT sponges used for spilled oil sorption. (I) sprinkled on the oil; (II) adsorb spilled oil; (III) collected by magnet; (IV) regeneration; (V) reuse.

by the sponges, the material was gathered by a magnet, collected and heated (to 220 °C to release the gasoline vapor or 300 °C to release diesel oil). The temperature required for vaporization can be controlled and kept slightly above the boiling point of the oil. After regeneration, the sponge can be reused for spilled oil sorption. The oil vapor can be recovered by passing it through oil or through an appropriate organic solvent at low temperature. Based on this heat treatment and mechanical compression, the Me-CNT sponge was cycled more than 1000 times. Compared with other regeneration methods (such as mechanical compression, washing with solvents or burning) heat treatment is a simpler, inexpensive, and easily completed technique.

The sponge has large mass sorption capacities $(m - m_0/m_0)$ for oil, taking up about 56 times its weight in diesel oil and 49 times its weight in gas oil (Figure 3a). These capacities are larger than those of polymer sponges and porous nanofibers.[29−31] The weight of the sponge does not change measurably, and the mass sorption capacity of the CNT sponges is largely retained after they have been used for many cycles. For example, the mass sorption capacity for diesel oil is 52 g/g after 200 cycles and over 43 g/g after 1000 cycles, which is 76% of the original capacity. This is the first report of a sorbent with such high reusability. The excellent recycling properties could reduce the cost of spilled oil recovery, implying that the sponges could be employed as efficient oil sorbents in practice.

The mass sorption capacities of the sponge can increase linearly with the density of the oil, and are not constant for different oils or solvents, as has been previously shown for many other sorbents.[5,9,32] This means that the value of mass sorption capacity alone cannot fully characterize the sorbent. Mass sorption capacity is also very sensitive to small changes in the density of the sorbent material, especially for superlow density sorbents. However, it is widely used in literature as a property parameter to describe and compare sorbents. The volume sorption capacity $([(m - m_0)\rho_0/\rho m_0 x])$, where ρ_0 is the density of the sorbent and ρ is the density of the oil or solvent, x is the porosity of the sorbent, as described by Korhonen, may better characterize the sorption capacity of a material.[32] x is approximately 100% for low density sorbents.

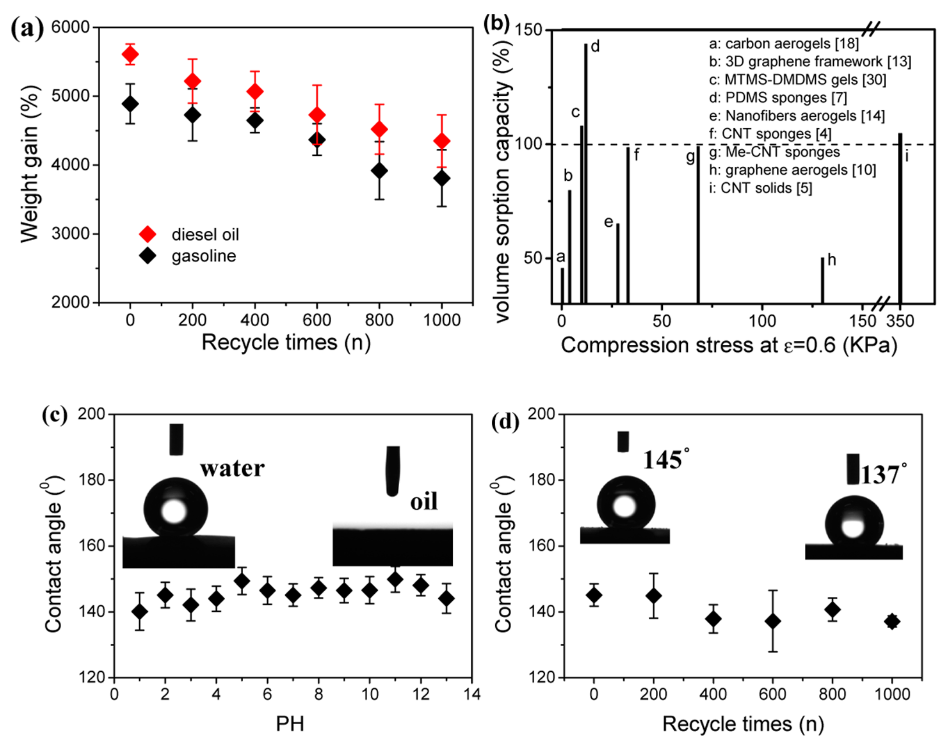


Figure 3. Recyclability of Me-CNT sponges. (a) Mass sorption capacities of the sponges as a function of cycling for up to 1000 cycles. (b) Volume sorption capacity and mechanical strength of Me-CNT sponges and various other sorbents. (c) Contact angles of the as-prepared sponges after floating on aqueous solutions with different pH values for 24 h. (d) Superhydrophobic character of the sponges after 1000 cycles.

dx.doi.org/10.1021/am4015007 | ACS Appl. Mater. Interfaces 2013, 5, 5845−5850

Table 1. Sorption Capacities, Mechanical Strength and Reusability of Different Sorbents

sorbent	sorption capacities (g/g)[a]	compressive stress at set strain of 60% (KPa)	desorption methods	recycle used times	sorbent density (mg/cm^3)	ref
Me-CNT sponges	66	68	heat treatment	1000	15	this work
PDMS sponges	~8	12	squeezing	20	180	7
MTMS−DMDMS gels	~9	10	squeezing	10	120	30
graphene aerogels	~38	130			13.2	10
CNT solids	~43	350	burning/ squeezing		24.3	5
carbonaceous nanofibers aerogels	~62	28	burning	6	10.5	14
CNT sponges	135	33	burning/ squeezing	10	7.3	4
3D graphene framework	~380	4	burning	9	2.1	13
carbon aerogels	~326	~0.3	heat treatment	10	1.4	18

[a]The sorption capacity was normalized by the density of solvent (gasoline or hexane).

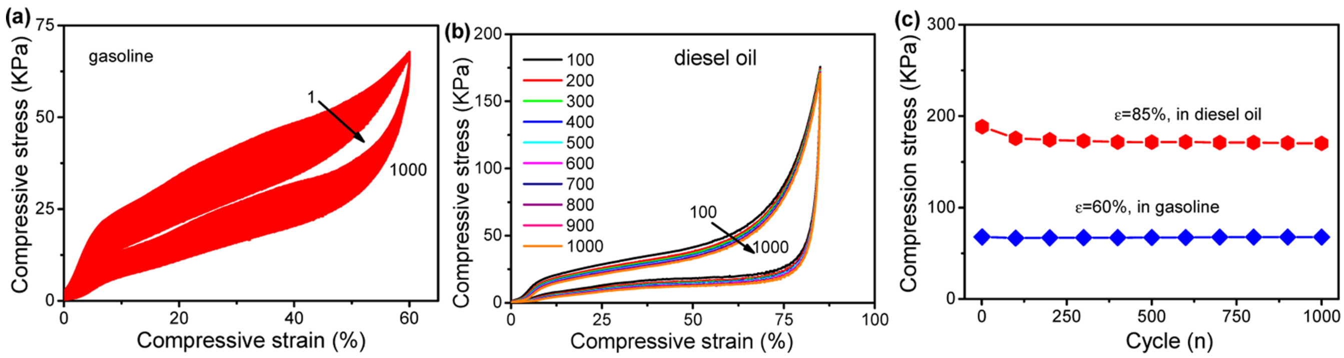


Figure 4. Mechanical properties of magnetic Me-CNT sponges as a function of cycling. Compressive stress−strain curves of the sponges placed in (a) gasoline and (b) diesel oil for 1000 cycles. (c) Stress during 1000 cycles at constant strain in diesel oil and gasoline.

Volume sorption capacity is independent of solvent density. The volume sorption capacity of Me-CNT sponges and other sorbents are calculated and showed in Figure 3b. For the data reported in the literature, the mass sorption capacity of the sorbent was normalized by the density of adsorbed solvent (gasoline or hexane). And the volume sorption capacity was calculated as ($v_m\rho_0/\rho x$), where v_m is the mass sorption capacity. It is about 99% for both Me-CNT sponges and our previously reported CNT sponges. This means that almost the entire volume of the samples is available for sorption, which is a larger proportion than that found for carbon-based aerogels (Figure 2b). Some sorbents have volume sorption capacities of more than 100%, as calculated from literature mass sorption capacity data. This may be caused by the surface adhesion of a large amount of solvent or because the material itself expands during sorption.

The Me-CNT sponge not only has high volume sorption capacity, but also appropriate mechanical strength (Figure 3b). The compressive stress for the Me-CNT sponge is 66 kPa at a constant strain of 60%, which is much greater than that of carbon aerogels (0.3 kPa) and a 3D graphene framework (4 kPa) at the same compressive strain. Table 1 compares the sorption capacities, mechanical strength and reusability of Me-CNT sponges with those of several typical sorbents reported in the literature. The sorption capacity of sponges is not as high as that of some super low-density sorbents, such as carbon aerogels or graphene aerogels,[13,18] but it does possess much higher mechanical strength and high reusability.

The sorption properties of the sponge are due to its nanoporous nature and hydrophobic and oleophilic surface properties, which results in large capillary action for wetting by oil. As show in the inset to Figure 3c, the water CA is large than 140°, and oil CA is below 4°. Moreover, the sponges have excellent long-term stability and chemical stability in air, different oils and organic solvents, even floating on aqueous solutions with pH values ranging from 1−13 for 24 h, as shown in Figure 3c. The sponge retains its hydrophobicity for at least one year under atmospheric conditions. This suggests that the sponges can be used under the demanding conditions found in oil recovery. Importantly, the Me-CNT sponges keep their hydrophobicity after more than 1000 usage cycles (Figure 3d).

The Me-CNT sponges are structurally stabile during spilled oil recovery. The sponges can sustain large-strain deformations, recover most of their material volume elastically, and resist structural fatigue under cyclic stress conditions in liquid oils. When compression testing the sponges under liquid oil, we observed that the samples recovered almost fully to their original shape, even after 1000 cycles. The stress vs strain curves for different cycles follow almost the same route during loading and unloading processes (Figure 4). During compression, absorbed oil is extruded out of the sponge pores and then sucked in again upon unloading. The sponges can maintain a similar compressive stress at the maximum strain in every cycle both in diesel and gasoline, indicating little degradation of mechanical strength after 1000 cycles (Figure 4c). These features are favorable for the application of the sponges over many cycles. The highly structure and chemical stability is the origin of Me-CNT sponges for high recyclability.

An interesting property of the Me-CNT sponge is the possibility of separating one particular oil or solvent from a mixture of solvents. After immersing one end of a piece of sponge in oil or solvent, the oil could diffuse up into the sample under capillary action. The capillary force is related to the pore size and structure, the properties of the oil and the wetting of the CNTs by the oil. Therefore, for different oils or solvents, the capillary force is different, resulting in different sorption and diffusion rates. The equilibrium sorption height can be expressed by the Laplace equation, $h = 2\cos\theta\gamma/\rho g R$, where θ is the CA of the CNT and oil, γ is the interfacial tension of CNT and oil, ρ is the density of the oil, g is the acceleration due to gravity, and R is the pore radius. Figure 5 shows the upward diffusion rates of diesel oil and gasoline in Me-CNT sponge. The gasoline diffuses faster than the diesel oil. The sorption height is 52 mm after 20 min of sorption for gasoline; however, it is only 33 mm for diesel oil. On the basis of this feature, the sponge could be used to separate solvents, as has already been reported for superwetting nanowire membranes.[33]

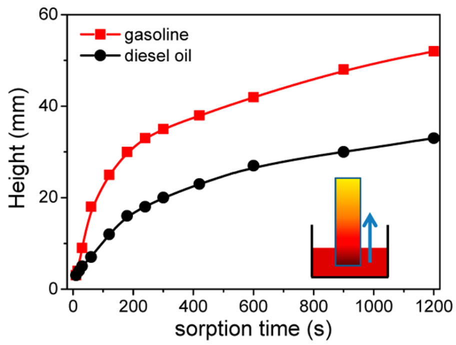


Figure 5. Sorption height of the sponge for different oils. A piece of sponge was immersed in oil, and the oil diffused upward into the sponge under capillary action.

CONCLUSION

Magnetic CNT sponges were used as sorbents for spilled oil recovery. They showed highly mass sorption capacity (up to 56 g/g) and volume sorption capacity (up to 99%), excellent recyclability (more than 1000 times) and stable performance. Although the sorption capacity of the sponges is lower than that of superlight carbon aerogels, the sponges have higher mechanical strength and better recyclability, since they can be reclaimed using a magnet and recovered by simple heat treatment. The structures, contact angle and sorption capacities do not change greatly even after 1000 usage cycles. The sponges also show different sorption and diffusion rates for diesel oil and gasoline, indicating that they can separate for different oils. In light of the rapid research progress in the field of spilled oil recovery, our results enhance the prospects for environmental applications of CNT.

AUTHOR INFORMATION

Corresponding Author

*E-mail: guixch@mail.sysu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (Grant 51102286), the Guangdong Natural Science Foundation (Grant S2012040007893), the Beijing City Nanotechnology Special Program (Grant Z121100001312005), and the Fundamental Research Funds for the Central Universities (12lgpy16).

REFERENCES

(1) Cheng, M. J.; Gao, Y. F.; Guo, X. P.; Shi, Z. Y.; Chen, J. F.; Shi, F. *Langmuir* **2011**, *27*, 7371−7375.

(2) Deng, D.; Prendergast, D. P.; MacFarlane, J.; Bagatin, R.; Stellacci, F.; Gschwend, P. M. *ACS Appl. Mater. Interfaces* **2013**, *5*, 774−781.

(3) Gui, X. C.; Li, H. B.; Wang, K. L.; Wei, J. Q.; Jia, Y.; Li, Z.; Fan, L. L.; Cao, A. Y.; Zhu, H. W.; Wu, D. H. *Acta Mater.* **2011**, *59*, 4798−4804.

(4) Gui, X. C.; Wei, J. Q.; Wang, K. L.; Cao, A. Y.; Zhu, H. W.; Jia, Y.; Shu, Q. K.; Wu, D. H. *Adv. Mater.* **2010**, *22*, 617−621.

(5) Hashim, D. P.; Narayanan, N. T.; Romo-Herrera, J. M.; Cullen, D. A.; Hahm, M. G.; Lezzi, P.; Suttle, J. R.; Kelkhoff, D.; Munoz-Sandoval, E.; Ganguli, S.; Roy, A. K.; Smith, D. J.; Vajtai, R.; Sumpter, B. G.; Meunier, V.; Terrones, H.; Terrones, M.; Ajayan, P. M. *Sci. Rep.* **2012**, *2* (363), 1.

(6) Zhao, M. Q.; Huang, J. Q.; Zhang, Q.; Luo, W. L.; Wei, F. *Appl. Clay. Sci.* **2011**, *53*, 1−7.

(7) Choi, S. J.; Kwon, T. H.; Im, H.; Moon, D. I.; Baek, D. J.; Seol, M. L.; Duarte, J. P.; Choi, Y. K. *ACS Appl. Mater. Interface* **2011**, *3*, 4552−4556.

(8) Wu, J.; Wang, N.; Wang, L.; Dong, H.; Zhao, Y.; Jiang, L. *ACS Appl. Mater. Interface* **2012**, *4*, 3207−3212.

(9) Zhao, J. P.; Ren, W. C.; Cheng, H. M. *J. Mater. Chem.* **2012**, *22*, 20197−20202.

(10) Wang, J. L.; Shi, Z. X.; Fan, J. C.; Ge, Y.; Yin, J.; Hu, G. X. *J. Mater. Chem.* **2012**, *22*, 22459−22466.

(11) Bi, H. C.; Xie, X.; Yin, K. B.; Zhou, Y. L.; Wan, S.; He, L. B.; Xu, F.; Banhart, F.; Sun, L. T.; Ruoff, R. S. *Adv. Function. Mater.* **2012**, *22*, 4421−4425.

(12) Dong, X. C.; Chen, J.; Ma, Y. W.; Wang, J.; Chan-Park, M. B.; Liu, X. M.; Wang, L. H.; Huang, W.; Chen, P. *Chem. Commun.* **2012**, *48*, 10660−10662.

(13) Zhao, Y.; Hu, C. G.; Hu, Y.; Cheng, H. H.; Shi, G. Q.; Qu, L. T. *Angew. Chem., Int. Ed.* **2012**, *51*, 11371−11375.

(14) Liang, H. W.; Guan, Q. F.; Chen, L. F.; Zhu, Z.; Zhang, W. J.; Yu, S. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 5101−5105.

(15) Wu, Z. Y.; Li, C.; Liang, H. W.; Chen, J. F.; Yu, S. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 2925−2929.

(16) Xiao, N.; Zhou, Y.; Ling, Z.; Qiu, J. S. *Carbon* **2013**, *59*, 530−536.

(17) Niu, Z. Q.; Chen, J.; Hng, H. H.; Ma, J.; Chen, X. D. *Adv. Mater.* **2012**, *24*, 4144−4150.

(18) Sun, H. Y.; Xu, Z.; Gao, C. *Adv. Mater.* **2013**, *25*, 2554−2560.

(19) Lee, C.; Baik, S. *Carbon* **2010**, *48*, 2192−2197.

(20) Futaba, D. N.; Miyake, K.; Murata, K.; Hayamizu, Y.; Yamada, T.; Sasaki, S.; Yumura, M.; Hata, K. *Nano Lett.* **2009**, *9*, 3302−3307.

(21) Lee, C. H.; Johnson, N.; Drelich, J.; Yap, Y. K. *Carbon* **2011**, *49*, 669−676.

(22) Li, Y. H.; Du, Q. J.; Liu, T. H.; Sun, J. K.; Jiao, Y. Q.; Xia, Y. Z.; Xia, L. H.; Wang, Z. H.; Zhang, W.; Wang, K. L.; Zhu, H. W.; Wu, D. H. *Mater. Res. Bull.* **2012**, *47*, 1898−1904.

(23) Viswanathan, G.; Kane, D. B.; Lipowicz, P. J. *Adv. Mater.* **2004**, *16*, 2045−2049.

(24) Srivastava, A.; Srivastava, O. N.; Talapatra, S.; Vajtai, R.; Ajayan, P. M. *Nat. Mater.* **2004**, *3*, 610−614.

(25) Gui, X. C.; Zeng, Z. P.; Cao, A. Y.; Lin, Z. Q.; Zeng, H. Q.; Xiang, R.; Wu, T. Z.; Zhu, Y.; Tang, Z. K. *J. Mater. Chem.* **2012**, *22*, 18300−18305.

(26) Thanikaivelan, P.; Narayanan, N. T.; Pradhan, B. K.; Ajayan, P. M. *Sci. Rep.* **2012**, *2*, 1−7.

(27) Zhu, Q.; Tao, F.; Pan, Q. M. *ACS Appl. Mater. Interface* **2010**, *2*, 3141−3146.

(28) Calcagnile, P.; Fragouli, D.; Bayer, I. S.; Anyfantis, G. C.; Martiradonna, L.; Cozzoli, P. D.; Cingolani, R.; Athanassiou, A. *ACS Nano* **2012**, *6*, 5413−5419.
(29) Zhu, Q.; Pan, Q. M.; Liu, F. T. *J. Phy. Chem. C* **2011**, *115*, 17464−17470.
(30) Hayase, G.; Kanamori, K.; Fukuchi, M.; Kaji, H.; Nakanishi, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 1986−1989.
(31) Li, A.; Sun, H. X.; Tan, D. Z.; Fan, W. J.; Wen, S. H.; Qing, X. J.; Li, G. X.; Li, S. Y.; Deng, W. Q. *Energy Environ. Sci.* **2011**, *4*, 2062−2065.
(32) Korhonen, J. T.; Kettunen, M.; Ras, R.; Ikkala, O. *ACS Appl. Mater. Inter.* **2011**, *3*, 1813−1816.
(33) Yuan, J. K.; Liu, X. G.; Akbulut, O.; Hu, J. Q.; Suib, S. L.; Kong, J.; Stellacci, F. *Nat. Nanotechnol.* **2008**, *3*, 332−336.