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Porous Materials Hot Paper

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Pumping through Porous Hydrophobic/Oleophilic Materials: An Alternative Technology for Oil Spill Remediation**

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Abstract: *Recently, porous hydrophobic/oleophilic materials (PHOMs) have been shown to be the most promising candidates for cleaning up oil spills; however, due to their limited absorption capacity, a large quantity of PHOMs would be consumed in oil spill remediation, causing serious economic problems. In addition, the complicated and time-consuming process of oil recovery from these sorbents is also an obstacle to their practical application. To solve the above problems, we apply external pumping on PHOMs to realize the continuous collection of oil spills in situ from the water surface with high speed and efficiency. Based on this novel design, oil/water separation and oil collection can be simultaneously achieved in the remediation of oil spills, and the oil sorption capacity is no longer limited to the volume and weight of the sorption material. This novel external pumping technique may bring PHOMs a step closer to practical application in oil spill remediation.*

Frequent oil spills have caused severe damage to the ecosystems of oceans and coastlines, and are difficult to clean up.[1] Currently the most commonly used technologies for oil spill remediation include booms, skimmers[2] solidifiers,[3] dispersants,[4] bioremediation,[5] and in situ burning.[6] However, except for skimmers, which are designed to recover the spilled oil, yet are only effective on high-viscosity oil, these techniques only focus on cleaning up, ignoring their adverse effects on the environment.

Recently, functionalized membranes with bio-inspired surfaces, including steel meshes[7] and fabrics,[8] have aroused great attention owing to their high separation efficiency and low cost.[7b] Unfortunately, it is extremely difficult to collect oil spills and filter them by these membranes.[9] Although a novel tubular vessel with hydrophobic and oleophilic metal meshes on the wall could remove oil from the water surface,[10] the oil recovery ability of this technology is ineffective in handling thin floating oil due to its low oil sorption capacity, and it has not been demonstrated to be effective on moving water surfaces. Porous hydrophobic and oleophilic materials (PHOMs), such as polymethylsilsesquioxane aerogels,[11] nanowire membranes,[12] carbon based sponges,[13] porous boron nitride,[14] and functional polymer sponges,[9,15] are an attractive alternative for oil spillage remediation, because PHOMs have the possibility to completely remove an oil film (especially thin and low viscosity oil) from the water surface. However, present studies focus excessively on the oil sorption capacity (amount of oil absorbed per unit weight of sorbent), ignoring the high material and transport costs of these lightweight, but bulky sorbent materials. Moreover, facing the shortage of fossil fuels in the future, the recovery of oil from absorbents is also a necessary process. Although the oil can be recovered from the PHOMs by squeezing[15a,c,16] and distillation,[13c] these time-consuming and lengthy procedures with questionable durability and demand for high cost devices are obstacles for their practical and commercial application.

Herein, we describe an oil collection apparatus based on a simple combination of PHOMs with pipes and a self-priming pump (Figure 1) to realize consecutive collection of oil in situ from the water surface. Our simulation shows that the key to this design is the capillary pressures at oil–air and oil–water interfaces of PHOMs, which spontaneously regulate with the suction power applied to the PHOMs. This prevents the permeation of air and water into the PHOMs (Supporting Information, Figure S1); only the floating oil is absorbed by the PHOMs and flows along the pipes to the collecting tank, leaving the PHOMs consistently able to uptake the oil present. This self-controlled oil collection system will not only save a large amount of PHOM material, but will also make the collection of oil spills easier and faster. We also demonstrate that PHOMs with a suction force applied can efficiently separate oil and water from a water surface with simulated waves. We believe that this novel external pumping

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Supporting information for this article, including materials and methods, simulation of the self-controlled oil collection design, a photograph of a hydrophobic polymer sponge, a diagram of experimental setups, the collection of large area floating oil, the collection of floating crude oil, an illustration of an integrated oil collection apparatus, the viscosity of the oils, and the test parameters, is available on the WWW under http://dx.doi.org/10.1002/anie.201310151.

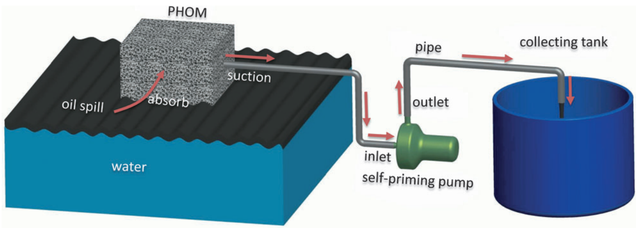

Figure 1. A pumped PHOM device for oil spill remediation. A pipe connected to the inlet of a self-priming pump is inserted into a PHOM and the outlet of the pump is connected to a collection vessel by another pipe. The PHOM is then placed on the oil spill site. When the pump is turned on, the oil on the water surface is selectively absorbed by the sorbent and flows along the pipe into the collecting vessel until all oil is consumed.

technique will bring PHOMs a step closer to practical application in oil spill remediation.

To demonstrate the principal of the design, hydrophobic polymer sponges (HPSs) were chosen as typical PHOMs. The HPSs were obtained by modifying commercially available polymer sponges (PSs) with a hydrophobic SiO_2 nanoparticle/polydimethylsiloxane (PDMS) coating through a facial dip-coating method (Figure 2 a). Commercially available PSs with open macropores can be easily modified by scalable dip-coating for various applications, such as supercapacitor electrodes,[17] elastic conductors,[18] gas, and oil sorbents.[15d,19] The original PS (Figure 2 b) with an open macroporous structure (Figure 2 c) is an excellent absorber for water and organic solvents. After being dipped in a hydrophobic SiO_2 nanoparticle/PDMS composite solution, the whole PS was filled with the composite solution quickly. They were then pulled up and aired to remove the solvent at room temperature, followed by curing at a higher temperature to produce the HPS (Figure 2 f). Some pores of the PS were caulked (Figure 2 g), whereas most of them remained, which ensured enough passage of oil inside the sponge. Figure 2 h shows the skeleton of the PS (Figure 2 d) covered with a thick hydrophobic SiO_2 nanoparticle/PDMS composite coating. In the magnified SEM images, it can be clearly seen that the surfaces of the skeleton changed from smooth (Figure 2 e) to randomly rough at the micrometer and sub-micrometer scales (Figure 2 i) after the modification process. It should be noted that this facile solution-processed dip-coating method of modifying PSs can be easily scaled up for practical application (Figure S2).

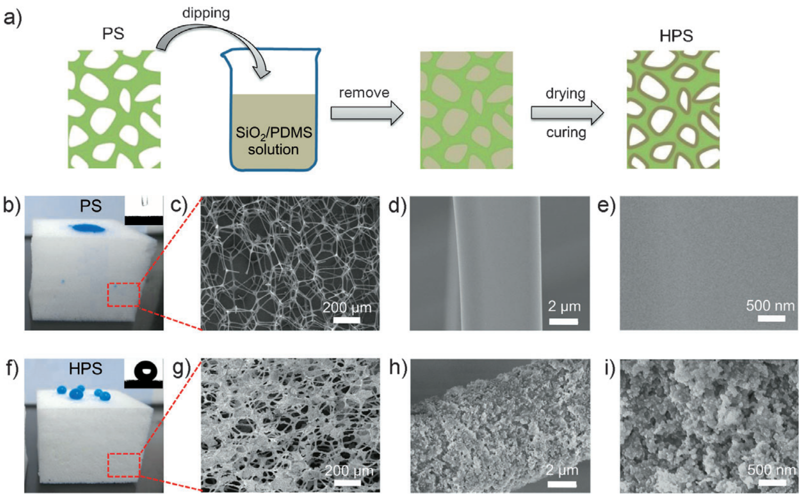

Figure 2. a) The fabrication of modified polymer sponge (PS) by a dip-coating process. b) Image of the PS; inset: water contact-angle measurement of the PS. c–e) SEM images of the original PS with different magnification. f) Image of the as-synthesized HPS; inset: water contact-angle measurement of the HPS. g–i) SEM images of the HPS with different magnification.

Compared with the flat skeletal surfaces of the original PS, such hierarchical roughness and low-free-energy SiO_2 nanoparticles/PDMS provide the capability of repelling water and absorbing oil. Figure 3 a shows that when the HPS was immersed into water by external force, air bubbles were trapped around the surface of the HPS, forming a silver, mirror-like surface, demonstrating the high resistance of HPS to water permeation. In addition, provided any part of the HPS was over a water surface or in contact with oil, water would never penetrate into the HPS, except under heavy pumping (Figure S3 and Movie S1). On the other hand, HPS exhibits good absorption capability for organic solvents and oil. As shown in Figure 3 b, *n*-hexane (dyed red) quickly spreads through the whole macroporous system of the HPS by capillary force. When a suction force was applied to the top of the HPS, the *n*-hexane absorbed by the HPS could be pumped away, while the *n*-hexane around the HPS continued to be absorbed (Movie S2).

Based on the different behavior of the HPS towards oil and water, we built up a bench-scale oil collection apparatus (Figures 3 c and S4). A sample oil, *n*-hexane could be selectively absorbed into the macropores of the HPS by immersing the HPS into the *n*-hexane/water mixture. After turning on the self-priming pump, the *n*-hexane absorbed by the HPS was pumped to collecting vessel. At the meantime, *n*-hexane around the HPS was consecutively absorbed into the HPS. When the *n*-hexane on the water surface disappeared, the *n*-hexane above the nozzle of the pipe in the HPS was further pumped away and an air channel formed in the HPS to terminate the *n*-hexane collection. In the pumping process, 25 mL of *n*-hexane was collected from the water surface in 10 seconds, and no water was observed in the collection vessel, thus showing the high oil/water separation efficiency and oil recovery rate of this system (Movie S3). We also performed the collection of crude oil on a water surface with our apparatus, and the result was that all the crude oil was collected successfully, which further demonstrated the potential of our self-regulating system for practical application in oil spillage remediation (Figure S5 and Movie S4).

The self-regulating properties of the system are largely due to the capillary action at the oil–air and oil–water

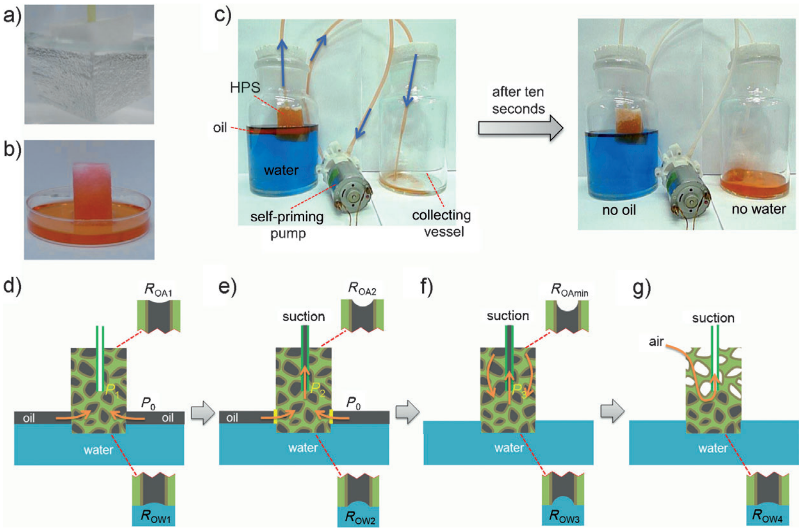

Figure 3. a) Photograph of a HPS immersed in water showing a silver mirror-like surface. b) Photograph of the HPS placed on the thin layer of *n*-hexane (dyed red). c) Photographs of continuously collecting *n*-hexane in situ from a water surface with the apparatus. d–f) Changes in the oil–air and oil–water interfaces of the HPS during the suction process. P_1 and P_2 are the pressures at the nozzle of the pipe before and after implying suction force. P_3 is the pressure at the nozzle of the pipe just when the floating oil is consumed during the suction processes. P_0 is the standard atmospheric pressure. R_{OA} and R_{OW} are the curvature radius of the oil–air interfaces and oil–water interfaces, respectively.

interfaces of HPS, as illustrated in Figure 3 d–g. The floating oil was first absorbed throughout the macropores of the HPS by capillary pressure at the oil–air interface (Figure 3 d). As the capillary pressure is inversely proportional to the radius of curvature of the interfaces, after imposing a suction force to the HPS (Figure 3 e), the capillary pressure at the oil–air and oil–water interfaces spontaneously increased by decreasing the curvature radius of the corresponding interfaces to reach a new equilibrium with decreased pressure (from P_1 to P_2) at the nozzle of the pipe. However, the equilibrium between the pressure of the oil surface (P_0) and the pressure at the nozzle of the pipe was broken, then the oil penetrated into the HPS through its surface, which was in contact with the floating oil (yellow line in Figure 3 e) and was pumped away to the collecting vessel. When the floating oil on the water surface began to vanish (Figure 3 f), the flow rate of oil decreased, which caused the pressure at the nozzle of the pipe to decreased further until the curvature radius of the oil–air interface decreased to its minimum value (R_{OAmin}). Then the pressure at the oil–air interface could not withstand the suction force and the oil above the nozzle of the pipe was pumped further away (Figure 3 f) until an air channel formed in the HPS, leaving behind the oil that was below the nozzle of the pipe (Figure 3 g).

Such self-controlled behavior means that a small piece of HPS can collect a large area of floating oil easily and quickly (Figure S6 and Movie S5). Based on the high efficiency of our pilot model apparatus, one can imagine a ship pulling a floating collection net made of pipes, HPSs and pumps to deal with the oil spill instead of carrying a large amount of oil-sorption materials (Figure S7). In consideration of the harsh sea conditions, such as strong wind and waves, we also studied the oil collecting performance of the apparatus on a water surface with simulated waves (Figure 4). The shaking of the HPS on the water surface did not affect the oil separation efficiency because of its buoyancy ability (Figure S8). In fact, the oil on a moving water surface was more quickly collected into a beaker without taking in water (Movie S6). This kind of oil collection apparatus, small in volume, light in weight, and easy to carry, was also demonstrated to be useful as an emergency facility for tankers and offshore drilling platforms, in case of oil leakage (Figure S9 and Movie S7).

The flow rate of oil recovery is also an important parameter to assess the potential application of the oil collection apparatus. We fixed the size of HPS ($2\times2\times4$ cm^3, about 1.1 g of weight) and investigated the dependence of the oil recovery rate on the power of a self-priming pump, the oil viscosity, and the altitude between the nozzle of pipe and oil surface. According to Darcy's law, the oil recovery rate can be expressed by Equation (1):

$$Q = (-k\,A\,\Delta P)/(\mu\,h) \tag{1}$$

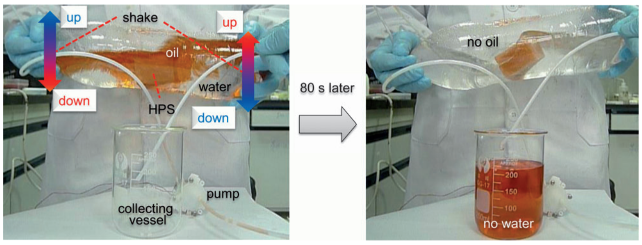

Figure 4. Photographs of the oil collection apparatus continuously collecting floating oil (*n*-hexane dyed in red) on a moving water surface.

Where Q is the oil recovery rate, k is the permeability of the HPS, A is the cross-sectional area of HPS, ΔP is the pressure decrease at the nozzle of the pipe, μ is the viscosity of the oil, and h is the altitude between the nozzle of the pipe and the floating oil surface. ΔP increases as the the pump power increases. When the pump power is within a low range, the capillary pressure of oil–air interfaces can regulate itself to give an equilibrium with ΔP, then the HPS is fully filled with oil (Figure 5 a) and Q increases as the pump power increases. However, when under heavy pumping, the curvature radius of the oil–air interfaces reaches its minimum value and decrease to the nozzle of the pipe, getting its maximum oil recovery rate, then the floating oil is pumped away along with air (Figure 5 b). This is consistent with the experimental result shown in Figure 5 c. The flux of oil increased quickly and almost linearly with the voltage of the pump from 0 V to

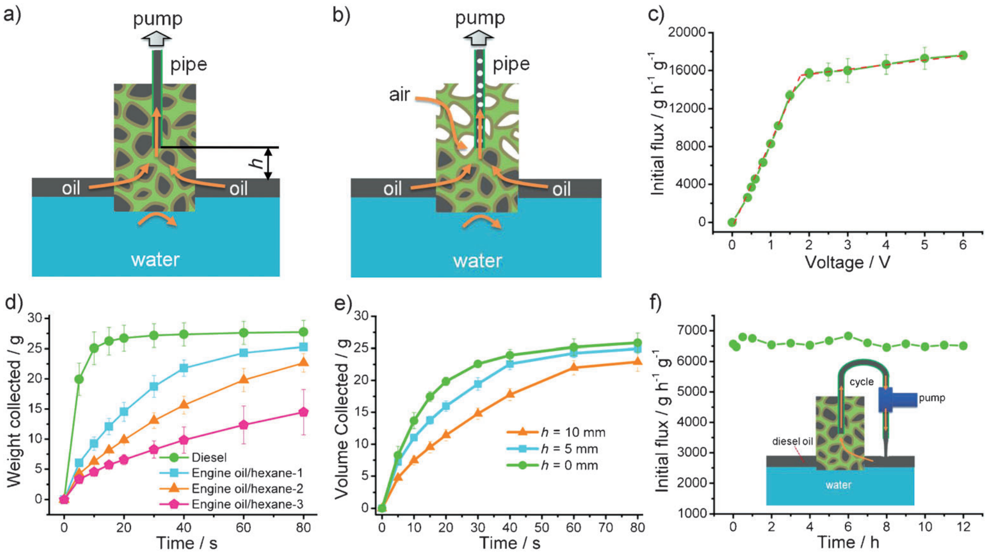

Figure 5. a and b) Oil transportation mechanisms with the HPS fully filled with oil, and with an air channel created in the HPS, respectively. c) Plot of the initial flux of oil (diesel oil) versus the voltage of the self-priming pump. The flux of oil was calculated by dividing the weight of recovered oil by operation time and the weight of the HPS. d) Recovery of oil (25 mL) from a water surface with different viscosities: diesel (5.4 mPa s^{-1}), engine oil/*n*-hexane-1 (18.2 mPa s^{-1}), engine oil/*n*-hexane-2 (46.2 mPa s^{-1}), engine oil/*n*-hexane-3 (102 mPa s^{-1}). e) Recovery of oil (engine oil/*n*-hexane-1) with different heights (h) between the nozzle of the pipe and the oil surface. f) Plot of the flux of (diesel) oil versus time under a circulatory system. All of the test parameters are illustrated in Figure S10.

1.5 V, but when the voltage of the self-priming pump exceeded 2 V, the flux of oil remained almost constant, and air bubbles appeared in the oil collected. To study the impact of oil viscosity on the oil recovery rate, we prepared several oil mixtures with viscosities varying from 5.4 mPa s^{-1} to 102 mPa s^{-1} (Table S1). According to Darcy's law, Q decreases as the oil viscosity increases, which is in accord with the experimental result shown in Figure 5d. The oil recovery rate decreased with the viscosity of the oil. It takes 5 s, 40 s, or 80 s to recover about 20 g of diesel oil (5.4 mPa s^{-1} at 22 °C), engine oil/*n*-hexane-1 (18.2 mPa s^{-1}) and engine oil/*n*-hexane-2 (46.2 mPa s^{-1}), respectively, under the same conditions. The position of the nozzle of the pipe also influences the oil recovery rate. Darcy's law shows that Q decreases as h increases, which can be seen in Figure 5e. The oil recovery rate decreases as the distance between the nozzle of pipe and the oil surface increases. As a result, in order to get the maximum oil recovery rate at low energy cost, the distance between the nozzle of the pipe and the oil surface should be kept at a minimum, and the power of the self-priming pump should be increased until bubbles appear in the recovered oil. The long-time working stability of our design is also worth noting. Figure 5 f demonstrates that the collection of diesel could be maintained for over 12 h without a noticeable decrease in flux.

In summary, we have demonstrated a new model oil collection apparatus, which can continuously collect oil in situ from a water surface with high speed and efficiency. Traditional sorbent technology needs three steps: 1) spread a large amount of sorbent over the oil spill site; 2) collect the absorbed sorbents; 3) recover oil from the sorbents by squeezing or distilling. In comparison, our in situ oil collection design saves sorbents, labor, and operation time, and as a result largely decreases the cost of oil collection. In the future, for large-area oil spills, oil-collecting ships could "fish" the floating oil by pulling a large floatable oil collection net made of pips, hydrophobic polymer sponges (HPSs), and pumps. This foldable oil-collection net with unlimited oil-sorption capacity, small in volume, and easy to carry, may also be used as emergency facilities for tankers and drilling platforms in case of oil leakage. Because of the severe water pollution caused by the growing number of oil spill accidents and industrial organic solvent leakages, this study may prove particularly useful in the design of oil-collection equipment and have significant environment impact.

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[1] R. W. Field, *Nature* **2012**, *489*, 41.
[2] V. Broje, A. A. Keller, *Environ. Sci. Technol.* **2006**, *40*, 7914.
[3] a) S. Basak, J. Nanda, A. Banerjee, *J. Mater. Chem.* **2012**, *22*, 11658; b) A. Vidyasagar, K. Handore, K. M. Sureshan, *Angew. Chem.* **2011**, *123*, 8171; *Angew. Chem. Int. Ed.* **2011**, *50*, 8021; c) S. Mukherjee, B. Mukhopadhyay, *RSC Adv.* **2012**, *2*, 2270.
[4] a) E. B. Kujawinski, M. C. K. Soule, D. L. Valentine, A. K. Boysen, K. Longnecker, M. C. Redmond, *Environ. Sci. Technol.* **2011**, *45*, 1298; b) A. M. Al-Sabagh, E. M. S. Azzam, M. R. N. El-Din, *J. Dispersion Sci. Technol.* **2008**, *29*, 866; c) R. J. Fiocco, A. Lewis, *Pure Appl. Chem.* **1999**, *71*, 27.
[5] R. P. J. Swannell, K. Lee, M. McDonagh, *Microbiol. Rev.* **1996**, *60*, 342.
[6] I. Buist, J. McCourt, S. Potter, S. Ross, K. Trudel, *Pure Appl. Chem.* **1999**, *71*, 43.
[7] a) D. Tian, X. Zhang, Y. Tian, Y. Wu, X. Wang, J. Zhai, L. Jiang, *J. Mater. Chem.* **2012**, *22*, 19652; b) A. K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, *Nat. Commun.* **2012**, *3*, 1025; c) Z. X. Xue, S. T. Wang, L. Lin, L. Chen, M. J. Liu, L. Feng, L. Jiang, *Adv. Mater.* **2011**, *23*, 4270; d) C. Lee, S. Baik, *Carbon* **2010**, *48*, 2192.

[8] a) J. P. Zhang, S. Seeger, *Adv. Funct. Mater.* **2011**, *21*, 4699; b) G. Kwon, A. K. Kota, Y. X. Li, A. Sohani, J. M. Mabry, A. Tuteja, *Adv. Mater.* **2012**, *24*, 3666.
[9] P. Calcagnile, D. Fragouli, I. S. Bayer, G. C. Anyfantis, L. Martiradonna, P. D. Cozzoli, R. Cingolani, A. Athanassiou, *ACS Nano* **2012**, *6*, 5413.
[10] D. Deng, D. P. Prendergast, J. Macfarlane, R. Bagatin, F. Stellacci, P. M. Gschwend, *ACS Appl. Mater. Interfaces* **2013**, *5*, 774.
[11] G. Hayase, K. Kanamori, M. Fukuchi, H. Kaji, K. Nakanishi, *Angew. Chem.* **2013**, *125*, 2040; *Angew. Chem. Int. Ed.* **2013**, *52*, 1986.
[12] J. K. Yuan, X. G. Liu, O. Akbulut, J. Q. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nat. Nanotechnol.* **2008**, *3*, 332.
[13] a) Z.-Y. Wu, C. Li, H.-W. Liang, J.-F. Chen, S.-H. Yu, *Angew. Chem.* **2013**, *125*, 2997; *Angew. Chem. Int. Ed.* **2013**, *52*, 2925; b) J. P. Zhao, W. C. Ren, H. M. Cheng, *J. Mater. Chem.* **2012**, *22*, 20197; c) H. C. Bi, X. Xie, K. B. Yin, Y. L. Zhou, S. Wan, L. B. He, F. Xu, F. Banhart, L. T. Sun, R. S. Ruoff, *Adv. Funct. Mater.* **2012**, *22*, 4421; d) 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.
[14] W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, *Nat. Commun.* **2013**, *4*, 1777.
[15] a) Q. Zhu, Q. Pan, F. Liu, *J. Phys. Chem. C* **2011**, *115*, 17464; b) L. Zhang, Z. Zhang, P. Wang, *NPG Asia Mater.* **2012**, *4*, e8; c) Q. Pan, Q. Zhu, Y. Chu, *J. Mater. Chem. A* **2013**, *1*, 5386; d) X. Zhang, Z. Li, K. Liu, L. Jiang, *Adv. Funct. Mater.* **2013**, *23*, 2881.
[16] D. D. Nguyen, N. H. Tai, S. B. Lee, W. S. Kuo, *Energy Environ. Sci.* **2012**, *5*, 7908.
[17] a) J. Ge, H.-B. Yao, W. Hu, X.-F. Yu, Y.-X. Yan, L.-B. Mao, H.-H. Li, S.-S. Li, S.-H. Yu, *Nano Energy* **2013**, *2*, 505; b) W. Chen, R. Rakhi, L. Hu, X. Xie, Y. Cui, H. Alshareef, *Nano Lett.* **2011**, *11*, 5165.
[18] J. Ge, H.-B. Yao, X. Wang, Y.-D. Ye, J.-L. Wang, Z.-Y. Wu, J.-W. Liu, F.-J. Fan, H.-L. Gao, C.-L. Zhang, S.-H. Yu, *Angew. Chem.* **2013**, *125*, 1698; *Angew. Chem. Int. Ed.* **2013**, *52*, 1654.
[19] X. Chen, Y. Wu, B. Su, J. Wang, Y. Song, L. Jiang, *Adv. Mater.* **2012**, *24*, 5884.

