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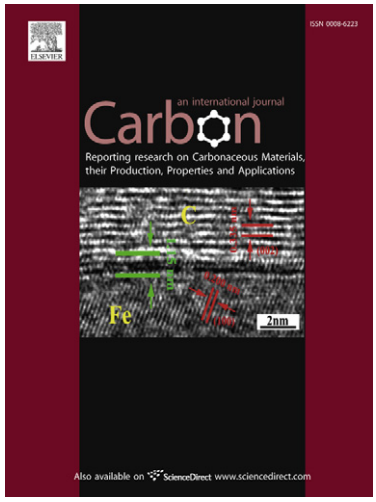

Oil sorption and recovery by using vertically aligned carbon nanotubes

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Oil sorption and recovery by using vertically aligned carbon nanotubes

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Abstract: We used carbon nanotubes as oil adsorbents and evaluated recycling performance by squeezing method. The sorption capacity of 3 mm long vertically aligned carbon nanotubes is almost 6.9 times higher than that of agglomerated carbon nanotubes due to the existence of large-sized macropores. Compared with exfoliated graphite (41 g/g), aligned carbon nanotubes exhibit higher sorption capacity (69 g/g) and better recycling performance due to their unique mechanical strength and excellent rebound resilience properties at high strains.

Treatment of oil spills remains a challenge to environmental scientists and technologists. Among all the existing techniques used for oil treatment, sorption is a popular technique because it is cheap, simple and effective [1]. Exfoliated graphite (EG), which is an important raw material for the industrial production of flexible graphite sheets, attracts our attention because of its very high

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sorption capacity of spilled heavy oils (40-80 g of heavy oil per 1 g). However, the recycling performance of EG is poor due to hard recovery of space or porosity among worm-like particles during filtration, centrifugation or compression [2]. Recently, carbon fiber felts exhibit excellent recycling performance, about 100% and 90% recovery of sorbed heavy oil and no decrease in sorption capacity even after eight cycles by centrifugation [3] and filtration under suction [4], respectively.

Carbon nanotubes (CNTs) are potential materials for energy-absorbing, mechanical dampening devices due to their unique mechanical strength (compressive stress) and compressibility (strain) [5]. For example, agglomerated CNTs [6, 7], vertically aligned CNTs (VACNTs) [5] and CNT-intercalated composites [8] could be repeatedly compressed at high strains. Considering the advantages of their cyclic compression property, as well as intertube porosity, CNTs were successfully used for the sorption of kerosene oil showing a capacitance of 69 g/g and excellent recycling performance in this paper.

Previous studies on the synthesis of VACNTs [9] and agglomerated CNTs [6] have been made. The synthesis of long VACNTs was carried out by the floating catalyst method using ferrocene as the catalyst precursor and cyclohexane as the solvent and carbon source in horizontal quartz tube. The concentration of the catalyst precursor in cyclohexane was 20 g/L. The cyclohexane solution at a feed rate of 5 mL/h was injected by a motorized syringe pump into a carrier gas of 90% Ar and 10% H_2 at a flow rate of 600 mL/min into the reactor. The carbon source was decomposed by in situ formed metal catalyst at 800 °C for 8 h. For comparison, EG (expanded volume: 250 mL/g) is also used as adsorbent, and the detailed procedure for preparation of EG has been described elsewhere [10].

To investigate the compressibility and recovery performances of those carbon materials under

the pressure, about 0.5 g of each powder was loaded to the cavity of a cylindrical die (diameter of 10 mm), and hydrostatic pressure (0.35 MPa) was applied through an oil jack to push the top of the padding. Expansion ratio is defined as t_2/t_1, where t_1 and t_2 are the height of loading and unloading, respectively [6]. The oil sorption process of carbon materials was designed as follows: Firstly, 0.2 g carbon materials were directly put into the injection syringe (diameter of 10 mm), then the excess kerosene oil (kinetic viscosity: 1.34 mPa s) was added and kept for 2 h. Finally, kerosene oil was decanted from the syringe and hanged for 2 h in order to drip off the excess oil. The recovery of adsorbed oil from carbon materials was carried out by squeezing the piston of syringe until no oil dropped (Fig. 1). This cycle of sorption and recovery was repeated up to ten times to determine the recycling performance of carbon materials. For comparison, the recovery process was also performed by removing the sorbed oil from carbon materials in the muffle at 400 °C for 2 h. The oil sorption capacities (g/g) of porous carbon materials were evaluated by the mass change of adsorbents before and after oil sorption.

In this work, two kinds of CNTs (VACNTs and agglomerated CNTs) were used for oil sorption as shown in Fig. 2. Scanning electron microscopy (SEM, Camscan Mx2600FE) images show that about 3 mm long VACNTs (Fig. 2a) is rather straight and the diameter of CNTs is 60 nm (Fig. 2b). Whereas, the primary aggregates of agglomerated CNTs produced by catalytic pyrolysis of propylene in a fluidized-bed reactor are about 1 μm [5], and the primary aggregates further combine with each other to form secondary aggregates (10 μm, Fig. 2c). Expansion ratios of VACNTs, agglomerated CNTs and EG during loading (0.35 MPa) and unloading cycles are shown in Fig.3a. The high expansion ratio of CNT material means good resilience properties [6, 7]. It can be observed that VACNTs exhibit excellence compressibility and recovery performance compared with agglomerated CNTs and EG at a relatively low pressure. For VACNTs, the resilience drops

rapidly in the first 4 cycles, suggesting that the interactions between long CNTs under compression, such as nanotube seizure and entanglement, and then stabilizes in the subsequent cycles.

The oil sorption capacities and recycling performance of carbon materials are shown in Fig.3b. Though BET surface areas of VACNTs (58 m^2/g) are less than that of agglomerated CNTs (241 m^2/g), it can be seen that long VACNTs exhibit a capacity of 69 g/g, much higher than that of agglomerated CNTs (10 g/g). Obviously, the oil sorption for CNTs depends not on the surface area of carbon materials. It is suggest that the high sorption capacity for VACNTs comes from the intertube space with large-sized macropores (3-300 μm, Fig. 4). The obtained results are also confirmed by two typical porous carbon materials. Actually, most granular activated carbons with a high specific surface area (e.g., 1000 m^2/g) give very small sorption capacities, about 1 g/g or less [11]. While worm-like EG (Fig. 2d) with surface area of 90 m^2/g exhibits a capacity of 41 g/g, macropores (1~50 μm, Fig. 2d) should be responsible for the present oil sorption by capillary forces. In this work, the sorption capacity of EG is less than previous reported capacity of 80 g/g [2, 12] due to its low expanded volume (250 mL/g). For EG, the sorption capacity decreases gradually with the increase of cycle number (Fig. 3b), suggesting that the macropores are easily destroyed after squeezing. Surprisingly, the excellent recycling performance is observed for both CNT adsorbents. In previous reports [6, 7], CNTs can be repeatedly compressed with excellent rebound resilience properties at high strains, and pore size distribution is almost no change when compressed to high pressure [6]. Therefore, almost 100% recovery of adsorbed oil can be obtained before 3 cycles, and follows a small reduction in sorption capacity upon recycling. This tendency is similar to expansion ratio of CNTs during loading and unloading cycles [7]. In addition, VACNTs also show excellent recycling performance using heat treatment method (Fig. 3c). After 10 cycles, the oil sorption capacity of VACNTs is about 4 times higher than that of EG. Therefore, VACNTs with high oil

sorption capacity and excellent recycling performance will be an advantage for spilled heavy oil, together with easy handling due to good mechanical properties and excellent recyclable efficiency.

In conclusion, in order to solve the question that it is very difficult to separate the oil adsorbed among worm-like particles of EG, we used CNTs as adsorbents to estimate oil sorption and recovery properties for the first time. The results show that aligned CNTs have high oil sorption capacity of 69 g/g and excellent recycling performance. This work opens up taking advantage of the excellent mechanical properties and the space in-between the nanotubes of CNTs for oil sorption and recovery. In view of high cost of CNTs, it is highly desirable to design porous CNT-based composite materials instead of pure CNTs as adsorbents in future work.

Acknowledgements

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Figure Captions

Fig.1 The experimental setup used for measuring the oil sorption capacities and recycling performance of porous carbon materials.

Fig.2 SEM images of VACNTs (a, b), agglomerated CNTs (c) and EG (d).

Fig.3 Expansion ratio of VACNTs, agglomerated CNTs and EG during loading (0.35 MPa) and unloading cycles(a), the oil sorption capacities and recycling performance of carbon materials by a simple compression (b) and treatment at 400 °C for 2 h in the muffle (c) (three specimens of each cycle were tested, and the standard error was ±5%).

Fig.4 Pore size distribution of VACNTs and agglomerated CNTs.

Figure 1

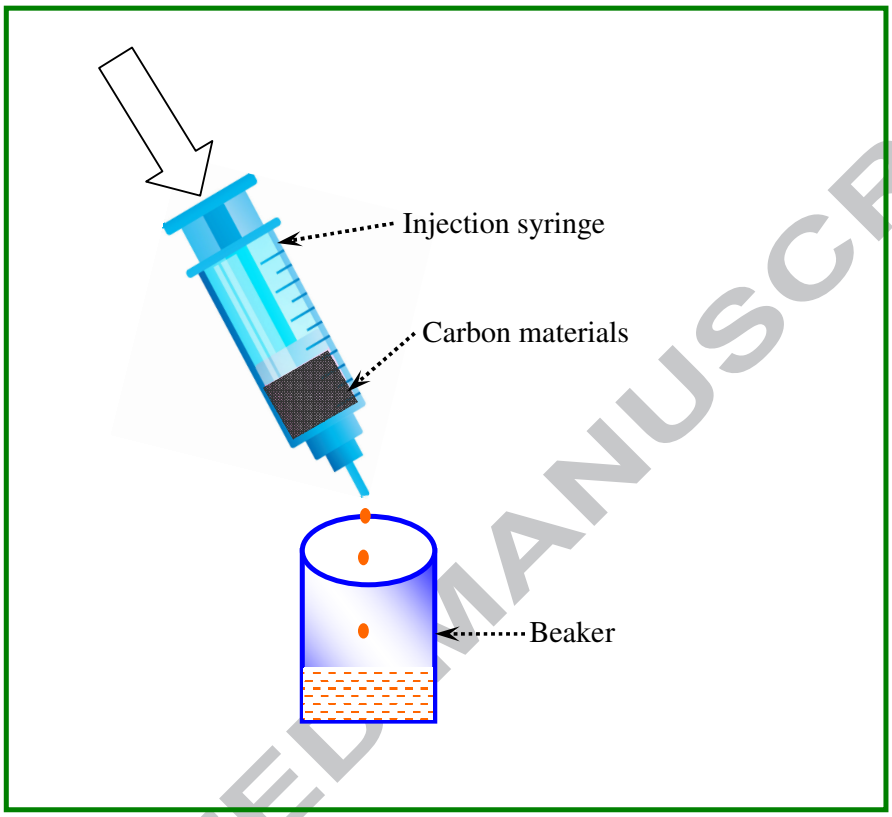

Figure 2

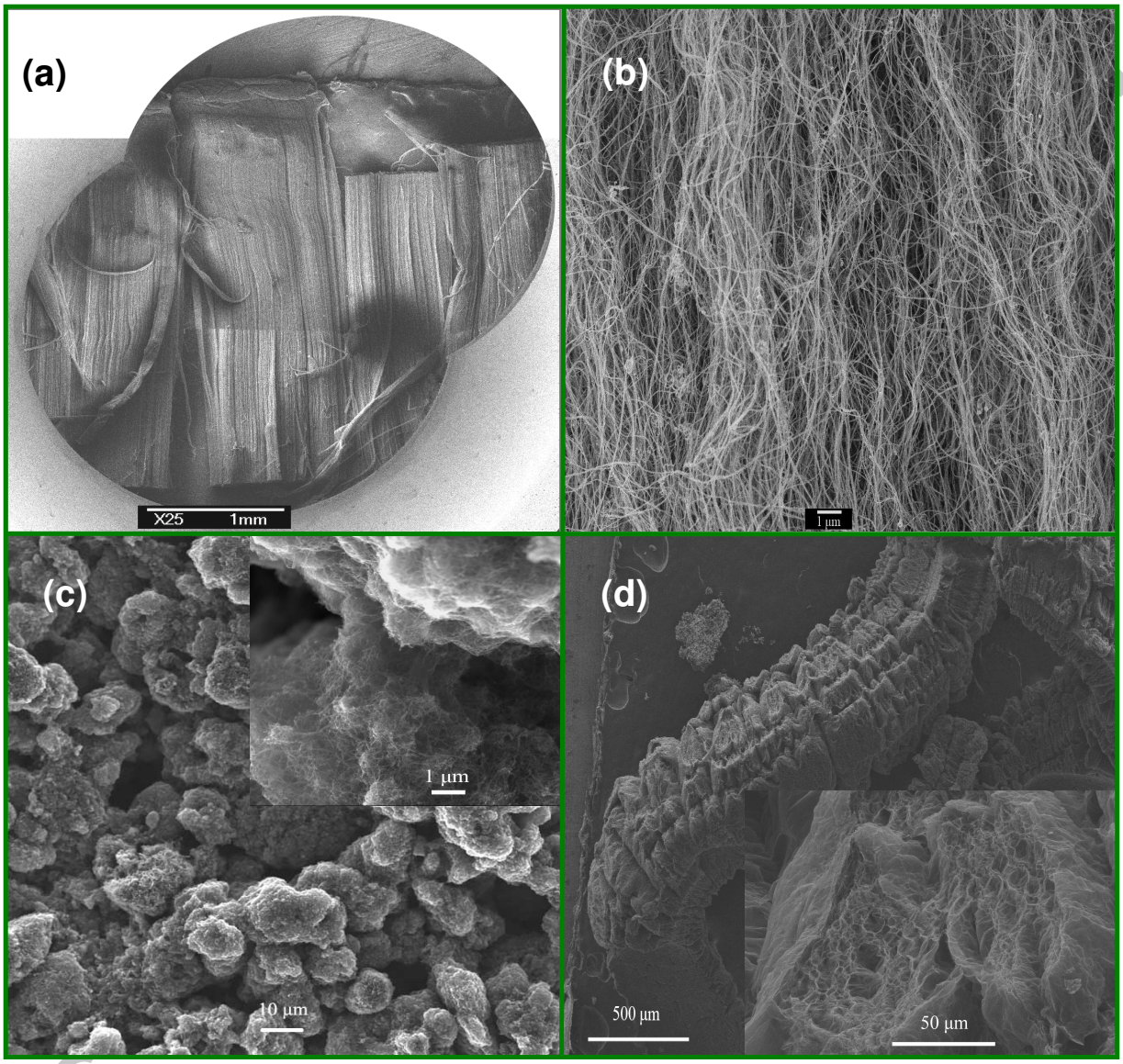

Figure 3

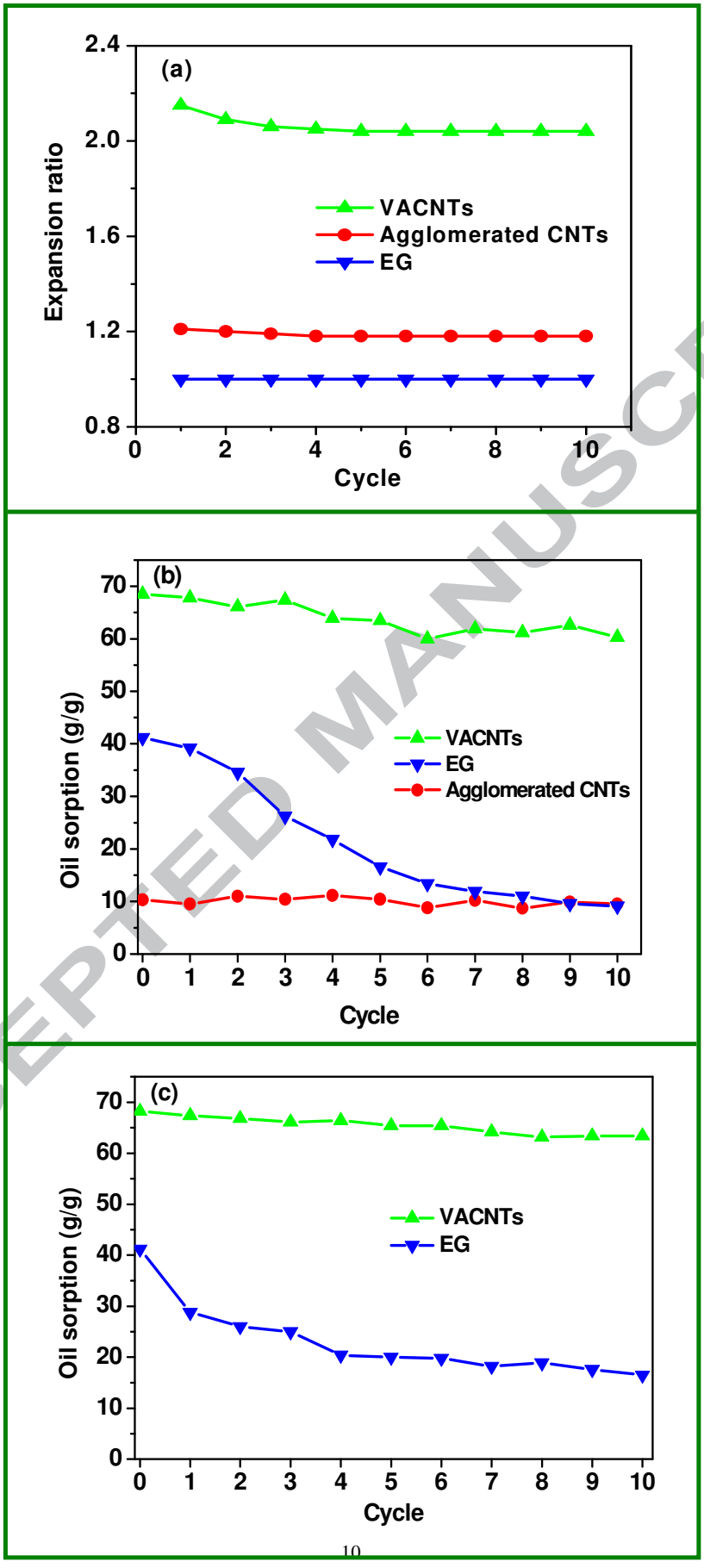

Figure 4