



Research paper

Improvement of oil adsorption performance by a sponge-like natural vermiculite-carbon nanotube hybrid

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ARTICLE INFO

Article history:

Received 21 September 2010
 Received in revised form 30 March 2011
 Accepted 8 April 2011
 Available online 20 May 2011

Keywords:

Vermiculite
 Oil adsorption
 Aligned carbon nanotube
 Intercalation
 Nanotechnology

ABSTRACT

Sponge-like exfoliated vermiculite (EV)/carbon nanotube (CNT) hybrids with different CNT content were prepared by intercalating aligned CNT arrays into natural vermiculite layers for oil adsorption. The intercalated growth of CNT arrays among EV layers of the EV/CNT hybrids was characterized by scanning electron microscopy and transmission electron microscopy. Thermogravimetric analysis under air atmosphere showed that CNT contents of the hybrids varied from 11.4% to 94.8% for different growth duration. Pore size distributions measured by an *ex-situ* Hg penetration method showed that large amount of pores can be formed in the hybrids after the intercalation of CNT arrays. N₂ adsorption results showed that the specific surface areas of all hybrids were significantly improved compared with original EV particles. Oil adsorption tests were conducted on a class of organic solvents and oils in baker and the recovery process was carried out in a syringe. It was found that the oil adsorption capacities of the as-obtained sponge-like EV/CNT hybrids were significantly improved compared with original EV particles due to the large quantity of pores produced by the intercalated growth of aligned CNT. The highest adsorption capacity of the EV/CNT hybrids was 26.7 g/g for diesel oil when the CNT content reached 91.0%, which also exhibited good recycling performance. Furthermore, the adsorption capacity for diesel oil can be further increased to 70.6 g/g by transforming the EV/CNT hybrids into fluffy EV/CNT cotton through high-speed shearing.

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1. Introduction

Clay minerals have drawn extensive attention due to their promising applications as catalysts or catalyst supports, and as nanofillers for clay polymer nanocomposites (Cheng, 1999; Ding et al., 2001; Ladewig et al., 2010; Zhang et al., 2006). This is because of their large surface area, strong acidity, and strong adsorption and ion-exchange ability. However, post modifications are always needed to improve the properties of clay mineral, such as cation exchange (Volzone and Ortiga, 2004), acid treatment (Venaruzzo et al., 2002), and surface modification (Dultz and Bors, 2000; Medeiros et al., 2009; Volzone, 2007), during which, the intercalation of carbon nanotube (CNT) is one of the mostly used process. The combination of one-dimensional (1D) CNT and two-dimensional (2D) clay mineral platelets also leads to three-dimensional (3D) hybrids, which are usually with unexpected properties for unique applications. For instance, the combination of 1D CNT with 2D clay mineral platelets formed a unique 3D nanostructured hybrid filler for making polymer hybrids (Bakandritsos et al., 2005; Xiang et al., 2009; Zhang and Li, 2010; Zhang et al., 2006; Zhao et al., 2010). The intercalated growth of

CNT arrays among the vermiculite layers led to the formation of hybrids of alternate CNT and inorganic layers, which were demonstrated to be of excellent energy adsorbing properties (Zhang et al., 2009a) and were promising for the large scale production of CNT arrays (Zhang et al., 2009b; Zhang et al., 2010). Further applications based on the combination of clay minerals and CNT are still to be explored.

Recently, the use of natural clay mineral for environmental protection became a hot topic for its sustainable and economic advantages (Medeiros et al., 2009; Rytwo et al., 2007; Volzone, 2007; Zadaka et al., 2007). Smectites and kaolinites, as well as their modified products, were demonstrated to be good solid adsorbents for pollutant gasses in natural conditions (Volzone, 2007). A variety of modified silicate mineral adsorbents were utilized for the removal of organic pollutants from water dispersion or by a filter (Rytwo et al., 2007; Zadaka et al., 2007). The petroleum product contamination from oil spills, such as the recent spill in the Gulf of Mexico, is a great risk for human that will affect wildlife in the oceans and on the shores for a long time, and will lead to substantial environmental and ecological problems. Many efforts have been devoted to oil removal. Exploring adsorbent materials with low cost, high adsorption capacity and good recovery property based on clay minerals comes to be a great challenge. Up to now, polymer sponge (Teas et al., 2001), exfoliated graphite (EG) (Inagaki et al., 2004; Toyoda et al., 2003; Zheng et al., 2004), biomass (Abdullah et al., 2010; Husseien et al.,

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2009), and natural clay mineral (Machado et al., 2006; Medeiros et al., 2009; Moura and Lago, 2009) have been widely explored as effective adsorbent materials.

Natural vermiculite, which is formed by weathering or hydrothermal alteration of biotite or phlogopite, shows a great potential to remove spilled oil due to the strong capillary action of the split shaped pores after exfoliation is carried out to form exfoliated vermiculite (EV) at high temperature (Medeiros et al., 2009). To develop the low-cost, environmentally benign, and resource-saving processes, several methods have been proposed to improve the adsorption capacity of the EV by changing its hydrophilic surface into hydrophobic with polymer coating (Machado et al., 2006; Medeiros et al., 2009), carbon coating (Medeiros et al., 2009), or surface modification (Moura and Lago, 2009). Meanwhile, CNT with certain graphene alignment, surface properties, and self-organized macroscopic morphology have also been developed to extend its adsorption capability for various heavy metal ions (Li et al., 2002; Li et al., 2010), inorganic (Li et al., 2001) and organic pollutants (Peng et al., 2003; Salam et al., 2010).

Recently, natural materials were used for the low-cost production of CNT, carbon nanofibers, and hybrids (Su, 2009). Hybrids of entangled CNT randomly distributed among vermiculite layers have been prepared and exhibited a remarkable 600% increase for oil adsorption (Moura and Lago, 2009). However, their adsorption capacity was still limited at 3.2 g/g for diesel oil. The reason lies in that the growth of entangled CNT can only introduce modification to the EV surface, while the pore structures of the as-obtained hybrids were always similar to that of original EV, which hindered the full utilization of the adsorption capacities of natural vermiculite nanocomposites. For an adsorbent material, adsorption capacity and recovery performance are two of the most important factors. The adsorption capacity depends on the surface hydrophobicity and pore structures of the material, while the recovery performance depends on its compression properties (Toyoda et al., 2003).

If the CNT can be grown into arrays with good alignment, the as-obtained CNT were always with a hydrophobic surface (Feng et al., 2002; Huang et al., 2008; Zhang et al., 2009c). Furthermore, there were abundance of macropores, mesopores and micropores in aligned CNT (Mi et al., 2007), and they were resilient and can be repeatedly compressed and recovered in over thousands of cycles (Cao et al., 2005). The objective is to explore new economical adsorbent materials with high performance for oil adsorption, a sponge-like EV/CNT hybrid composed of aligned CNT and natural vermiculite with certain 3D structure was prepared by direct chemical vapor deposition (CVD). The pore structure of the hybrid can be delicately tuned by varying the CNT content, and the combination of aligned CNT arrays and natural vermiculite led to a significant improvement of the oil adsorption properties.

2. Experimental

2.1. EV/CNT hybrids preparation

The EV was directly purchased from Lingshou, Hebei Province, P.R. China. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>99.0%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (>99.0%) were purchased from Beijing Chemical Reagents Company, P. R. China. H_2 (>99.99%) and Ar (>99.99%) were from Beijing Bei Temperature Gas Factory. Liquefied petroleum gas (LPG) (Commercial) was from Beijing LP Gas. Ethanol (>99.9%), hexane (>99.9%), chloroform (>99.9%), and p-xylene (>99.9%) were all from Beijing Chemical Reagents Company, P. R. China. Diesel oil with a range of CE was collected from local gas station. Soybean oil with the first grade (GB 7781, P. R. China) was purchased from local supermarket.

Firstly, 5.0 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.0 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in deionized water (100 mL) in a beaker (200 mL), which was then heated to 90 °C in a water bath. After that, about 10 g EV

particles were dispersed in the solution to form a uniform dispersion through strong stirring by a magnetic stirrer for 2 h while the temperature was kept at 90 °C. After filtration, the filter cake was dried in a drying cabinet at 100 °C for 6 h to get rid of the residual water. Then the Fe/Mo/EV catalysts for CNT array growth were obtained.

Growth of aligned CNT arrays was carried out using the catalytic CVD process. About 1 g of the Fe/Mo/EV catalyst was put into a quartz boat with a wideness of 10 mm, a length of 100 mm and a depth of 5 mm. The quartz boat was transported to the center of the horizontal quartz tube with an inner diameter of 20 mm and a length of 1200 mm by an iron wire. And then the quartz boat was put up side down and taken out, leaving the Fe/Mo/EV particles spayed uniformly at the center of the reactor. The quartz tube was inserted into an electric furnace (SK2-2.5-13D from Beijing Electric Furnace Works), which was then heated from room temperature to 650 °C with a temperature ramp rate of 20 °C/min under flowing Ar (600 mL/min) and H_2 (50 mL/min) controlled by mass flow meters. Fe/Mo nanoparticles can be formed on the surfaces of EV layers and served as the catalyst for the growth of aligned CNT after reduction of Fe/Mo/EV particles during this process. Once the temperature reached 650 °C, LPG (100 mL/min) was then introduced into the reactor. LPG was decomposed onto the Fe/Mo nanoparticles to start the growth of CNT arrays. The gas flows were all controlled by mass flow meters and passed through the quartz tube reactor from the left side to the right side. After certain growth durations, H_2 and LPG were turned off and the furnace was cooled down to room temperature under Ar atmosphere protection. Then the as-prepared EV/CNT hybrids were collected for further characterization and oil adsorption test. The samples obtained with different growth durations (X) were denoted as EV/CNT-X with X = 5, 30, 60, 90, and 120 min. EV/CNT-90 was placed in a high-speed shearer with a rotor capable of rotating at a speed of 24,000 rpm to be treated for 10 min in air to obtain fluffy EV/CNT hybrids.

2.2. Characterizations

The samples were characterized using a JSM 7401F (JEOL Ltd., Tokyo, Japan) scanning electron microscopy (SEM) operated at 3.0 kV and a JEM 2010 (JEOL Ltd., Tokyo, Japan) transmission electron microscopy (TEM) operated at 120.0 kV. For SEM analysis, the samples were mounted on round copper sample holders with double-sided conductive adhesive tapes. The samples for TEM were prepared by the sonication of about 5 mg of the as-grown products in ethanol and several drops were dropped onto a TEM grid using a glass capillary with an inner diameter of 0.5 mm and a length of 10 cm. The CNT content was obtained by thermogravimetric analysis (TGA) heated from room temperature to 900 °C under air atmosphere with a temperature ramp rate at 20 °C/min using a Thermal Gravimetric Analyzer (Q500, TA instruments, USA). The pore size distribution of samples was measured by an *ex-situ* Hg penetration method performed in a Quantachrome type PoreMaster 60 porosimeter (Autopore IV 9510, Micromeritics Instrument Corporation, USA). The Brunauer–Emmett–Teller (BET) specific surface area of all samples was measured by N_2 adsorption/desorption at liquid- N_2 temperature using Micromeritics Flow Sorb II 2300 (Shimadzu Corporation, Japan).

2.3. Oil adsorption experiments

The adsorption experiment in the present work was carried out according to the methods reported previously (Gui et al., 2010; Abdullah et al., 2010). The adsorption experiments here on a range of solvents and oils were carried out in a glass beaker (150 mL) covered with a piece of metal sieve instead of a wire-mesh basket. An amount of 0.2 g EV/CNT hybrids were put into the beaker first and then 50 mL

of the solvent or oil was poured into the beaker. After 5 min the beaker was placed upside down and left still to drain off the excess solvent or oil. The adsorption was fast and typically can reach the equilibrium stage in a few minutes. The EV/CNT hybrids were then collected by the metal sieve and weighed. The continued reuse of adsorbent was carried out in an injection syringe with a diameter of 15 mm and a volume of 10 mL. About 0.2 g EV/CNT-90 was directly put into the syringe, then the excess diesel oil was added and kept for 5 min. After that, the diesel oil was decanted from the syringe and the excess oil dripped off from the tip of syringe. The absorbed oil was removed from the EV/CNT-90 by squeezing the piston of syringe until no oil dropped. The cycle of adsorption and recovery was repeated 10 times to characterize the recycling performance. The oil adsorption capacity was calculated as $(S-S_0)/S_0$, where S is the weight of the

hybrids after oil adsorption and S_0 is the weight of the hybrids before oil adsorption.

3. Results and discussion

3.1. Characterizations of the EV/CNT hybrids

CNT arrays with different lengths were intercalated among the EV layers for different reaction durations. As shown in Fig. 1a and b, the length of the as-obtained EV/CNT hybrid after a 120-min growth was significantly enlarged from 1–2 mm of the original EV particles to 15–20 mm. SEM images showed that the EV/CNT hybrids consisted of alternate EV layers and porous CNT arrays. A 5-min reaction gave rise to CNT arrays with a length of ca. 1 μm

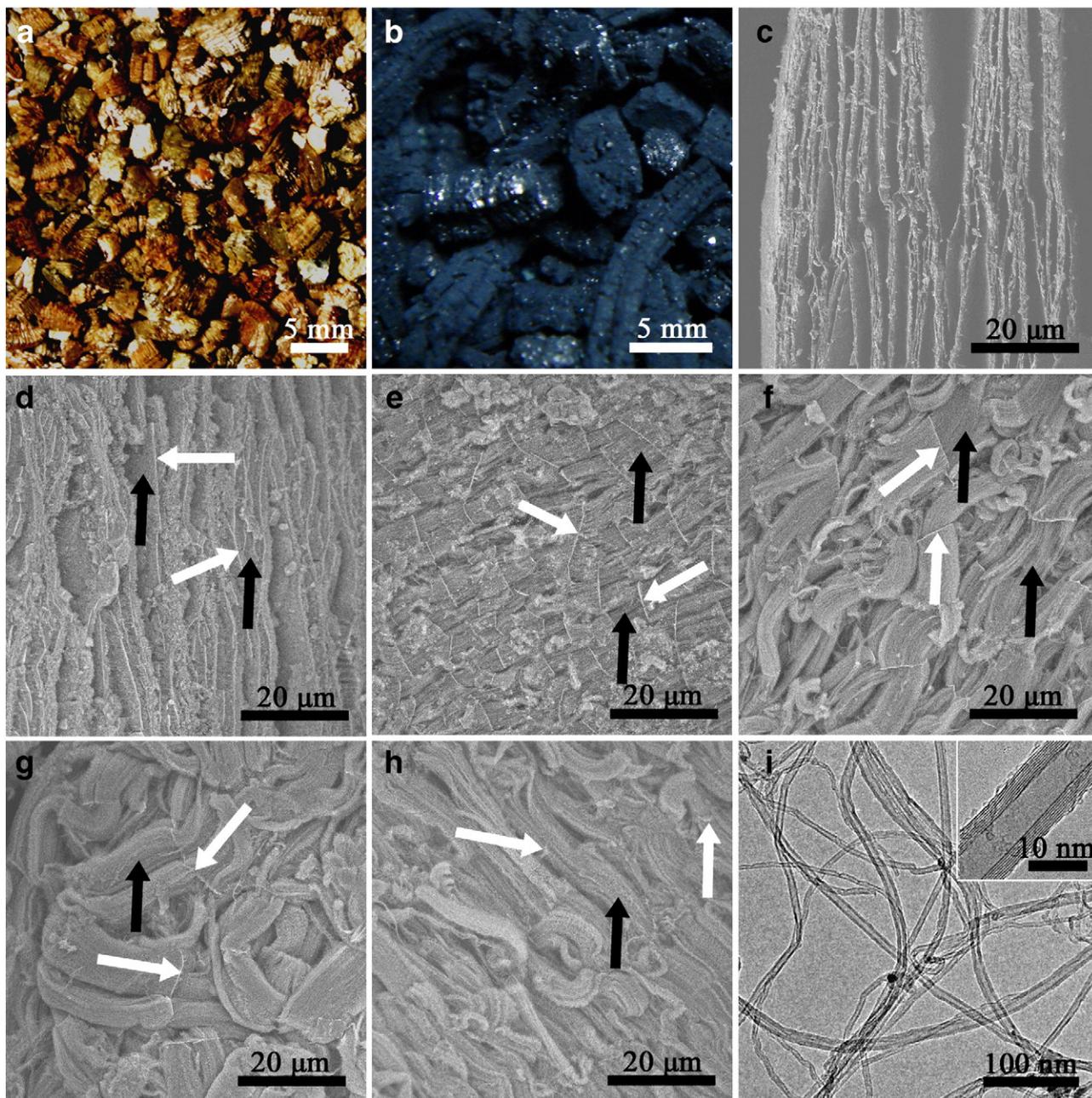


Fig. 1. Images showing the morphology of the (a) EV and (b) the as-obtained EV/CNT hybrids after a 120-min reaction; SEM images showing the morphology of the (c) EV and the EV/CNT hybrids with the CNT content of (d) 11.4% in EV/CNT-5 for a 5-min reaction, (e) 33.1% in EV/CNT-30 for a 30-min reaction, (f) 67.6% in EV/CNT-60 for a 60-min reaction, (g) 91.0% in EV/CNT-90 for a 90-min reaction and (h) 94.8% in EV/CNT-120 for a 120-min reaction; (i) TEM and inserted high resolution TEM images showing the tubular structure of the CNT in the EV/CNT hybrids. The EV layers in (d–h) are indicated by white arrows, while the aligned CNT arrays in (d–h) are indicated by black arrows.

and a content of 11.4% intercalatedly grown among EV layers, which resulted in a larger interlayer distance (Fig. 1c and d). The EV layers were further pushed apart when the CNT content increased to 33.1% for a 30-min reaction (Fig. 1e). Meanwhile, the different growth rates of CNT arrays at different parts of the EV particles caused stress among CNT arrays, which can damage the large EV layers into small pieces, as shown in Fig. 1d and e. The EV layers were almost ruined when the CNT content increased to 67.6% with a 60-min reaction, leaving much smaller pieces of EV sheets with aligned CNT grown on both sides accumulated together (Fig. 1f). The EV sheets were further damaged along with the increasing content of CNT arrays for continuing growth, as shown in Fig. 1g and h. Thus, the EV/CNT hybrids denoted as EV/CNT-X (X = 5, 30, 60, 90, and 120) were with the increasing CNT content. TEM and high resolution TEM images shown in Fig. 1i indicated that the as-grown CNT in the EV/CNT hybrids were with tubular structure and outer diameters of 5–10 nm.

3.2. Oil adsorption

The adsorption capacities of the EV/CNT hybrids were measured for a range of organic solvents and oils. As shown in Fig. 2a, the adsorption capacities for all solvents and oils were significantly improved after the intercalation of aligned CNT. The adsorption capacity increased with increasing CNT content in the EV/CNT hybrids, and the highest value was achieved when the CNT content reached 91.0%. With aligned CNT intercalated into the EV layers, there is a high degree of π electron delocalization conjugated system on the surface of CNT due to the sp^2 hybridization of the carbon atoms, which inclines to couple/stacking with other π or σ electrons. For aromatic compounds, such as p-xylene, π - π electron coupling/stacking

interaction will be formed (Wang et al., 2010). For the hydrocarbons, such as diesel oil and hexane, the σ electron in the absorbed molecules can couple with π electron on CNT. These promoted the oil adsorption on the EV/CNT hybrids. Besides, pore structure also played an important role in the adsorption performance. Similar to oil adsorption on EG, oil adsorption mainly occurred in large size pores, and the intraparticle pores of CNT and EV/CNT hybrids also assisted in the oil adsorption (Gui et al., 2010; Toyoda et al., 2003). As shown in Fig. 2b, with the increase of CNT content in the hybrid, the volume of mesopores and macropores increased significantly. This can be attributed to the fact that the EV layers can be gradually pushed apart along with the intercalated growth of CNT arrays to enlarge the pore size of the hybrid, and the apertures between CNT in the as-grown arrays also produced large amount of pores. These led to the improvement of the adsorption capacity. With further increase of the CNT content, the damage of EV layers caused the formation of large quantity of pores larger than 7.5×10^3 nm to further increase the adsorption capacity. However, when the CNT content was excessively high (>91.0%), the growing CNT tended to occupy the existing pore in the EV/CNT hybrid, leading to the decrease of the pore volume and the adsorption capacity, accordingly (Fig. 2a and b). For non-polar molecules, only surface adsorption was supposed to be effective. Thus the adsorption capacities were proportional to molecular weight for hybrids with the same pore structure (soybean oil > diesel oil > p-xylene > hexane), as shown in Fig. 2a. While for polar molecules, such as chloroform and ethanol, they can act as electron acceptor due to their electrophilic functional groups and the CNT can act as electron donors. The existence of strong electron donor-acceptor interactions between the absorbed molecules and the adsorbent materials (such as CNT) led to the large adsorption capacity even though they were with small molecular weight (Fig. 2a).

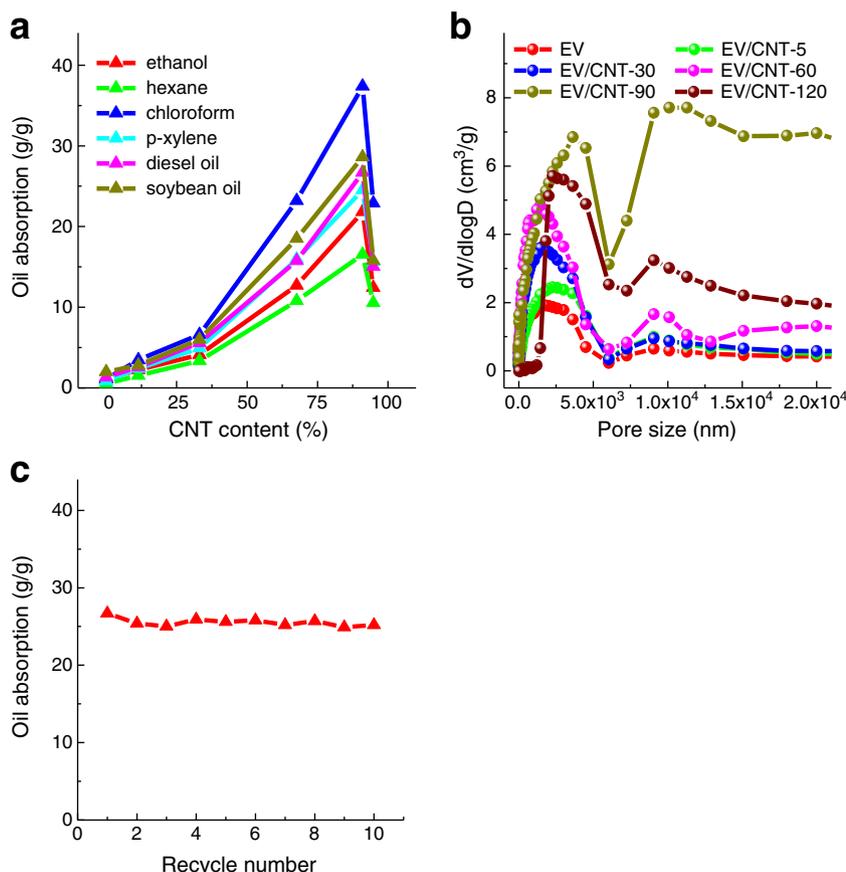


Fig. 2. (a) The adsorption capability of the EV-CNT hybrids with different CNT content measured for a range of organic solvents and oils; (b) the pore size distribution of the EV-CNT hybrids with different CNT content; (c) recycling performance of the diesel oil adsorption capacity on EV/CNT-90.

Table 1
Comparison of the general properties of the modified vermiculite through different methods.

Sample	BET surface area (m ² /g) ^a	Hg porosimetry (cm ³ /g) ^b	Carbon content (%) ^c	Packing density (g/cm ³)	Diesel oil adsorption (g/g)	Ref.
EV	2.2	3.6	0	0.20	1.3	This work
Amorphous carbon modified EV	7	/	0.7	/	1.7	(Moura and Lago, 2009)
SWCNT modified EV	15	1.8	2	/	3.2	(Moura and Lago, 2009)
Porous carbon coated EV	/	/	10.8	/	1.9	(Medeiros et al., 2009)
	/	/	6.0	/	3.2	
	/	/	3.4	/	3.7	
EV/CNT-5	42.8	4.0	11.4	0.18	2.6	This work
EV/CNT-30	148.8	6.2	33.1	0.069	5.6	
EV/CNT-60	289.3	14.0	67.6	0.030	15.8	
EV/CNT-90	384.0	15.2	91.0	0.021	26.7	
EV/CNT-120	327.4	14.8	94.8	0.019	15.0	

^a Measured by N₂ adsorption.

^b Measured by *ex-situ* Hg penetration.

^c Obtained from TGA.

Furthermore, the introduction of the flexible CNT made the resulting hybrids highly ductile and resilient. The as-obtained alternate CNT arrays and inorganic layers structure of the EV/CNT hybrids could be repeatedly compressed at high pressure and exhibited excellent energy-absorbing and cyclic compression properties (Zhang et al., 2009a). Thus, recycling performance of the diesel oil adsorption capacity on EV/CNT-90 was investigated. As shown in Fig. 2c, more than 94% of the diesel oil adsorption capacity can be preserved even after 10 cycles, indicating the good recycling performance of EV/CNT-90 on oil adsorption.

Compared with EV coated with porous carbon (Medeiros et al., 2009), or modified with amorphous carbon or single walled CNT (SWCNT) (Moura and Lago, 2009), the EV/CNT hybrids were with much higher BET surface area and Hg porosimetry, as shown in Table 1. The adsorption capacities of the EV/CNT hybrids were also much higher, with the highest value of 26.7 g/g for diesel oil occurred when the CNT content was 91.0%, which was about 20 times that of the original EV particles and 8 times that of the SWCNT modified EV. Besides, this novel material can be simply mass produced in fluidized-bed reactors (Zhang et al., 2009b; Zhang et al., 2010). Thus the EV/CNT

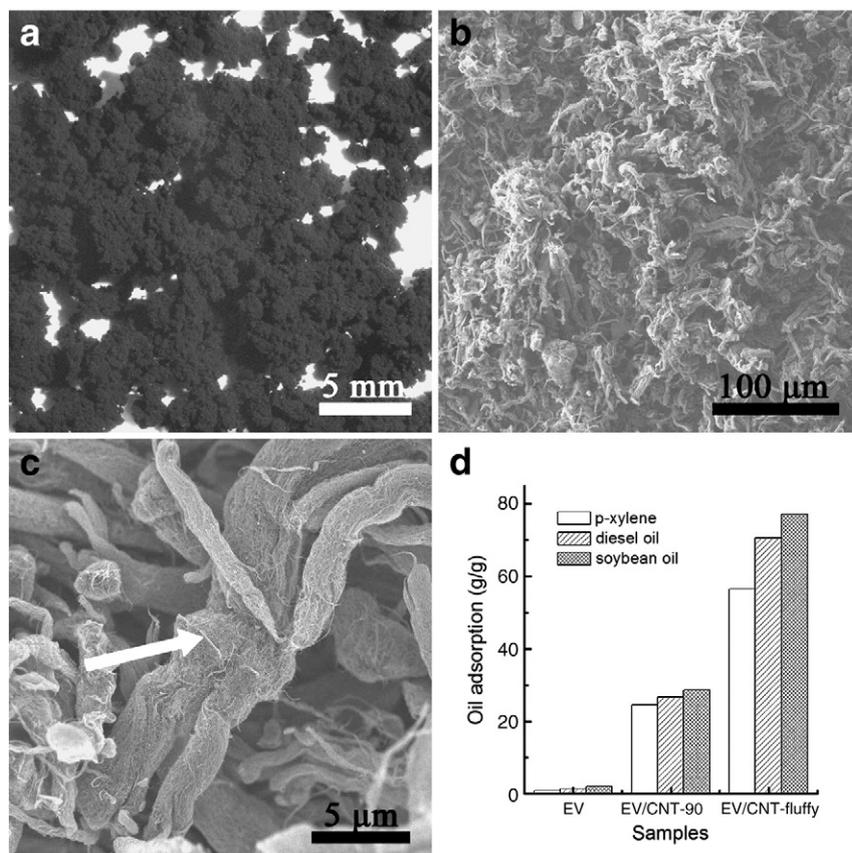


Fig. 3. (a) A photo showing the appearance of the EV/CNT fluffy; (b) and (c) SEM images showing the CNT bundles in the EV/CNT fluffy; (d) comparison of the oil adsorption capabilities of EV, EV/CNT-90 and EV/CNT fluffy.

Table 2
Comparison of diesel adsorption capability of different adsorbent materials.

Sample	Diesel oil absorption [g/g]	Ref.
Activated carbon	0.6	(Gui et al., 2010)
Loofash skeleton	1.5	(Gui et al., 2010)
Cotton towel	4.8	(Gui et al., 2010)
Nano-wire	20	(Yuan et al., 2008)
Kapok	20.8–36.7	(Abdullah et al., 2010)
Corn stalk	8.6	(Hussein et al., 2009)
Polyester sponge	26	(Gui et al., 2010)
Polyurethane sponge	45	(Gui et al., 2010)
Exfoliated graphite	53	(Bai and Liu, 2009)
CNT sponge	146	(Gui et al., 2010)
EV/CNT-90	26.7	This work
EV/CNT-fluffy	70.6	

hybrids are potential economical adsorbent materials with high adsorption capacity and good recycling performance.

3.3. Fluffy EV/CNT hybrid

To further improve the adsorption capacity, high-speed shearing was carried out to transform EV/CNT-90 into fluffy EV/CNT cotton. The EV/CNT fluffy with a low packing density of ca. 0.015 g/cm³ exhibited cotton-like macroscopic structure, which was composed of EV sheets interlinked with aligned CNT bundles on both sides stacked together (Fig. 3a–c). The adsorption capacities of the EV/CNT fluffy for p-xylene, diesel oil, and soybean oil were 56.5, 70.6, and 77.2 g/g, respectively, which were much higher than that of the original EV particles or EV/CNT-90 (Fig. 3d). This can be attributed to the formation of large quantity of pores as a result of the damage of the ordered EV sheets/CNT bundles structure, as shown in Fig. 3b. The adsorption capacities of the EV/CNT-90 and EV/CNT fluffy also exhibited higher values than most of the traditional adsorbent materials (Table 2). It should be noticed that CNT sponge was with the a much higher adsorption capacity, indicating that there is still space for the optimization of the CNT structure to achieve a more efficient hybrid adsorbent from natural materials.

4. Conclusions

In summary, high-performance and economical adsorbent materials of sponge-like hybrids with the structure of aligned CNT array intercalated vermiculite were obtained based on natural materials. The oil adsorption capacities of EV particles were significantly improved by the intercalated growth of CNT arrays among EV layers, which produced large quantity pore structures. The highest adsorption capacity (26.7 g/g) of the EV/CNT hybrids for diesel oil occurred when the CNT content reached 91.0%, which was also demonstrated to be resilient and exhibited excellent recycling performance. The adsorption capacity of the EV/CNT hybrids for diesel oil can be further increased to 70.6 g/g by the conversion of EV/CNT-90 into EV/CNT fluffy with high-speed shearing, which was about 50 times that of the original EV particles and 3 times that of the EV/CNT-90. Besides, this novel material can be simply mass produced in fluidized-bed reactors. It also can float on the surface of water due to its low bulk density and is promising to be used in environmental remediation especially in oil spills.

Acknowledgments

The work was supported by the Foundation for the Natural Scientific Foundation of China (No. 20736004, No. 20736007, and No. 2007AA03Z346), and the China National Program (2011CB932602).

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