



Catalytic growth of carbon nanotubes and nanofibers on vermiculite to produce floatable hydrophobic “nanosponges” for oil spill remediation

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ABSTRACT

In this work, chemical vapour deposition (CVD) synthesis of carbon nanotubes (CNT) and nanofibers on the surface of expanded vermiculite (EV) was used to produce a highly hydrophobic floatable adsorbent to remove oil spilled on water. XRD, SEM, TG and Raman spectroscopy showed that the carbon nanotubes and nanofibers grow on FeMo catalyst impregnated on the EV surface to form a “sponge structure”. As a result of these carbonaceous nanosponges the absorption of different oils remarkably increased ca. 600% with a concomitant strong decrease of the undesirable water absorption.

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1. Introduction

Catalytic chemical vapour deposition (CVD) synthesis of carbon nanotubes (CNT) using a large variety of catalysts, e.g. Fe/Mo, Ni, Co, and different carbon sources, e.g. CH₄, C₂ and C₃ hydrocarbons, CO, ethanol, has been extensively investigated in the last years [1,2]. Due to its relative simplicity, low cost, high yields and the possibility to control several features of the CNT the CVD process has proven to be the most promising large scale carbon nanotubes preparation process. Different oxides such as Al₂O₃, SiO₂, MgO have been used as support to grow CNT [3–6]. Well defined surfaces, such as silicon wafer have also been used to grow highly organized aligned CNT known as “carpets” [7,8].

In this work, we have used the surface of vermiculite to grow CNT and nanofibers via CH₄-CVD synthesis. Vermiculite, a clay mineral, is a very interesting layered material with many potential industrial and environmental applications [9,10]. Upon sudden heating at temperatures higher than 700 °C inter lamellae water molecules evaporate abruptly, separating packets of layers that produce a highly developed porous structure. This expanded vermiculite (EV) shows a volume up to 20 times greater and floats on water due to the decrease in density, ca. 0.05–0.30 g cm⁻³ [9,11]. This vermiculite has been used to remove oil spilled on water due to the strong capillary action of the slit shaped pores [12–16]. A strong drawback of vermiculite is the high water uptake and low

absorption of the hydrophobic organic contaminants due to the strong hydrophilic clay surface. Several works and patents report different processes to hydrophobize the vermiculite surface using, for example, siloxanes [17] and polymer coating [13]. However, all these processes were relatively complex and produced relatively low oil removal capacity.

Hereon, we report the CH₄ CVD on the vermiculite surface to produce a dense CNT and nanofibers complex entangled structure. This nanostructured carbon produces a highly hydrophobic material with a “sponge” effect conferring to the adsorbent a high oil removal capacity. This is one of the first environmental applications of carbon nanotubes.

2. Experimental

The vermiculite used in this work has the approximate composition (Al_{0.30}Ti_{0.04}Fe_{0.63}Mg_{2.00})(Si_{3.21}Al_{0.79})O₁₀(OH)₂Mg_{0.13}-Na_{0.02}K_{0.10}(H₂O)_n. The exfoliation was carried out by introducing the vermiculite in a quartz tube at 1000 °C for 60 s. The exfoliated vermiculite was impregnated with solutions of Fe(NO₃)₃ and MoO₂(acac)₂ using H₂O or methanol as solvents at different concentrations. The impregnated EV was dried at 80 °C for 3 h and submitted to the CVD process. The different prepared EV (ca. 1.0 g) was placed in a quartz tube of 40 mm diameter and heated at 10 °C min⁻¹ to the reaction temperature of 900 °C under H₂/Ar flow (150 mL min⁻¹) and the temperature was kept at 900 °C for 1 h to pre-reduce the catalyst precursors. The material was then immediately submitted to a CVD with CH₄/Ar (1/1 mixture at 1 atm and 600 cm³ min⁻¹) at 900 °C for 1 h. The reaction lasted for

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10 min, unless otherwise stated. After the reaction, the system was cooled under Ar flow.

The vermiculite–carbon composites were characterized by Raman spectroscopy (Renishaw) with the excitation wavelength of 633 nm and a laser spot size of 20 μm with confocal imaging microscope. The spectra taken at ten different points were averaged to minimize dispersion of the sample position.

The powder XRD data were obtained in a Rigaku model Geigerflex using Cu K α radiation scanning from 2° to 75° at a scan rate of 4° min⁻¹. Scanning electron microscopy (SEM) analyses were carried out in a Jeol JKA 8900RL. TG analyses were carried out in a Hi-Res TGA 2950 thermogravimetric analyser (TA) instrument, with a constant heating rate of 10 °C min⁻¹ under air flow (100 mL min⁻¹). BET surface area was carried out in an Autosorb 1 Quantachome using 22 cycles N₂ adsorption/desorption and the mercury porosimetry measurements were performed in a Quantachrome type PoreMaster 60 porosimeter.

The absorption experiments were carried simulating an oil spilling situation using 10 mL of contaminant, i.e. soy bean cooking, mineral oil and diesel, in 100 mL water. The produced hydrophobized vermiculite (100 mg) was then added to the suspension it of. After 5 min the vermiculite was removed using a simple metal sieve and left still for 3 min to drain the excess oil and water. Previous optimization experiments showed that the EV immediately saturates with both oil and water and contact times of 5 min are enough to reach equilibrium. Also, the drain time in the sieve has no significant influence on the amount of oil and water absorption. After absorption, the materials were weighed to determine the total amount of oil and water retained. For vegetable and engine oils the materials were dried at 80 °C overnight to remove water and weighed again to determine both the water and oil absorptions. For the experiments with diesel, the sample cannot be dried at 80 °C since a significant part of diesel will volatilize at this temperature. Therefore after absorption experiment the sample was weighed to determine the total amount of water and diesel absorbed. The sample was then extracted with 20 mL hexane and analyzed by gas chromatography (Shimadzu 17A equipped with FID capillary column Alltech EC-Wax 30m). From a simple calibration, the amount of diesel absorbed can be calculated from the total area of the peaks.

3. Results and discussion

3.1. Preparation and characterization of the composite EV/nanostructured carbon

The composites vermiculite/carbon nanostructures were prepared by impregnation of Fe(NO₃)₃ and Mo(acac)₂O₂ in different concentrations on the vermiculite surface from methanol or water solutions. Table 1 shows the prepared precursors with different Fe-Mo/EV contents and the solvent used in the impregnation.

Table 1

Conditions used to prepare the different vermiculite precursors for the CVD synthesis.

Sample	Fe (wt%)	Mo (wt%)	Solvent
EV	–	–	–
Fe ₁ (W)	1	–	H ₂ O
Fe ₂ (W)	2	–	H ₂ O
Fe ₃ (W)	3	–	H ₂ O
Fe ₁ (M)	1	–	MeOH
Fe ₂ (M)	2	–	MeOH
Fe ₁ Mo _{0.15} (M)	1	0.15	MeOH
Fe ₂ Mo _{0.30} (M)	2	0.3	MeOH

The precursors were pre-reduced under H₂/Ar flow at 900 °C for 1 h and immediately submitted to a CVD with CH₄/Ar at 900 °C also for 1 h.

The obtained materials were characterized by SEM, TG, Raman spectroscopy and XRD. After CVD all samples were completely black due to carbon deposition. The samples prepared using water as solvent in the impregnation step were very brittle and fragile with almost total collapse of the lamellar vermiculite structure. As a result of this collapse the Fe(W) samples showed a small decrease on the surface area (Table 2). On the other hand, samples prepared with methanol showed the lamellar and porous structure intact and mechanically resistant.

Fig. 1a shows the scanning electron microscopy of the exfoliated vermiculite before CVD with regular flat surface lamellae and a slit-type porous structure. After CVD, the sample Fe₁(W) appears very brittle and no filaments or deposited material could be observed (Fig. 1b and c). On the other hand, SEM images for the Fe₂(M) and Fe₂Mo_{0.30}(M) (Fig. 2d–i) suggests that the EV completely changes the texture. A further magnification of the SEM image clearly showed a surface completely covered with carbon filaments with nanometric diameters and several micrometers long (Fig. 1e–i).

These materials with different forms of carbon were characterized by Raman spectroscopy. Spectra obtained with the laser 633 nm (Fig. 2) showed the presence of broad G bands at ca. 1595 cm⁻¹ related to graphitic layers and the disorder D peak at 1330 cm⁻¹. The low I_G/I_D ratio of the samples Fe(w) without Mo (0.6–1.0) suggests the presence of high quantity of amorphous carbon or defects in the carbon structure. On the other hand, when Mo is introduced in the sample, i.e. Fe₁Mo_{0.15}(M) and Fe₂Mo_{0.30}(M), a very high I_G/I_D ratio of 3.2 and 7.9, respectively, was observed, suggesting the formation of well graphitized carbon. Also, it is interesting to observe that in the presence of Mo, the Raman spectra show strong bands at low wavenumber at 133–248 cm⁻¹ related to the formation of single wall carbon nanotubes (SWCNT) with calculated diameters between 0.9 nm and 1.8 nm [18].

TG analyses for all Fe(M)/EV and FeMo(M)/EV samples after CVD showed a weight gain from 150 °C up to 550 °C (Fig. 3). This

Table 2

General properties of the EV composites prepared.

Sample	BET surface area (m ² g ⁻¹)	Hg porosimetry (cm ³ g ⁻¹)	C ^a (%)	Forms of carbon ^b	Average oil absorption (g g ⁻¹)	Water absorption (g g ⁻¹)
EV	5	1.9	–	More amorphous	0.5	3.7
Fe ₁ (W)	3	–	Ca. 0.1	More amorphous	–	–
Fe ₂ (W)	3	–	Ca.0.1	More amorphous	–	–
Fe ₃ (W)	2	1.6	Ca.0.1	More amorphous	–	–
Fe ₁ (M)	7	–	Ca.0.7	More amorphous	1.7	0.5
Fe ₂ (M)	9	1.8	ca.2	More amorphous	1.3	0.5
Fe ₁ Mo _{0.15} (M)	15	1.8	ca.2	SWCNT and graphitic carbon	3.2	0.5
Fe ₂ Mo _{0.30} (M)	18	1.7	ca.2	SWCNT and graphitic carbon	2.0	0.5

^a From TG.

^b Obtained from the I_G/I_D ratio and from SEM analyses.

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