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Synthesis of graphene/hollow carbon fiber composite aerogels for oil spill cleanup

Cynthia E. Ibarra Torres,[a] Thelma E. Serrano Quezada,[a] Oxana V. Kharissova,[a] Hongbo Zeng,[b] Boris I. Kharisov,*[a] Edith Luevano Hipólito,[a] Leticia M. Torres-Martínez[a] and Lucy T. González[c]

[a] *Universidad Autónoma de Nuevo León, San Nicolás de los Garza, Nuevo León, Mexico, C.P. 66455.*
E-mail: bkhariss@hotmail.com
[b] *Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada*
[c] *Tecnológico de Monterrey, Escuela de Ingeniería y Ciencias, Monterrey, Nuevo León 64890, Mexico*

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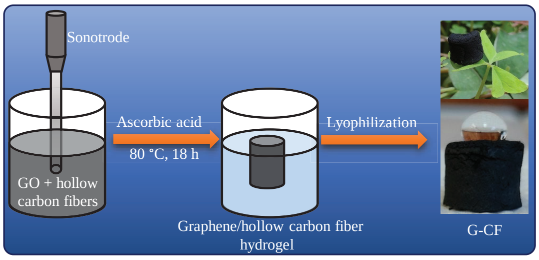
To solve environmental problems caused by the spill of oil and other organic liquids, we have developed graphene/hollow carbon fiber composite aerogels (G-CF) with a low density, high hydrophobicity, buoyancy, and adsorption capacity up to 42.7 g g^{-1}.



Keywords: carbon aerogels, graphene, hollow carbon fibers, sorbents, oil–water separation.

An oil spill is an accidental discharge of either crude or refined oil into the environment, predominantly into the ocean or coastal waters.[1,2] This pollution caused by human activity must be removed as soon as possible to prevent damages to the environment, human health, and economy.[3–5] Mechanical, chemical, thermal, and bioremediation techniques are mainly used for oil spill remediation; recently, an electrochemical process has also been studied. Sorbent materials (a mechanical technique) are an ideal solution because of their low cost, high efficiency, reusability, and fast and easy operation.[6–9] Recently, carbon sponges,[10] mesoporous carbon materials,[11] and special carbon aerogels[12] have been studied as the sorbent materials.

Carbon aerogels are of considerable current interest due to their ultralow density, large surface area, high porosity, high thermal and chemical stability, and good mechanical properties, because of which these materials have a great potential as petroleum adsorbents.[13,14] Graphene-based aerogels have excellent properties and various applications,[15,16] and they were extensively investigated as oil adsorbents and demonstrated excellent results.[17] Among them are graphene aerogels (sorption capacities of 52–105.93 g g^{-1}),[18,19] functionalized or doped graphene aerogels like polyvinyl alcohol–graphene aerogel (sorption capacities of 114–285 g g^{-1}),[20] *N*-doped graphene aerogels (sorption capacities up to 42 g g^{-1}),[21] graphene aerogels with poly(dimethylsiloxane),[22] hybrid or composite graphene aerogels like graphene/carbon nanotube aerogels (adsorption capacities of 30.5–501 g g^{-1}),[23–26] carbon fibers/reduced graphene oxide aerogels (adsorption capacities up to 206.38 g g^{-1}),[27] and hollow carbon spheres/graphene aerogels (adsorption capacities up to 108 g g^{-1}).[28] Hybrid or composite aerogels synergistically combined the individual properties of components to obtain improved properties.

The purpose of this work was to obtain graphene/hollow carbon fiber composite aerogels for applications in oil spill cleanup. For their synthesis, suspensions of 50 mg of graphene oxide (GO) and hollow carbon fibers (2.5, 5.0, and 7.5 mg) obtained by pyrolysis of cotton at 700°C were prepared in 20 ml of water; then, a sonotrode (500 W, 20 kHz, 40% amplitude) was used for 30 min to form stable suspensions. Next, ascorbic acid (20 mg) was added, and the mixture was heated at 80 °C for 18 h without stirring to form a hydrogel (GO reduction reaction), which was lyophilized to obtain a corresponding aerogel (G-CF25, G-CF50, or G-CF75). Graphene aerogel without hollow carbon fibers (GA) was obtained for comparison. The adsorption tests were carried out in triplicate as indicated in the ASTM F726-99 standard.[29]

The FTIR spectrum of graphene/hollow carbon fiber aerogels (G-CF) in Figure 1(*a*) has no characteristic bands corresponding to oxygen functional groups due to the successful reduction of GO and the carbonization of cotton fibers, which caused the absence of the characteristic functional groups of cellulose. Figure 1(*b*) shows the XRD patterns of all the materials, which contain peaks at 26°, 44.5°, and 81.5° corresponding to the (002), (100), and (110) planes, respectively, and these peaks correspond to a graphitic structure. The SEM micrographs shown in Figures 1(*c*) and 1(*d*) exhibit a three-dimensional and interconnected network, composed of graphene sheets with embedded randomly oriented hollow carbon fibers (CFs), which form a porous structure.

The nitrogen adsorption–desorption isotherms of type IV characteristic of mesoporous materials were obtained using a physisorption technique. Table 1 shows that the surface area increased upon adding CFs (G-CF50) to the pristine GA; however, the surface area decreased drastically with the amount of CFs (G-CF75) and became closer to that of CFs.

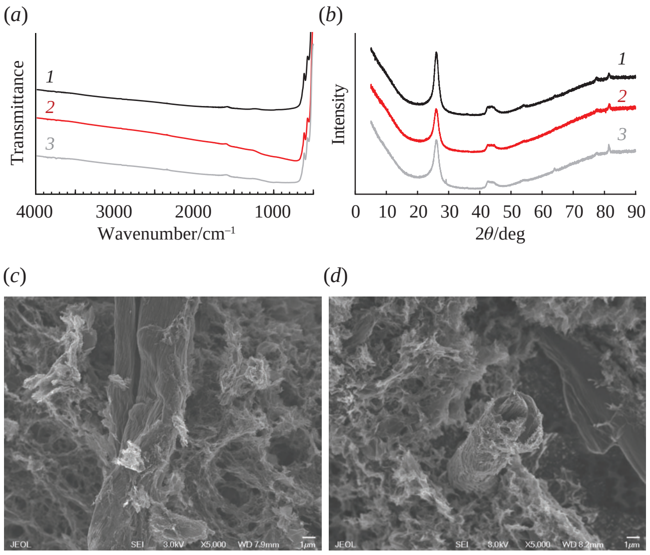


Figure 1 (*a*) FTIR spectra and (*b*) XRD patterns of (*1*) G-CF25, (*2*) G-CF50 and (*3*) G-CF75; SEM micrographs of (*c*) G-CF50 and (*d*) G-CF75.

Table 1 Surface areas and porosity of aerogels.

Sample	BET surface area/ m^2 g^{-1}	Total pore volume/ cm^3 g^{-1}	Pore radius/ Å
GA	153.248	1.515	16.606
G-CF50	313.087	0.876	16.496
G-CF75	29.000	0.269	16.558
CF	12.568	0.003	16.448

The contact G-CF angles did not show important changes in the materials; however, an increase to 120° was observed in the G-CF75 sample [Figure 2(*a*)]. According to Figure 2(*b*), only the G-CF50 sample showed a notable increase in adsorption capacity due to its high surface area of 313.087 m^2 g^{-1}, as compared to that of GA (153.248 m^2 g^{-1}).

Figure 2(*c*) shows the results of reusability tests for G-CF50. The sample exhibited a stable behavior throughout ten adsorption–combustion cycles upon adsorbing ethanol and retained 94.4% of the initial adsorption capacity in the tenth cycle. On the other hand, when adsorbing oil, a noticeable decrease in the adsorption capacity to 29.6% was observed in the tenth cycle. A retained fraction of the adsorbed oil formed a film, which decreased the surface area and pore size of the material to result in a lower adsorption capacity.

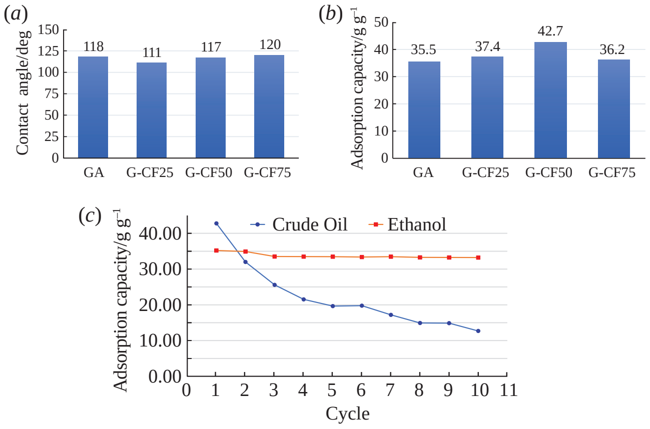


Figure 2 (*a*) Contact angles and (*b*) adsorption capacities for aerogels in question, as well as (*c*) reusability tests for G-CF50.

In conclusion, G-CF50 exhibited the highest adsorption capacity of 42.7 g g^{-1}, 20.28% higher than that of GA, due to its high surface area of 313.087 m^2 g^{-1}, hydrophobicity, and porous structure. This material presented excellent reusability for ethanol adsorption with a stable behavior throughout ten adsorption–combustion cycles and retained 94.4% of the initial adsorption capacity in the tenth cycle, Thus, it is likely that other organic liquids with high volatility and low viscosity can be adsorbed and aerogels can be regenerated efficiently.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.042.

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