Journal of Industrial and Engineering Chemistry 22 (2015) 8–18

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Fabrication of nanoporous graphene by chemical vapor deposition (CVD) and its application in oil spill removal as a recyclable nanosorbent

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A R T I C L E I N F O

Article history:
Received 28 January 2014
Received in revised form 13 June 2014
Accepted 16 June 2014
Available online 21 June 2014

Keywords:
Crude oil
Nanoporous graphene
Sorption
Recovery
CVD
Hydrocarbon

A B S T R A C T

In this research, nanoporous graphene which is used as nanosorbent was synthesized by CVD method and the product was characterized by SEM, TEM, BET, TGA, XRD. FT-IR and Raman spectroscopy. The sorption of two samples of crude oil and also hydrocarbons which cause severe environmental pollution especially in water, on to nanoporous graphene was studied. Due to the high pore volume (1.17 cm^3/g), large specific surface area (410 m^2/g) and small pore size, high sorption capacity was achieved. Maximum sorption capacity of this nanoporous graphene for two samples of crude oil (A) and (B) was 102.17 and 105.39 g crude oil/g nanosorbent, respectively. The maximum sorption capacity of this nanosorbent for hydrocarbons was obtained at 155.46 g hydrocarbon per gram nanosorbent.
Crude oils and hydrocarbons sorbed into nanoporous graphene could be recovered by three methods of heat treatment, extraction with solvent and filtration under mild suction with the proper recovery ratio. The recovery capacity by three methods was obtained, 99.01, 98.50, 98.05%, respectively. By means of these recycling methods, crude oil can be separated from nanosorbent and reused after the recovery. According to proper performance and good shaping ability of this nanosorbent, it can be used as a good candidate in the removal of oil spills.

Introduction

Oil spills in sea waters have caused many serious environmental problems worldwide, not only polluting the waters but also causing great oil loss. With recent large oil spills, there is now a growing worldwide concern about the urgent need to control the accidental and deliberate releases of oil during transportation and storage [1]. The adverse impacts of ecosystems and the long-term effects of environmental pollution by releases, call for an urgent need to develop a wide range of materials for cleaning up oil from the oil impacted areas, especially as the effectiveness of oil treatment varies with time, the type of oil and spill, amount of spilled oil, location, destination, season of the year and the weather conditions [2,3].

A common treatment technique used in oil spill accidents on sea is the containment with large floating barriers (so called oil fences) followed by skimming through specialized ships that either vacuum the oil off the sea or soak it up with the absorbent materials [4,5].

Sorbent materials are attractive for some applications because of the possibility of collection and complete removal of the oil from the oil spill site. Suitable sorbents have a significant capacity for oil recovery from the surface of the sea, minimum harmful effects on ecosystems, and a low price. Sorbents recover the spilled oil by either adsorption or absorption mechanisms. Adsorption is the distribution of the adsorbate over the surface of the adsorbent, while absorption is the distribution of the absorbate throughout the body of the absorbent [6].

The addition of sorbents to the oil spill areas facilitate a change from liquid to semi-solid phase and once this change is achieved, oil can be easily recovered by the removal of the sorbent structure. Furthermore, these materials can be recycled. Some properties of the good sorbent materials include hydrophobicity and oleophilicity, high uptake capacity, high rate of uptake, retention over time, oil recovery from sorbents, and the reusability and biodegradability of the sorbents [7,8].

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http://dx.doi.org/10.1016/j.jiec.2014.06.018
1226-086X/

Table 1
Heavy oils used.

Type	API	Specific gravity	Viscosity at room temp. (poise)
Bahregan (A)	28.01	0.89	28.4
Sorush Nowrooz (B)	18.89	0.94	750.7

In recent years, graphene has received considerable attention in different fields of research and has become a "star" material due to its amazing properties [9–18].

It has been found that the nanoporous graphene has a high capacity for the sorption of crude oil and petroleum products, fats, alkanes, toluene, as well as the other organic solvents, without any further modification or treatment. So it can also sorb a large amount of oil suspended on water in a short time [19].

In this research, nanoporous graphene was used as nanosorbent and two kinds of crude oil with different characterization and hydrocarbons with different carbon chain lengths, which are common pollutants in both daily life and industry are used for the experimentation. In all the cases, nanoporous graphene showed an excellent sorption.

Three methods of heat treatment, filtration under mild suction in room temperature and washing with solvent can be applied for recycling the crude oil and hydrocarbons and regeneration of the nanoporous graphene.

Experimental procedure

Preparation of nanoporous graphene

Nanoporous graphene was prepared by our special CVD (chemical vapor deposition) method [20] in a catalytic basis. The chemical vapor deposition (CVD) technique was carried out in an electrical furnace consisting of a quartz tube with a diameter of 50 mm and 120 mm length. The furnace provided programmable heating up to 900–1100 °C for 5–30 min. The reaction was carried out using methane as the carbon source and hydrogen as the carrier gas in a ratio of 4:1.

The synthesized material was purified as follows [21]. In order to obtain pure nanoporous graphene, and remove the metal nanocatalysts, the product was stirred in 18% HCl solution for about 16 h at an ambient temperature. Then the sample was washed for several times with distilled water. The washing process continued until the neutral material was obtained. The treated product was dried at 100 °C and characterized by SEM, TEM, BET, XRD, TGA and Raman spectroscopy.

Characterization of the synthesized material

Scanning electron microscopy (SEM) images were taken with a Camscan MV2300 Microscope with an operating voltage of 15 kV to investigate the morphology of the sample. The nano-porous graphene was dispersed in 2-propanol and then the product was examined by transmission electron microscopy (TEM) images using a JEOL 1200 EXII microscope to verify the desired structure of the synthesized nano-porous graphene.

To evaluate the purity of nano-porous graphene, thermogravimetric analysis (TGA) was performed in air with a temperature ramp of 5 °C/min.

Fourier transform infrared (FT-IR) spectra was recorded on a Bruker IFS 88 Fourier transform infrared spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region to study the nanoporous graphene oxidation.

In addition, Raman spectroscopy, using an Almega Thermo Nicolet and 532 nm Ar-ion laser excitation source was carried out to reveal the quality of the nano-porous graphene. The most prominent features in Raman spectra of sp^2 hybridized carbon materials are the G band appearing at about 1580 cm^{-1} and the 2D band at 2400–2600 cm^{-1}. In the presence of a certain amount of disorder or edges within the structure, D band appears at 1200–1400 cm^{-1}. Raman spectroscopy indicates the number of graphene layers via a change in the position and intensity of the G and 2D band [22].

The surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K using an ASAP-2010 porosimeter from the Micromeritics Corporation, GA. The sample was degassed at 350 °C and 1.33–0.67 kPa overnight prior to the adsorption experiment. The pore size distribution (PSD) was evaluated from the adsorption isotherms using the Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) available as a built-in software from Micromeritics and the standard Brunauer–Emmett–Teller (BET) method was used for the calculation of the surface area.

X-ray diffraction (XRD) patterns were recorded on Bruker D8 Advance (CuKα radiation 0.154 nm) operating at 40 kV and 40 mA. Graphene distance layer can be calculated based on Bragg's law [23,24]:

$$n\lambda = 2d_{(hkl)}\sin(\theta) \quad (1)$$

where λ is the wavelength of the X-ray, θ is the scattering angle, n is an integer representing the order of the diffraction peak, d is the interplane distance of the lattices, and (hkl) are Miller indices.

The mean crystallite size of the powder composed of relatively perfect crystalline particles can be determined via so-called Scherrer equation [23,24]:

$$L_{hkl} = \left(\frac{k\lambda}{\beta_0 \cos\theta}\right) \quad (2)$$

where L_{hkl} is the mean dimension of the crystallite perpendicular to the plane (hkl); β_0 is the integral full widths at half maximum in radians; k is a constant dependent on the crystallite shape (0.89). However, the number of graphene layers (N) can be obtained through using the following equation [25]:

$$N = \frac{L_{hkl}}{d_{hkl}} \quad (3)$$

Sorption experiments

Sorption capacities of nanoporous graphene

Experiments have been carried out to clean up two oil samples, presented in Table 1, and hydrocarbons as pollutants from the surface of the water. Physical properties of nanoporous graphene which have been used as nanosorbent are shown in Table 2. In each experiment, a specified amount of either oil or other pollutants was added to a 600-ml beaker containing 400-ml of distilled water at a constant temperature of 30 °C in a water bath and stirred for a while. Immediately after the stirring stopped, the oil or hydrocarbons are floated on the surface of the water. Onto this floating

Table 2
The G band and D band position and their intensity, intensity of D band G band ratio and 2D band position of nanoporous graphene.

Sample	D band position (cm^{-1})	G band position (cm^{-1})	I_G	I_D/I_G	2D band position (cm^{-1})
Nanoporous graphene	1292.5	1583.5	192.32	1.32	2551