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Chemical Physics Letters 373 (2003) 272–276

CHEMICAL PHYSICS LETTERS

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Naturally produced carbon nanotubes

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Received 30 January 2003; in final form 3 April 2003

Abstract

Carbon nanotubes represent an impressive kind of materials with diverse unexpected properties, and different methods to artificially produce them have been developed. Recently, they have also been synthesized at low temperatures, demonstrating that these materials might exist in fluids or carbon rocks of the Earth's crust. A new type of natural encapsulated carbon nanotubes found in a coal–petroleum mix is presented. These findings show that all allotropic carbon forms known up to date can be produced in Nature, where pressure, catalysts particles, shear stress and parameters other than exclusively very high temperature, seem to play an important role for producing nanotubes.

1. Introduction

Fullerenes and carbon nanotubes have attracted a great deal of attention due to their unique structural features, amazing properties and potential technological applications. Nowadays, a number of methods have been demonstrated to artificially produce carbon nanotubes, from arc discharge [1,2], pyrolysis of hydrocarbons over catalysts [3], laser vaporization of graphite [4], electrolysis of metal salts with graphite electrodes [5] to hydrothermal methods [6]. Also, novel layered materials have been synthetically developed to mimic fullerene-like structures such as BN [7], BC_2N [8], MoS_2 [9] and WS_2 [10]. Synthetic nanotube-encapsulated materials have been produced by introducing different particles by oxidative opening of carbon nanotubes [11]. C_{60} and C_{70} fullerenes [12] and recently single-walled carbon nanotubes [13,14] have been produced in the laboratory by utilizing a coal carbon source instead of the standard graphite electrodes in the arc discharge. As for naturally occurring fullerenes, reports of an impact crater on the Long Duration Exposure Facility (LDEF) spacecraft, carbonaceous meteorites [15] and different geological samples (particularly the case of fulgurite specimens) [16,17], led to think that extreme tempera-

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0009-2614/03/$ - see front matter © 2003 Published by Elsevier Science B.V.
doi:10.1016/S0009-2614(03)00615-8

ture conditions were mandatory to find naturally occurring fullerenes and nanotubes. However, other methods in which lower temperatures are successfully utilized to produce carbon nanotubes have been reported [6,18,19], demonstrating that the various carbon phases can be obtained under less astringent conditions. In fact, the natural processing of carbon can present different temperature conditions; a clear example is peat being transformed into coal at increased pressure and as a result of relatively low temperatures. Moreover, carbonaceous coal presents different ranks, depending on the degree of metamorphism, determined by the heating conditions on moist mineral-matter-free [20], so natural products can have different allotropic carbon forms, inasmuch as the amorphous carbon has graphitic transitions at different temperatures when specific metals are in contact with carbon and act as catalysts [21]. This effect has been employed in the production of carbon nanotubes with increased yields when a catalyst is utilized [22,23]. Other important finding in this regard is the recent report of graphite formation by tectonic stress [24], which helped to understand the manner in which both pressure and shear stress facilitate graphitization at lower temperatures, which allows to explain the occurrence of graphite within the continental crust as related to the progressive metamorphism of coal. In addition, a recent study [6] describes a new hydrothermal technique able to produce carbon nanotubes under conditions that are comparable to those of a geological environment, which has led some authors [6,13] to suggest the possibility of finding nanotubes produced by a number of natural process. In fact, some years ago microstructured particles were found in diesel soot [25] and more recently, fullerenes and fullerene-like carbon particles were reported in Permian–Triassic boundary sediments [26] and petrol soot [27], respectively. The latter with similar features than those produced by the arc method. It is also important to remark that others carbonaceous materials (soot charcoal, graphite and diamond) have been somehow familiar to human beings, from the pre-historic era [28]. Accordingly, a new type of natural carbon nanotubes found in a coal–petroleum mix is presented.

2. Experimental

The sample was obtained from an actual oil well, identified by PEMEX (the Mexican Petroleum Company) as P1. The well, corresponding to a Jurasic Superior Kimmeridgian (JSK) geological stratum, produces an American Petroleum Institute (API) grade 32 oil and is located in Mexico's southeast shore. The oil contains 2 wt% of asphaltenes, 3 wt% of sediment and is extracted from a depth of 5600 m. The specimen analyzed in this report was extracted by 30 min centrifugation from the oil sediment at 2000 rpm. The liquid was separated by decantation and the paste-looking precipitate was dispersed in ethanol and deposited in Cu grids for analysis in TEM (Transmission Electron Microscope, JEOL JEM 100CX-II, at a voltage of 200 keV) with EDS (Noran voyager) microanalysis, the sample was analyzed also in micro-RAMAN Dilor with 457 nm and spectral resolution of 3 cm^{-1}.

3. Results and discussion

TEM images of the specimens are shown in Figs. 1a–e. The outer diameters of the nanotubes found vary from few to several tenths of nanometers and up to nearly 2 μm long. In most cases, nanotubes present closed end cap (Fig. 1a), however, we found also open end cap carbon nanotubes (Fig. 1b) where several nanotubes contained different nanoparticles. It is possible that the nanotubes in Fig. 1a are not composed only by carbon, inasmuch as the stripped structure seems to be formed by other elements. The image of Fig. 1c shows a nanosized structure attached to a structure resembling a nanorod, since this structure seems to be solid structure, unlike the nanotubes, which present walls and a central hollow. The micrograph of Fig. 1b shows nanotubes that are thinner than those of Fig. 1a and containing nanoparticles. It must be pointed out that these images are different from the typical carbonaceous material of the arc discharge approach, where generally nanotubes are found closely bound to other carbon forms, whereas the present micrographs show the carbon nanotubes generally iso-

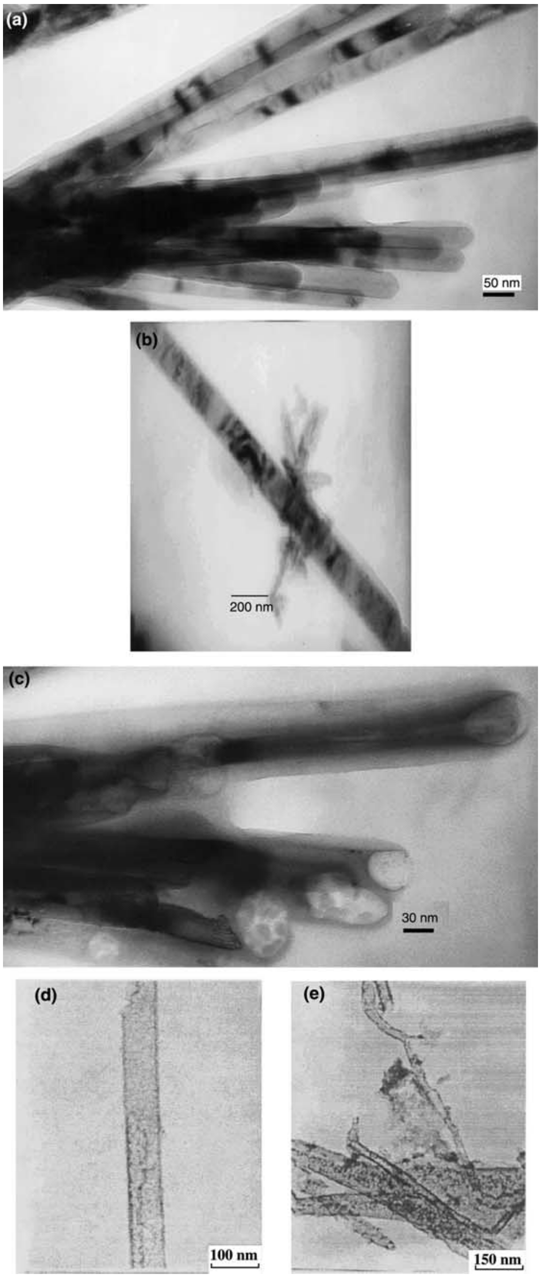

Fig. 1. (a) A bundle of carbon nanotubes with closed end cap and fringed structure due to mineral particle trapped. The straight line in each nanotube is very clear and the average diameter is 60 nm; (b) open cap carbon nanotubes-encapsulated with different mineral particles; (c) a nanoform with branched structure over the wall; (d) synthetic multiwalled carbon nanotube produced at low temperature (reproduced with the author's permission) [18]; (e) synthetic carbon nanotube growth process (reproduced with the author's permission) [18].

lated with only a limited quantity of other carbon forms and few of the nanotubes have other carbonaceous particles attached to their structure. Interestingly, and opposed to the synthetic ones, the natural carbon nanotubes contain many particles embedded. This indicates that carbon nanotubes produced by Nature present different features as compared to their laboratory-made counterparts. Indeed, open and close end cap, and encapsulated nanoparticles have been obtained in the laboratory, but the stripped structures of Fig. 1a, which are very common throughout the samples analyzed in this work, are reported here for the first time. Interestingly, these samples present a structure similar to the carbon nanotubes artificially produced by Wang et al. at low temperatures (200 °C) [18], as shown in Fig. 1d. Also, the carbon form attached to the carbon nanotube in Fig. 1c bears some resemblance to the carbon nanotubes grown in the aforementioned low temperature synthesis technique [18] (Fig. 1e), where the catalyst and reaction time play a much more important role than temperature. Moreover, in the literature, it has been established that the carbon nanotubes diameters depend critically on the production conditions. This would explain why the diameter of the natural carbon nanotubes presents a relatively wide distribution, since Nature does not have a strict control of the conditions as synthetic routes, where the growth conditions can be controlled [29,30]. The EDS microanalysis spectrum of the nanotubes reveals that they are indeed fundamentally formed by carbon, in addition to traces of heavy elements, corresponding to the included nanoparticles, stripe-shaped mineral deposits and others elements which could act as natural catalysts (Fe, for instance), as can be observed in Fig. 2.

The RAMAN spectra presented in Figs. 3a and b correspond to natural carbon nanotubes and multiwalled carbon nanotubes, respectively. (The samples of multiwalled carbon nanotubes were purchased from MER Corporation and analyzed by the authors as compared to natural carbon nanotubes.) In both cases, two characteristic bands appear at 1574 (G line) and 1348 cm^{-1} (D line). The first band corresponds to one of the E_2g modes, which has been assigned to the movement

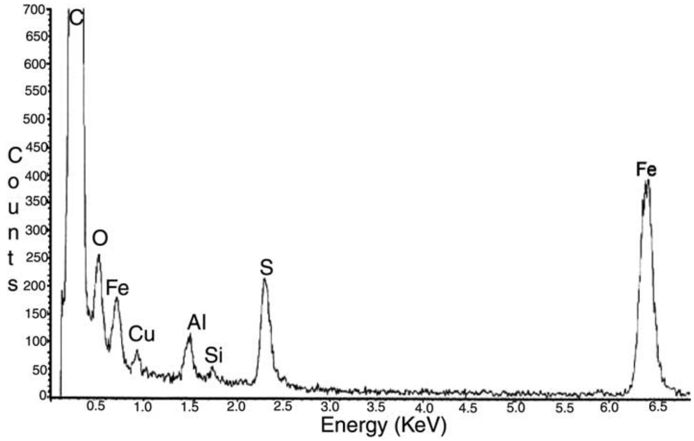

Fig. 2. EDS spectrum of natural carbon nanotubes.

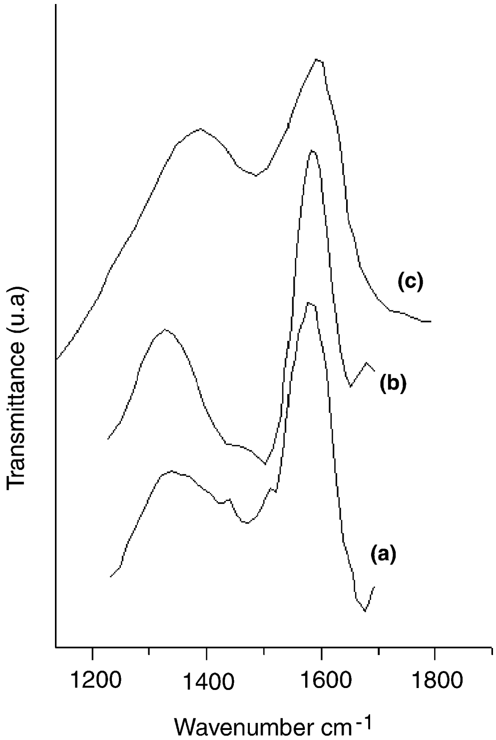

Fig. 3. First-order RAMAN spectra: (a) natural carbon nanotubes; (b) multiwalled carbon nanotubes arc discharge approach; (c) multiwalled carbon nanotubes produced at low temperature (reproduced with the author's permission) [18].

of two neighboring carbon atoms in opposite directions in a graphite sheet. The second band is due to defects in the curved graphene sheets tube end [31,32] this disorder is a feature related to the region near the *k* point of the graphite Brillouin zone [33]. Both peaks are presented by other carbonaceous materials but with shifts in the wavenumber and changes in intensity. For example, the Highly Oriented Pyrolytic Graphite (HOPG) shows the G band at 1580 cm^{-1} and does not show the D band; glassy carbon has the G band at 1584 cm^{-1} and the D band at 1348 cm^{-1} [32], which is more intense than the G peak. This does not occur in neither carbon nanotubes or natural graphite spectra, the latter presenting both peaks at 1580 (G line) and 1350 cm^{-1} (D line) and the intensity of the G band being greater than the D band [34]. These data are relevant, for the detailed molecular structure of the various forms of carbon is known to depend on the ratio between the integrated intensities of the D band and of the G band [31]. RAMAN has been also used to study residual carbonaceous matter, such as coals anthracites, keregens and graphitoids from metasedimentary series, and these samples all showed shifts of the aforementioned bands, depending on the grade of metamorphism. In the samples studied here, both bands agree very well with the bands reported from multiwalled carbon nanotubes and other nanosoot obtained by both laser pyrolysis and arc methods [35]. The spectrum of filled natural carbon nanotubes (Fig. 3a) is also similar to the spectrum of nanotubes synthetically produced at low temperatures [18,19] (Fig. 3c).The present results evidence that natural processes can indeed produce all the different allotropic carbon forms known to date. The variation in the graphitization degree, likely depending on the different variables (temperature, pressure, shear stress, metal catalysts) that occur in Nature, particularly in the Earth's crust, influences the crystalline structure of natural materials.

Acknowledgements

The authors are indebted to Sergio Jimenez for his assistance in the Raman measurements and to Yi Xie for permission to utilize his images.

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