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Bulk synthesis of carbon nanocapsules and nanotubes containing magnetic nanoparticles via low energy laser pyrolysis of ferrocene

M. Bystrzejewski [a,b,*], H.W. Hübers [c], A. Huczko [b], T. Gemming [a], B. Büchner [a], M.H. Rümmeli [a]

[a] IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany
[b] Dept of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland
[c] German Aerospace Center, Rutherfordstr.2, D-12489 Berlin, Germany

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ABSTRACT

A one-step synthesis route to carbon nanocapsules and nanotubes containing Fe and Fe_3C nanoparticles is reported. Low power laser assisted pyrolysis of ferrocene yielded carbon nanocapsules (30–100 nm in diameter) and multi-wall carbon nanotubes (30–80 nm in diameter). The developed route is fast and enables one to synthesize the products at a rate of 84 mg/min. The iron content in the product (10–42 wt.%) can be varied by modulating the buffer gas pressure during the synthesis process.

1. Introduction

Magnetic nanoparticles attract the attention of the materials science community because of their unique magnetic, optical, electronic and mechanical properties [1,2]. Metal–carbon nanocomposite materials, where the metallic nanoparticles are tightly encapsulated in carbon nanocapsules (CNCs) or within carbon nanotubes (CNTs), are also of great interest. The graphitic walls preserve the specific properties of the nanoparticles and perfectly protect them from oxidation and agglomeration. These nanocomposite materials also have various prospective applications, which include magnetic data storage [3], catalysis [4], solid sorbents [5] and numerous biomedical applications [6].

Many techniques are used to synthesize metal-containing carbon nanocomposites, e.g. thermal plasma methods [7], explosive reactions [8], and various approaches based on chemical vapor deposition (CVD) [9]. Ferrocene is a metalorganic compound which is often used in synthesis of CNCs and CNTs (greater details can be found in a review by Nyamori et al. [10]). The benefits of using the ferrocene arise from its low decomposition temperature (500–650 °C), above which the ferrocene pyrolyses to Fe nanoclusters and carbon species. In this Letter we present the studies on ferrocene decomposition induced by a low energy CO_2 continuous laser beam. This laser-based approach differs substantially from traditional thermal CVD and explosion methods, because it provides a highly localized high temperature region for the reaction.

2. Materials and methods

The carbon nanostructures were synthesized using a continuous wave low power (30 W) CO_2 laser system, which is described in details elsewhere [11]. In brief, the laser beam was focused on to a target, which contained 70 wt.% of ferrocene and 30 wt.% of MgO in the form of a compressed disk. The role of MgO was to improve the laser coupling to the target and the heat exchange between the ferrocene crystallites. The experiments were performed under flowing nitrogen atmosphere at two pressures: 1000 mbar and 1 mbar (Table 1). In the low pressure experiment a pressure of 1 mbar was maintained by evacuating with a diaphragm pump. The reactor was thoroughly flushed with N_2 prior to the pyrolysis in order to eliminate parallel oxidation processes. The reaction time was 30 s and each run was repeated 4 times. After the pyrolysis a black product was seen to have formed on the target surface. The product could be easily separated by cutting it off. The mass loss of the target and the mass of the collected product was monitored in each test. This enabled an estimate of the average target ablation rates and product condensation rates (see Table 1) to be determined. These convenient parameters are valuable indicators of pyrolysis dynamics and will be discussed later.

The as-obtained products were purified by 5 h boiling in 4 M nitric acid. This treatment was applied to remove the un-protected metallic nanoparticles and MgO crystallites. Then, the samples were thoroughly rinsed with excess of water and ethanol, and finally dried in air at 80 °C. The product morphology was studied by transmission electron microscopy (TEM, Tecnai F30–300 kV). The structural characteristics were

* Corresponding author. IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany. Tel.: +49 48228220211; fax: +49 48228225996.
E-mail address: mibys@chem.uw.edu.pl (M. Bystrzejewski).

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Table 1
Experimental parameters and product characteristics.

	1000 mbar	1 mbar
Target ablation rate [mg/s]	3.0 ± 0.4	4.1 ± 0.2
Product condensation rate [mg/s]	1.4 ± 0.3	0.5 ± 0.1
Product recovery ratio [%]	45 ± 4	56 ± 5
Fe content [wt.%]	10.8 ± 0.4	42.0 ± 1.5
G/D intensity ratio	0.49 ± 0.03	0.51 ± 0.04

analyzed by powder X-ray diffraction (Cu K-alpha radiation) and Raman spectroscopy (1064 nm excitation laser). The iron content was evaluated via thermogravimetry. A sample (typically 50 mg) was burned in flowing air at 1000 °C and the mass of the as-formed residue was precisely weighed. The burning process led to the complete gasification of carbon, whilst Fe and Fe_3C nanoparticles were oxidized to Fe_2O_3 (iron oxide was the sole component of the residue). The Fe content was then calculated from the stoichiometric composition of Fe_2O_3.

3. Results and discussion

When the laser beam is fired on to the target two simultaneous processes occur due to the high temperature gradient of the laser beam at the interface, these are: (i) pyrolysis of ferrocene (at the point where the laser beam impinges on the target and the temperature regime is at its highest), (ii) sublimation of ferrocene (in the vicinity of the laser spot). The dynamics of the pyrolysis process may significantly change with the pressure of the buffer gas, which is known to be one of the parameters that can control carbon nanotubes growth [9,10]. In this case, the target erosion rate is higher at lower pressures (1 mbar) as shown in Table 1, because the lower pressure favors the sublimation of ferrocene (Clausius-Clapeyron relation) and the target energy loss to the surrounding gas is less. It should be highlighted that the laser irradiation is sufficient to pyrolyse the organometallic precursor. The maximum temperatures reached on the target at the laser spot are between 800 and 1100 °C [11]. However, this is insufficient to lead to phase transitions of the MgO matrix. The

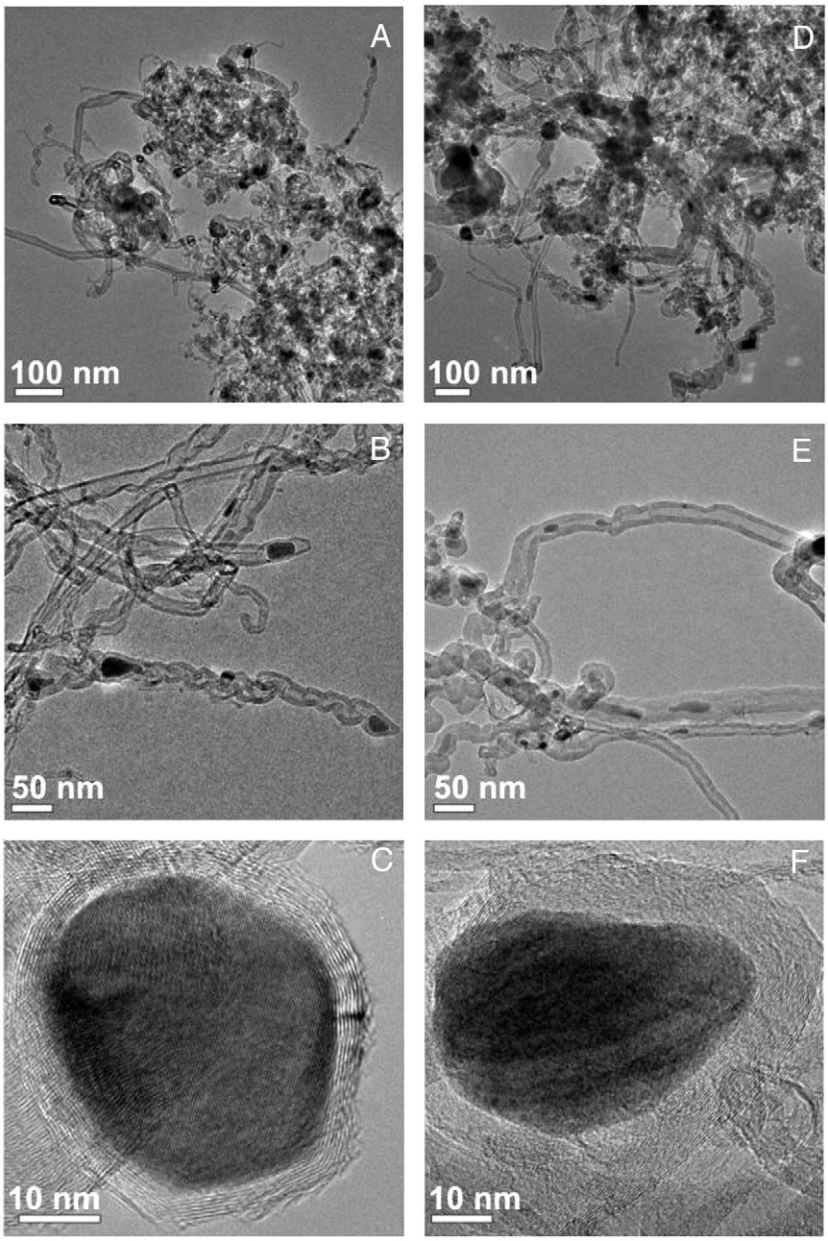

Fig. 1. TEM images of product obtained at 1000 mbar (A–C) and 1 mbar (D–F).