Original Article

A study on carbon nanotubes/nanofibers production via SHS method in C-Al-Fe$_2$O$_3$ system

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A B S T R A C T

In this research carbon nanotubes (CNTs) and carbon nanofibers (CNFs) were synthesized via self-propagation high-temperature synthesis (SHS). The exothermic reaction between aluminum and iron oxide was used for preparing the heat required for SHS. In addition, the iron produced from the reaction can play as a role of catalyst for growing the CNTs/CNFs in the presence of activated carbon. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman analysis, Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) method were used to characterize the samples. It was found that the amount of activated carbon in the initial powders has an essential effect on the reaction products. In less than 5 wt% activated carbon, the SHS process is performed completely otherwise, the activated carbon does not participate in the chemical reaction and acts as strong diluents as well as controller of the reaction factors.

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1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], great effort has been devoted to the understanding of their potential applications and to the development of reliable and efficient methods for their production. CNTs can be produced by various methods including arc-discharge [1–3], laser ablation [4,5], and chemical vapor deposition [6,7]. Recent papers have shown that CNTs could be synthesized by other techniques such as mechanochemical processing [8] or combustion reactions [9,10]; another name for this last method is self-propagation high temperature synthesis (SHS) or, in brief, combustion synthesis (CS). Indeed, SHS is a well-known reaction used to fabricate new compounds and structures [11–13]. Once started, the reaction continues with the help of the energy provided by itself rather than from outside the system. The suitability of CS for the large-scale manufacturing of carbonaceous nanomaterials has been proven for carbon black [14] and fullerenes [15]. Rapid solidification of products
in CS, creates nanostructures that would be otherwise difficult to make [16]. Furthermore, analysis of material produced by means of CS has revealed the presence of carbonaceous nanostructures [17,18] and isolated CNTs [19]. For example, Alekseeve et al. [20,21], used carboniferous materials (soda, limestone, and Teflon) and reducers (magnesium, lithium, and sodium) with the addition of a nickel or iron as a catalyst. The yield of CNTs has shown to be weakly sensitive to the amount of catalyst. They have also found that the carbon source is an important factor: carbonaceous materials which were used required energy to decompose and to take part in the formation of nanostructures and it implies that there are no diluents in the reaction. These conditions cause agglomeration and condensation of the materials, preventing the formation of carbon nanostructures [22,23]. In this paper, we used a very simple reaction, the so called thermite, to produce CNTs and CNFs just in one step. The following reaction was used as a combustion reaction under an inert gas atmosphere:

\[
\text{Fe}_2\text{O}_3 + 2\text{Al} + \text{XC} \rightarrow 2\text{Fe} + \text{Al}_2\text{O}_3 + \text{XC} + \text{enthalpy of reaction}
\]  

(1)

Ignoring the kinetic aspects such as particles surface contact and heat leakage, adiabatic temperature \((T_{ad})\) can be calculated as follows:

\[
-\Delta H_{298} = \int_{298}^{T_{ad}} (C_p(\text{Al}_2\text{O}_3)) \,dT + 2 \int_{298}^{T_{ad}} (C_p(\text{Fe})) \,dT + X \int_{298}^{T_{ad}} (C_p(\text{C})) \,dT
\]

(2)

Adiabatic temperature has a significant influence on the reaction rates because it represents the quantity of local heat generated by the reaction, and the reaction rate increases with increasing temperature. This temperature can be varied by the amount of diluents (The coefficient of \(X\) in Eq. (1)), which here is activated carbon. The letter \(C\) refers to activated carbon, which was used as the source of carbon as well as a diluent. The results show that, through control of the amount of reactants, it is possible to obtain carbon nanotubes and carbon nanofibers by a simple thermite reaction.

2. Materials and methods

Activated carbon (extra pure, Scharlau, <50 µm), Iron (III) Oxide (LOBA CHEMIE Co., <200 µm, purity > 97%) and pure aluminum powder (<100 µm, purity > 99%) were used as carbon source, oxidizer and reducer agents, respectively. SEM micrographs of the starting powders are shown in Fig. 1.

The powders were mixed and homogenized in a low energy ball mill for one hour. The mixtures, which were composed of Al and Fe₂O₃ powders with a 2:1 molar ratio (according to thermite reaction stoichiometry: \(2\text{Al} + \text{Fe}_2\text{O}_3 = 2\text{Fe} + \text{Al}_2\text{O}_3\)), together with different activated carbon amounts were charged into a stainless steel vial. The milling media were stainless steel balls with a ball-to-powder weight ratio (BPR) of 30:1. The adiabatic temperature and the heat released from the reaction were controlled by varying the percent of activated carbon (Table 1).

For performing of SHS experiments, the powder mixture was cold pressed to form cylindrical pellets 4 mm in diameter and 20 mm in height. In order to achieve better condensation, 0.2 mL of Hexamine was added to 2 g of the mixture. Pellets were dried in an oven at a temperature of 100 °C for half an hour. The pellets were then combusted inside a stainless steel chamber. Sample heating was provided by an electrical heat resistant coil placed around a graphite crucible containing the pellets. All experiments were performed under a high-purity argon (99.9%) atmosphere. Ignition temperatures were measured by placing a K-type thermocouple under the pellet surface. Propagation rates were determined from video recordings of the reaction fronts. Solid combustion products containing fiber-like nanostructures were refluxed with nitric acid for two hours to remove iron particles resulting from the reaction and were then heated for 2 h at 380 °C to oxidize amorphous carbon. Observations and characterizations of the samples were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray analysis (EDX), transmission electron microscopy (TEM), thermo gravimetric analysis (TGA), Raman analysis and atomic absorption spectrometry (AAS). The XRD investigations were performed using an ARL X’TRA powder X-ray diffraction analyzer with Cu-Kα radiation. SEM observations were performed using a LEO-1450VP at an accelerating voltage of 15 kV. Structural observations analysis of the products by TEM was carried out with a LEO-912AB microscope and thermo gravimetric analyses (TGA) were performed using a Shimadzu apparatus TGA-50 at a heating rate of 10 °C/min up to 900 °C in air.

3. Results and discussion

For a system to be suitable for the synthesis of CNTs, three components are essential: (i) a source of carbon; (ii) a source of heat; and (iii) the presence of metal catalytic particles. We intentionally chose an activated carbon as the carbon source rather than conventional graphite because the activation
Table 1 – Composition of reactant mixtures, adiabatic temperatures, and rates of front propagation.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Activated carbon (%wt)</th>
<th>Tad (K)</th>
<th>Reaction rate (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5AC</td>
<td>5</td>
<td>3130</td>
<td>3.5</td>
</tr>
<tr>
<td>10AC</td>
<td>10</td>
<td>2922</td>
<td>1</td>
</tr>
<tr>
<td>15AC</td>
<td>15</td>
<td>2741</td>
<td>0.4</td>
</tr>
</tbody>
</table>

![Illustration of carbon fragments](image1)

Fig. 2 – (a) Illustration of curved carbon fragments, containing pentagonal and heptagonal rings as well as hexagons, and (b) conventional HRTEM micrographs showing general appearance of fresh activated carbon [30].

![TGA graph](image2)

Fig. 3 – TGA graph for activated carbon and pure graphite.

![X-ray diffraction pattern](image3)

Fig. 4 – X-ray diffraction pattern of pure graphite and activated carbon.

![Raman spectra](image4)

Fig. 5 – Raman spectra of synthesized CNTs.

The process results in an ‘open’ structure which is more susceptible to the production of carbon nanotubes and nanofibers. Activated carbon may be prepared from a variety of carbonaceous precursors, including coal, peat, and nutshell, which are carbonized and then ‘activated’ either by oxidation with CO₂ or steam or even by treatment with acids, bases or other chemicals. The resulting carbon typically has a surface area of 1500 m² g⁻¹ and an average pore size of approximately 3 nm. This type of carbon has a disordered and porous microstructure consisting mainly of tightly curled single carbon layers. Also, it contains highly curved atom-thick walls throughout its 3D structure and they are all assemblies of defective graphene layers [24,25]. Additionally, it has been proved that this type of carbon has a fullerene-related structure including pentagonal and heptagonal rings (see Fig. 2a and b) [26,27].

Fig. 3 shows the results of thermo gravimetric analysis (TGA). The results indicate that the activated carbon used in the current research is more active than graphite because its burning temperature is about 100 °C lower than pure graphite. Fig. 4 shows a comparison of XRD graphs for activated carbon
and pure graphite. As can be seen, activated carbon has a very low crystallinity in comparison to pure graphite.

From the point of thermodynamic stability view, this lower crystallinity aids activated carbon to change its morphology and stabilize its structure as CNT or CNF after SHS reaction. The second component for CNTs production is a heating system; here, the source of heat is the thermal energy released during the exothermic reaction ($\Delta H_{298}^{\circ}$). The final essential

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**Fig. 6** – SEM micrographs of products formed upon combustion of Al-Fe$_2$O$_3$-activated carbon mixture in different magnifications.

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**Fig. 7** – TEM micrographs of products formed upon combustion of Al-Fe$_2$O$_3$-activated carbon mixture in different magnifications, (a), (b), and (c) 5AC sample, (d) 15AC sample.
The component needed for synthesis of CNTs is the catalytic metal. Here, the iron produced through thermite reaction plays this role (see Eq. (1)).

The lattice vibrations of ordered carbon materials can be analyzed by Raman spectroscopy [28]. Fig. 5 shows the Raman spectra of CNTs. As it can be seen there are two clear peaks in this pattern. The peak at \( \sim 1330 \text{ cm}^{-1} \) is related to the band D, caused by the defects in the structure of the sp\(^2\) carbon and can be due to the lattice defects in the graphite sheet that make up CNTs. Also, this band indicates deposition of amorphous carbon, or nanotubes with large diameters, or even nanofibers, which have more defects than nanotubes [29]. The peak at around \( 1580 \text{ cm}^{-1} \) is related to the band G, which is generated by the tangential modes of vibration of carbon sp\(^2\). Actually, it is intensified by the presence of nanotubes of small diameter, which have few defects, and demonstrates the presence of crystalline graphitic carbon [29].

Fig. 6 shows numerous fibrous nanostructures formed upon combustion of the Al-Fe\(_2\)O\(_3\)-activated carbon mixture under different magnifications. Combustion products contained elongated nanostructures of about 100 nm in diameter and several micrometers in length (Figs. 6 and 7).

Fig. 7a–d shows TEM images of these purified nanofibers. As it can be seen from Fig. 7, some products are nanoparticles encapsulated ended with a hollow inside which means that they are nanotubes (indicated in Fig. 7b) and some others are solid (indicated on Fig. 7a) which means that they are nanofibers. Some fibers, such as those observed in Fig. 7a, have open endings, which imply that the fibers have an empty channel inside. The amount of iron produced through thermite reaction was measured by means of AAS. For this purpose, the achieved solution after refluxing was applied and the iron solved in nitric acid was measured. The sample contained 5 wt% activated carbon (5AC) clearly exhibited these CNT and CNF structures; however, the sample with 10 wt% activated carbon (10AC) exhibited a very small quantity of observable and measurable of CNTs and CNFs, it was while the sample containing 15 wt% activated carbon (15AC) exhibited none. For sample 5AC, the highest temperature in the region of SHS reaction was estimated at above 3100 K (2827 °C), but it existed for a very short time, as determined by the rate of reaction propagation. This amount of time, though, is enough for the isolation of carbon in the form of fibers or nucleation of a graphene layer on the surface of a nanodrop [31,32].

The study of the catalytic pyrolysis method to CNTs using metallic iron (Fe) as catalyst showed that the growth of CNTs had two stages: the formation of the primary CNTs on the surface of the metallic catalyst, and the deposition of carbon on the primary CNTs [33]. The mechanism of primary CNT formation can be explained by the vapor–liquid–solid mechanism [34], by which the carbon passes through a dissolve–diffuse–precipitate process inside of the catalyst then moves to the surface of the catalyst for deposition as CNT and CNF. We believed that sample 5AC experienced such a situation because of the higher adiabatic temperature and heat released from the reaction. In samples 10AC and 15AC, conversely, activated carbon played the role of diluents, and the heat released from the SHS reaction was not so high nor the rate of reaction suitable for forming nanodrops and growing CNTs and CNFs; As can be seen in Fig. 6d only a few encapsulated particles with carbon were detected. In Fig. 8 the suggested formation mechanism was shown schematically.

4. Conclusions

Both CNTs and CNFs by SHS reaction were fabricated in C-Al-Fe\(_2\)O\(_3\) system under argon atmosphere. Microscopic evaluations show that the iron metallic nanoparticles produced by SHS process act as a catalyst in CNT and CNF formation. Activated carbon is a suitable carbon source and has the catalytic potential for CNT formation because of its special structure. For the first time, the SHS method was used with the cheap powders (Al and Fe\(_2\)O\(_3\)) together with the carbonaceous material (activated carbon) to synthesize carbon nanostructures. This technique offers a simple and rapid method to synthesize CNTs and CNFs; it also offers advantages such as flexible synthesis conditions and simple setup.

Conflicts of interest

The authors declare no conflicts of interest.
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REFERENCES
