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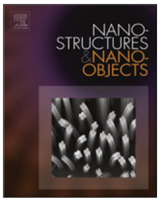

Role of pyrolysis reaction temperature and heating-rate in the growth and morphology of carbon nanostructures

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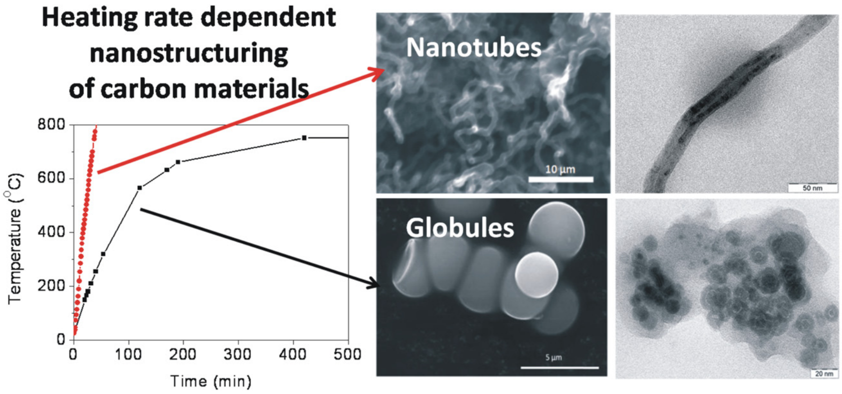
HIGHLIGHTS

- A low-cost, one-step pyrolysis route is devised to synthesize carbon nanostructures.
- High and low heating-rates favor formation of carbon- nanotubes and globules, respectively.
- Heating zone-length has no role on product morphology but increases product-yield.
- Higher graphitization and reduced Fe_3C phase is observed with increasing $T_{synthesis}$.
- Air-calcination decomposes Fe_3C into smaller Fe-particles and forms annular graphitic layers.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of reaction temperature, heating rate of the precursors and length of the reaction zone of the furnace on the morphology of carbon nanostructures synthesized via a single-step pyrolysis route is studied. When the furnace was heated at a slow heating rate the synthesized products have highly amorphous globular morphology regardless of the length of the heating zone and the reaction temperature. The amorphous globules contain a dispersion of Fe-based particles. Higher graphitization around the Fe-based particles is observed upon increasing the synthesis temperature. The heating rate has the highest influence on the morphology of the products. When the furnaces were heated (naturally) at a low rate of ~3 °C/min up to the reaction temperature amorphous carbon globules formed, while carbon nanotubes formed when the heating rate was increased to 20 °C/min in a controlled manner. When the synthesized samples were calcined in air at 400 °C for 1 h, the amorphous carbon graphitizes and the graphitic phase forms agglomerated nanotube-like structure.

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1. Introduction

Carbonaceous materials have become indispensible and highly promising in the fields of electronics [1–3], catalysis [4–11], organic synthesis [12–14], sensors [15], energy harvesting [16–19] and storage [1,20,21], biomedicine [1,22,23], ferrofluids [24,25], hyperthermia materials [26], MRI contrast agents, magnetic data storage and metamaterials [27,28] etc. Among the carbon based

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materials, carbon nanotubes (CNT) and graphene have been in the limelight since their discovery [1,29]. Owing to their large surface area these carbonaceous materials can also be used in adsorption of various chemical species [30]. Nitrogen-doped graphene and CNT have appeared to be promising replacement for the expensive platinum group catalysts (Pt, Pd, Ru) in fuel cells for oxygen reduction reaction [17]. Recent reports also mention promising supercapacitive behaviour of graphene [20], multi-walled CNT and their polymer composites [21]. For the inorganic materials, carbon encapsulation is a cost-effective tool to prepare heterostructures of nanoparticles and protecting them from oxidation [31,32]. Various methods have been developed for their synthesis including; chemical vapour deposition (CVD) [33,34], solvothermal [35], laser ablation [36], chemical exfoliation [37], pyrolysis [38] etc.

CVD is the most popular among these techniques for mass production of carbon materials, but it requires precise instrumentation and high operating costs [33,34]. It operates at moderate temperature and produces nanotubes in larger quantities than arc discharge or laser ablation techniques. Usually, gaseous carbon precursors (acetylene, methane etc.) along with a catalyst source (ferrocene, nickelocene etc.) are passed through a quartz tube and these precursors are deposited on a substrate which results in the formation of CNTs. Metal particles are generally formed by the reduction of the metal precursors. At high temperatures carbon atoms dissociate from the precursors and deposit over the metal nanoparticles, which then nucleates and facilitates the growth of carbon nanostructures. This technique allows a continuous production of carbon materials. Fullerenes, graphene and carbon fibres can also be synthesized by tuning the growth conditions. The quality of CNTs is mostly governed by the choice of catalyst, synthesis temperature, substrate material and flow rate of carrier gas. Variations in any of these parameters drastically change the diameter and morphology of the CNTs. Another major issue with this technique is the poisoning of catalyst, mostly by the amorphous carbon, which prevents nanotube growth. This limitation has to be overcome for the formation of pure nanotubes.

Another technique, electric arc discharge synthesis [39], is well known to generate highest quality carbon nanotubes and fullerenes. The method involves passing a current of ∼50 A between two graphite electrodes in helium atmosphere. CNTs form when the graphite from the anode evaporates and condenses on the cathode. Using pure graphite electrodes mainly multi-wall nanotubes are produced by this method, while the growth of single-walled nanotubes requires a metal catalyst such as Co, Fe or Ni. A large amount of amorphous carbon is generally formed by this method which renders this method difficult to scale up.

The laser ablation technique [36] requires a pulsed laser to be targeted at a graphite specimen in an inert environment. CNTs are formed on a substrate at the end opposite to the graphite target. There are a few parameters to be controlled and the shape and structure of the CNTs is controllable. Although lesser amount of amorphous carbon forms by this method, the drawback is its low product yield (although higher than arc-discharge method). The cost of production of CNTs is high since controlling pressure is required along with high operating temperatures which needs very precise instrumentation. An alternative method needs to be devised to avoid these difficulties.

In comparison to all the above methods, pyrolysis method is a significantly simplified version of the CVD technique. The CNT growth occurs on the reactor wall or on a substrate like quartz. The amount of amorphous carbon can be simply controlled by the synthesis temperature. This method is cost-effective and offers a wide scope in choosing the precursor media [40]. Low cost single-step procedure can be devised [41] excluding the use of any inert gas flow. In this study the synthesis aims at reducing the cost of carbon based materials (CNTs and other carbonaceous composite materials), by excluding "inert gas flow" and stringent process controls. The synthesis parameters can vary depending on the furnace structure (length of heating zone) and working parameters (heating rate, temperature etc.). This work highlights the important parameters governing the growth of CNTs and other carbonaceous materials (globules). When we include the cost of infrastructure and energy consumption during synthesis, a closed CVD system like ours is very useful. Using our setup, we have also scaled up the synthesis to achieve few-gram level of synthesis of CNTs as part of our ongoing research.

Using the pyrolysis technique it had been previously reported that benzene–ferrocene mixture exclusively gives rise to carbon nanotubes and boron doping is essential to synthesize carbon encapsulated magnetic nanoparticles without nanotubes [42]. However, in this report we demonstrate that boron doping is not an essential condition; rather a variation of the synthesis parameters can lead to the growth of carbon encapsulated magnetic particles. Further modifications can lead to simultaneous growth of amorphous carbon encapsulated nanoparticles and carbon nanotubes. Furthermore, we studied the effect of reaction temperature, heating rate of the furnace (and the precursors) until the reaction temperature, length of the heating zone and post-calcination of the reaction products on the morphology of the carbon structures.

2. Fabrication of the furnaces and their temperature calibration

For identifying the role of the reaction zone-length, we built two tube furnaces indigenously, Furnace 1 and Furnace 2, with lengths of the maximum constant temperature zones of 4 and 10 cm, respectively (Fig. 1) and calibrated the temperatures. The technical details of the furnaces are mentioned in Table 1. Kanthal heating elements (wires) were used. For Furnace 1, the wires were directly wound on the ceramic (alumina) tube, while for the Furnace 2, the wires were first rolled in the form of a continuous spiral of 1 cm diameter and the spiral was then carefully wound on the tube. The length of the tubes is so chosen that the heat from the furnace is not dissipated into the environment easily. The heating elements were then fixed using high temperature refractory cement. Each setup was properly dried for 5 days at a constant low heating (using its own coil) to avoid cracking. The tube was then placed in a steel cylinder such that the heating zone (coil) lies at the centre of the furnace. The interior between the steel cylinder and the alumina tube was completely insulated using ceramic/glass wool. The heating elements were powered by a Variac by manually controlling the input voltage. The temperature of the furnaces was monitored using an external K-type thermocouple at different input voltages. The variation of temperature with distance is plotted on the right hand side of each furnace, in Fig. 1 (position of one end of the steel cylinder is assigned as zero). The curves from top to bottom show the temperature profile when the furnace was in steady equilibrium condition at the respective input voltage. The plateau region corresponds to the maximum temperature achieved for the particular set voltage. Both the furnaces show a plateau region of temperature with temperature gradient on either side, dividing the furnace into three temperature zones. Clearly, the Furnace 2 (having higher winding-length) shows a clear and longer plateau in the temperature profile. The different temperature zones were labelled as A, B and C as given in Fig. 1. Fig. 2 shows the calibration curve for the final (equilibrium) temperature versus input voltage for Furnace 1 and 2. The plot varies linearly according to the following equations [(1) and (2)] for Furnaces 1 and 2; respectively:

$$\mathrm{T}\,(^{\circ}C) = 10.72 \times V_{\mathrm{i}} + 25 \tag{1}$$

$$\mathrm{T}\,(^{\circ}C) = 8.01 \times V_{\mathrm{i}} + 25 \tag{2}$$

where, T is the temperature at the centre of the furnace in °C and V_{i} is the input voltage. From the equations one can select an applied voltage for achieving a particular final temperature, up to a temperature limit of 1100 °C.

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