

Processing and Properties of Nanocarbon Reinforced Iron Nanocomposites by Self-Catalytic Propagation High-Temperature Synthesis for Cancer Therapy

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Abstract

Combustion synthesis in a self-catalytic propagation High-temperature Synthesis mode was used with the aim to synthesize 1D carbon nanostructures, by the sodium Azide NaN_3 reduction of the Teflon PTFE (CF)_n, either in argon or in air, at ambient pressure (0.1 MPa) or at 1 MPa. In the same time, several possible catalysts were tried, such as $\text{Fe}(\text{CO})_5$, $\text{Co}(\text{CO})_8$, $\text{Ni}(\text{CO})_4$ powders. Through the presence of NaF in the product, the deep reduction of PTFE is shown. In order to produce fullerenes and carbon nanotubes, On the other hand, we obtain nanocarbon reinforced iron nano-composites by nanocarbon encapsulated iron metal nanoparticles in nanocarbon coke were obtained in our samples with high yield, opening the process to new possible and nanobiomedical applications.

Keywords: PTFE; 1D nanostructures; Nanocarbon encapsulated metal nanoparticles; Nanocomposites; Nano-biomedical applications

Introduction

Among the recent progress in carbon chemistry, the discovery of nanostructures based on graphitic planes, such as fullerenes [1,2], carbon nanotubes [3] and graphene [4-6] are of prime interest. The specific properties of these materials are the subject of intensive research, since they may be significantly modified by the presence of foreign atoms [7,8], either through chemical bonds with the carbon, or through encapsulation. Also, the structure of single graphitic planes, either in single wall CNTs or, more specifically of graphene induces specific electric properties that make these semiconductors of prime interest for high speed electronics [9,10], and their synthesis [11-13] and their properties [14-16] are the subject of intensive research.

Our goal is here to produce carbon-based nanostructures encapsulating metal or carbide nanopowders and/or nanorods. However, it the most known method to produce graphene is through deposition on silicon carbide [17], it is much more

difficult to synthesize on metals, as carbon would dissolve into the metal as a solid solution, or, at higher concentration, produce carbides. To avoid such a disastrous side effect, the fast, high-temperature stage of the carbon layer must be followed by a rapid cooling down. Apart from the Huffman-Krätschmer arc process [18], SHS reactions are a promising way to produce such hetero-structures [19-32,33-35]. Among the other possible synthesis processes, one could also cite RF plasma torch [36], magnetron and ion beam co-sputtering [37], high temperature annealing of the mixtures of carbon-based materials and metal containing powders [38], catalytic carbonization process [39,40,41], and laser induced pyrolysis [42]. The very idea of encapsulating metals or metal carbides inside nanotubes or fullerene-like structures partly comes from the very specific magnetic properties in the nanoscale range, the carbon layer ensuring the particles to be stable, resistant, harmless, with many possible industrial applications [21]

Experiment

SHS process in PTFE / NaN_3 /Fe(CO)₅ systems

As a source of carbon, Teflon (PTFE from Sigma-Aldrich, purity >99%, CaCO_3 from Sigma-Aldrich, >99%) were reduced using NaN_3 powder (Sigma-Aldrich, >99%). The blends were prepared in a high energy Fritsch planetary ball mill (Pulverisette 6) using a rotation speed within the range 400–600 rpm for a duration of 30-45 min to assure high homogenization, fractioning, and cold welding of the particles. In order to avoid oxidation during alloying, the ball mill was filled with high purity argon gas. The powders were then mixed with $\text{Fe}(\text{CO})_5$ powders (-325 mesh), used as catalysts and not compacted. Finally, reactions were carried out under reactive (air) or neutral atmosphere (argon) in a high-pressure reactor, in the self-propagating High-temperature Synthesis (SHS) mode (Figure 1), at an initial

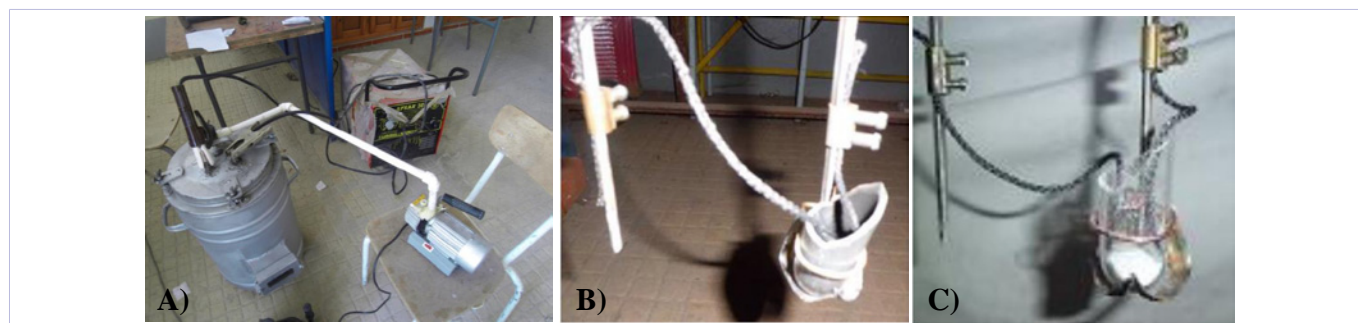


Figure 1: (A) Overall view of the self-catalytic propagation High-temperature synthesis system, (B) Powder after reaction ignited by graphite cord, (C) Powder before reaction.

Table 1: Characteristics of the reacting mixtures.

Expected reaction	Composition, w%	Catalyst (wt %)	DS°, J.kg ⁻¹ .K ⁻¹	DH°, kJ.kg ⁻¹	DG°, kJ.kg ⁻¹	T _{ad} °, K	Q _r , kJ.kg ⁻¹
$2CF + 2NaN_3 = 2NaF + 2C + 3N_2$	CF/NaN ₃ (67.8/32.2)		947	- 4005	- 4288	3125	3700
$2CF + 2NaN_3 = 2NaF + 2C + 3N_2$	CF/NaN ₃ (67.8/32.2)	Fe (CO) ₅ (10)	2007	-3513	-4111	2175	3100

pressure of up to 1.0 MPa (10 atm): the reaction was initiated by an intensity electrical current 60 Amperes and terminated within less than one minute. The characteristics of the expected reactions, including the composition of the mixtures, their standard thermodynamic parameters, and the measured heat of reactions Q_r are given in Table 1. The effect of the processing parameters-such as the reacting mixture composition (PTFE / NaN₃/Fe(CO)₅ weight ratio), initial combustion pressure (1-10 atm) and nature of the surrounding atmosphere (air, argon, CO, and nitrogen)-was studied. Products were characterized by XRD, electron diffraction and High-Resolution Transmission Electron Microscopy (HRTEM), and Raman spectroscopy.

Purification procedure for combustion products

The soot-like products, obtained in both types of synthesis processes, have to be subjected to purification procedure in order to remove non-encapsulated metal and carbide. The purification procedures have to remove simple inorganic salts, such as fluorides. In order to remove these salts it is necessary to anneal the combustion reaction products for 6 hr in 50% nitric acid HNO₃ at 323K, and then to flush by distilled water until complete removal of the acid is achieved [33].

In order to remove non coated iron or carbides, the samples have to be boiled in 2M HCl (24 h), and then washed in distilled water and subsequently in ethanol and annealed in dry air atmosphere at 350K. In order to remove amorphous carbon, the chemical oxidation by KMnO₄ dissolved in 50% sulfuric acid could be used. Again the sample has to be washed thoroughly in distilled water and annealed in dry air atmosphere.

Results and Discussions

Figure 2 presents the X-ray diffraction patterns and electron diffraction (Figure 3) of the products obtained after reaction of the systems PTFE/NaN₃ with and without Fe(CO)₅. From this figures,

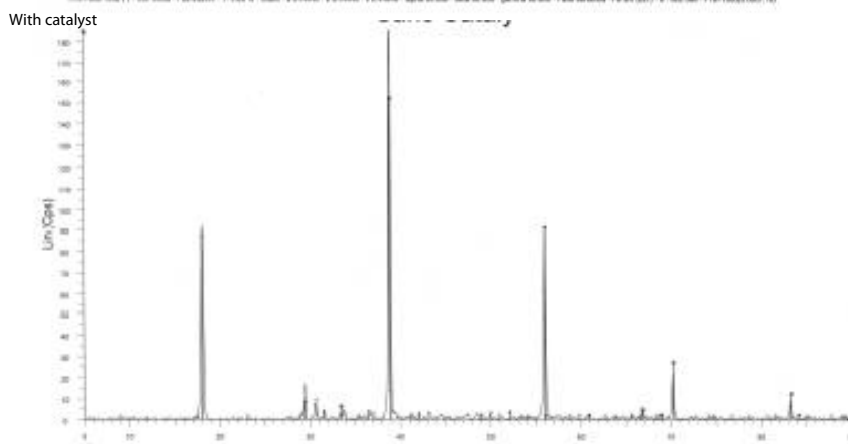
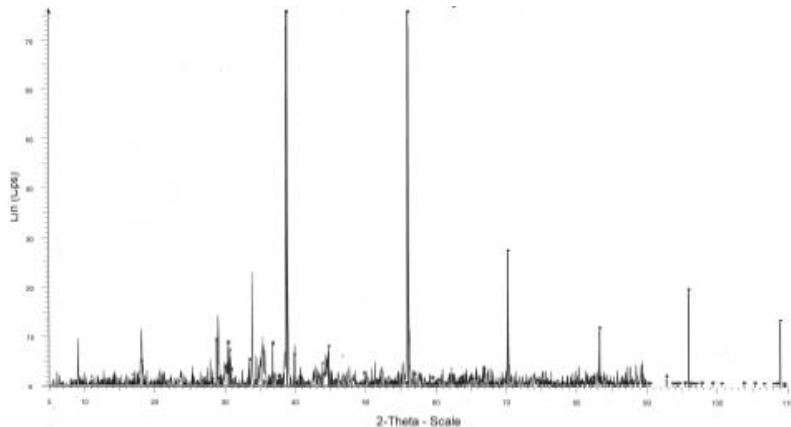
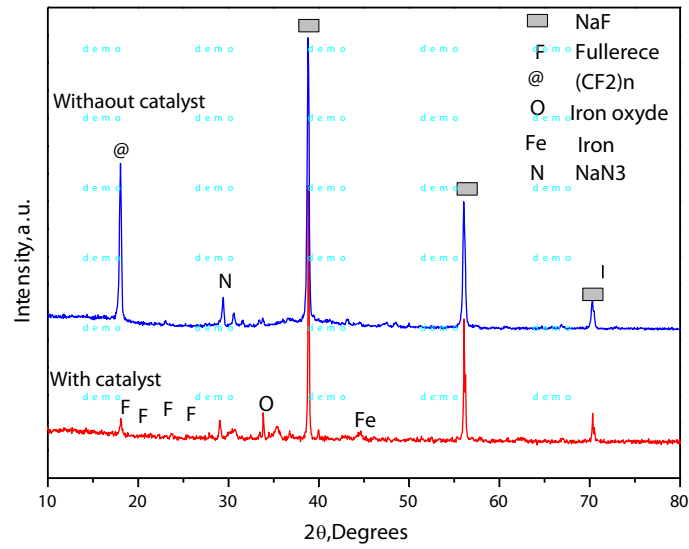
we observe the presence of nanocrystalline NaF, which is a proof that a reaction reducing at least partially the PTFE occurred, of various organic materials, fullerenes and of carbon in the form of 1D nanostructure and remaining CO₂ from the catalyst. Finally, it must be pointed out that our results, even when fiber-like products are not dominant, is capable of producing encapsulated products, would it be reduced metals (Fe), as observed by HRTEM, Figure 3, from the sodium Azide-induced reduction of PTFE in the presence of iron catalyst in the form of gas phase Fe(CO)₅. A good adherence of the particle with its graphitic surroundings is observed, although there obviously is a significant growth of this graphitic layer during the reaction with high yield. The inset (Figure 3) represented the electron diffraction of the nanocarbon coke and iron nanocrystallite encapsulated. We have obtained a nanocarbon reinforced metallic matrix nanocomposite in core shell nanostructures.

Summary

Under the applied conditions, the presence of nanocrystalline NaF, fullerenes and 1D carbon nanostructures in the products is confirmed by XRD analysis when the reaction takes place under a neutral atmosphere, which points to the deep conversion of PTFE. This experiment's is directed towards the achievement of higher content of Fe-containing nanoparticles, control of particle size distribution, and also the structure of the particles, e.g. using thermal boosters to increase the overall adiabatic temperature by using of PTFE reduced by NaN₃ in the gas phase metallocene Fe, Ni, Co(CO)₅ as catalyst metal nanoparticles is achieved to obtain nanocarbon reinforced metallic matrix nanocomposite in core shell nanostructures for cancer therapy.

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Without catalyst

Figure 2: XRD pattern of the combustion products obtained from the reacting mixtures: (1) PTFE/NaN₃ without metal catalysts, (2) PTFE/NaN₃ with Fe(CO)₅ catalyst, All experiments were performed under 0.1 MPa Argon.

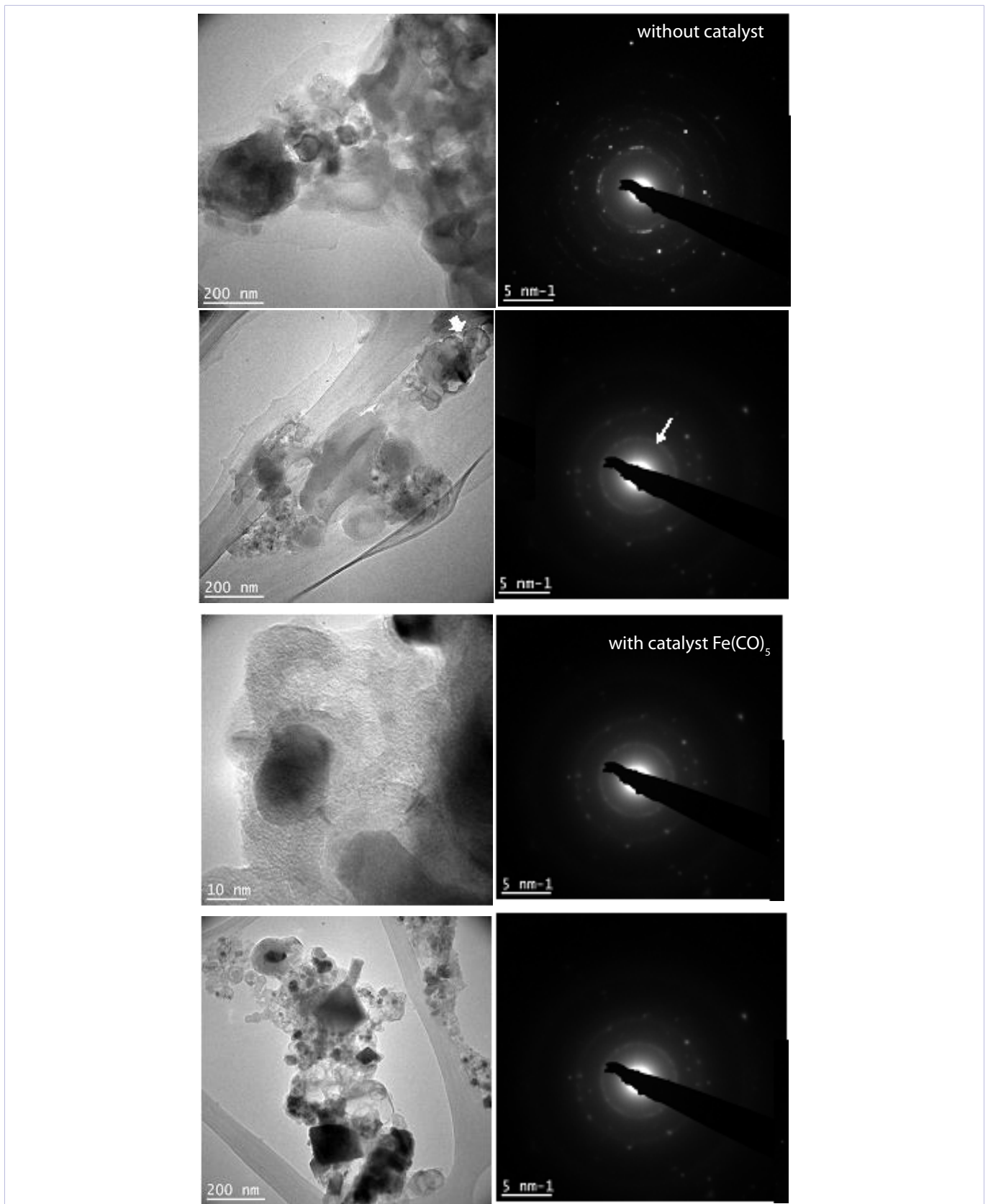


Figure 3: HRTEM represented metallic nanoparticle encapsulated in core shell nanocarbon nanostructure forming a metallic matrix nanocomposite , without and with catalyst Fe(CO)₅ from top to bottom with electron diffraction (ED).

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