



## Pharmacological molecule based on nanocarbon container encapsulated ferromagnet by combustion synthesis for cancer therapy

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### Abstract

Combustion synthesis in electrothermal explosion mode can be regarded as an efficient method to obtain new nanomaterials. Different starting mixtures of magnesium powder with various carbonates ( $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{FeCO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ ) were tried and the self-thermal reactions were carried out under both reactive (air) and neutral atmosphere (argon) with an initial pressure of 10 atm to yield novel nanomaterials. Fe, Co, Ni, Pd, Nd, Ta, Ti, Nb, W and NiO powders were used as catalysts and their synthesis and purification have been optimized. Under the applied conditions the presence of crystalline MgO and  $\text{NaO}_2$  in products confirmed by XRD analysis, even for the reaction under neutral atmosphere, points to the deep conversion of carbonates. For producing fibrous products the  $\text{Na}_2\text{CO}_3$  system proved to be the most promising one (in other of tested carbonate systems, except  $\text{Li}_2\text{CO}_3$ , the content of fibrous phase was insignificantly small). SEM images show the morphology of the products with some 1-D nanostructures resembling carbon nanotubes and nanosized metal/carbon composite (carbon-encapsulated metal-based iron nanoparticles with a core-shell structure with interesting magnetic properties by combustion was obtained. Different magnetic metals (Fe, Ni, and Co) that can be encapsulated by the carbon shell, graphite layers and nanofibers. After purification procedure, we will only obtain core-shell or graphite layers encapsulated by metal magnetic nanoparticles without impurity like noncoated iron or carbides and amorphous carbon. The characterization techniques include the chemical analysis, HRTEM, XRD and FESEM. The VSM and Mössbauer Spectroscopy (in the case of Fe-containing samples) will be performed in the near future. Model of the kinetic formation of pharmacological molecule based on nanocontainer carbon ferromagnet is given. The obtained novel pharmacological molecular nanostructure will be injected in the cancer tumor cell (prostate) after sterilization. The nanocontainer will be heated by microwave at the Laboratory Central of Anatomie and Cytology Pathology of the CHU Annaba. The reaction will be observed in the HRTEM.

**Keywords:** Electrothermal explosion reaction; 1-D nanostructures; core-shell structure; graphite layers; nano container carbon ferromagnet, nanofibers.

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## 1. Introduction

For very long time carbon was known as the fundamental component of different chemical species. These compounds create foundation of living organisms, including plants and animals. It is therefore understandable that these compounds were subject of intensive research, creating an immense branch of science known as organic chemistry.

The investigations in these areas were very intense, resulting in many discoveries which affected not only scientific understanding of fundamentals of chemistry, physics and biology but also transformed many areas of industrial activity and deeply changed our everyday life. It is therefore surprising, that the subject was not exhausted; on the contrary, recent discoveries channeled interest of many researchers in this direction. Among significant achievements in the area, the most prominent was the discovery of nanosize carbon structures, such as fullerenes [1, 2], carbon nanotubes (CNTs) [3] or graphene [4–6] and related materials [44]. These discoveries heralded advent of new branch of science and nanotechnology.

The molecular nanostructures of carbon (CNTs) have interesting optical and electrical properties, which can be modified by introduction of foreign atoms [7]. It is also important that this development was connected with the progress in the most important characterization tool. High Resolution Transmission Electron Microscopy (HRTEM) that allowed studying these structures with atomic precision. Another discovery of self-standing graphene attracted more attention to this area [4–6]. This discovery was even more surprising, as graphene is intimately related to graphite, the material known for centuries. The electric properties of graphene made this material a focal point of the semiconductor research promising new very attractive applications in high-speed electronics [8, 9].

Application of graphene-based devices requires deposition of graphene on a mechanically strong support. The optimal choice would be fabrication of graphene on a carbon-based material such as silicon carbide. It was therefore fortunate that graphitic films can be grown on SiC surfaces [10–12]. It was recognized only recently that few atomic carbon layers have the electronic transport properties of graphene [13]. It is evident that most important is the structure of the SiC–graphene interface. Therefore the atomistic structure was intensively investigated [14, 15]. Despite some progress, the relations between the atomistic structures of carbon layers deposited on SiC surfaces are not well understood.

Another aspect of the interaction of graphite-like carbons layers with solid supports is related to carbon–metal structures. In contrast to graphene–SiC structures, which are relatively easy to obtain, the carbon–metal structures are more difficult to synthesize. This is related to the fact that carbon is easily dissolved in liquid metals, creating solid solutions or in higher concentrations, metal carbides [16]. Therefore in order to synthesize such structures, rapid high-temperature methods have to be used. Fast, high-temperature stage of the synthesis of carbon layers on metal surfaces should be followed by rapid cooling down of the system in order to prevent dissolution of carbon layer in the metal interior. Among the processes that are able to fulfill such criteria, the most effective are: Huffman–Krätschmer arc process [17] and combustion synthesis [18, 19]. Therefore combustion synthesis is a technologically important process. In particular, application of the combustion process to creation of Me–C structures.

It has to be noted that carbon encapsulation of metal nanoparticles changes their properties. These particles create a new-type material combining magnetic and other physical properties of metals with chemical resistance of carbon. They create a new type of structural nanosize materials, which demonstrate the potential of nanotechnology. As such their properties are extremely interesting from the point of materials science and also for

their potential applications. Therefore their properties are intensively investigated [20]. The results of the characterization of such systems by many methods will also be reviewed. Their properties open routes to many applications in industry and medicine and other branches of human activity [21]. Therefore such possibilities of potential applications will also be discussed.

## 2. Experimental Procedure

Combustion was carried out in a electrothermal explosion (ETE) reactor (Figure 1). The effect of process parameters such as reactant composition (powdered Mg/carbonate), initial combustion pressure (1–10 atm) and atmosphere (air, argon, CO and nitrogen) was studied.

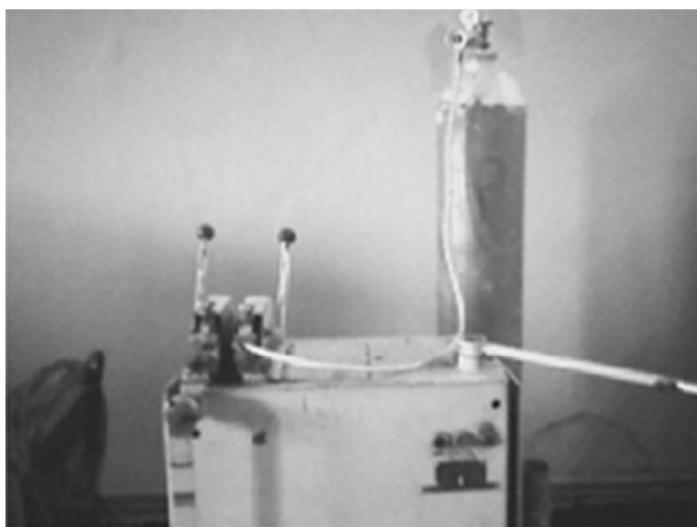
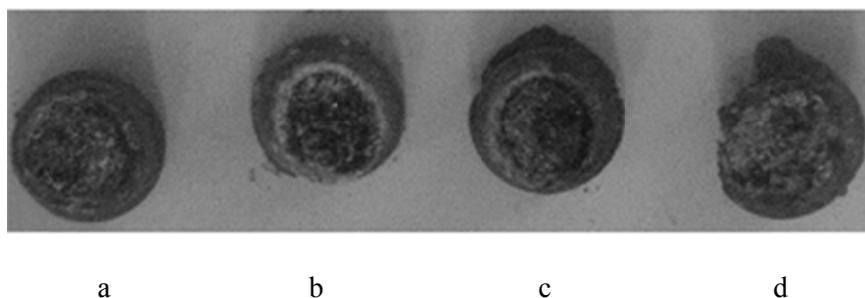


Fig. 1: Overall view of the electrothermal explosion reactor.

The products (Fig. 2) were characterized by XRD, scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. Purification procedure of the products was proposed and will be performed. The powder mixture of reactants was placed in a cooper tube deccres the projection of the materials by shock-wave induced by the reaction; they was initiated by heavy-current heating and terminated usually within less than 2 min.



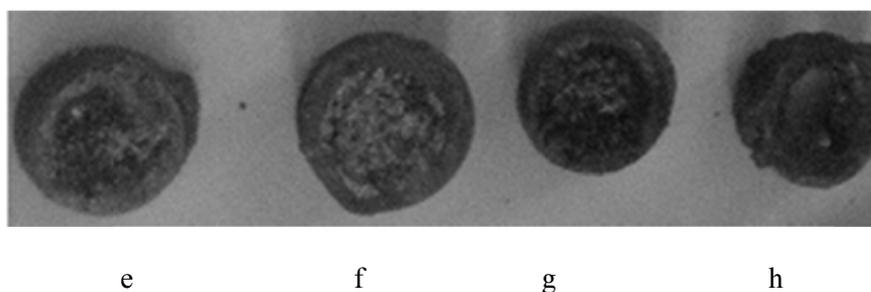


Fig. 2: Samples pictures of the combustion products obtained from carbonate systems with and without metals catalysts incorporated in cooper tubes: (a)  $\text{Na}_2\text{CO}_3/\text{Mg}$ , 1 atm argon,(b)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Fe}$ , 1atm argon,(c)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Ni}$ , 1 atm argon,(d)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Co}$ , 1 atm argon, (e)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Ta}$ , 1 atm , (f)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Ti}$ , 1 atm , (g)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Pd}$ , 1 atm, (h)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Nd}$ , 1 atm.

### 2.1. ETE Process in Carbonate Systems

Different starting homogenous mixtures of Mg powder (Sigma–Aldrich, >99%) with various carbonates  $\text{Na}_2\text{CO}_3$  from Sigma Aldrich, >99% and  $\text{CaCO}_3$  from Sigma–Aldrich, >99% as a source of elemental carbon, were tried; reactions were carried out under reactive (air) or neutral atmosphere (argon) at an initial pressure of 10 atm. The blends were prepared in a high energy Fritsch planetary ball mill. The rotation speed could be varied within the range 400–600 rpm. In order to avoid oxidation during alloying, the ball mill was filled with high purity argon gas. The vial was opened after 30–45 min to assure high homogenization, fractioning, and cold welding of the particles. The powders were compacted into small discs [(2–3) × 13 mm] at the compacting pressure  $P=6000$  psi and put into a cooper tube; Fe, Co, Ni, Pd, Nd and NiO powders (325 mesh) were used as catalysts.

Assumed reactions, composition of the mixtures, their standard thermodynamic parameters and measured heats of reactions are given in Table 1. High adiabatic temperatures, especially these in excess of 2000 K (Table 1), make the combustion method as perspective as carbon arc plasma methods, also capable to provide extremely high temperatures, above 3000 K [17, 20]. For comparison, the last column in Table 1 presents the measured values of reaction heats (at constant volume). They are seen to correlate with calculated standard enthalpy of reactions.

Table 1: Assumed rections compositions and thermodynamic parameters

Assumed reactions	Composition, wt.%	Catalyst wt.%	$\Delta S^\circ$ , J/kg·K	$\Delta H^\circ$ , kJ/kg	$\Delta G^\circ$ , kJ/kg	$T_{ad}$ K	$Q_r$ , kJ/kg
$\text{Na}_2\text{CO}_3 + 3\text{Mg} = 3\text{MgO} + \text{C} + 2\text{Na}$	$\text{Na}_2\text{CO}_3/\text{Mg}$ (70/30)	Fe, (10) Ni, Co, NiO	2392	-3750	-4463	2300	2388
$\text{CaCO}_3 + 2\text{Mg} = 2\text{MgO} + \text{CaO} + \text{C}$	$\text{CaCO}_3/\text{Mg}$ (70/30)	Fe, (10) Ni, Co, Pd, Nd, NiO	2007	-3513	-4111	2175	3100

## 2.2 Purification Procedure for Combustion Products

Carboniferous material with other products of reactions remained on the bottom of the reactor. The material will be rinsed with water to remove sodium, treated in boiling nitric acid for 3 h to remove sodium oxide and then will be rinsed with water again. After that the solution will be filtered, and the remaining powder dried [36].

The soot, sponge or salts-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. In order to remove these salts it is necessary to anneal combustion products at 323 K for 6 h in 50 % HNO<sub>3</sub> and then to flush by distilled water until complete removal of the acid is achieved [26, 38, 43]. In order to remove uncoated 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 350 K. In order to remove amorphous carbon, the chemical oxidation by KMnO<sub>4</sub> dissolved in 50 % sulfuric acid could be used. Again the sample has to be washed thoroughly with distilled water and annealed in dry air [41, 42, 45].

## 3. Results and Discussion

### 3.1 Characterization of Products

The presence of crystalline MgO, organic materials, NaO<sub>2</sub> and carbon as a source of 1D nanostructures the in the products was confirmed by XRD (Fig. 3).

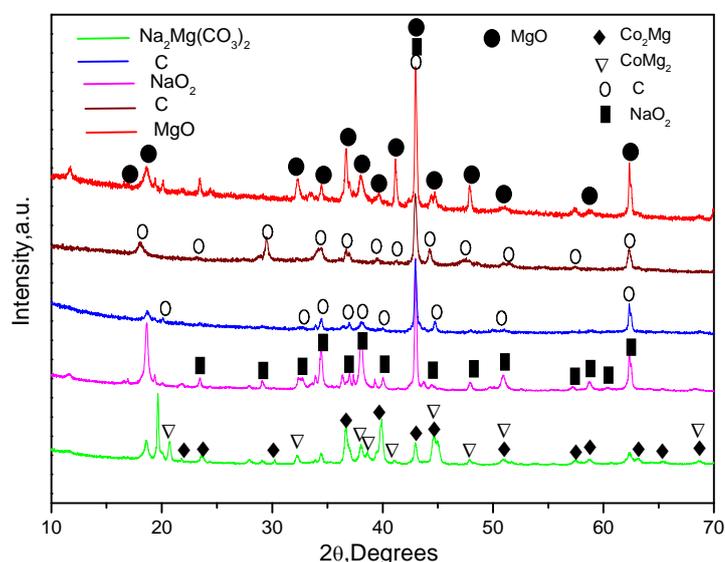
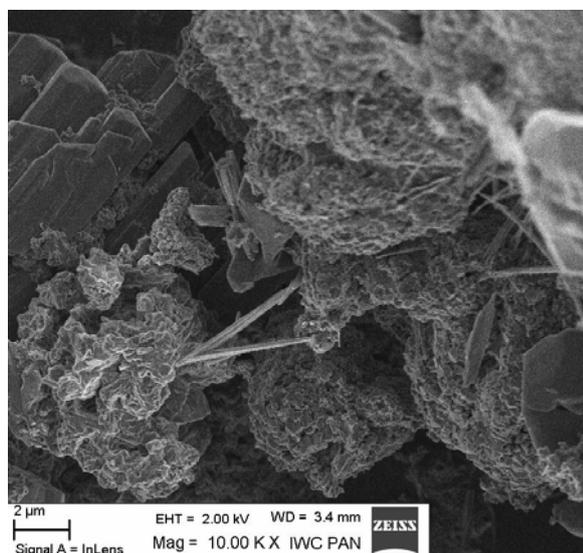


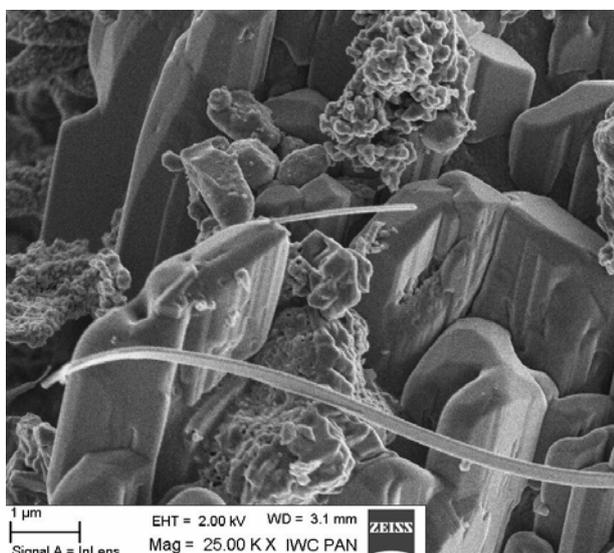
Fig. 3: XRD pattern of the combustion products obtained from carbonate systems with and without metals catalysts: (green line) Na<sub>2</sub>CO<sub>3</sub>/Mg, 1 atm argon, (bleu line) Na<sub>2</sub>CO<sub>3</sub>/Mg/Fe, 1 atm argon, (pink line) Na<sub>2</sub>CO<sub>3</sub>/Mg/Ni, 1 atm argon, (dark red line) Na<sub>2</sub>CO<sub>3</sub>/Mg/Co, 1 atm argon, (rot line) CaCO<sub>3</sub>/Mg, 1 atm argon.

The noncoated iron or carbides and encapsulated iron is not detected because is segreget with small concentration. The EDX analysis (Fig. 6), demonstrate that the reaction under neutral atmosphere leads to a deep conversion of carbonates. For producing fibrous

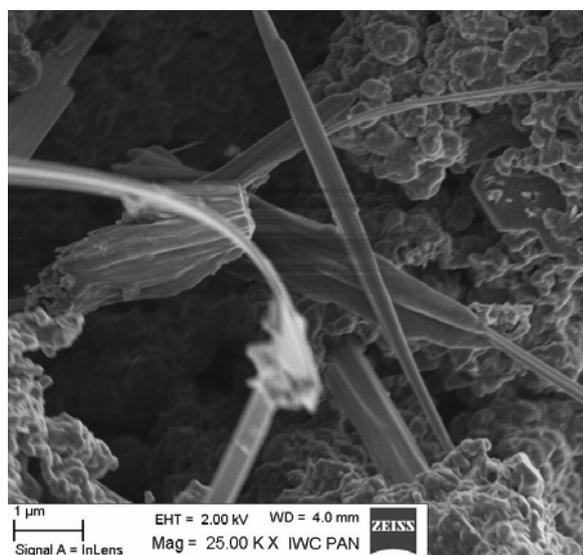
products (Fig. 4), the  $\text{Na}_2\text{CO}_3$  system proved to be the most promising one; in other tested carbonate systems, except  $\text{Li}_2\text{CO}_3$ , the content of fibrous phase was negligibly small. The FESEM pictures (Fig. 4) show the morphology of the products with some 1D nanostructures resembling carbon nanotubes (CNTs) and nanofibers (Fig. 4) without and with Fe, Ni, Pd and Co catalysts (Fig. 4(a)–(m)), in comparison with the nanostructures reported in [40] (Fig. 4(f), (g), (h)).



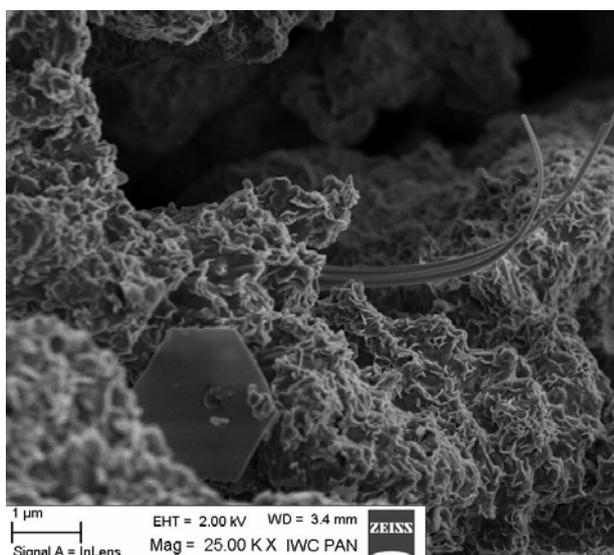
(a)



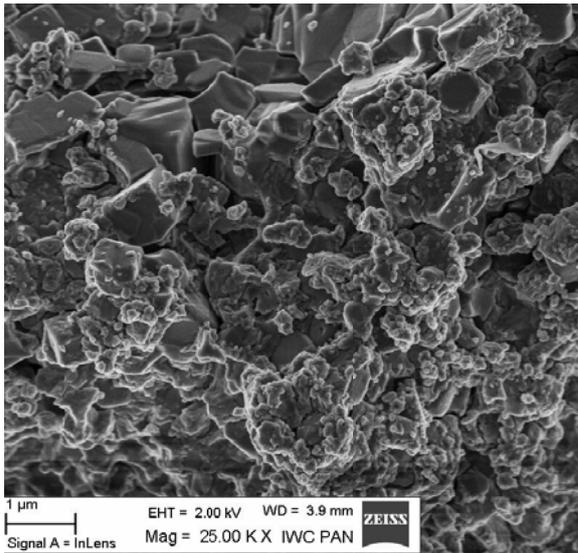
(b)



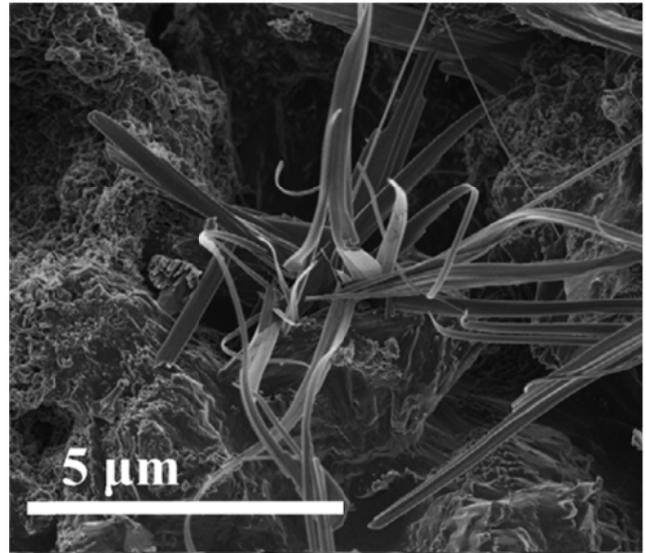
(c)



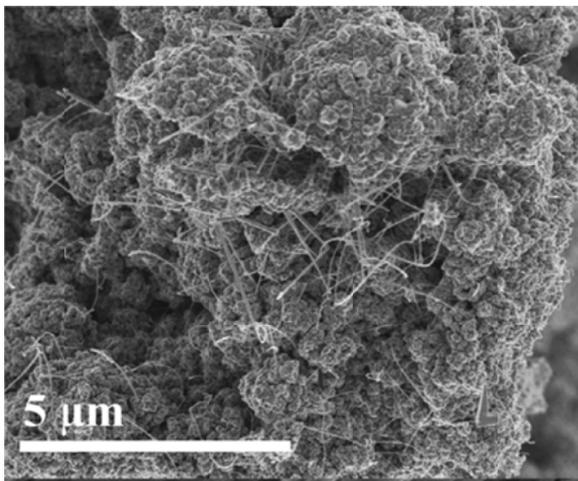
(d)



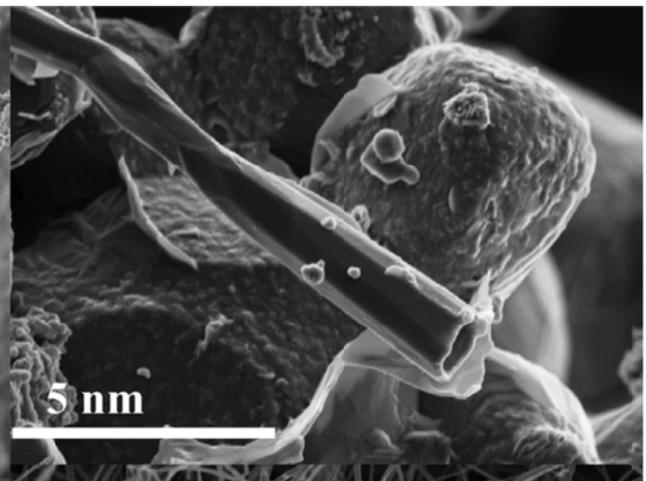
(e)



(f) [40]



(g) [40]



(h) [40]

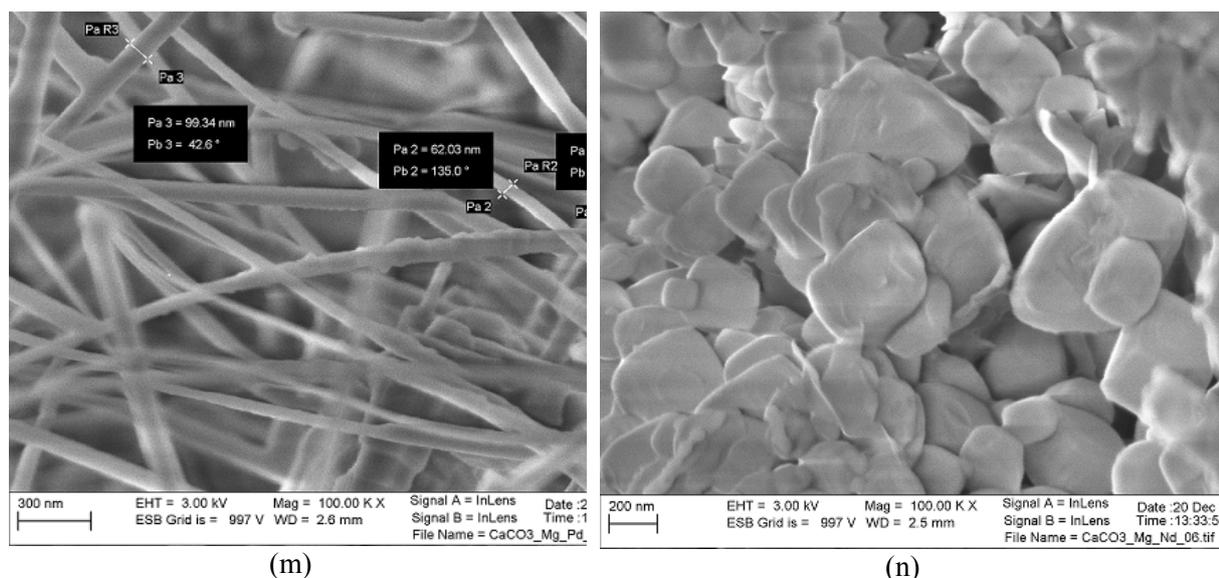


Fig. 4: FESEM pictures of the combustion products obtained from carbonate systems with and without metals catalysts: (a)  $\text{Na}_2\text{CO}_3/\text{Mg}$ , 1 atm argon, (b)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Fe}$ , 1 atm argon, (c)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Ni}$ , 1 atm argon, (d)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Co}$ , 1 atm argon, (e)  $\text{CaCO}_3/\text{Mg}$ , 1 atm argon, (f)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Co}$ , 10 1 atm (f), air, (g)  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{PTFE}/\text{Fe}$ , 10 atm, air [40], (h)  $\text{FeCO}_3/\text{Mg}$ , 10 atm, air [40], (m)  $\text{CaCO}_3/\text{Mg}/\text{Pd}$ , 1 atm argon, (n)  $\text{CaCO}_3/\text{Mg}/\text{Nd}$ , 1 atm argon.

In fact, Huczko *et al.* [26] and Alekseev *et al.* [36] have shown that condensing carbon vapors by combustion of carbonates (produced via SHS) can yield CNTs. Also, Bendjemil *et al.* [37, 38] reported on production of carbon nanotubes upon gas combustion (decomposition of  $\text{Fe}(\text{CO})_5$  at low pressures and moderate temperatures, one should mention that  $\text{CO}_2$ ), which is in fact, an intermediate reactant of our carbonate decomposition under combustion synthesis conditions, can be reduced to CNTs by metallic Li [39].

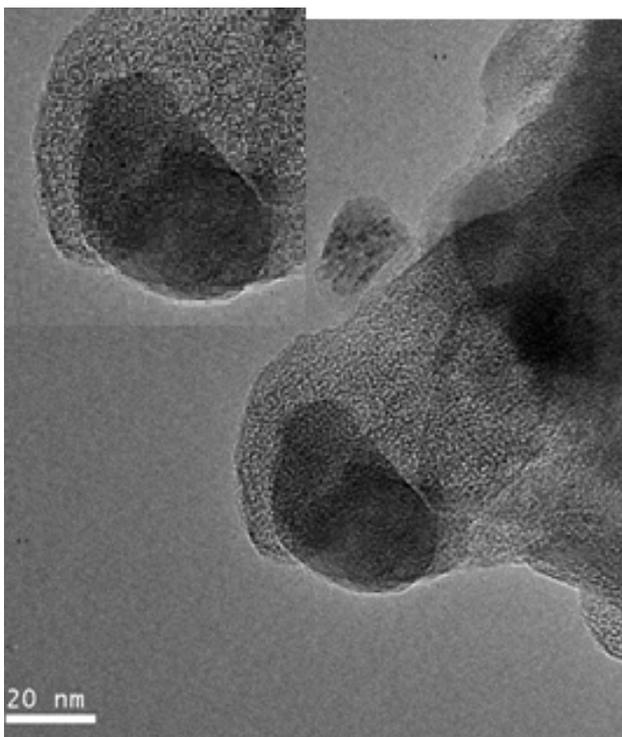
The images of the typical carbon-shell, graphite layers, Fe or  $\text{Fe}_3\text{C}$  containing encapsulates are presented in Fig. 5 (a)–(d). In these images the following particles are observed: Fe or  $\text{Fe}_3\text{C}$  nanoparticles, surrounded by graphitic envelope, adhered to the metal nanoparticles; the nanoparticles surrounded by thin graphite envelopes on which secondary, much thicker graphite layer is created (Fig. 5(a)–(c)) and nanotubes. Such thick graphite structures are created due to nonuniform enveloping of the grains surfaces, resulting in encapsulation of the grain in the zones of considerably different temperatures. The series of images demonstrates transition from amorphous carbons structure, presented in (Fig. 5(d)), the presented nanoparticles are shown in the insets located in the corners. Fig. 5 (e), (f), (g), (h) corresponding to  $\text{Na}_2\text{CO}_3/\text{Mg}$ , systems 1 atm argon, that represented organic and mineral materials resulting from the reactions and nanotubes.



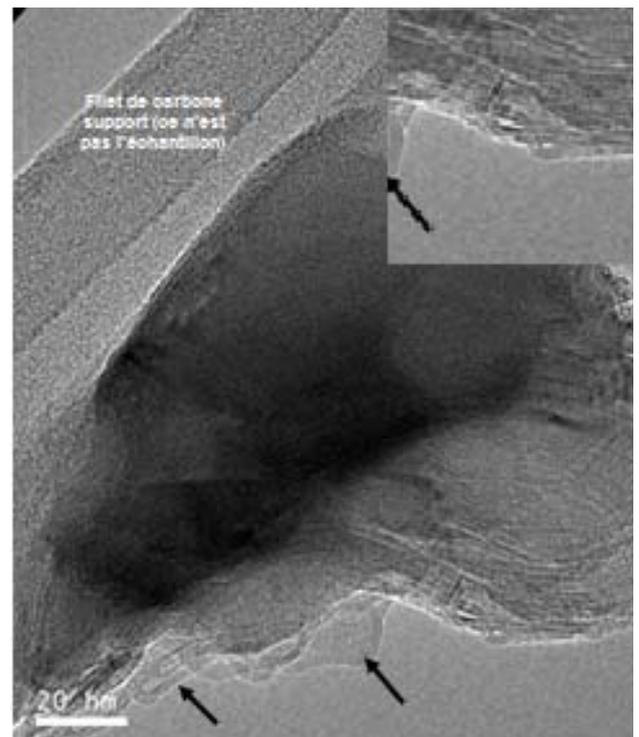
(a)



(b)



(e)



(g)

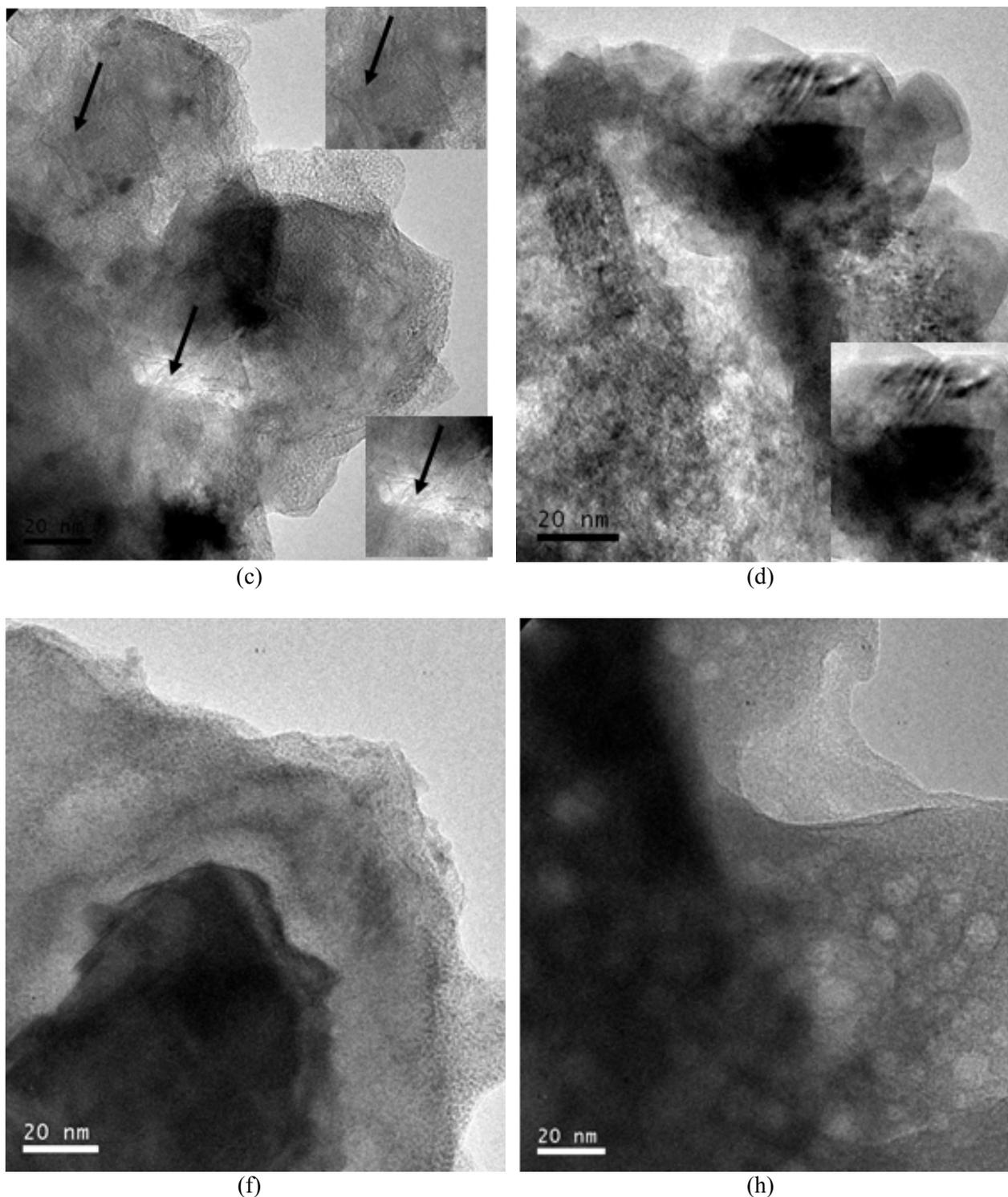
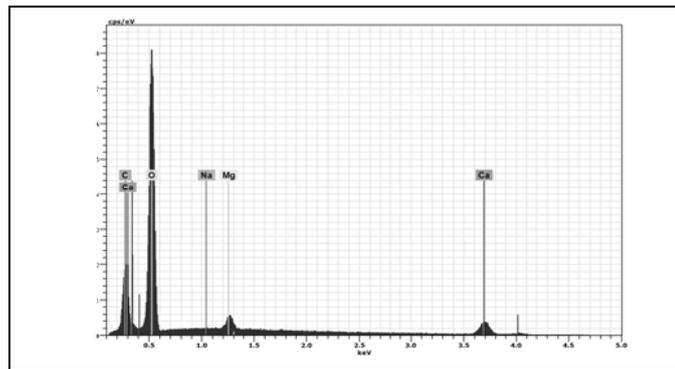


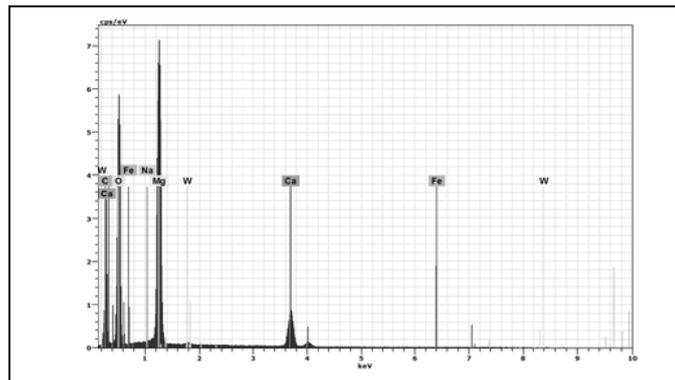
Fig. 5: (a), (b), (c), (d) corresponding to the HRTEM pictures of the nanostructures obtained in combustion synthesis of  $\text{Na}_2\text{CO}_3/\text{Mg}/\text{Fe}$  systems, 1 atm argon, showing encapsulation of Fe or  $\text{Fe}_3\text{C}$  nanoparticles of about 20 nm thick by graphitic layers: inset in the right corner shows the magnified part of the nanoparticle Fe and  $\text{Fe}_3\text{C}$ ; (c) amorphous carbon; (b) and (d) nanoparticles by additional thick graphite layers growing on the thin C- particles, (e), (f), (g), (h) corresponding to  $\text{Na}_2\text{CO}_3/\text{Mg}$ , systems 1 atm argon, that represented organic and mineral materials resulting from the reactions, nanotubes and graphite layers.

It has to be noted that the combustion synthesis suffers from some drawbacks at the moment. This are related to relatively small portion of useful Me-containing products. This

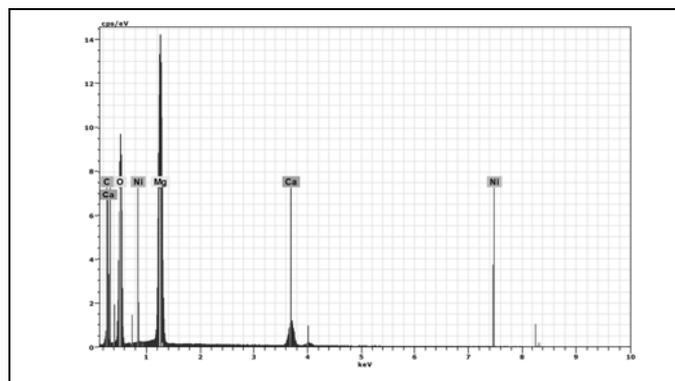
is partially caused by relatively low temperature of the process. Still the adiabatic temperatures, listed in table 1 are high exceeding 2000 K for some cases, close to those attained by arc-discharge technique. Thus, low efficiency is partially related to the fact that the area is in the early stage of development. Therefore intensive research of the process is necessary to develop combustion detonation and shock synthesis (CDS), before the method could be industrially attractive. This research will be directed towards achievement of higher content of Me-containing particles, control of particle size distribution and also the structure of the particles.



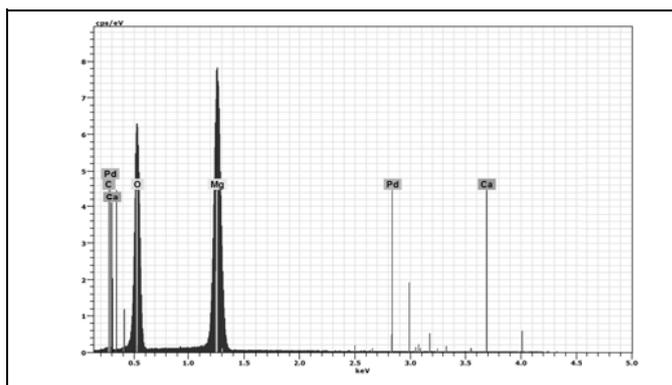
(a)



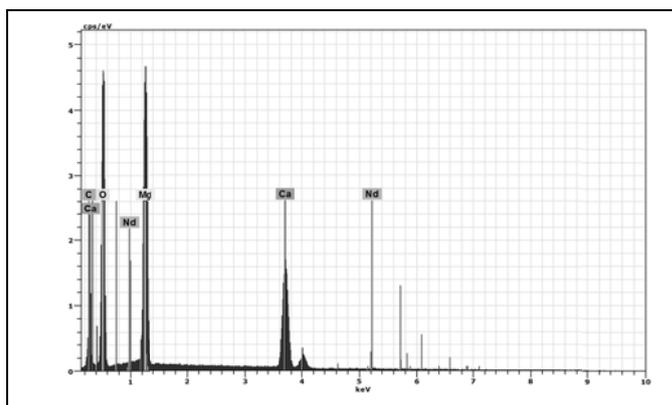
(b)



(c)



(d)



(e)

Fig. 6: EDS spectra of the combustion products obtained from carbonate systems with and without metals catalysts: (a)  $\text{CaCO}_3/\text{Mg}$ , 1 atm argon, (b)  $\text{CaCO}_3/\text{Mg}/\text{Fe}$ , 1 atm argon, (c)  $\text{CaCO}_3/\text{Mg}/\text{Ni}$ , 1 atm argon, (d)  $\text{CaCO}_3/\text{Mg}/\text{Pd}$ , 1 atm argon, (e)  $\text{CaCO}_3/\text{Mg}/\text{Nd}$ , 1 atm argon.

### 3.3 Kinetic Model Formation of Pharmacological Molecule Based on Core-Shell (Nanocontainer Carbon Ferromagnet)

Their core is nonokristallit ferromagnet. It is chemically fonctionnalized by nanoparticle for biologically active nanocapsule is hypothetically, be placed in a manner controlled with the magnetic field head for human organism (drug delivery, cancer therapy). The figure shows the model of kinetic formation use for the pharmacological molecule. Such new nanomaterial preceded must be research their possible actions and reactions with the graphitic core or matrix

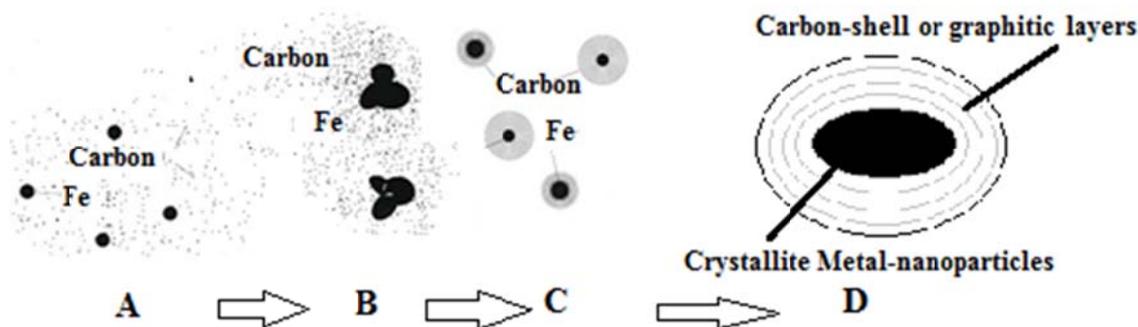


Fig. 7: Model of the kinetic formation of pharmacological molecule based on nanocontainer carbon ferromagnet.

#### 4. Conclusion and Perspective

Under the applied conditions the presence of crystalline MgO and carbon as source of 1D nanostructures the in the products confirmed by XRD analysis, the reaction under neutral atmosphere, points to the deep conversion of carbonates. For producing fibrous products the  $\text{Na}_2\text{CO}_3$  system proved to be the most promising one (in other of tested carbonate systems, except  $\text{Li}_2\text{CO}_3$ , the content of fibrous phase was insignificantly small). FESEM pictures show the morphology of the products with some 1-D nanostructures resembling to carbon nanotubes and nonofibers.

Carbon encapsulated magnetic nanoparticles belong to the newest, rapidly developed branch of nanotechnology science. These structures were developed recently as a part of wide are of investigations of carbon based nanostructures: fullerenes, nanotubes, graphene, etc.

Starting from purely carbon domain these structures penetrated into more sophisticated design: combination of metals and carbon. This combination offers new perspectives, not available to standard carbon-based structures. Magnetic properties of iron, cobalt, nickel etc. can be preserved in nanoscale small volumes. Carbon encapsulation makes the nanoparticles stable, resistant, harmless. They could preserve their unique properties for very long time in extremely aggressive chemical environment, at high temperatures or both. In conjunction with the small size and possibility of control by magnetic field, this offers wide area of applications, such as magnetic data storage, xerography, electronics, magnetic resonance imaging and catalysis [21]. Other important applications remain in nanomedicine, e.g. transport of anticancer drugs or fine surgical interventions.

Many different synthesis techniques were used to obtain such nanocarbon encapsulated nanoparticles: carbon plasma arc-discharge [17, 20], RF plasma torch [31], magnetron and ion beam co-sputtering [32], high temperature annealing of the mixtures of carbon-based materials and metal containing powders [33], pyrolysis of organometallic compounds [18] and catalytic carbonization process [34, 38, 45], laser induced pyrolysis [35] and finally the combustion synthesis [18-30, 40]. The latter method, discussed in the present review is the only one capable to scale-up to large size mass production technique that could be fast, efficient and highly reproducible. Potentially, this technique could be very pure, as all additional products are very reactive ionic species which could be effectively removed by etching in acids, which could be removed by flushing in pure water. This condition is

especially important for medical applications where chemical purity requirements are particularly stringent.

Experiments are now in progress using the reaction mixture:  $2CF_4 + 2NaN_3 = 2NaF + 2C + 3N_2$  using metallocene  $Me(CO)_5$  ( $Me = Fe, Co, Ni$ ) as source of metal magnetic nanoparticles encapsulated carbon in core shell structure according to the (Figure 7). This research will be achievement of higher content of Me-containing particles, control of particle size distribution and also the structure of the particles. The combustion synthesis will be critically compared in the near future with combustion detonation and shock synthesis (CDS).

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