

# COMBUSTION SYNTHESIS AS A FAST ROUTE TO PRODUCE NOVEL NANOMATERIALS

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**Abstract:** Combustion synthesis was applied as a novel approach to produce carbon-related nanostructures. Redox reactions in the systems Mg/Si/GO/SiF<sub>x</sub> yielded interesting products like silicon carbide nanowires (SiCNWs) and graphene-related nanostructures.

**Keywords:** COMBUSTION SYNTHESIS, SILICON CARBIDE NANOWIRES, GRAPHENE-RELATED NANOSTRUCTURES

## 1. Introduction

There are two basic approaches to synthesize nanomaterials, characterized by novel and specific properties: top-down and bottom-up. In the latter one (following the Feynman's idea<sup>1</sup>) molecules, atoms and ions combine together forming larger structures, specifically called nanomaterials if their size is smaller than 100 nm in one direction. There are many ways to atomize the matter but usually they involve high-energy activation. We propose here a Combustion Synthesis CS (also called Self-Propagating High-Temperature Synthesis, SHS) which is a relative simple (but still not widely explored) technique to produce novel nanomaterials on a bottom-up platform, this due to high temperatures and high pressure gradients resulting in quench conditions far from thermodynamic equilibrium<sup>2-4</sup>. As an example, we showed elsewhere<sup>5-8</sup> that SiCNWs can be efficiently produced from the mixture of simple reactants Si/Teflon®. Here we aim at the formation of novel nanocarbons like graphene<sup>9-11</sup> and graphene/SiCNWs composites which due to low dimensionality have a unique variety of properties, which make them promising candidates for various applications.

## 2. Experimental

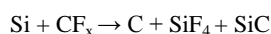
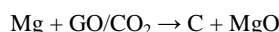
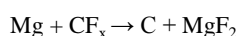
The experimental set-up and approach in CS is simple: the solid-phase reaction between a strong reducer and a strong oxidant results in a very short exothermic process leading to the formation of novel exotic compounds (via reactants intermediate atomization) this happens due to high temperature and pressure gradients, and fast quench. This usually very fast process (within seconds) is carried out in a high-pressure stainless-steel chambers (Fig. 1).



Fig. 1 Experimental set-up for combustion synthesis (stainless-steel reactors

of a volume 340 cm<sup>3</sup>, 550 cm<sup>3</sup> and 2700 cm<sup>3</sup>).

Magnesium and silicon elemental were used as reducers while graphene/graphite oxide (GO) and fluorinated graphite (CF<sub>x</sub>) were the oxidants. The following equations describe the chemical transformations in the systems under investigation



Before the combustion the reactants were loaded into the quartz crucible and placed in the reactor, which was then filled with the combustion gas (Ar, CO, CO<sub>2</sub>...) and the combustion pressure was adjusted as pre-planned (between 1 and 50 atm). The reaction was started by resistive heating of the crucible content with the igniter (carbon, kanthal or tungsten tape). The combustion was usually terminated within a fraction of second. The solid products were collected to evaluate the progress of the combustion, the conversion degree and the composition/morphology using different techniques. Those include: XRD, SEM, TEM, EDX, Raman spectroscopy, elemental analyzes, and others.

## 3. Results and Discussion.

We present here the preliminary results of combustions regarding the following solid-phase reaction systems and starting reactants mixtures:

-Mg/CF<sub>x</sub>

-Mg/GO

-Mg/CO<sub>2</sub>

-Si/CF<sub>x</sub>

-Si/GO

For such systems the following operational parameters were tested:

- different molar ratio of reactants
- different morphology of starting reactants
- different combustion atmospheres
- different starting pressures
- different mass of reactants

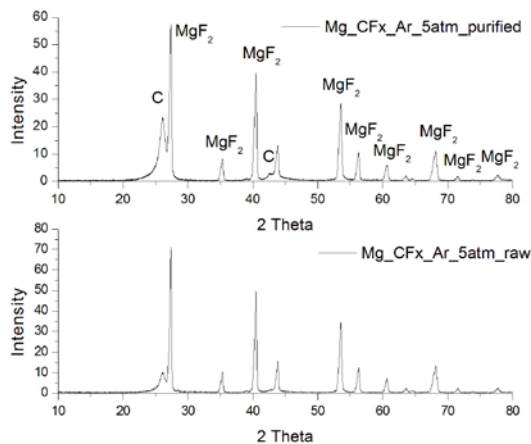
The highly exothermic reduction of carbon-bearing reactants with magnesium or silicon firstly results in atomization of all reactants. This is followed, on the quench stage, by the formation of solid magnesium oxide and/or SiCNWs while the remaining carbon vapors form also solid carbon. Surprisingly, this condensation leads towards the formation of graphite-like carbon. More interestingly, novel graphene- and carbon-related

nanostructures are also formed this happens due to fast condensation under thermal conditions close to graphitization. Such interesting preliminary results definitely call for more-in-depth research since graphene is currently considered as a wonder material of XXI century and new, efficient ways of its production are still extensively sought. To isolate the carbon phase, the raw products were leached with 3M HCl (removal of MgO and unreacted Mg) or with 30% KOH (removal of Si and SiO<sub>2</sub>).

We present below XRD measurements (phase composition of products) of selected reactants and the results of SEM observations (morphology of products).

**4.1. System Mg/CFx**

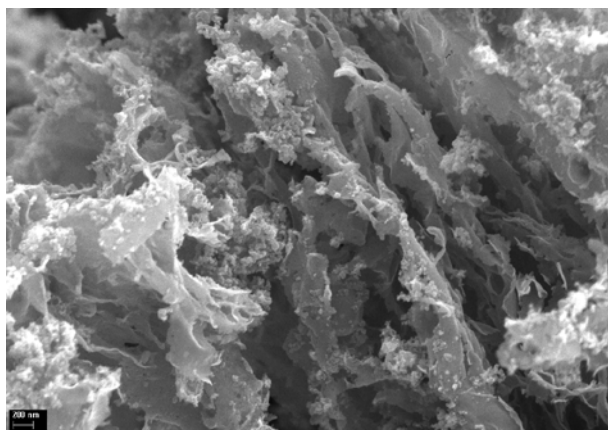
Fig. 2 shows the results of XRD analysis of products from Mg/CFx combustion in Ar (5 atm), for raw and purified material.



**Fig. 2.** XRD analysis of raw and purified product from Mg/CFx combustion

The phase composition shows that MgF<sub>2</sub> and carbon are the main components of products thus confirming the expected combustion. After the purification, the carbon peak is much more pronounced. Surprisingly, there is still some MgF<sub>2</sub> in final product thus pointing to its partial carbon encapsulation.

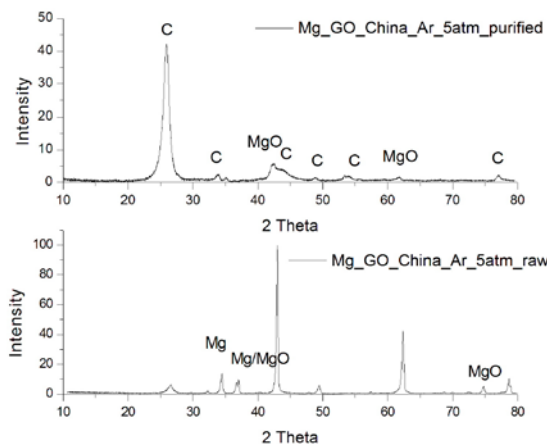
Fig. 3 presents the SEM image of the purified product. A petal-like layered microstructure of carbon resulting from de-fluorination and partial exfoliation of fluorinated graphite is evident.



**Fig. 3.** SEM spectrum of purified product (Mg/CFx combustion in Ar, 5 atm)

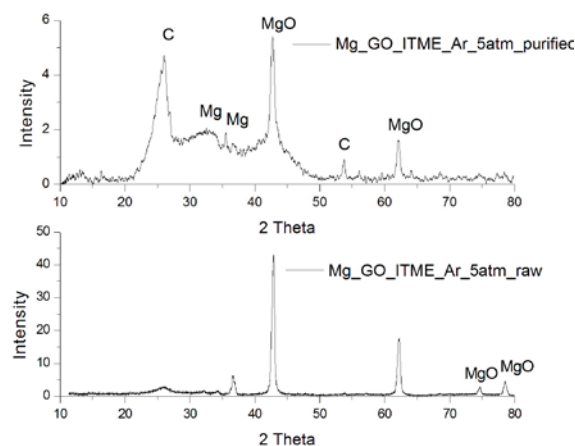
**3.2. System Mg/GO**

Fig. 4 presents the XRD spectra of products from Mg/GO combustion in Ar (5 atm), for raw and purified material (graphene oxide GO of Chinese origin).



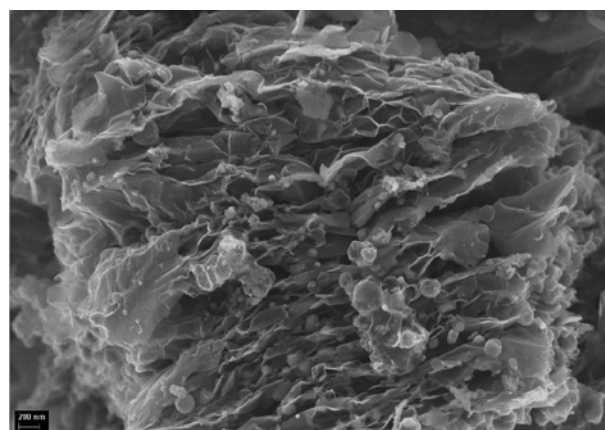
**Fig. 4.** XRD analysis of raw and purified product from Mg/GO combustion (GO of Chinese origin)

As before, those results confirm the combustion with MgO formed as the product of Mg oxidation and free carbon. The purification stage enriches the final product in carbon but there still exists some MgO, probably carbon-encapsulated. Much the same results were obtained in case of graphene oxide of Polish origin (Fig. 5)



**Fig. 5.** XRD analysis of raw and purified product from Mg/GO combustion (GO of Polish origin)

Fig. 6 shows the morphology of purified product from Mg/GO (of Chinese origin) combustion.



**Fig. 6.** SEM spectrum of purified product (Mg/GO combustion in Ar, 5 atm, GO of Chinese origin)

Again, the product has a layered microstructure. Some un-leached (this is probably due to carbon encapsulation) nanocrystallites of Mg or MgO can be also spotted in the image.

### 3.3. System Mg/CO<sub>2</sub>

Fig. 7 shows the results of XRD analysis of products from Mg combustion in gaseous CO<sub>2</sub> (20 atm), for raw and purified material.

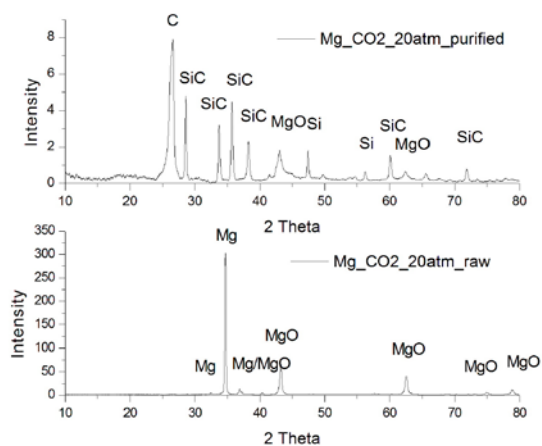


Fig. 7. XRD analysis of raw and purified product from Mg combustion in CO<sub>2</sub>

Carbon oxide is efficiently reduced with magnesium. The purified product is almost pure, well graphitized carbon.

Fig. 8 shows the SEM images of purified combustion product (starting pressure of CO<sub>2</sub> 20 atm).

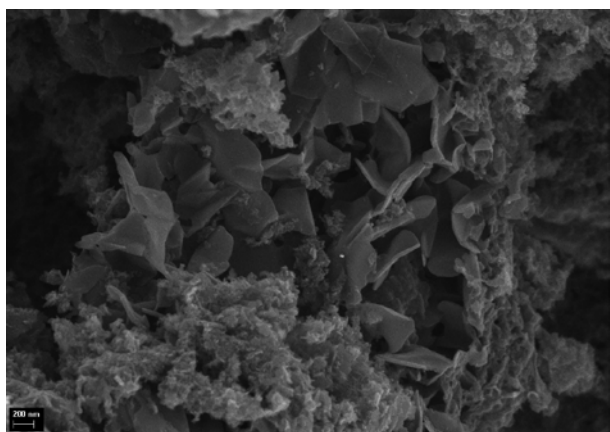


Fig. 8. SEM spectrum of purified product (Mg combustion in CO<sub>2</sub>, 20 atm)

The product is composed of both nanocarbon (soot?) and well-crystallized layered microstructures. EDX measurements are under way to qualitatively identify those interesting components.

### 3.4. System Si/CFx

Fig. 9 presents the XRD spectra of products from Si/CFx combustion in Ar (5 atm), for raw and purified material.

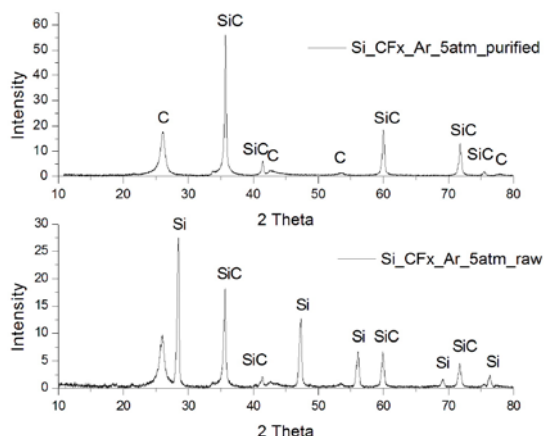


Fig. 9. XRD analysis of raw and purified product from Si/CFx combustion

Raw product contains carbon, unreacted Si and SiC while the purified product is highly enriched in carbon phase.

The morphology of the purified product is shown in Fig. 10.

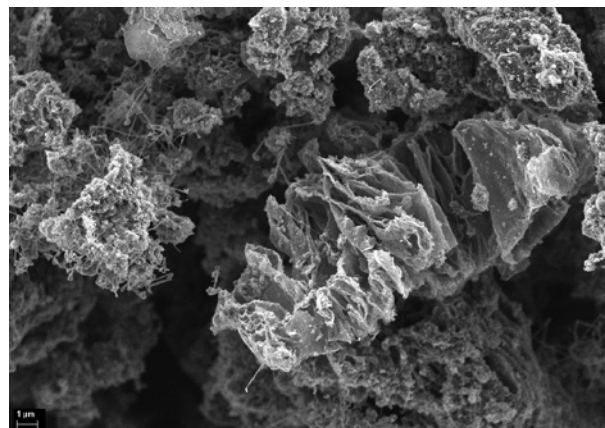


Fig. 10. SEM spectrum of purified product (Si/CFx combustion in Ar, 5 atm)

Both nanowires of SiC and exfoliated de-fluorinated starting oxidant (layered morphology) can be seen in the image. Si elemental evidently extracts fluorine and the exothermic effect of this reaction not only initiates exfoliation but also probably generates some free carbon which reacts with Si forming SiCNWs.

### 3.5. System Si/GO

Fig. 11 presents the XRD spectra of products from Si/GO combustion in Ar (5 atm), for raw and purified material (graphene oxide GO of Polish origin).

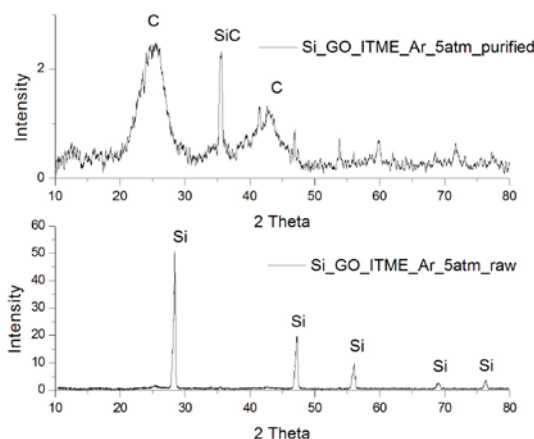
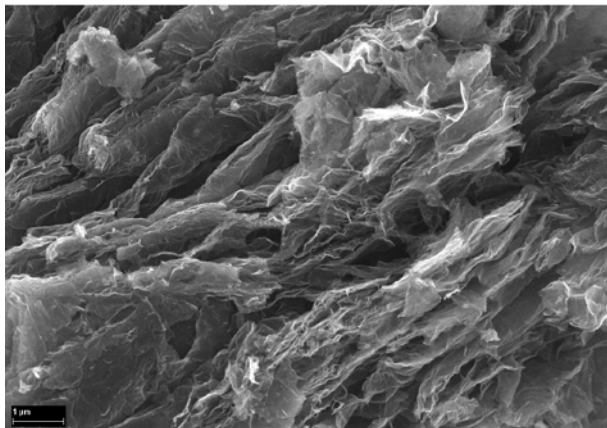


Fig. 11. XRD analysis of raw and purified product from Si/GO combustion (GO of Polish origin)

Si is much weaker reducer comparing to Mg but still can reduce graphene oxide. Surprisingly, not silica but SiC is a reduction product thus confirming such combustion is governed by kinetics (not by the thermodynamics).

The SEM image of the product is presented in Fig. 12.



**Fig. 12.** SEM spectrum of purified product (Si/GO combustion in Ar, 5 atm)

Fine and layered microstructure of the product is clearly demonstrated confirming very efficient de-oxygenation/exfoliation of the starting graphene oxide. TEM observations (under way) should provide the more-in-depth profiles of the carbon of which the thickness of sheets is of crucial importance.

#### 4. Summary

We show here that the combustion synthesis is a novel and fast route to efficiently produce interesting nanomaterials like silicon carbide nanowires and layered nanocarbons. Those preliminary results of research call, however, for a more-in-depth optimization of sought processes.

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