

# COMBUSTION SYNTHESIS: FROM SIMPLE REACTANTS TO CARBON-RELATED NANOMATERIALS

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**Abstract:** Combustion synthesis (CS) is a technique for the synthesis of various nanopowders and complex compounds. This manuscript describes principles, some recent developments in CS and its exemplary applications: formation of silicon carbide nanofibers (SiCNFs) and transformation of synthetic and natural (Nepali dolomite) carbonates into graphene-related carbon nanostructures.

**Keywords:** COMBUSTION SYNTHESIS, SILICON CARBIDE NANOFIBERS, GRAPHENE-RELATED NANOMATERIALS

## 1. Introduction

The ability of exothermic reactions to release heat has attracted the attention of researchers for ages. The exothermic reactions are also utilized for the preparation of materials. The approach of combustion synthesis uses the self-generated heat during rapid exothermic reactions which usually occur in condensed systems<sup>1</sup>. Thus, the accompanying high temperatures favor the formation of nanomaterials usually via the "bottom-up approach". The new nanomaterials synthesized via CS can find wide applications in different industrial fields such as energy conversion and storage, optical devices, catalysis, advanced ceramics and polymers, electronics, and biomedicine. The diversity of CS processing was reviewed by Morsi<sup>2</sup>.

Mukasyan and Manukyan have demonstrated a great potential of CS which can produce atomically thin two-dimensional materials for energy applications<sup>3</sup>. In fact, novel carbon nanomaterials (fullerenes, carbon nanotubes and encapsulates, graphene) are nowadays widely applied in numerous fields which utilize their unique structural and functional features<sup>4</sup>.

Graphene, a carbon honeycomb with only one-atom thickness, has superior physical properties that open great possibilities resulting in real time applications in every field of science and technology. It is efficiently produced via the 'bottom-up' techniques involving the high-temperature formation of carbon-bearing gaseous intermediates followed by the condensation of carbon gas. Among various techniques to atomize carbon-related precursors, CS opens a novel effective direction for the synthesis of graphene<sup>5,6</sup>. As for example, Zhao et al.<sup>7</sup> prepared graphene sheets by the calcination of calcium carbonate with magnesium powder.

We present here two examples which demonstrate the applications of combustion synthesis in efficient production of different carbon-related materials, namely silicon carbide nanofibers and graphene-related nanocarbons.

## 2. Experimental

All combustions were successfully accomplished using the experimental system and the protocol described in details elsewhere<sup>8</sup>. The stoichiometric mixture of powdered reactants was placed (in a quartz crucible with the immersed heating tape) in the stainless-steel pressure-resistant reactor. After adjusting the initial pressure (Ar) the combustion was ohmically initiated. After the reaction the system was cooled and the raw products were collected, purified and characterized using SEM, XRD and chemical analyses. The material balance of the combustion was also carried out. The reaction vessel enables the registration of the light emitted during combustion reaction. The example of such progressive onset of an emitted incandescence signal is shown in Figs. 1 and 2.

The combustion is very fast indeed. For both runs, the reaction duration can be estimated as only ca 1.1 s and 2.4 s, respectively. The second reaction proceeds evidently with oscillations.



Fig. 1. Example of reaction evolution vs. time (run II-1)



Fig. 2. Example of reaction evolution in time (run II-2)

## 3. Results and discussion

### 3.1 Si-(C<sub>2</sub>F<sub>4</sub>)<sub>n</sub> System

We have shown earlier<sup>9</sup> that the reaction



can be easily and efficiently accomplished as a thermally autogeneous redox process to produce silicon carbide nanofibers (SiCNFs). Here we compare the process yield using as the oxidizer both relatively expensive synthetic commercial standard TEFLON<sup>®</sup> (from Merck) and the waste polytetrafluoroethene TARFLEN<sup>®</sup> (from Grupa Azoty S.A., Tarnów). Table 1 presents the operational parameters of two combustions. Run I-1 was performed with the stoichiometric mixture of pure Si and TEFLON<sup>®</sup> whilst in run I-2 TARFLEN<sup>®</sup> waste was used as an oxidizer.

**Table 1.** Operational parameters of combustion synthesis of SiCNFs

Run #	Starting reactants	Combustion atmosphere, initial pressure, at	Peak pressure, at	Starting mass of reactants, g	Mass of raw products, g	Un-reacted Si in raw product, wt%	Total conversion of Si, %
I-1	Si/TEFLON <sup>®</sup> (36/64)	CO, 10.3	32.5	6.57	1.95	4.8	96.0
I-2	Si/TARFLEN <sup>®</sup> (36/64)	CO, 10.9	52.0	6.96	2.36	5.2	95.1

The powdered starting mixture was totally converted into greyish raw product which tightly filled the reactor (Fig. 3). Its sponge-like morphology is due to the fibrous nature.

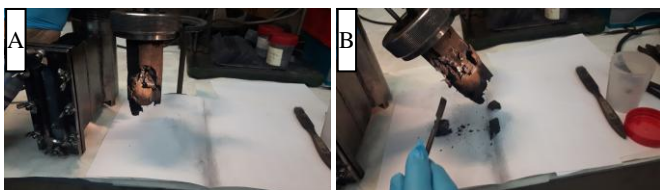


Fig. 3. Collecting the raw product (run I-2)

Fig. 4 presents the typical SEM images of the raw product (run I-2) which has nearly the same morphology for both tests performed.

The raw product is dominated by nano-sized SiC fibers (the outer diameter ca 20 nm, see Fig. 4 C) with some ball-like nanoparticles. The starting silicon is almost completely converted into SiC and SiF<sub>4</sub> (Table 1). The purification of the raw product (not reported here) along with the combustion material balance shows that SiC yield ranges between 20 and 30%. Thus, the waste polymer can be easily converted into SiC nanofibers.

### 3.2 Mg-MeCO<sub>3</sub> System

Both standard and natural (dolomite, Nepal origin) magnesium carbonates were reduced with magnesium under neutral atmosphere according to the following equation:



to produce solid carbon along with MgO. It was expected that high temperature may favor the formation of highly-graphitized carbon structure. The raw products were chemically purified (leaching with 3M HCl) to remove the un-reacted Mg and MgO. Table 2 presents the operational parameters of both runs.

The peak pressure during the combustion is much higher comparing to the starting pressure and this finding confirms high combustion temperature. Relatively low mass decrease of reactants after the combustion indicates mostly solid phase transformation of carbonates (see equation (2)) with low emission of CO<sub>2</sub> (this is probably due to the short reaction time). The elemental analysis showed that the purification procedure is very efficient and the final product contains much more elemental carbon (resulting from carbonate reduction) comparing to the starting mixture. In the case of combustion treatment of standard carbonate the final product is mostly composed of carbon elemental (74.8 wt%) the balance related to carbon-encapsulated Mg-related entities.

To better follow the transformation of reactants during the combustion the XRD spectra were measured (not shown here). The phase identification (quite complex) is under way but some important findings are already evident.

The spectra of starting material and raw product are quite different proving the deep decomposition of reactants during combustion.

The spectra of raw and purified product are different confirming the efficient purification protocol (removal of un-reacted Mg and MgO).

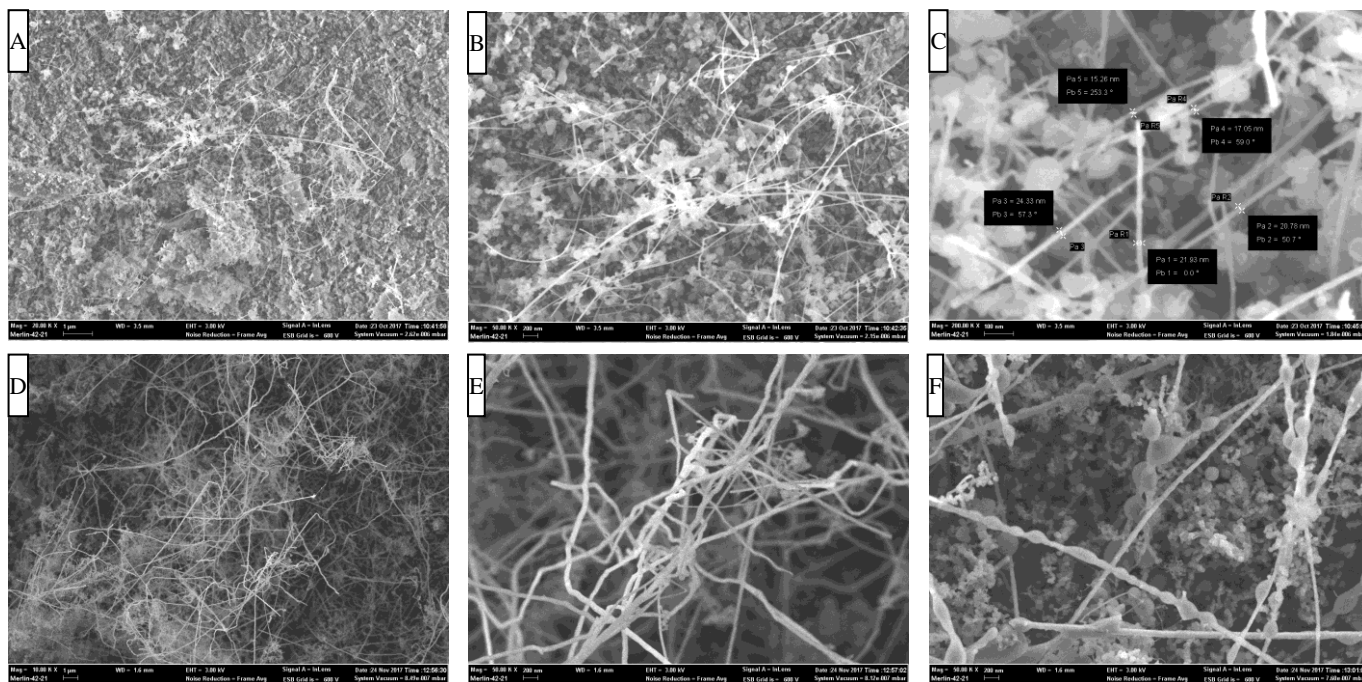


Fig. 4. Representative SEM images of the raw product (run I-2)

**Table 2.** Operational parameters of magnesium reduction of standard and natural magnesium carbonates

Run #	Starting reactants	Combustion atmosphere, initial pressure, at	Peak pressure, at	Mass of starting reactants, g	Mass of raw product, g	Mass decrease, %	C content in raw product, wt%	C content in purified product, wt%
II-1	10 Mg + 3 MgCO <sub>3</sub> ·Mg(OH) <sub>2</sub> ·3H <sub>2</sub> O	Ar, 10	60	10.37	9.95	4.1	6.1	74.8
II-2	4 Mg + CaCO <sub>3</sub> ·MgCO <sub>3</sub>	Ar, 10	20	10.05	9.96	0.9	1.8	5.0

In the spectrum of purified product a strong peak at  $2\theta = ca\ 26^\circ$  indicates the presence of carbon-related material as expected.

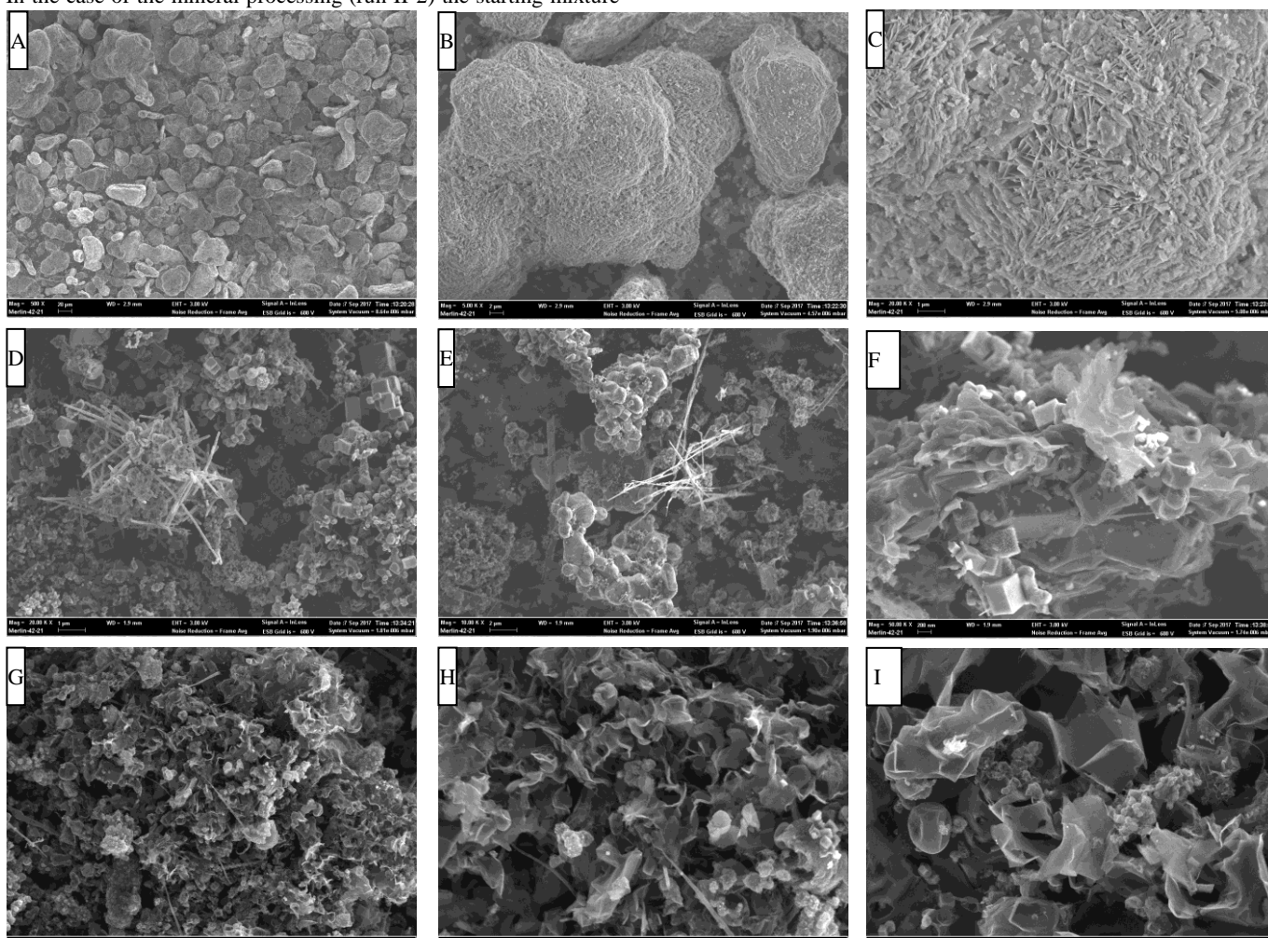
Fig. 5 and 6 present the representative SEM images of both starting mixtures and the products resulting from Mg reduction of standard carbonate (run II-1) and dolomite (run II-2), respectively. The starting mixture (run II-1) is composed of microsized particles of elemental magnesium and conglomerates of magnesium carbonate (Fig. 5). The raw product is mostly composed of well-crystallized nanocrystallites of MgO along with 1-D nanoparticles. The purified product contains nanosized petal-like (multi-layered graphene?) carbon nanoparticles, 1-D yet-unidentified objects (carbon nanofibers?) and still cubic MgO nanocrystallites. Thus, condensing carbon vapors (resulting from carbonate decomposition and atomization) partially cover MgO nanocrystallites preventing them from HCl leaching.

In the case of the mineral processing (run II-2) the starting mixture

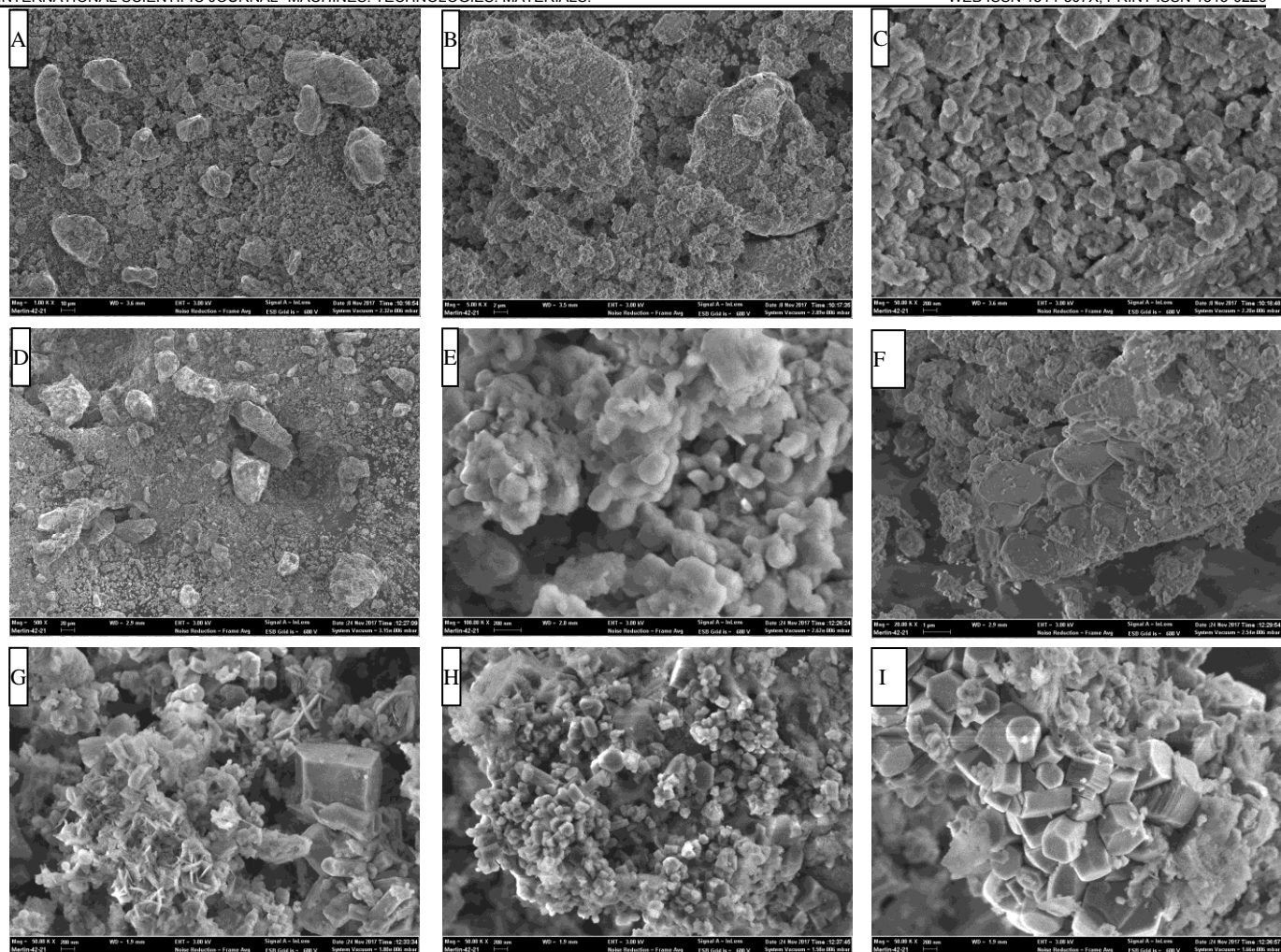
is composed of microsized particles of magnesium elemental and dolomite (Fig. 6). The raw product still contains some un-reacted starting microsized components but well-crystallized nanocrystallites of MgO can be also easily spotted. They still dominate in the purified product in which also some petal-like nanostructures are visible. This again confirms that at least partial atomization (this due to high temperature during the reduction) of the reactants takes place and the as-condensing carbon vapors partially cover MgO nanocrystallites.

#### 4. Conclusions

Combustion synthesis is characterized by high temperature which initiates the decomposition and partial atomization of the reactants followed by the fast expansion and quenching (within a fraction of second) of mostly gaseous reactants and their solidification. This creates favorable conditions for the growth of nanoobjets such as



**Fig. 5.** Representative SEM images of the starting mixture (A-C), raw product (D-F) and purified product (G-I); run II-1



**Fig.6.** Representative SEM images of the starting mixture (A-C), raw product (D-F) and purified product (G-I); run II-2

SiC nanofibers and graphene-related carbon resulting from carbonate processing.

## 5. References

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