Graphene, a unique two-dimensional (2D) array of monolayer carbon atoms packed into a dense honeycomb crystal, has attracted much attention because of its diverse and extraordinary properties, i.e., electronic, magnetic, thermal, lubricant, chemical, optical, and mechanical.1 Graphene-related materials are also postulated to be used in energy conversion and storage.2 Thus, graphene and graphene-related materials have shown many applications in nanoelectronics,2 sensors,3 composite materials,4 and in an environmental engineering.5 Carbon and graphitic materials have also been for decades a workhorse material in electrochemistry.6 Graphene was first produced by Novoselov et al. by mechanical exfoliation of graphite in 2004.8 Since then many techniques have been proposed to obtain graphene with a main approach via energy- and time-consuming wet chemistry route of graphite exfoliation. Jankovský et al.9 presented recently in details the thermal exfoliation/reduction of graphite oxide.

The focus of this work is to obtain hierarchical layered carbons. Such few-layered graphene is also called 3D graphene10 which, in fact, has many potential applications including energy storage (capacitors, electrodes), gas sensing, catalysis, biomedicine (biocompatible scaffolds), adsorption, hydrogels, and composites. As for example, Zhang et al. reported recently the synthesis of porous 3D graphene-based material with excellent properties for such applications.11

Herein we apply a self-propagating high-temperature synthesis (SHS), also called combustion synthesis (thermolysis) which has been widely used for years for fabrication of many compounds with large negative heat of formation.12,13 Such fast process usually progresses in a self-sustaining and energy self-efficient regime.1 In fact, we have shown elsewhere that SiC nanowires can be efficiently synthesized from simple starting reactants (Si/Teflon).14,15 Zhao et al. presented recently16 an approach for synthesizing graphene through a magnesiothermic reduction of calcium carbonate, while Poh et al.17 synthesized graphenes for electrochemical applications via reduction of CO2 by lithium.

The aim of this work was to test such a synthetic strategy for converting carbon-containing Ca/Mg oxalates into 3D graphene-related materials. The electrochemical measurements were performed to evaluate the potential application of the carbon material in the energy storage. The exploratory study was also carried out to test the adsorption properties of this material.

**Results and Discussion**

All thermolyses were carried out in the high-pressure reactor following the protocol outlined elsewhere.18 A wide range of stoichiometry of the reactants and the operational parameters were tested (Table I). Please note that the reactions were carried out using the stoichiometric ratio of the reactants, and the excess and the insufficient amount of the reducing agent (Mg).

Well-mixed reactants were placed in a quartz crucible, with a carbon thread (an electrical igniter) which was immersed inside. All combustions proceeded spontaneously following the reaction scheme

\[
\text{Mg} + \text{Ca} + \text{C}_2\text{O}_4 \rightarrow \text{Mg} + \text{Ca}_2\text{O} + \text{CO}_2
\]

The anhydrous Ca/Mg oxalates and MgC2O4 hydrate (POCH Gliwice, Poland) were mixed with fine (grains size ca. 40 μm) and coarse (grain size ca. 240 μm) magnesium (Merck). The runs were mostly carried out under neutral atmosphere (Ar, atmospheric and high pressure). In the run J the carbon thread was replaced with tungsten wire to test whether the wire can interfere the process as a potential source of carbon in solid products. Two combustions (K and L) were performed under CO2 atmosphere to check whether carbon dioxide can be also concomitantly reduced with Mg to solid carbon as was reported elsewhere.19

After the thermolysis the reactor was cooled down and the fluffy and blackish solid product was collected both from the crucible and the reactor walls. The as-obtained (raw) product was mixed and analyzed (XRD, SEM) before the purification. The unreacted Mg and the as-produced Ca/Mg oxalates were leached with 3 M HCl solution (at 90°C for 30 min). The purified product was washed with ethanol and dried overnight before the analyses (XRD, SEM, TGA and Raman spectroscopy). The electrochemical properties of the produced carbon material were studied using a method described elsewhere.20 The adsorption performance was tested via the removal of 4-chlorophenol from water. The concentration of stock solutions varied between 150 and 1360 nmol/dm³. 25 mg of tested carbon material was added to a vial containing 25 cm² of the stock solution. The equilibrium concentration was measured using UV-Vis spectrophotometer after 24 h.
Table I. Operational parameters of all runs (including both Ca and Mg oxalate).

| Run # | Composition     | Molar ratio of reactants | Atmosphere and starting pressure, MPa | Mass of starting composition, g | Mass of solid products, g | C content in product, wt% |
|-------|-----------------|--------------------------|----------------------------------------|---------------------------------|---------------------------|--------------------------|
| A     | Mg/CaC$_2$O$_4$ | 1:1$^a$                  | Ar; 0.1                                | 4.52                           | 3.45                      | 2.25                     |
| B     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | Ar; 0.1                                | 4.37                           | 3.58                      | 3.98                     |
| C     | Mg/CaC$_2$O$_4$ | 9:1$^a$                  | Ar; 0.1                                | 4.52                           | 4.32                      | 0.56                     |
| D     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | Ar; 0.1                                | 5.08                           | 2.99                      | 2.47                     |
| E     | Mg/CaC$_2$O$_4$ | 9:1$^{(stoich.)}$       | Ar; 0.1                                | 5.24                           | 4.15                      | 0.73                     |
| F     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | Ar; 1.0                                | 4.81                           | 3.92                      | 4.84                     |
| G     | Mg/CaC$_2$O$_4$ | 9:1$^a$                  | Ar; 1.0                                | 4.50                           | 4.33                      | 0.38                     |
| H     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | Ar; 1.0                                | 5.51                           | 5.51                      | 2.93                     |
| I     | Mg/CaC$_2$O$_4$ | 9:1$^b$                  | Ar; 1.0                                | 5.96                           | 5.70                      | 0.97                     |
| J     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | Ar; 1.0                                | 13.88                          | 12.10                     | 17.08                    |
| K     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | CO$_2$; 2.0                            | 5.25                           | 5.02                      | 1.14                     |
| L     | Mg/CaC$_2$O$_4$ | 3:1$^{(stoich.)}$       | CO$_2$; 2.0                            | 2.82                           | 2.62                      | 1.30                     |

$^a$fine Mg.
$^b$coarse Mg.

Signal Diagnostics (LSD) approach has been developed$^{21}$ which enables the on-line determination of the reaction duration and tracking of its progress.

The combustion time differs significantly for the tested compositions, as the example this parameter starts from less than 0.80 s for run C; 1.0 s for run B and even up to 24 s for run A. The flame oscillations and the spread of red-hot material in the combustion chamber were observed.

The combustions were accompanied by a pressure jump reaching 4 MPa (for runs with starting pressure 1 MPa) which results from high temperature expansion of, partially gaseous, intermediate reactants. As reported elsewhere,$^{21}$ the average combustion temperature determined from emission spectroscopy for a relatively mild reducer (compositions Si/PTFE) is close to 2000 K. In case of much stronger reducer (Mg) the combustion temperature is obviously much higher, not only exceeding the Mg melting point (923 K), but also the boiling point (1364 K) can be easily reached. Thus, one can reasonably expect that the thermolysis proceeds partially in gas phase.

The XRD diffractograms of the selected products (Mg/CaC$_2$O$_4$, runs A-C, both the raw and purified material) along with the diffractogram for the initial reactant mixture are shown in Figure 2. The graphs confirm the deep transformation of the reactants into sought products, with the total disappearance of the starting oxalate in the as-obtained products. The raw products are dominated by MgO and CaO, along the presence of some unreacted Mg. The increase of its content is in line with the content of Mg in the initial mixture. The side reaction is also evidenced by the presence of Mg carbonate resulting from the reaction of MgO with carbon dioxide, which evolves during the thermal decomposition of the oxalate. The phase composition of the product collected from the crucible was almost identical with the product recovered from the reactor’s walls, thus confirming that the combustion is progressing with the partial expansion of the voluminous product outside the crucible. The purified product is dominated by turbostratic carbon with the best graphitization obtained for a stoichiometric composition (run B). Surprisingly, the purified product also contains some CaO which, presumably, was not leached in the acid during purification and plausibly CaO crystals are encapsulated in protective carbon coatings.$^{22,23}$ The highest graphitization of carbon for the stoichiometric composition (run B) was confirmed by TGA analyses (Figure 3) which showed the highest oxidation resistance for the purified product from run B.

Figure 4 shows the representative SEM images of the products. The raw non-homogeneous product is dominated by, mostly cubic, nano- and micro-crystallities of carbon-coated metal oxides (ca 50–200 nm in diameter) with some un-reacted round-shaped Mg particles (surface-decorated with carbon and metal crystallites). This observation confirms that some particles of Mg are melted during the combustion process. The layered carbon nanostructures and spherical shells are, however, also spotted in a raw product. Such few-layer graphene shells were also obtained recently by Bachmatiuk et al.$^{24}$ The presence of carbon-related material is clearly evidenced in the SEM images of the purified product. This material is dominated by petal-like 3D graphene material forming both a kind of a ‘Swiss cheese’ carbon matrix and hollow carbon nanospheres, clearly resulting from the etching of metal oxide and Mg.$^7$

The purified products were also studied using Raman spectroscopy (Figure 5) and the acquired spectra were deconvoluted and fitting using Lorentzian function (the goodness of fit- $R^2$ factor was 0.99). All spectra are dominated by G, D and 2D bands as expected.$^{25}$ The lowest D/G ratio (the lowest density of defects), equal to 0.33, was 0.33.
Figure 2. XRD spectra of selected samples: starting composition (B), raw and purified products.

again found for the stoichiometric composition (run B). The highest 2D/G ratio (3.30) was also obtained for this product thus confirming the best ordering and the thinnest layered carbon.

The combustion processes were also carried out with a coarse-grained Mg powder, under atmospheric (runs D and E) and higher pressure (H and I). The XRD diffractograms of raw and purified products do not essentially differ (not shown here) from the runs with fine-grained reducer at atmospheric pressure (A-C). However, the unreacted oxalate was also spotted in a raw product thus indicating the lower conversion yield of the reactants. This finding was confirmed by the balance of mass which showed the lower content of carbon in products. Thus, melting and evaporation of the reducing agent
(Mg) is less advanced, as expected, for the coarse-grained Mg. This observation does not strictly hold under higher pressure (1 MPa) when the conversion yield is higher. At higher pressure the expansion of gaseous reactants is evidently hampered and results in higher reaction temperature which finally favors Mg phase transformation. Thus, even the coarse-grained reducing agent particles can partially vaporize and the factor of limited diffusivity is not pronounced any longer. The XRD diffractograms of purified products are dominated by carbon, with the traces of MgO and CaO. It again confirms the partial carbon encapsulation of the resulting metal oxides. Regardless the pressure, the graphitization of carbon is lower for the coarse-grained reducer. The SEM images of the products (Figure 6) are similar to the ones obtained for the fine-grained reducing agent. The purified products are composed of petal-like layered graphite and/or hollow spherical
The purified samples were also analyzed using the Raman spectroscopy. The results (spectra not presented here) show the lowest amount of defects of carbon network for stoichiometric compositions (with a coarse-grained Mg) with the 2D/G ratio equal to 7.83 and 5.16 for combustion initial pressure equal to 0.1 and 1 MPa, respectively. The product from run D can be regarded as a few-layered turbostratic graphene.\textsuperscript{26}

The purified samples were also analyzed using the XRD of the products (not presented here) show slightly lower amount of defects of carbon nanostructures (higher 2D/G ratio) for the run under higher pressure.

To confirm the versatility of the proposed approach the combustions with Mg/MgC\textsubscript{2}O\textsubscript{4} compositions (runs J-L) were carried out, both at higher pressure in Ar and CO\textsubscript{2} atmosphere. The morphology of the raw and purified product from Mg/MgC\textsubscript{2}O\textsubscript{4} (run J with tungsten wire instead of carbon thread as an igniting element) composition does not differ from the thermolysis of CaC\textsubscript{2}O\textsubscript{4} (Figure 8). Thus, the carbon thread can be excluded as a potential source of carbon material in products. The magnesium grains ‘glued’ in the fine Mg oxalate (starting mixture) are completely transformed into the mixture of carbon and cubic MgO nanocrystallites. Surprisingly, the raw product contains also 1D nanostructures and their identification (plausibly carbon nanotubes) is under way. The purified product partially resembles the raw product thus confirming the ‘carbon shielding’ of the products during their formation. However, the 1D nanostructures are still perfectly identified, too, along with the punctured (the removal of Mg/MgO) product thus confirming the ‘carbon shielding’ of the products during their formation.

From the data presented in Table I the mass balance of all combustions was carried out and the total conversion of oxalates (see Eq. 1) was estimated. The transformation of the starting carbon (i.e. in the Mg/oxalate mixtures) into solid carbon in the purified product depended upon the operational parameters and varied between 6.03 and 76.83\%, with the highest conversion for the stoichiometric composition. The transformation yield for the Mg/MgC\textsubscript{2}O\textsubscript{4} composition (run J) was higher than 100\% and this finding clearly reveals the extensive carbon encapsulation of Mg-related compounds.

The relatively low yield of solid carbon from the reduction of hydrated magnesium oxalate in CO\textsubscript{2} atmosphere (runs K and L) points to the partial removal of formed carbon (both from oxalate and the reduced CO\textsubscript{2}) via the water vapor conversion. The thermal decomposition of the oxalate with the evolution of carbon dioxide is also expected to be hampered under these conditions (Le Chatelier’s principle). The expected reduction of CO\textsubscript{2} (combustion atmosphere) with Mg also seems to be negligible since the morphology of the raw and product and was acid-etched during the purification protocol. The Raman spectra of the products show the lowest amount of defects of carbon network for stoichiometric compositions (with a coarse-grained Mg) with the 2D/G ratio equal to 7.83 and 5.16 for combustion initial pressure equal to 0.1 and 1 MPa, respectively.
purified product resembles the carbon produced in Mg/CaC₂O₄ runs, regardless the applied initial pressure of carbon dioxide (Figure 9).

The produced 3D graphene (the purified product from run B) was tested as an electrode for the supercapacitors applications. In fact, Hu et al.²⁷ obtained recently mesoporous carbon materials for binder-free supercapacitor. Figure 9a shows the cyclic voltammetry (CV) curves of a prepared electrode at various scan rates. The CV curves at various scan rates show that the current increases with an increase of the scan rate and the potential expands gradually. The maximum area enclosed in the cyclic voltammograms is an indication of increasing conductivity and better capacitive performance. The shape of the voltammograms appears nearly identical, suggesting high cyclic stability of the electrode material. Figure 10c shows the charge/discharge curve of a sample at various applied currents in the potential range of 0–0.8 V. The specific capacitance \( C_{sp} \) of the electrode was calculated according to the following equation

\[
C_{sp} = \frac{I \Delta t}{\Delta V \times m}
\]

where: \( I \) is the discharge current (A), \( \Delta t \) is the discharge time (s), \( \Delta V \) is the potential window (V), and \( m \) is the mass (g) of the active carbon material. The specific capacitance of the prepared electrode was 187 F g⁻¹ at the current of 1 A/g. Those results clearly justify high potential of the produced carbon material in terms of its application in supercapacitors. To further evaluate the electrochemical behavior of the prepared material the EIS measurement was also carried out. Figure 10c presents the Nyquist plot of the sample. The impedance spectra are composed of one semicircle (Figure 10b) in the high-frequency range corresponding to the double-layer capacitance and a straight sloping line in the low-frequency range is corresponding to the diffusive resistance proving the Warburg behavior. Further, the diameter of the semicircle corresponds to the charge transfer resistance resulting from a charge transfer through the electrode–electrolyte interface. Such result demonstrates that the prepared electrode material can provide a convenient pathway for the ion and electron transport.

The adsorption properties of the purified material from run B were investigated in the removal of 4-chlorophenol from water. The adsorption isotherms (Figure 11) were determined for the purified and activated material. The activation procedure included annealing at 600°C using KOH as the activation agent (the mass ratio of carbon material and KOH was 1:3). The activation process resulted in the mass loss of 20%. The purified material has relatively weak adsorption properties and its equilibrium adsorption capacity is ca. 60 mmol·g⁻¹, whilst the activated material increases its adsorption performance by the factor of four (260 mmol·g⁻¹).

Conclusions

We report an extremely fast (within a fraction of a second) thermolysis of magnesium-Mg/Ca oxalate mixtures which results in the formation of solid products containing partially carbon-covered MgO/CaO nanocrystallites and layered turbostratic graphene-related material. The extensive parametric studies showed that the highest yield of the sought products was obtained for the stoichiometric composition of reactants and at higher pressure. At lower Mg content only a part of the oxalate is deeply reduced (to solid carbon) and the thermal decomposition of the starting salt (with the evolution of carbon oxides) may prevail in the system while in case of an excess...
of the reducer the reaction heat is partially consumed for the phase transitions of Mg (melting/vaporization) only. The higher pressure obviously favors higher reaction temperature preventing the expansion of reactants. The interesting morphology of the produced 3D graphene-related material suggests its suitability for the prosperous applications. Indeed, the remarkable electrochemical and adsorption properties were preliminarily assessed.

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