

Large scale production of few layer graphene from novel plasma reactor system

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ABSTRACT

We are presenting a novel method of catalyst-free continuous large scale production of graphene from a gaseous hydrocarbon feedstock in our proprietary plasma reactor system. Controlling the operation parameters of the non-equilibrium inert/hydrocarbon gas plasma from our in-house designed systems allows for hydrocarbon conversion efficiencies of up to 90 % at flow rates of up to 30 L/min. We are showing the strong dependence of crystallinity and morphology of the product on plasma properties according to varied operating parameters such as gas composition and power rating. Transmission electron microscopy was employed to determine the nanostructure of material from different sets of parameters. Crystallinity of samples was determined by Raman spectroscopy and thermogravimetric analysis. BET surface area measurements of as synthesized samples reached up to 300 m² g⁻¹ with a narrow mesopores range of 7.2-9.9 nm corresponding to stacks of about 15 graphene sheets. Small amounts of a gaseous by-product evolved during plasma processing was qualified and quantified by gas chromatography.

Keywords: Graphene, nanocarbon, atmospheric pressure microwave plasma, methane

1 INTRODUCTION

Graphene is believed to have the potential to revolutionise our everyday life due to its exceptional mechanical properties (high strength and elasticity), high electrical and thermal conductivity, impermeability to gasses or transparency to light¹. However, the market of wide and versatile range of graphene applications may be impeded as we are lacking a large scale and cost efficient graphene production method. It is predicted that advanced graphene electronics requiring relatively perfect films of big area will not leave a laboratory space soon². Therefore, the growth is predicted for graphene nano-platelets mainly for applications in composite materials (enhancing their strength, electrical and thermal conductivity), conductive paints and inks (conductive coatings, antistatic and electromagnetic shielding, corrosion protection, gas barrier applications etc.), and energy storage and generation^{1,2}.

In order to exploit the large scale potential of graphene, we focused on a plasma approach as a synthesis technique.

Plasma synthesis of graphene flakes is a bottom-up technique of which arcs^{3,4} and inductively coupled⁵ plasmas have been reported in the literature. However, these plasmas require the use of expensive noble gases (helium or argon), vacuum or low pressure operation, high purity graphite electrodes with a complicated cooling system. They also face the difficulty of being continuous, rather than batch ones. Therefore, microwave plasma processes run at the atmospheric pressure are especially promising^{6,7,8}.

Microwave plasma lacks of thermodynamic equilibrium between electrons and other plasma species (radicals, ions, particles). Thus, processes occurring in plasma are determined mostly by electrons' temperature, making them less sensitive to thermal processes and the temperature of the gas as in thermal type of plasma. This allows the potential of running processes under milder conditions, with reduction in the complexity of the process and increased energy efficiency. Also it offers the possibility to exceed conventional processes in efficiency and selectivity, enabling the use of cheap reagents like methane, which otherwise in thermal processes would be decomposed with poor yield and high energy input necessary⁹.

2 EXPERIMENTAL

Research was conducted on a novel, double vortex, 6 kW atmospheric pressure, microwave (2.45 GHz) plasma reactor, developed by GasPlas AS, of which a schematic is presented in Fig. 1. The power supply allowed for the microwave power to be continuously changed up to 6 kW. Thanks to the tuning system, efficient power transfer from the magnetron to the reactive gas could be achieved: the reflected MW power was therefore low, below 2% of incident power.

Table 1. Plasma parameters used for synthesis of carbon samples.

Sample	Power [kW]	N ₂ flow [L min ⁻¹]	CH ₄ flow [L min ⁻¹]
A	1.5	27	3
B	2	24	6
C	3	14	16

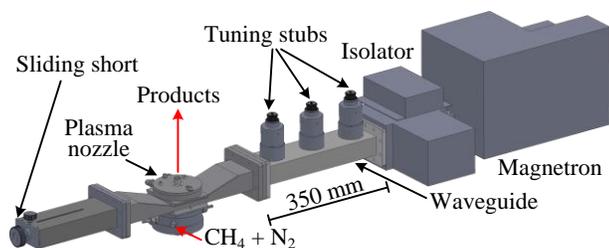


Figure 1: Schematic of GasPlas 2.45 GHz, 6 kW atmospheric pressure microwave plasma reactor.

Plasma system was supplied with a mixture of nitrogen and methane. Total flow rate of the input gas mixture was kept constant at 30 L min^{-1} but the composition varied (Table 1). At the gas output a quartz tube with an internal diameter of 17 mm was connected to the plasma nozzle. Solid carbonaceous product was collected for further analysis from the inner walls of the tube. The concentration of gas components exiting the system was measured with a detector and gas chromatograph. Solid carbon samples were collected after plasma processing at parameters listed in Table 1.

3 RESULTS

Both gaseous and solid products of plasma reactions were subjected to analysis. In ideal case, the only product of methane splitting would be hydrogen and carbon, according to equation (1). In practice the complete splitting is unachievable and also unavoidable recombination of plasma reactants takes place synthesising acetylene, ethylene and ethane in the ratios as presented in Fig. 2 for 1.5 kW process. The 2 and 3 kW processes resulted in similar amounts of components (up to 1.5 % difference).

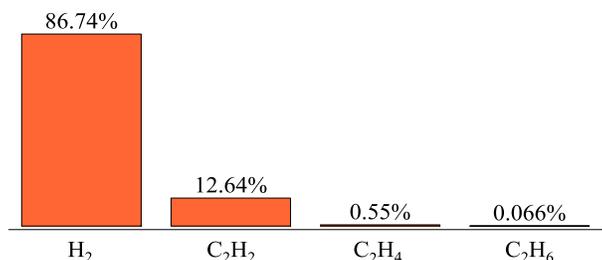


Figure 2: Volumetric composition of synthesised gaseous products in output gas during 1.5 kW, $27 \text{ L min}^{-1} \text{ N}_2$, $3 \text{ L min}^{-1} \text{ CH}_4$ plasma processing.

The carbonaceous product varied in physical properties depending on the plasma operating parameters. As imaged by transmission electron microscopy (TEM), carbon structures synthesised at 1.5-2 kW of absorbed power,

appeared in the form of thin graphene-like flakes and sheets (Fig. 3a, b), folded, crumpled and overlapped on a TEM grid. When magnified the folding places, number of graphitic layers could be estimated (Fig. 3c-e) which was the most commonly below 20. Double and single layer graphene was also captured frequently within the sample (Fig. 3d, e). These low power samples were selective and uniform in terms of graphene-like structure type. Amorphous and disordered graphite structures were absent. Operating at 3 kW microwave power resulted in mainly disordered graphitic carbon material, broadly described as carbon black (Fig. 4a-c). Graphene-like structures could be also noticed (Fig 4b) but not with the purity and selectivity, as in samples A and B. Graphitic structures were of high number of layers (tens to hundred) which were disordered towards each other (Fig. 4c). Graphitic spheres (Fig. 4a) and tubular structures were also noticed. Although some of the amorphous carbon spheres appeared after runs at 3 kW, they were in minority and uncommon.

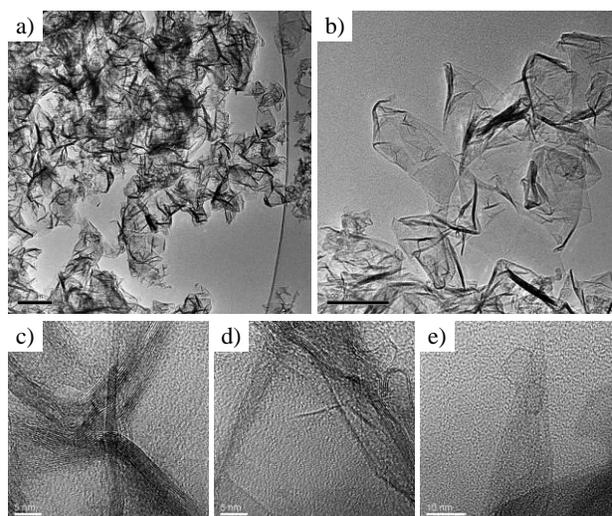


Figure 3: TEM micrograph of carbon sample B (2 kW): a), b) overview of graphene-like structures folded and overlapped; c), d), e) graphene folds magnified with single and double layer graphene in d) and e).

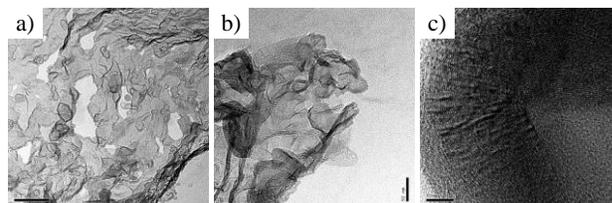


Figure 4: TEM micrograph of carbon sample C (3 kW): a) overview of disordered graphitic structures; b) graphene-like structures circled embedded within disordered carbon black; c) magnification of thick disordered graphitic sheets.

Morphologically, the low power structures appeared as tens of nanometres rods (Fig. 5a), while 3 kW power structures were spherical and bigger, 90-150 nm diameter

(Fig. 5b), as imaged by scanning electron microscopy (SEM).

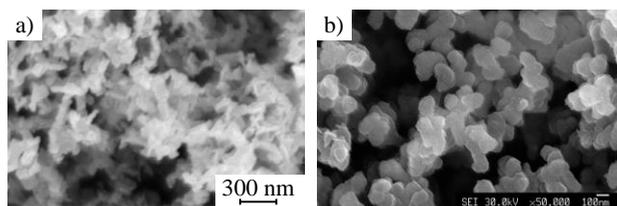


Figure 5: SEM micrograph of carbon samples prepared in a) 1.5 kW, b) 3 kW processing.

Table 2. BET surface area of carbon samples.

Sample	A (1.5 kW)	B (2 kW)	C (3 kW)
BET surface area [$\text{m}^2 \text{g}^{-1}$]	262.4 ± 1.5	264.6 ± 1.7	197.5 ± 1.1

BET surface area (nitrogen adsorption and desorption isotherms at 77 K) for samples A and B was similar, and higher than for the sample C (Table 2). The B sample was subjected to 85 min ultrasonication process at room temperature in chloroform, in order to investigate whether graphene platelets further delaminate and surface area increases. No changes in surface area were measured.

In order to check samples crystallinity Raman spectroscopy of He-Ne 633 nm laser ($\sim 2 \mu\text{m}$ spot size) was performed on powders. Spectra were taken on several spots within the same sample. Fig. 6 presents the averages for samples B (2 kW) and C (3 kW). Spectrum of sample A (1.5 kW) was very similar to the B one. Raman spectra present three dominant peaks: *D*, *G*, and *2D* bands. Presence of the *D*-band at about 1328 cm^{-1} , also called a disorder-induced band, is attributed to sp^3 bonding, often associated with impurities, poor graphitisation, and disordered graphitic structures. However, when analysing graphene material this peak cannot be explicitly attributed to impurities or structural defects. Edges of graphene sheets always appear as sp^3 structures, giving the rise to *D*-band. In the conditions of these measurements, where laser spot size is bigger than a single sheet, these edges were for sure captured. However, even when present, the *D*-band is narrow, and its relative intensity to *G*-band is between 0.50-0.76 for researched samples. The position of *2D* band is similar for A and B samples, but shifted towards lower wavenumber when compared to the sample C. This shift can be attributed to reduced number of graphitic sheets within 1.5-2 kW structures in comparison to 3 kW ones [12]. This conclusion is also supported by TEM observations.

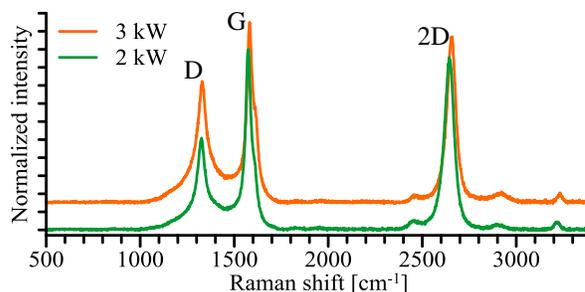


Figure 6: Raman spectra of carbon samples from 2 and 3 kW plasma processing normalised versus *G*-band. 3 kW spectrum is shifted vertically for clarity.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) performed on the samples in flowing air atmosphere confirms complexity of structures, observed before by TEM. From the thermal analysis as presented in Fig. 7 for B sample (2 kW), two significant mass loss regions can be easily distinguished, suggesting polymorphism of the structures within the sample. The oxidation temperature of carbonaceous material depends on wide range of factors like the degree of graphitization, density of crystalline defects, porosity, the conformation of the graphitic planes (zig-zag is easier to oxidise, armchair harder) and the crystallite size. From TEM was observed that 1.5 and 2 kW samples were consisted of graphene-like platelets with different number of graphitic sheets. It is speculated that the first main mass loss region of about 19% between $500\text{-}600 \text{ }^\circ\text{C}$ can be associated with oxidation of a few layer and small in size graphene platelets. The major mass loss of about 80% in the temperature range of $600\text{-}700 \text{ }^\circ\text{C}$ is believed to be a result of thicker and larger platelets oxidation. As seen by TEM they indeed were in majority. 3 kW sample had wider oxidation temperature range ($450\text{-}800 \text{ }^\circ\text{C}$) with no significantly dominant phase, which is in agreement with presence of thicker graphitic plates and bigger variety of formations shown by TEM.

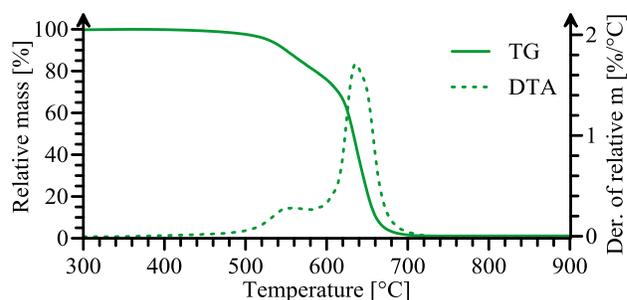


Figure 7: Thermogravimetry (TG) and differential thermal analysis (DTA) of B carbon sample (2 kW) performed in flowing air atmosphere. Two distinctive mass loss regions are clearly distinguished.

Carbon material was not collected quantitatively during presented plasma processes. However, solid carbonaceous material synthesis rate could be estimated basing on the composition of input and output gas as indicated by conducted gas chromatography. Doing so it was calculated that the potentially valuable graphene-like structures were synthesised at the rate of about 0.15 and 0.73 g min⁻¹ during 1.5 and 2 kW processing respectively.

4 CONCLUSION

This contribution presents the clear possibility for synthesis of graphene structures in a gas-phase in the atmospheric pressure microwave plasma reactor, without a use of either substrate or catalyst. High purity samples were synthesized at powers 1.5 and 2 kW. With increased power (3 kW) samples polymorphism increases, resulting in thick disordered graphitic formations, but also graphene-like and amorphous carbon inclusions. TGA/DTA confirms samples' lack of homogeneity. Although Raman *D* to *G* bands intensity is irrelevant as the direct samples quality indicator, sharpness and narrowness of the peaks proves good crystallinity of 1.5-2 kW samples which deteriorates for the 3 kW one. Formed particles are less than 150 nm in size and differ morphologically from smaller rods (1.5-2 kW) to bigger spheres.

GasPlas atmospheric pressure microwave plasma reactor enables graphene-like structures to be synthesised at the scale larger than reported so far in the literature. Although more work is needed to achieve material uniformity, ideally as the mono or double layer graphene, we believe that this procedure will emerge as the most efficient among known so far processes of graphene harvesting or synthesis.

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