Influence of plasma discharge instability on the synthesis of graphene nanosheets in dual-channel microwave plasma torch at atmospheric pressure

J. Toman[1], O. Jasek[1], M. Snirer[1] , V. Kudrle[1] & J. Jurmanova[1]

[1]*Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic*

Abstract: Influence of the interplay between central (Q_C) and secondary (Q_S) channel gas flow as well as delivered microwave power (P_{MW}) during graphene nanosheets synthesis in microwave plasma was investigated. Argon was used as a working gas as well as a carrier gas for ethanol precursor. In dual channel configuration, plasma discharge can be sustained even at high flow rates of ethanol due to the separation of working and carrier gas. Depending on the Q_C, Q_S flow rates and delivered microwave power, high quality carbon nanostructures with controlled properties were prepared.

Keywords: graphene, nanosheet, microwave, plasma, torch, decomposition, synthesis

1. Introduction

Decomposition of various hydrocarbon precursors in plasmas sustained by microwave (MW) radiation at atmospheric pressure conditions is widely used technique for synthesis of broad range of carbon nanomaterial. Graphene nanosheets is one of the last studied. Considerable amount of research has been done since 2008 in the problematics of controllable and scalable production of graphene nanosheet material at atmospheric pressure conditions. It was shown by Dato et al. [1] that MW plasma synthesis is one-step process suitable for time-effective, continuous production of graphene nanosheet nanomaterial. Based on his research, it was hypothesized, that ethanol together with dimethyl ether (DME), exhibiting identical stoichiometry, could have the ideal ratio of C, H and O atoms for controllable graphene synthesis [2]. Work done by Fronczak et al. [3] investigated aliphatic monoalcohols (from ethanol to decanol) by decomposition in radio frequency thermal plasma jet, with similar results, supporting previous hypothesis. In 2013, a single-step method was developed by Tatarova et al. [4] using MW atmospheric pressure plasma driven by surface waves. Their early work discussed decomposition of ethanol vapours in surface wave microwave discharge, complemented with theoretical model made by Tsyganov et al. [5] , which could model and experimentally map the particle and thermal fluxes in the reactor. Identical approach was recently applied to investigate use of methane as a precursor, with much narrow range of operational conditions resulting in growth of graphene nanosheets [6].

2. Experimental

A schematic view of the experimental set-up used with a detailed view of the nozzle configuration is shown in Fig. 1. The experimental equipment consisted of a microwave generator, working at standard frequency of 2.45 GHz, 2 kW maximum power P_{MW}, connected to a standard rectangular waveguide and transmitting the MW power through a coaxial line to a hollow nozzle electrode. Argon for plasma ignition and sustainment was supplied to the discharge chamber through the central channel of the carbon electrode, and secondary channel served for ethanol precursor delivery. Reactor chamber consisted of 20 cm long quartz tube with 8 cm diameter. terminated by aluminium flange. Synthesized nanopowder was collected from the reactor wall or on the Si/SiO_2 substrates placed in the z-axis of symmetry, 10 cm above the tip of the electrode. External parameters involved in the study were central channel argon flow rate Qc ranging from 220 to 920 sccm, secondary channel argon gas flow rate Qs ranging from 300 to 1400 sccm and MW power changed from 140 to 350 W.

Optical emission spectroscopy (OES) was performed to obtain necessary information needed to associate the changing material properties with specific change of plasma parameters in dependence on changing external parameters. Ethanol decomposition resulted in presence of CN, C_2 molecular bands and C, Hα and Ar atomic lines in visible range. Rotational temperatures were obtained from fitting CN band spectra and were used to approximate neutral gas temperature using simulation in Massive OES software [7]. Digital photographs were analysed by (SSIM) similarity image analysis [8] to determine level of stability of MPT discharge.

To obtain more detailed information about the material structure Raman spectroscopy and XPS were used. The synthesized carbon nanostructures were analyzed by Raman spectroscopy at the range of 1000 to 3200 cm^{-1} by changes in the shape and integrated intensity of D (~ 1350 cm^{-1}) and 2D (~2690 cm^{-1}) peaks normalized to the "graphite" G (~ 1580 cm^{-1}) peak. The XPS analysis of C1s region was carried out with aim to investigate bond structure of carbon material. The peaks centred at 284.4±0.1 eV and 285.2±0.1 eV were assigned to sp^2 and sp^3 hybridized carbon. Carbon atoms bound to oxygen are also detected with peaks centred at 286.2±0.2 eV, 286.9±0.2 eV and 288.1±0.2 eV assigned to C-O , C=O carbonyl and O-C=O carboxyl groups, respectively. The morphology of synthesized nanostructures was studied by SEM and TEM analyses.

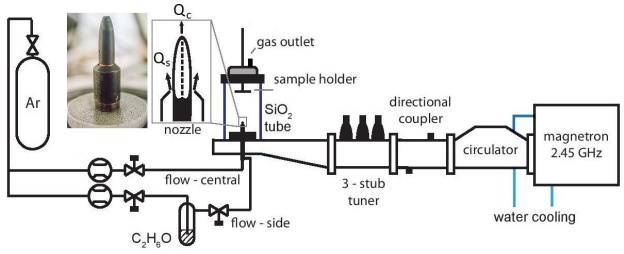

Fig. 1. MPT set-up with detailed scatch and photography of the dual-channel carbon electrode.

3. Results and Discussion

3.1 Unique electrode design

The dual channel electrode configuration (Fig. 1) used for carbon nanomaterial synthesis, including graphene nanosheets, was designed to study the process of synthesis parametrically, so we are able to determine the particular effect of each of the parameters independently.

It was necessary to split the carrier and working gas flow, so it is possible to control the residence time of building blocks ruled by Qc and the amount of ethanol vapours by increasing Qs. Moreover, the geometry of secondary channel was designed in such manner, that its cross section was much higher then the cross section of the central channel and the corresponding gas velocity of argon carrying ethanol vapours was of order of magnitude lower than the Qc velocity. Dividing the channel for plasma sustainment and precursor delivery allowed us to work in much stable regime of MPT discharge and to use larger amounts of molecular precursor entering the ethanol decomposition and subsequent formation of graphene.

3.2 MPT discharge structure

MW plasma torch discharge at atmospheric pressure in Ar/ethanol mixture represents high temperature system (T_n ~ 4000 - 5000 K) and was especially prone to fluid dynamics, thermal and plasma instabilities. Process of plasma chemical synthesis of graphene nanosheets is strongly dependent on structure of plasma discharge. Fig.2a. represents side and top view of the MPT discharge with marked active plasma and assembly zones. Interestingly, digital photography taken from the discharge axis showed hollow cylindrical arrangement of assembly zone surrounding active plasma zone. When the supersaturation is reached the nuclei of graphene nanosheets are formed on the border of the plasma zone [4]. Further downstream graphene nanosheet assembly zone develops.

The shape and dimensions of each zone was susceptible to the Qc and Qs flow rates, as can be seen on digital photographs of three particular gas flow combinations (Fig.2). Digital photographs analysed with similarity image analysis showed dual character of instabilities occurring during the decomposition of ethanol in the synthesis process. Laminarity, representing high level of similarity ~98% (Fig.1a) begins to be gradually disturbed, when Qc exceeds 500 sccm (16.6 m/s, Fig. 2c), or Qs

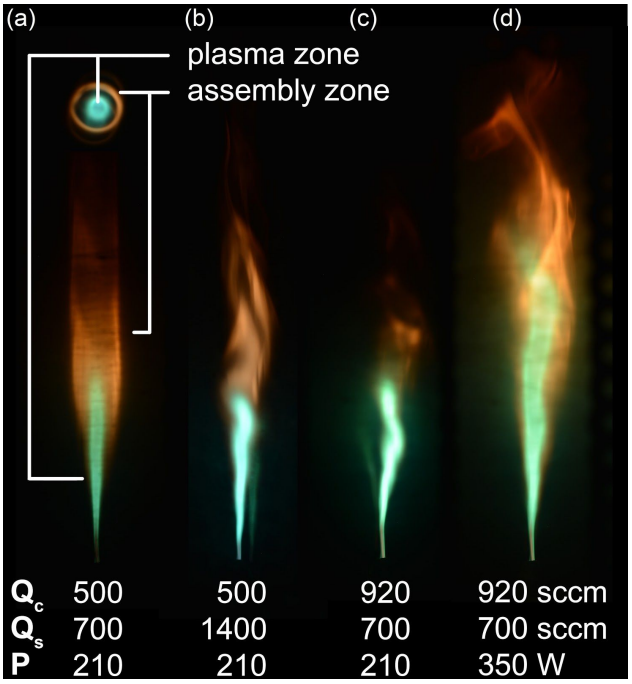

Fig. 2. Structure of MPT discharge characteristic for (a) laminar regime, (b) helical regime. (c) low MW power turbulent regime, (d) high MW power turbulent regime.

exceeds 900 sccm (0.24 m/s, Fig.2b). The former was clearly a consequence of transition to turbulent flow regime with similarity index dropping to ~94%. The design of secondary channel did not allow such transition. Observation supported by similarity analysis (same value as at laminar regime ~98%) has led to a conclusion, that the "instability" caused by high Qs is, basically, a stable regime with fully developed helical structure of plasma flame moving in the gas flow direction.

3.3 Graphene nanosheet formation

Relatively small variation in P_{MW} delivered into the plasma in combination with moderate change of gas flow were able to shift the synthesis between diverse carbon allotropes. This observation is in contradiction with conclusions made by Dato & Frenklach [2] who observed no significant effect on the graphene nanosheet synthesis in much broader range of MW power (350 - 1100W).

Graphene nanosheets synthesis is strongly influenced by plasma temperature and nucleation density of active species such as C_2 and C in the plasma. These parameters are closely related to the energy delivered into the plasma by MW power source and the amount of ethanol vapour carried by Qs supplied to MPT discharge. The residence time of active plasma species is predominantly determined by Qc flow rate.

OES measurements showed considerable rise in C_2/C plasma species ratio with increasing Qs (Fig. 3a). The rotational (neutral gas) temperature (Fig. 3b) also increased from 4500 K to 5100 K, for 140 W and 350 W, respectively.

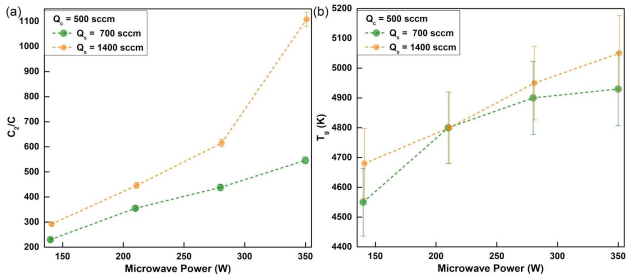

Fig. 3. Microwave power dependencies of (a) carbon species proportion from OES, (b) neutral gas temperature Tg; for three combinations of Qc/Qs representing different discharge regimes.

3.4 Carbon nanomaterial characterisation

In all cases I_{2D}/I_G ratio was increasing from ~0.2 to ~0.9 with microwave power (140 - 350 W). The structure of prepared material changed from mostly amorphous carbon at low P_{MW} = 140 W, through highly defective nanoplatelets/ graphene nanosheets to well graphitized few layer graphene nanosheets at higher MW power and relatively broad range of gas flow combinations. Fig. 4. compares carbon nanomaterial synthesized at two different Qc/Qs combinations (and two different MW power) representing laminar and turbulent flow regimes. Relatively high I_{2D}/I_G ratio together with well defined, narrow, low intensity D peak represent few layer graphene nanosheets with relatively low defect density (Fig. 4a).

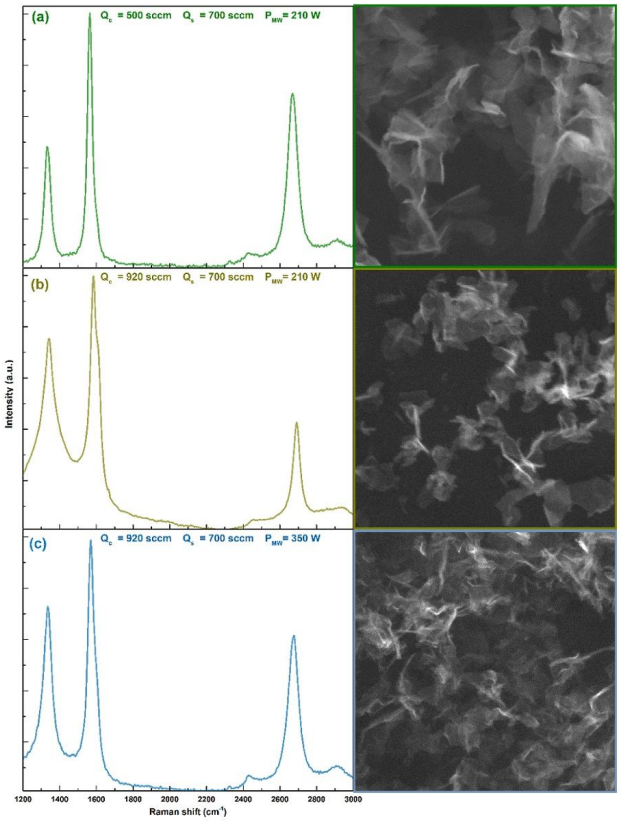

Fig. 4. Raman spectra and corresponding 1x1μm SEM micrographs of carbon nanostructures formed at specific combination of deposition conditions representing (a) laminar flow regime, (b) low MW power turbulent flow regime, (c) high MW power turbulent flow regime.

On the other hand, C nanomaterial synthesized at turbulent regime showed lower I_{2D}/I_G ratio together with high intensity D peak and broad D region, representing much thicker structures with higher defect density. However, when the energy delivered by MW power into the plasma was increased (to 350W), the synthesis process shifted towards formation of nanosheets. SEM micrographs on Fig. 4. show nanomaterial corresponding to Raman spectra.

XPS analysis of C1s peak showed differences in bond structure of above discussed experiments. High percentage of sp^2 hybridized carbon (~68%), accompanied with low percentage of sp^3 hybridized carbon (~15%) and oxygen functionalities (~8%) was typical for graphene nanosheets synthesized at laminar regime or at turbulent regime with elevated MW power. Analysis of low power turbulent regime showed almost equal percentage of sp^2 (~37%) and sp^3 (~37%) hybridized carbon together with higher oxygen functionalities (~19%).

In general, the optimum conditions of nucleation of graphene nanosheets could be achieved when an increase of Qc flow rate was accompanied by P_{MW} increase, otherwise multi-layer defective structures were predominant product of the synthesis.

4. Conclusion

Microwave plasma torch discharge at atmospheric pressure conditions was used for graphene nanosheet synthesis and detailed study of synthesis process. Using dual channel gas delivery system, we described particular effect of argon gas flows, amount of ethanol and MW power on hydrodynamics, plasma-chemistry and stability of the process. By simultaneous control of residence time and MW power delivered into the plasma it is possible to manage main plasma parameters i.e. concentration of active plasma species and gas temperature and shift the synthesis towards formation of higher quality graphene nanosheet structures.

Acknowledgements

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