

## GRAPHENE NANOSHEETS SYNTHESIZED IN MICROWAVE PLASMA AND LIQUID EXFOLIATED GRAPHENE: STRUCTURAL CHARACTERIZATION STUDY

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### Abstract

Graphene based nanomaterials produced by liquid exfoliation techniques and microwave plasma decomposition of ethanol were studied by scanning electron microscopy (SEM), Raman spectroscopy and X-Ray powder diffraction (XRD). Graphene oxide (GO) and reduced graphene oxide (r-GO) prepared by liquid exfoliation technique consisted of several types of structures - thin flakes with thickness of 10-15 nm and lateral dimensions of several micrometers and graphite like structures, 100  $\mu\text{m}$  in size, with not fully exfoliated graphene layers. The graphene nanosheets prepared in microwave plasma torch (MWGNs) were several nm thick and rectangular in shape with size of several hundred nanometers. Contamination by elements S, Mn and K was detected by EDX analysis in both GO and r-GO samples. Similarly, Fe was detected in MWGNs. This contamination was caused by synthesis process in all cases. The Raman spectroscopy analysis showed presence of D ( $1360\text{ cm}^{-1}$ ) and G ( $1580\text{ cm}^{-1}$ ) band and second order 2D ( $2690\text{ cm}^{-1}$ ) and D+G ( $2920\text{ cm}^{-1}$ ) in the measured spectra. The  $I_D/I_G$  intensity ratio was 2.2 and 2.5 for GO and r-GO samples, respectively. The graphene nanosheets Raman spectra exhibited  $I_D/I_G$  ratio of 0.5 and high intensity 2D peak at  $2690\text{ cm}^{-1}$ . XRD analysis revealed graphite like structure, graphite peak (002), of all samples and presence of contamination (Fe, intercalation compounds) in agreement with EDX analysis results. XPS analysis confirmed results of XRD and Raman analysis and  $\text{sp}^2/\text{sp}^3$  ratio of carbon C1s peak was increasing with decreasing  $I_D/I_G$  intensity ratio.

**Keywords:** Graphene, microwave plasma, liquid exfoliation, material analysis

### 1. INTRODUCTION

There exists wide range of methods to prepare advanced carbon materials like carbon nanotubes (CNT), nanofibers, graphene, nanoribbons or nanoflakes [1]. Liquid exfoliation belongs to most frequently used techniques for preparation of graphene and graphene oxide. The method is based on separation of individual graphene layers from graphite flakes by means of ultrasonication, intercalation or shear forces. The method generally involves three steps a) dispersion in a solvent, b) exfoliation and c) purification. During the preparation the graphite source and graphene based output material are exposed to number of chemicals (acids, reduction compounds) and processing steps. To avoid these elaborate procedures, an alternative to liquid exfoliation was developed in a form of synthesis of graphene nanosheets in microwave plasma. It was shown that ethanol decomposition in microwave plasma at atmospheric pressure leads to successful formation of graphene nanosheets [2]. This method was further investigated by Tatarova and Tsyganov [3] using microwave plasma surface wave discharge at atmospheric pressure in Ar/ethanol gas mixture. By further analysis and modelling they found that  $\text{C}_2$  molecule promotes nucleation and growth of graphene and atomic C leads to deposition of amorphous and  $\text{sp}^3$  phase. We have showed recently that microwave plasma torch operated at atmospheric pressure can also be used for such synthesis [4].

In this work we compare structure and composition of product of both methods: liquid exfoliation by Hummers method and decomposition of ethanol in microwave plasma torch at atmospheric pressure.

## 2. EXPERIMENTAL

Graphene oxide (GO) and reduced graphene oxide (r-GO) powder was prepared by Hummers method [5]. High purity artificial graphite dissolved in concentrated  $\text{H}_2\text{SO}_4$  and  $\text{NaNO}_3$  was added to the mixture. The mixture was magnetically stirred for 10 min and kept at the temperature of 0 °C in ice bath. Then anhydrous  $\text{KMnO}_4$  was added to the mixture and kept for 20 min at 0 °C followed by the heating to 35 °C for 30 min. The sample was then hydrolyzed in water and  $\text{H}_2\text{O}_2$  was added. Finally the sample was washed by deionized water and dried in air. To prepare the r-GO, the prepared GO was reduced at 350 °C for 1 hour. More details about the preparation technique could be found in [6, 7].

As prepared powder was dispersed in ethanol and ultrasonicated for 10 minutes. The prepared suspension was then transferred by drop casting onto Si wafer and left in the fume hood under heating for 5 minutes to evaporate the solvent. Second set of samples was prepared by direct transfer of nanopowder to double-sided carbon adhesive tape.

The graphene nanosheets were synthesized by ethanol decomposition in microwave plasma torch at atmospheric pressure. The setup consisted of a microwave (MW) generator (2.45 GHz, 2 kW) with a standard rectangular waveguide, transmitting the MW power through a coaxial line to a hollow nozzle electrode. The gases were supplied to the discharge chamber through the carbon or iron nozzle which has two gas channels. The central channel (0.8 mm diameter), in the nozzle axis, was used for introduction of working gas - argon (360 - 920 sccm) and subsequent ignition of plasma. The secondary channel (annulus with outer radius 8.4 mm and inner radius 7.7 mm) was used for introduction of carrying gas - argon (500 - 1400 sccm) with precursor (ethanol 2-25 sccm) vapours into the plasma environment. The gas flows were controlled by Bronkhorst electronic flow controllers. Reactor chamber consists of a quartz tube (8 cm diameter, 20 cm long) terminated by dural flanges. Synthesized nanopowder was collected from the reactor wall or on the Si/SiO<sub>2</sub> (92 nm) substrates fixed in the holder, quartz tube with fastening mechanism, 10 cm from the plasma nozzle.

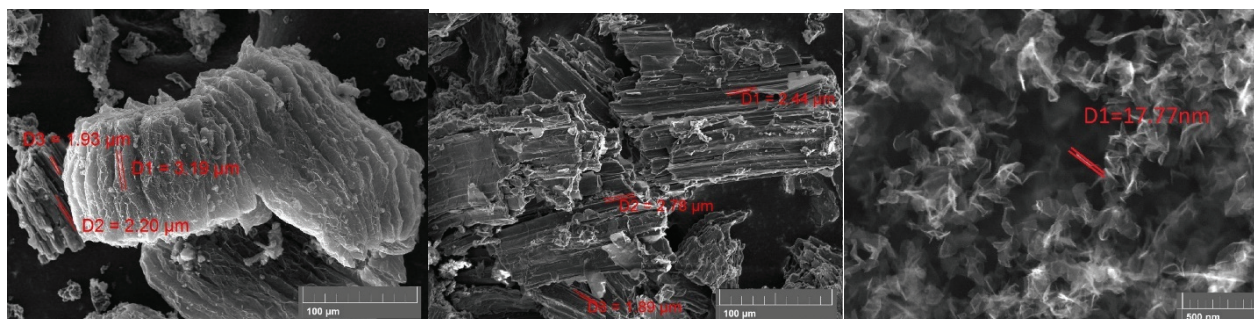
Raman spectroscopy was carried out using HORIBA LabRAM HR Evolution system with 532 nm laser, using 100x objective and 25 % ND filter in the range from 1000 to 3200  $\text{cm}^{-1}$ . Samples were imaged with TESCAN scanning electron microscope (SEM) MIRA3 with Schottky field emission electron gun equipped with secondary electron (SE) and back-scattered electron (BSE) detectors as well as characteristic X-ray detector Oxford Instruments EDX analyzer. XRD analysis was carried out with X-Ray Diffractometer SmartLab Type F from Rigaku capable of small angle X-ray scattering (SAXS) technique and equipped with with copper anode and vertical theta-theta goniometer with horizontal sample site with independent source and detector movement. XPS analysis was performed using ESCALAB 250Xi (Thermo Scientific, UK) X-ray photoelectron spectrometer equipped with a conventional hemispherical analyzer. Monochromatized Al K $\alpha$  (1486.6 eV) X-ray source was focused into elliptical spot size at 650  $\mu\text{m}$ .

## 3. RESULTS AND DISCUSSION

### 3.1. SEM Structural Characterization

Graphene oxide and reduced graphene oxide were observed in two ways: in the natural state (pieces of material adhered to a double-sided adhesive tape) and in a more coherent layer (dissolved in pure ethanol, shaken by an ultrasonic cleaner and dried on a silicon wafer) using secondary electron (SE) and back-scattered electron (BSE) mode. There are differences between the two preparation techniques which are expressed in the alignment of graphite flakes on the substrate. The drop casted sample from liquid formed thin layer showing individual pieces of (reduced) graphene oxide (**Figure 3**). The adhesive tape technique formed thicker layer and was better suited to obtaining information on the total elemental composition by EDX (Energy Dispersive X-Ray (Spectroscopy)) analysis, while the first one better depicts the topology of the resulting graphene oxide. The graphene nanosheets obtained by microwave plasma synthesis were imaged as

collected directly on the substrate. A typical shape of the produced nanopowders was captured on the following micrographs **Figure 1**.



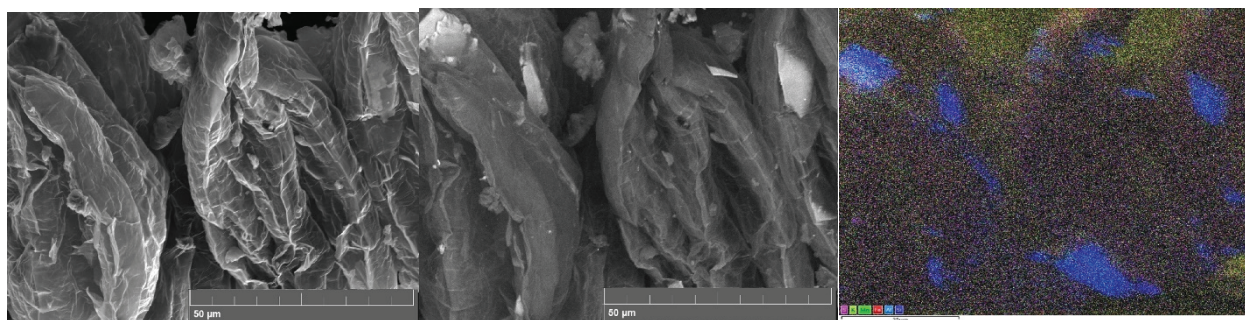
**Figure 1** Topological structure of the studied nanomaterials. r-GO on the left, GO in center and MWGNs on the right

One can see that the GO crystals are partially exfoliated on the edges and one can observe large pieces, hundreds of  $\mu\text{m}$ s, as well as small thinner and smaller flakes of material, several  $\mu\text{m}$ s. The reduction process of GO formed its reduced form r-GO and changed nanopowder structure as well. The exfoliation on the edges was more pronounced and the large graphite flakes started to disintegrate. The structure of MWGNs was completely different in comparison to GO structure. The bottom-up approach of synthesis resulted in foam like ordering of individual curved graphene nanosheets with thickness of several nanometers and lateral dimensions of hundreds of nanometers.

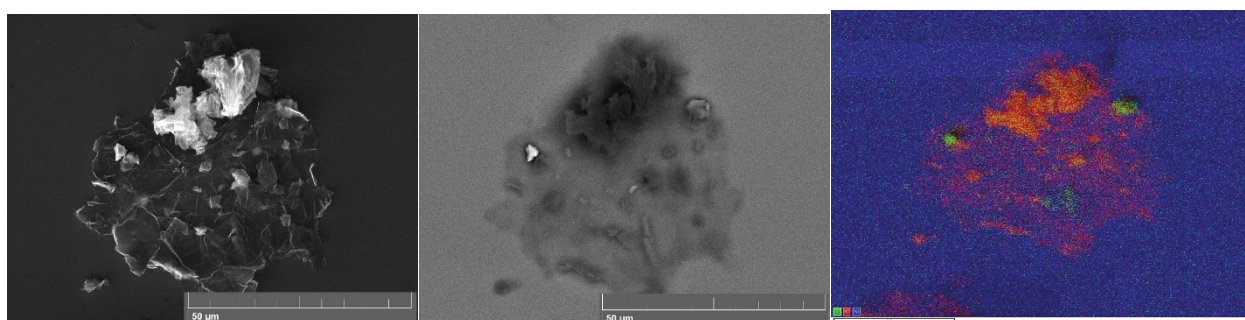
### 3.2. Contamination characterization by EDX

The GO and r-GO materials, due to the way they were prepared, are expected to be contaminated with the chemicals used in preparation process. Sample contamination may be already revealed by the images obtained with the BSE detector, where brighter spots represented heavier elements than carbon and oxygen. Precise chemical analysis of such a site was performed using an EDX analyzer. In the following figures, **Figures 2 - 4**, contamination maps are given without carbon and oxygen (EDX cannot detect hydrogen), which are main constituents of the material. Because EDX can only determine elemental composition of contaminants but not its crystalline form, we cannot determine by this method chemical state of the used compounds after the exfoliation process. Not including oxygen bonded to the foreign elements, the r-GO sample contained 1.5 atomic percent of contamination (N, Si, S, Al, K, Mn, Fe in order of concentration) and the GO sample contained about 4 atomic percent of contamination (S, N, Si, Al, Fe, Mn, K in order of concentration). It is necessary to note that due to the particle form of studied samples and its chemical inhomogeneity, the information obtained by local EDX analysis needed to be complemented by more global technique such as XRD. EDX analysis clearly demonstrated a different ratio of carbon and oxygen in the reduced graphene oxide, about 90:10, and GO about 75:25. The detail of the topological structure of graphene oxide in SE mode, the chemical compounds contamination imaged by BSE mode with visible places of chemical inhomogeneities (the brightness is determined by the atomic number of the elements) can be seen in **Figure 2** for large flake of r-GO, in **Figure 3** for small flake of r-GO and in **Figure 4** for GO flakes. Contamination of graphene nanosheets was very small, below 1 percent. Iron nanoparticles, 10 - 200 nm in diameter, formed by sputtering of the nozzle electrode could be found in the deposit and were clearly visible on the images in BSE mode **Figure 5**. The composition of bright spots was determined by EDX analysis as iron coming from plasma nozzle. This contamination could be almost completely eliminated by using carbon as nozzle material. The assumption that the plasma discharge could cause breakage of carbon nozzle and contaminate the sample with large graphite particles was not confirmed and such objects could not be found in the deposit.

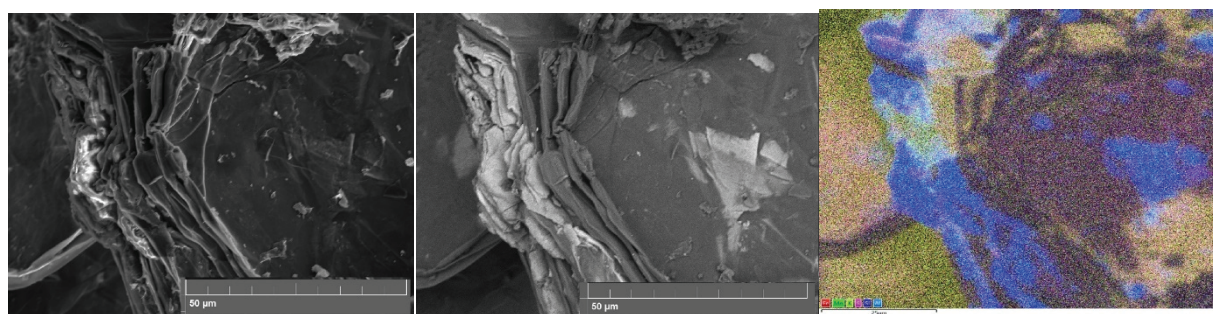




**Figure 2** Reduced graphene oxide r-GO - a typical sample structure. Images taken by SE detector (on the left), BSE detector (in the center) and EDX detector (on the right), HV=8kV. Elements color key: S - violet (0.4 at%), K+Mn - green (0.2+0.2 at%), Fe - red (0.1 at%), Si,Al - blue (0.4, 0.2 at%).



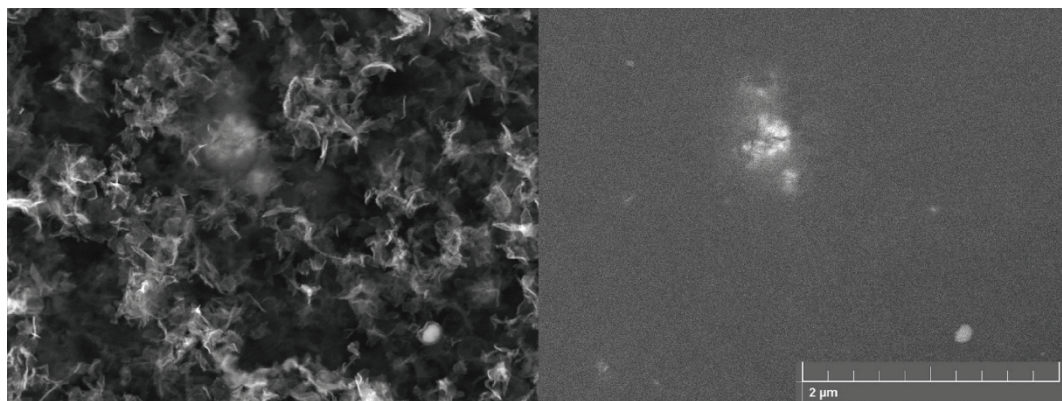
**Figure 3** Detail of individual reduced graphene oxide flake. Images taken by SE detector (on the left), BSE detector (in the center) and EDX detector (on the right), HV= 15 kV. Elements color key: C - red (50.1 at%), O - green (1.0 % at), Si substrate - blue (48.9 at%).



**Figure 4** Graphene oxide GO - a typical sample structure. Images taken by SE detector (on the left), BSE detector (in the center) and EDX detector (on the right), HV=8kV. Elements color key: Fe - red (0.5 at%), K+Mn - green (0.1+0.2 at%), S - violet (2.0 at%), Si,Al - blue (2.1, 1.5 at%).

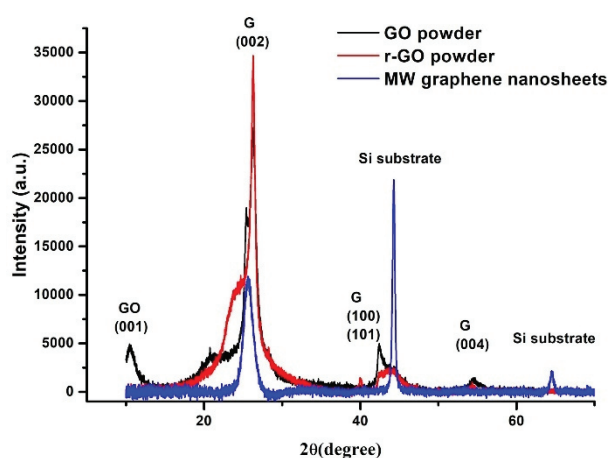
### 3.3. Material characterization by Raman spectroscopy and XRD

Further information about material structure and composition was obtained by Raman spectroscopy and XRD. XRD analysis of graphene nanomaterial powder was carried out by Bragg-Brentano technique from 10 to 100 2 $\theta$  angle (**Figure 6**). In all types of materials strong graphite (002) diffraction at 26.7° (0.335nm) could be observed, but this peak appears to be slightly shifted to lower angle values in MWGNs sample. Weaker graphite diffraction peaks (100), (101) and (004) could be observed in GO and r-GO samples as well.

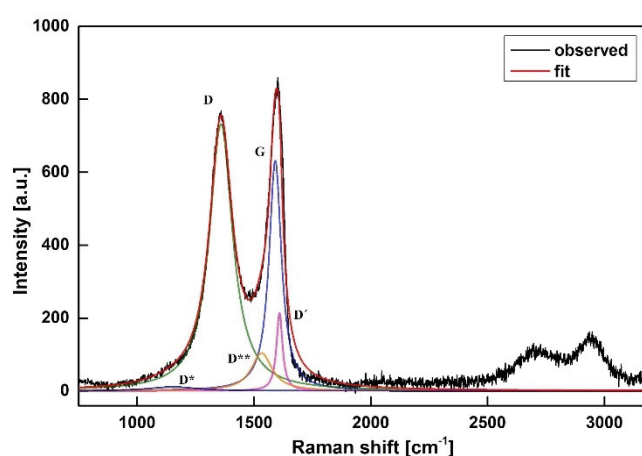


**Figure 5** Detail of graphene nanosheets and its contamination by iron nanoparticles. Images taken by SE detector (on the left) and BSE detector (on the right), HV=15kV.

GO powder analysis also showed presence of strong GO peak at  $10.4^\circ$  (0.855nm) typical for intercalated graphite structure of graphite oxide [8]. This peak was not found in r-GO powder nor microwave plasma graphene nanosheets sample. Further wide peaks between  $20\text{--}25^\circ$  and at  $40^\circ$  could be assigned to contamination by intercalation compounds such as  $\text{KMnO}_2$  etc. MWGNs sample also exhibited presence of diffractions at  $44.3, 64.5, 81.8$  and  $98.5^\circ$  assigned to Si substrates and some small intensity peaks could be assigned to Fe. The amount of contaminants was consistent with results of EDX analysis.



**Figure 6** XRD pattern of prepared nanopowders



**Figure 7** Raman spectra of prepared GO sample

Raman spectroscopy analysis showed presence of D, G, 2D and D+G bands [9]. **Figure 7** represented Raman spectra of both GO and r-GO samples which were very similar. The main feature of the spectra corresponded to the conventional D and G bands with peaks centered at  $\sim 1360\text{ cm}^{-1}$  and  $\sim 1590\text{ cm}^{-1}$ . Additional three peaks appeared during deconvolution of the region described as  $D^*$ ,  $D^{**}$  and  $D'$  centered at  $1130\text{ cm}^{-1}$ ,  $1520\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$ . The occurrence of broad and intensive D peak in combination with  $D^*$  and  $D^{**}$  peaks were a sign of defective and disordered structures caused by exfoliation process. On the contrary, Raman spectra of MWGNs exhibited sharp D peak of low relative intensity (0.5) to G peak and intensive 2D peak (FWHM  $65\text{ cm}^{-1}$ ) as expected from few layer graphene.

Results of previous analyses were supported by XPS analysis of MWGNs. The results showed 98 % content of carbon with small addition of oxygen (2 %) in the sample. The  $\text{sp}^2$  bonded structure was confirmed by fitting C1s peak profile with 95 %  $\text{sp}^2$  (284.4 eV) and small content of  $\text{sp}^3$  (285.4 eV) and carbon - oxygen bonds (286-287 eV) [10]. This result confirmed higher quality of MWGNs in comparison to GO and r-GO structures.



#### 4. CONCLUSIONS

We have compared structure and composition of two kinds of graphene related materials - graphene oxide and its reduced form prepared by Hummers methods and graphene nanosheets prepared by microwave plasma decomposition of ethanol. The structural study by SEM proved that top-down preparation method of GO and r-GO led to only partial exfoliation of large portion of graphite flakes. This exfoliation on the flakes edges further increased after reduction process and formation of r-GO. The amount of oxygen substantially decreased from 25 to 10 % in r-GO structure as shown by EDX and XRD analysis, but the structure still exhibited very similar XRD diffraction pattern to graphite. Therefore, it would be better to call this structure reduced graphite oxide. On the contrary, bottom-up approach of microwave plasma synthesis was successfully used for synthesis of graphene nanosheets only several atomic layers thick, and therefore, much closer to graphene structure, but their lateral size was order of magnitude smaller than GO structures. As a consequence of preparation process both types of material contained impurities from processing chemicals (K, Mn, S, N) or plasma torch nozzle material (Fe). The structural and compositional characteristics were confirmed by Raman spectroscopy ( $I_D/I_G$  intensity ratio), XRD (graphite (002) crystal diffraction) and XPS (C1s energy spectra) measurements. In the future the amount of contamination could be reduced by modifying preparation process of both types of nanomaterial.

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