

Characterization of nanoblister on HOPG surface

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We report on influence of the surface functionalization on the properties of highly oriented pyrolytic graphite. The samples were processed in nitric acid and characterized by XPS, Raman and EDX spectroscopies, AFM, SEM and optical microscopy. It is shown that interaction of nitric acid with the surface of HOPG leads to two types of reactions: oxidation of the graphite and intercalation of the nitrate ions at the blistered areas.

Key words: graphite, nitric acid, surface, delamination, topography

1 Introduction

Under normal conditions, graphite is the most stable allotropic form of carbon. Variation of its physical and chemical properties define the application range of graphite from pencil leads to cutting-edge calibration etalons in scientific applications. Thermal characteristics of graphite make it interesting for aerospace applications [1]. Intercalation of compounds can further spread properties of graphite and increase is application potential.

Both HOPG (highly oriented pyrolytic graphite) and HAPG (highly annealed pyrolytic graphite) exhibit pronounced layered structure. HOPG consists of hexagonal carbon planes situated in ABAB positions. Due to Van der Waals bonding between the planes this material is utilized for study and preparation of graphene structures. The interplanar distance between layers can be changed by intercalation of metals.

Graphene nanoblister and nanobubbles are partially delaminated areas of one or several graphite layers. Both can be prepared on graphite itself or on interfaces of graphite with substrates from other materials. The nanobubbles are of interest because they can trap molecules from gases [2]. There are several methods of graphite nanobubbles formation on HOPG surface: pure chemical, electrochemical, plasma processing, *etc* [3]. Formation of blisters consists of penetration of the reagent through defects into near-surface layers and oxidation of graphite. In result, formation and dissociation of carbonic acid leads to blistering.

Braking of interplanar bonds at HOPG near-surface area and appearance of round-shaped blisters were reported before [4]–[6]. Our study contributes to this field by confirmation of the theoretical work of Tang and Cao

[7] about stronger adsorption of NO_3 in comparison to other nitrogen oxides. The NO_3 anion could be detected by Raman spectroscopy at the blistered areas. We also demonstrate by XPS and Raman spectroscopies presence of NH_2 group which is important for surface functionalization for biomedical application [8].

Appearance of blisters, delamination and "bubbles" could also occur during films deposition using carbon materials as substrates. Since control of the surface condition of the substrate is important part of deposition technologies [4, 5], modified carbon surfaces are thus of interest also for growth control during deposition of thin films [11].

2 Experiment

HOPG samples of ZYB quality (purchased from TipsNano OÜ) were exfoliated by tape and exposed to 65% nitric acid (HNO_3) under ambient conditions for 8 minutes. After the exposition, the samples were washed using demineralized water. Optical imaging of the samples before treatment and after treatment is shown in Fig. 1. The position of AFM probe is shown in Fig. 1(a).

The obtained surfaces were studied using atomic force microscopy (AFM) in semi-contact mode in order to not damage the surface features [7, 8]. The blistered areas tend to form "bubbles" on the surface with height up to $1 \mu\text{m}$ (see Fig. 2). It was suggested by Burgess *et al.* [14] that the blistering occurs due to functionalization of the surface defects by oxygen-containing bonds [15].

The blistered areas were also observed by SEM (scanning electron microscopy): maximum diameter of the nanobubbles was up to $3 \mu\text{m}$ (see Fig. 3).

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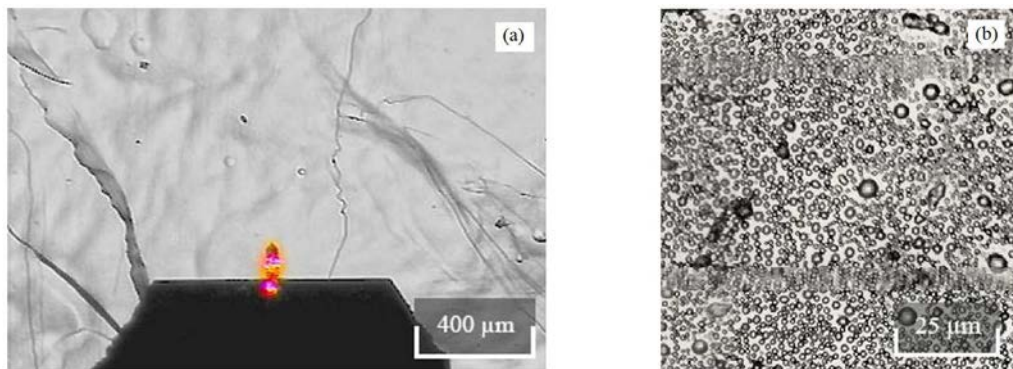


Fig. 1. Optical images: HOPG (ZYB) surface: (a) – before and, (b) – after 8 minutes of processing by HNO_3

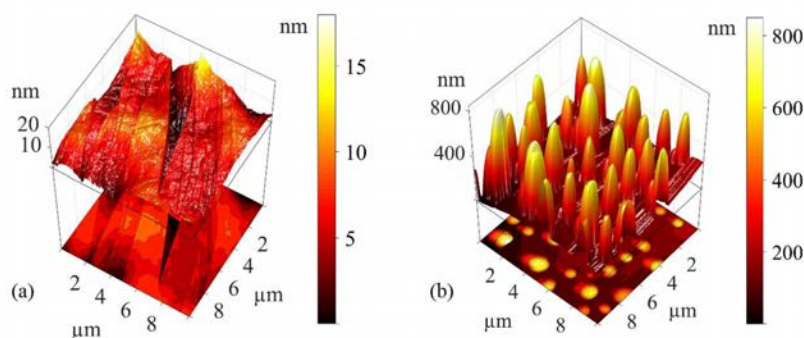


Fig. 2. AFM images: HOPG (ZYB) surface: (a) – before, and (b) – after 8 minutes processing in HNO_3 .

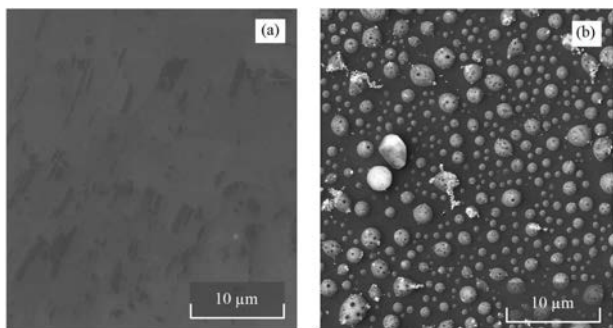


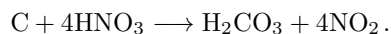
Fig. 3. SEM images: HOPG (ZYB) surface: (a) – before, and (b) – after 8 minutes of processing by HNO_3

Concerning chemical analysis, XPS showed presence of several peaks after treatment of HOPG surface with nitric acid (see Fig. 4). The N1s nitrogen peak occurring at ~ 400 eV is usually assigned to C–NH₂ bond and its appearance corresponds with theory [14]. However, only 2 minutes of etching by 5 keV argon ions is sufficient to almost completely remove N1s peak, Fig. 4(b). It happens because of preferential etching of nitrogen which occurs by Ar irradiation. The other peak that emerged after HNO_3 treatment is the oxygen peak O1s at 532.4 eV corresponding to the C–O bond. To remove the O1s peak entirely, much longer Ar exposition would be required:

even after 20 minutes of etching remnants of this peak persist, Fig. 4(c). Ion beam etching was performed in situ in the XPS chamber. The samples were not exposed to air in order to avoid influence of atmospheric oxygen to the surface condition.

Additionally, EDS (Energy Dispersive X-Ray Spectroscopy) was used for determination of oxygen abundance in the near-surface area. Although EDS did not prove the presence of nitrogen (which was observed by XPS due to its higher sensitivity to surface condition), oxygen content in the measured samples increased from 0.59 up to 1.02 atomic % after treatment.

The amount of oxygen increased twice after treatment, which confirms redox reaction between HOPG and HNO_3 . First, surfactant elements from the acid create chemical bonds with graphite surface during reactions:



Subsequently, the carbonic acid instantly decomposes into carbon dioxide and water:



The produced stress occurs between the reacted near-surface area and the rest of the sample. The delamination of the layers and formation of blisters occurs where Van der Waals bonds are broken. Finally, Raman spectroscopy is widely used for characterization of carbon materials. We used Renishaw InVia spectrometer with laser power of 1 mW and wavelength 532 nm [16]. The observed Raman peaks (see Fig. 5) correspond to graphite intercalation

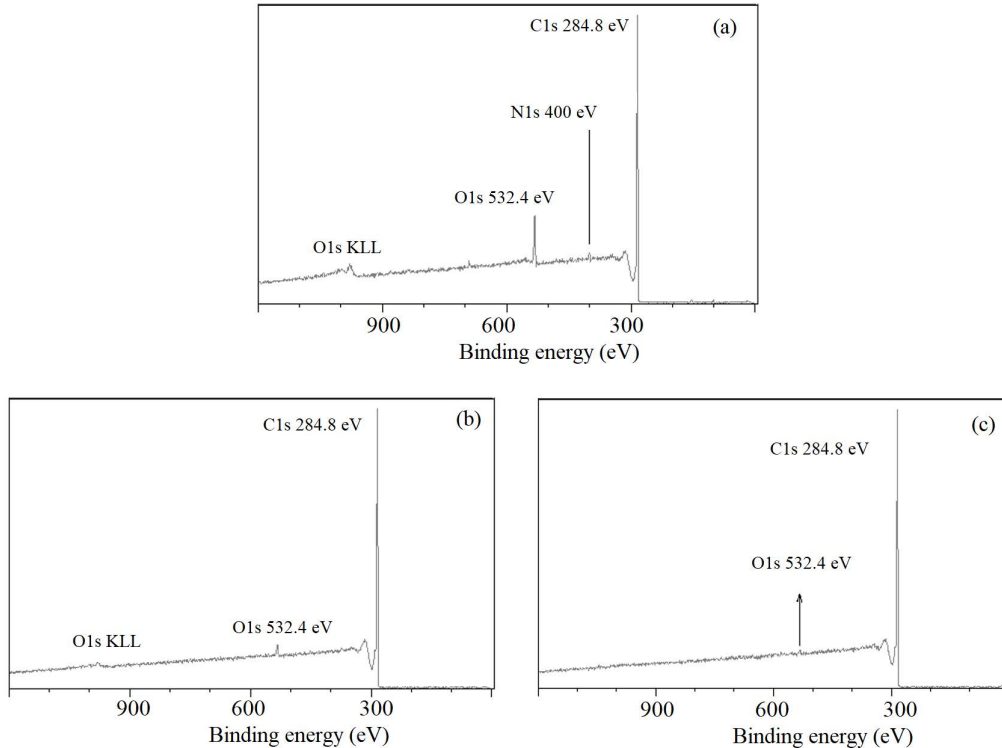


Fig. 4. Wide XPS spectra of HOPG treated with HNO_3 during 8 minutes: (a) – before Ar etching, (b) – 2 min Ar etching, and (c) – 20 min Ar etching

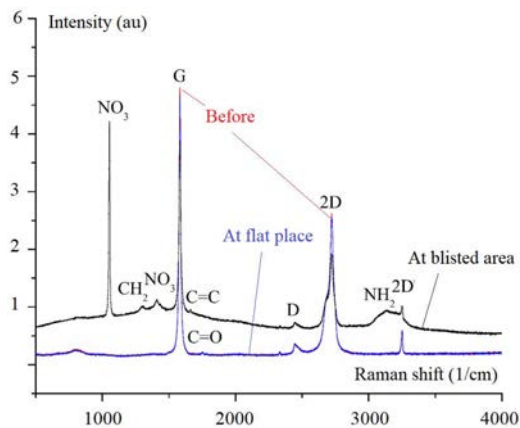
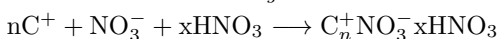
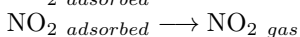
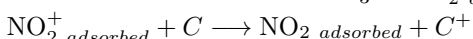
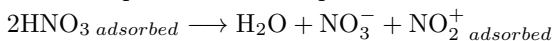


Fig. 5. Raman spectra: HOPG (ZYB) surface before and after 8 minutes of processing by HNO_3

compounds. According to Dunaev and Shapoev [17] the intercalation process could be presented as:



The main differences in comparison to pristine HOPG are in spectra from the blister areas. The common areas are observed at 1582 cm^{-1} and 2721 cm^{-1} which are positions of G and 2D peaks of HOPG [18]. Doublet of 2450 cm^{-1} and 3248 cm^{-1} is assigned to D and 2D modes of HOPG, correspondingly [19]. The blister areas show, however, additional features:

- peak at 1053 cm^{-1} refers to macro-cation NO_3 trapped between the graphite layers and the rest of non-dissociated HNO_3 [20],
- peak at 1300 cm^{-1} is connected with transverse vibrations of CH_2 group [21],
- appearance of the 1409 cm^{-1} peak can be attributed to incorporated nitrate anion [22],
- features of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ stretching modes are noted by 1660 cm^{-1} and 1748 cm^{-1} peaks, correspondingly [23],
- peak at 3130 cm^{-1} occurs due to NH_2 groups [24].

Thus, the Raman measurement confirms presence of bonds which result from intercalation and oxidation reactions [25]. In order to check the inner structure of the surface features which occurs after the acid treatment the depth-scan Raman measurement was done. The largest blister on the surface was funded by optical microscope for this aim, Fig. 6(a). Contrasted images for NO_3 peak and G-peak at the surface, in middle (and at the bottom) are investigated (Fig. 6(b)-(d)). The results indicate presence of NO_3^- ions and intensive G-peak on the surface. G-peak decreases during scanning inside the blisters and growths with approaching to the HOPG bulk. The content of nitrogen oxide is higher in the middle of the blister. Peak ratio demonstrates presence of several carbon layers on the surface of the delaminated area and higher amount of the nitrogen compounds (NO_3 and NH_2) below them.

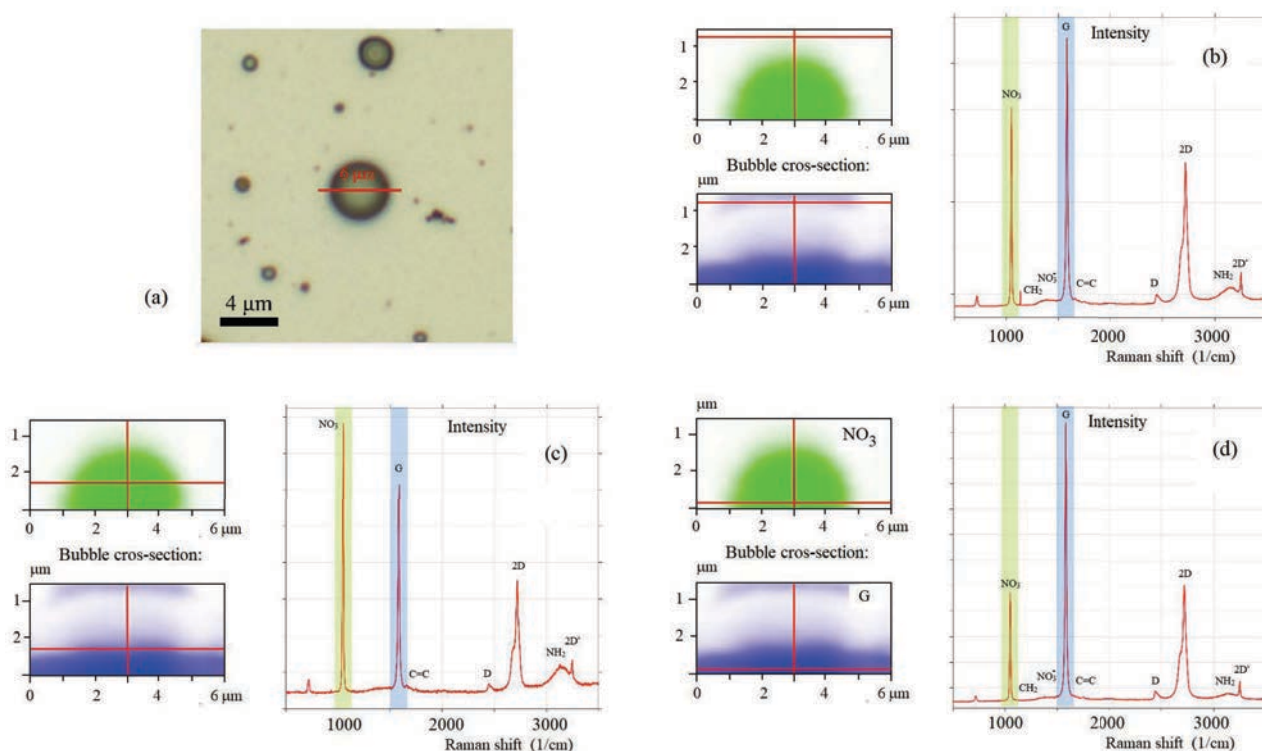


Fig. 6. Raman spectra of the blistered area in depth: (a) – optical top view of the blister for Raman depth-scan, (b) – blister cross-section, top view, (c) – blister cross-section, middle view, and (d) – blister cross-section, bottom view

3 Conclusion

Treatment of the surface by HNO_3 created blistered areas. AFM, SEM and optical images demonstrate formation of nanoblister with different size but similar shape. According to EDS, there are changes in oxygen abundance in the near-surface area after processing by HNO_3 .

In summary, nitric acid attacks graphite as oxidant by taking forth an electron (three electrons participate in plain covalent bonding). It is expected that CO_2 , NO_2 and water occur in result of reaction between HNO_3 and graphite. Intercalated elements consist of products of redox reactions between graphite and HNO_3 . We observed the presence of electron acceptor NO_3^- at the blistered areas. XPS and Raman data confirmed surface functionalization by NH_2 group.

All these defects influence physical and chemical properties of the surface and also affect the performance of the material in its potential applications. In particular, formation of blisters should be considered when HOPG is used as a substrate for epitaxy and heterostructures preparation.

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