Structure analysis of carbon nanomaterials using black silicon-based SERS substrate

Lena Golubewa[1,2], Yaraslau Padrez[1], Hamza Rehman[2], Renata Karpicz[1], Tatsiana Kulahava[1], Olga Levinson[3], Polina Kuzhir[2]

[1]*Department of Molecular Compound Physics, Center for Physical Sciences and Technology, Lithuania*
[2]*Department of Physics and Mathematics, Institute of Photonics, University of Eastern Finland, Finland*
[3]*Ray Techniques Ltd., Israel*
lena.golubewa@ftmc.lt

1. Introduction

Surface Enhanced Raman Spectroscopy (SERS), as compared with Raman spectroscopy, where compound analysis is strongly depended on the substance quantity (it should be high), has significant advantage as it allows receiving the 'fingerprints' of trace amounts of analytes and analysing single monolayers, strongly diluted solutions with concentrations for up to 10^{-12}-10^{-9} M), etc. The efficiency and sensitivity of this method is determined by a substrate used. Black silicon (bSi) refers to silicon surfaces with a layer of "needle" or "pyramidal"-like microstructures on top which suppress reflection and enhance the scattering and absorption of light. Sputtered with gold, high curvature cone-like structures can serve as active sites for electromagnetic field enhancement. In the present study we implied bSi sputtered with gold (bSi/Au) for fluorescence graphene quantum dots (GQDs) structure analysis and their modification under the action of various oxidants in biological systems, and for characterization of fluorescent nanodiamonds (NDs) obtained by laser synthesis.

2. Result and discussion

Raman spectrum of GQD suspension and SERS spectra of untreated GQDs and GQDs exposed to hydrogen peroxide, NaClO or oxygen plasma are presented in Fig.1. Structural features and presence of specific functional groups are not resolved in Raman spectra, while SERS spectrum shows that GQDs are strongly passivated with oxygen-containing groups, with high inclusion of epoxy-groups. GQDs exposed to NaClO lose their fluorescence but are not affected by H_2O_2. SERS spectra demonstrate the degradation of GQD structures under the action of NaClO and C-O-C bands vanishing allows assuming that the degradation mechanism of GQDs is through the targeting epoxy-groups in them. It was also demonstrated that NDs obtained by laser synthesis have similar passivation with oxygen-containing groups, however, the difference in the fraction of epoxy-groups (NDs contain less) likely explains the insensitivity of NDs to the NaClO exposure.

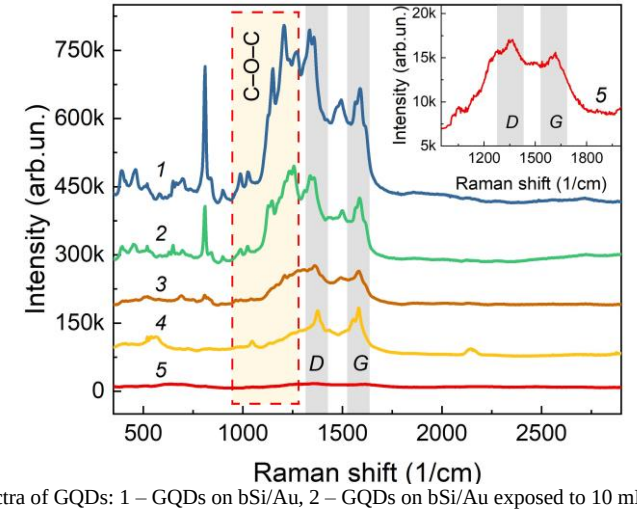

Fig. 1. SERS and Raman spectra of GQDs: 1 – GQDs on bSi/Au, 2 – GQDs on bSi/Au exposed to 10 mM H_2O_2 (30 min), 3 – GQDs on bSi/Au exposed to 10 mM NaClO (30 min), 4 – GQDs (treated with oxygen plasma) on bSi/Au, 5 – GQDs in water.

3. Conclusions

Gold-coated bSi-based SERS substrate is a powerful tool for carbon nanomaterials analysis, which allowed revealing specific features of GQDs and NDs and structural changes underlying the mechanism of biodegradation of GQDs by NaClO.

4. Acknowledgements

This work was supported by H2020 RISE DiSeTCom (No 823728) and H2020 RISE Graphene 3D (No 734164)