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GRAPHENE QUANTUM DOT CHARACTERIZATION USING BLACK SILICON BASED SERS SUBSTRATE

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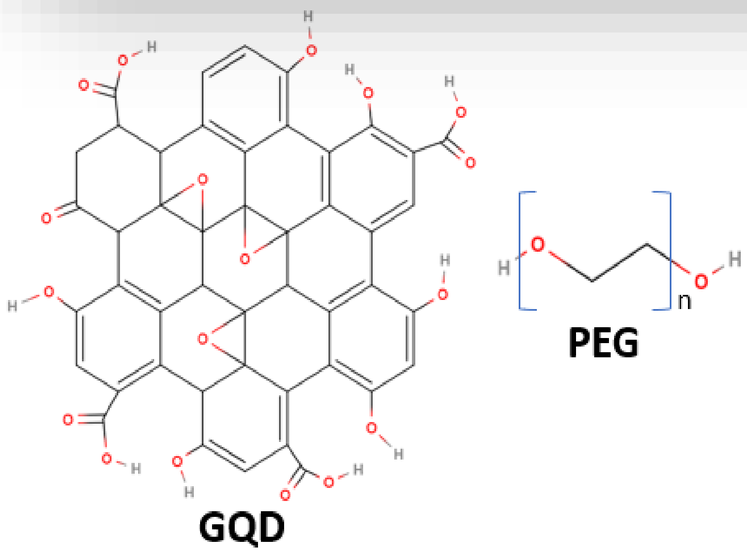

Fluorescent graphene quantum dots (GQDs) are promising nano-agents for optically guided targeted drug delivery. GQDs structure determines the efficiency of their application as imaging and diagnostic agent and surface chemistry governs the interaction of GQDs with living cells and tissues. Raman spectroscopy and SERS are highly specific methods of investigation and characterization of QGs. Black silicon-based substrate (bSi/Au, fig.2) [1] has outstanding SERS properties and was applied for GQD analysis.

Discussion

Typical Raman spectrum of GQD water suspension is featured with characteristic D band (A_{1g} mode) and G band (E_{2g} mode) [2] at 1358 cm^{-1} and 1589 cm^{-1}, respectively. During the analysis of the Raman and SERS spectra of GQDs (see Fig. 1, line 1, 4 and inset) additional lines were found. Investigation of GQD water suspension using bSi/Au SERS-active substrate made it possible to reveal the presence of additional surfactant used by the supplier to solubilize GQDs and identify PEG 1500 (or PEG of higher MW) as this surfactant (see Fig. 1, line 4 for GQD-PEG, line 2 for PEG).

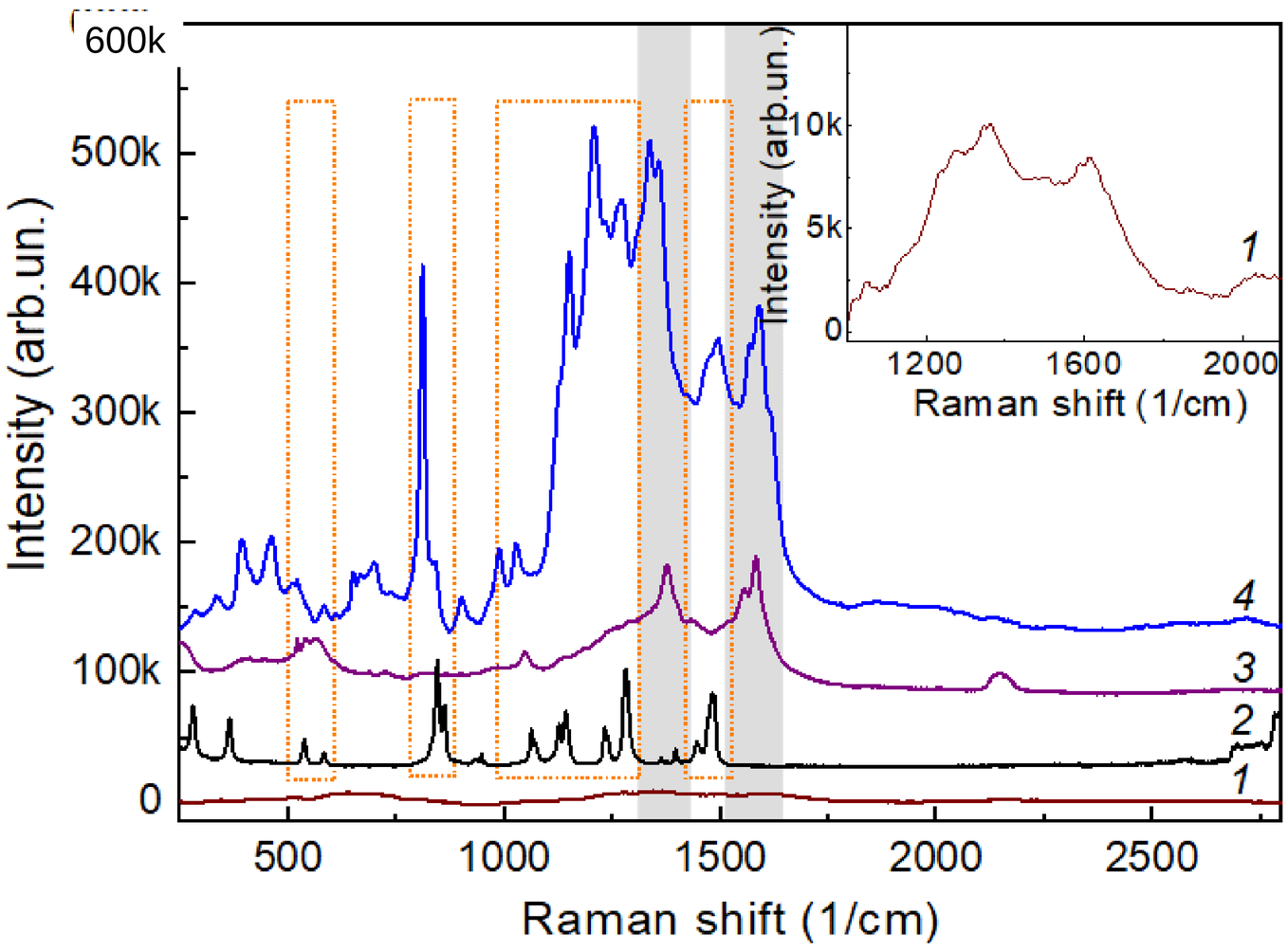

Figure 1. Raman/SERS spectrums:
line 1 - Raman spectrum of GQDs dispersed in water;
line 2 - Raman spectrum of PEG-2000;
line 3 - GQDs (1 mg/mL) after additional treatment for organics removal on bSi/Au;
line 4 - SERS spectrum of GQDs (1 mg/mL) on the bSi/Au substrate;
Inset - enlarged range 1000-2100 cm^{-1} of GQDs Raman spectrum (line 1).

Conclusions

Investigation of GQD water suspension using bSi/Au SERS-active substrate made it possible to demonstrate, that GQD-PEG treatment with oxygen plasma and additional washing effectively remove GQD functionalization with PEG leaving only GQDs (see Fig. 1, line 3).

Thus, GQD structure quality control and surface chemistry analysis could be successfully performed using bSi/Au SERS substrate.

Materials and methods

Graphene Quantum Dots (GQDs). GQDs (green luminescent, water-dispersed, CAS 7440-44-0, Sigma-Aldrich, USA) dispersed in water (1 mg/mL) were used throughout experiments. Due to data provided by supplier topographic height is about 1.0-2.0 nm, diameter is < 5 nm.

bSi/Au production. A silicon <100> oriented wafer (p-type) with 1-20 Ohm·cm resistivity was etched using ICP-RIE technique. The Au films were deposited on the bSi substrates using a Quorum Q150T ES Plus-Turbomolecular pumped coater.

Cleaning GQDs. Plasma cleaner Harrick Basic Plasma Cleaner PDC-32G-2. Partial removal of the surfactant from the GQD-containing bSi/Au substrate was carried out with O_2 plasma (1 mbar).

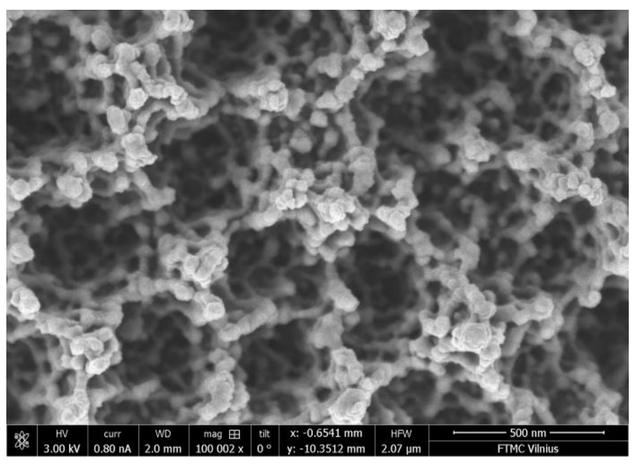

Figure 2. SEM-imagine of bSi substrate with Au film.

References:
1. L. Golubewa et al. *ACS Appl Mater Interfaces* **12(45)** p. 50971-50984 (2020);
2. R. Justin et al. *Carbon N. Y.* **97** p. 54-70 (2016).