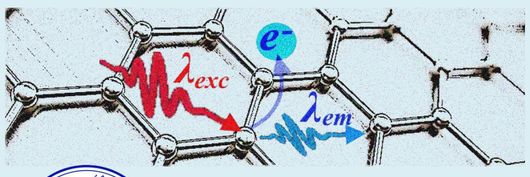

Workshop: 2th Photon-graphene interaction: phenomena and applications
Satellite to 21 st International Conference on Dynamical Processes in Excited States of Solids

CHANGES IN THE STRUCTURE AND PROPERTIES OF GRAPHENE OXIDE SURFACES DURING REDUCTION AND MODIFICATION

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The aim of the current study was to find changes in the structure and state of the surface of graphene oxide (GO) under the conditions of its reduction and modification by hetero atoms of nitrogen and amino acids. Reduction of GO was performed with hydrazine hydrate (R-GO), doping with nitrogen atoms - urea impregnation and subsequent heat treatment (N-GO), and the surface of GO was modified with sulfur-containing amino acid – L-cysteine by nucleophilic addition (L-GO). The samples obtained were characterized by analytical methods, such as Raman scattering, IR spectroscopy, TPD-mass-spectrometry, dynamic light scattering spectroscopy.

Materials. Initial GO samples were obtained from "Grafren AB" (Sweden) as a dark brown 20–25 % water-soluble paste, which was synthesized in accordance with ISO/TS 80004-13:2017 (E) "Graphene and related two-dimensional (2D) materials". According to the certificate: the number of layers is 10–15, the size of the flakes – 0.1–200 μm, the atomic ratio C/O is 2.5–2.6. Reducing of samples was performed using hydrazine hydrate according to the method specified in [1]. Reduced GO samples were designated R-GO. To obtain nitrogen-containing GO (N-GO) derivatives, a portion of the oxidized sample was immersed in a 10 % urea solution and evaporated to constant weight, 1 h in an inert atmosphere (700–800 °C), then washed with distilled water to neutral pH and dried for 4 hours at 105 °C. Sulfur-derived GO derivatives, in particular GO, modified with the aminoacid *L*-cysteine (*L*-GO) were obtained.

Structural characteristics of GO, its reduced and modified forms

Table 1. The values of some basic parameters of the characteristic bands manifested in the micro-cattle of GO samples and its restored and modified forms and their values according to the results of deconvolution in the form of Gauss - Lorentz bands

Samples/ parameters	D, cm^{-1}	G, cm^{-1}	D_{FWHM}, cm^{-1}	G_{FWHM}, cm^{-1}	$2D_1$, cm^{-1}	$2D_2$, cm^{-1}	$2D_3$, cm^{-1}	$2D_{1FWHM}$, cm^{-1}	$2D_{2FWHM}$, cm^{-1}	$2D_{3\,FWHM}$, cm^{-1}	I_D, rel. un.	I_G, rel. un.	I_D/I_G	I_{2D1}/I_G	I_{2D1}, rel. un.	I_{2D2}, rel. un.	I_{2D3}, rel. un.	L_a, nm	number of layers
GO-initial	1358.5	1592.4	172.3	104.6	2704.0	2944.5	3159.0	406.6	152.6	181.4	23.7	29.0	0.82	0.12	3.5	3.0	2.0	16.0	15±1
R-GO	1354.0	1586.0	109.6	105.3	2700.0	2955.0	3221.0	227.9	198.2	126.3	11.9	9.2	1.3	0.14	1.3	1.4	0.3	10.5	9±1
N-GO	1358.5	1586.0	137.7	111.3	2697.5	2948.45	-	279.5	153.6	-	9.6	9.5	1.0	0.1	0.9	0.8	-	13.6	12±1
L-GO (cystic acid)	1358.5	1581.3	139.8	94.3	2721.0	2959.0	3172.0	278.8	186.4	157.4	23.0	20.3	1.1	0.17	3.4	4.1	1.7	12.4	11±1

The thickness of the graphene particle La was calculated according to the following formula [2]:

$L_a(nm) = (2.4 \times 10^{-10})\lambda_l^4 \left(\frac{I_D}{I_G}\right)^{-1}$ (1), where: λ_l is the wavelength of the excitation radiation (in our case it is 488 nm), I_D is the intensity of the D-band, I_G is the intensity of the G-band. (Table 1)

The particle size distribution was determined using the dynamic light scattering method. Practically stable suspensions of GO and its modified forms have a narrow monomodal particle size distribution (Fig. 1), which in the spherical approximation have the following average hydrodynamic diameters: GO ≈ 1.5 μm, R-GO ≈ 1.9 μm, N-GO ≈ 2.3 μm, L-GO ≈ 0.64 μm.

***a* – graphene oxide (source); *b* – reduced graphene oxide; *c* – nitrided; *d* – modified with *L*-cysteic acid.**

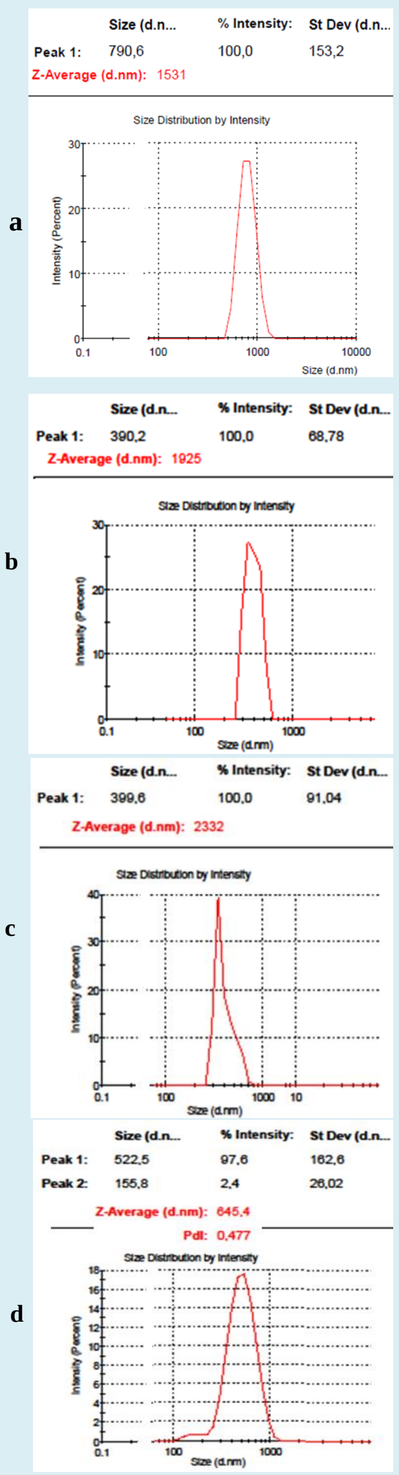

Fig. 1. Particle distribution by radius

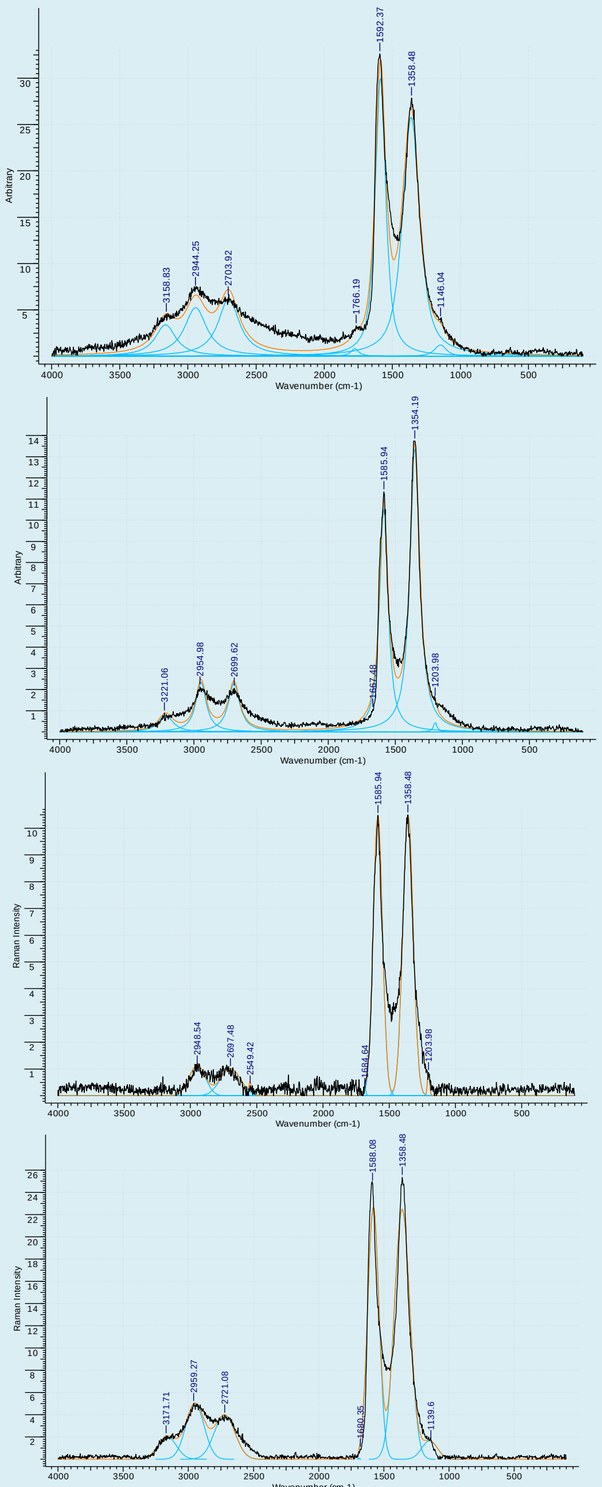

Fig.2. Spectra of Raman scattering and deconvolution of these spectra in the form of Gauss-Lorentz bands after manual subtraction of the baseline. Shooting conditions:λ=488 nm, P=1 mW

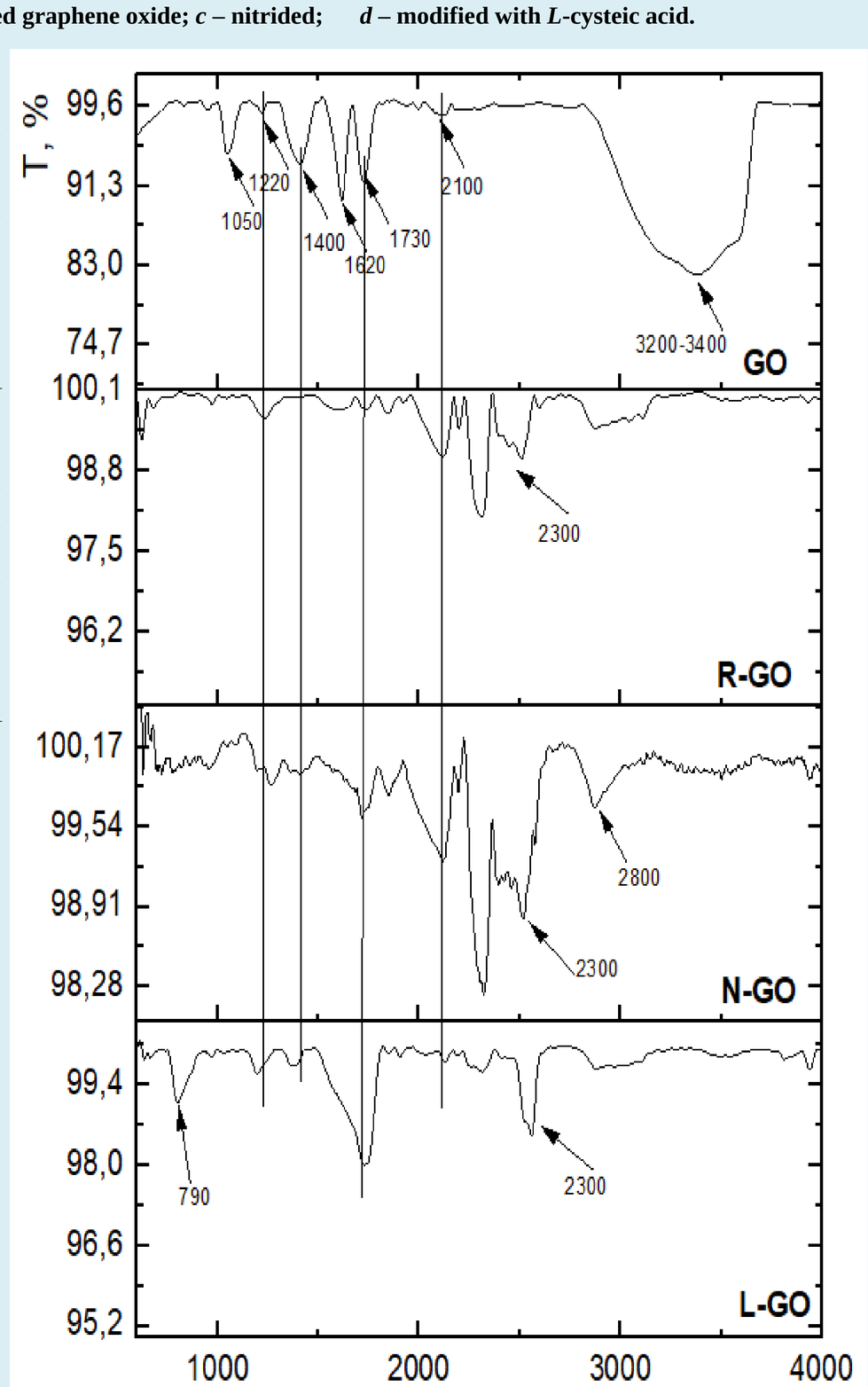

Fig.3. IR spectra of obtained samples

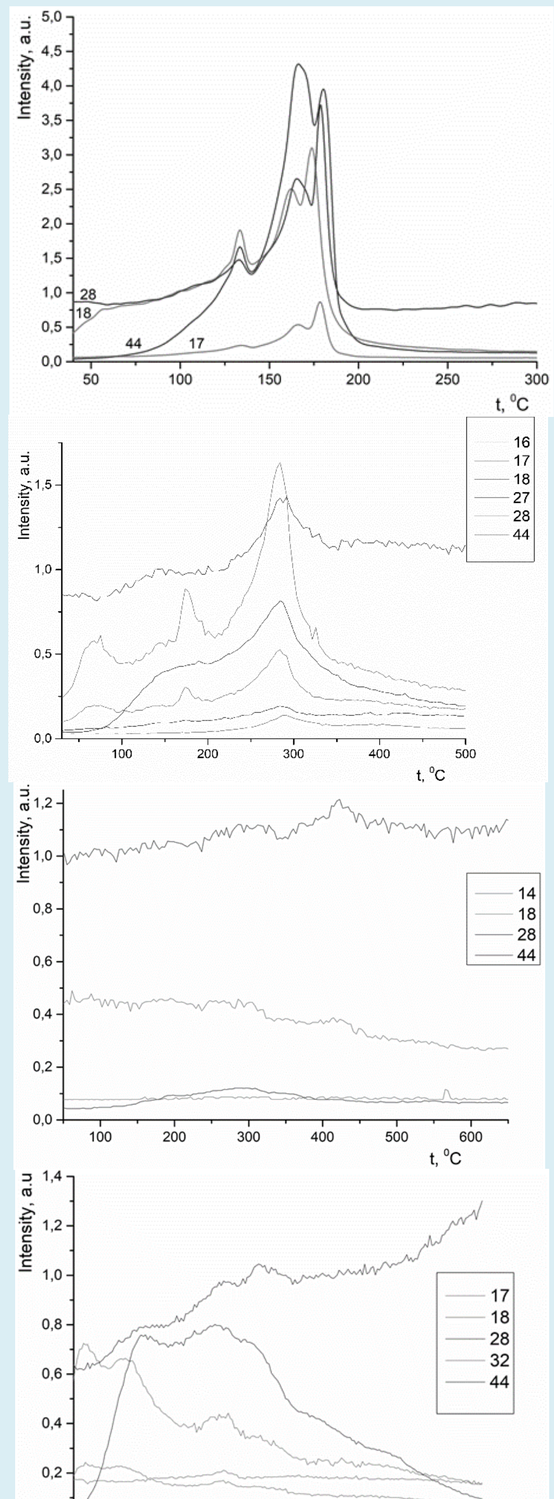

Fig. 4. TPD-MS spectra

Conclusion. Comprehensive studies conducted by Raman, DLS, IR spectroscopy, thermo-programmed mass spectroscopy have shown that the reduction of graphene oxide with hydrazine hydrate, its modification with nitrogen by impregnation with urea and subsequent heat treatment and sulfur-containing compound obtained by the addition of *L*-cysteic acid are effective, lead to significant changes in its structure and surface chemistry. Empirical studies [3] have shown that such changes affect the capability of the obtained samples to scavenge free radicals and this property increases in a row: *L*-GO > GO > N-GO > R-GO.

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