Names and affiliations of applicants (* indicates experimentalists):

*Kristina Kvashnina, ESRF, Grenoble
*Anna Romanchuk, Stepan Kalmykov, Anastasiya Kuzenkova, Evgeny Gerber,
Lomonosov Moscow State University
*Alexandr Talyzin, Umea University, Sweden

Report:

Graphene oxide (GO) is one layer of carbon with various functional oxygen-containing groups (epoxy, carboxyl, carbonyl, phenolic, etc.). The high sorption ability of GO to various radionuclides and heavy metals has been repeatedly demonstrated previously. However until now, it is unknown which exactly oxygen-containing groups of GO bind to radionuclides and keep them on the surface.

There are several ways of graphite oxidation to produce samples of graphene oxide with the predominance of various functional oxygen-containing groups. The most famous of them are Hummer's, Tour's and Brodie's methods. As a result of the Hummer's method (HGO), samples with a predominance of carbonyl and carboxyl groups are obtained [1,2]. The Tour's method (TGO) is a modification of the Hummer's method that is quite popular today including industrial production [3]. Materials synthesized by Brodie's method (BGO), contain the predominance of hydroxyl groups [2,4]. In this study, we aim to determine which groups preferentially bind to the radionuclides, how they are distributed over the surface, how the synthesis method of the GO samples and its defectiveness affect the sorption mechanism. Three samples of graphene oxide BGO, HGO and TGO were compared.

We studied sorption process of different cations such as U(VI), Cs(I) and Eu(III) which demonstrate quit different chemical properties. Charge states of absorbed atoms and its local atomic geometry were studied by means of XAS spectroscopy in conventional fluorescence mode and in fluorescence mode with high energy resolution at U L_3, Eu L_3, Cs K edges. Experimental spectra were analyzed using IFFEFIT data analysis package[5].

1) Samples with U(VI) sorbed onto three GO samples at different pH values (2.8, 3.2, 4.7 and 6) HERFD showed the evidence of the U(VI) oxidation state of all samples. At the same time the shape of the U spectra of different GOs at the U L3 edge are quite similar (fig.1a). Contrarily to HERFD XANES, the EXAFS spectra showed tiny difference in local atomic structures of U atoms (fig.1b). First oxygen shell is very similar for all studied samples and corresponds to axial oxygen atoms Second (oxygen or carbon) shell at ~2 Å corresponds to oxygen atoms at 2.4-2,5 Å, in case of TGO and HGO samples the shapes of second EXAFS peak are very similar too. However the intensity of the second peak in BGO EXAFS spectra is much lower the in case of TGO and HGO, this could be explained by splitting of the second oxygen coordination shell in local atomic environment of uranium. In particular the U-O/C bond in BGO sample is longer for compare to

U sorbed on TGO and HGO samples. It was also observed that upon increasing pH disordering in the system are increasing too.
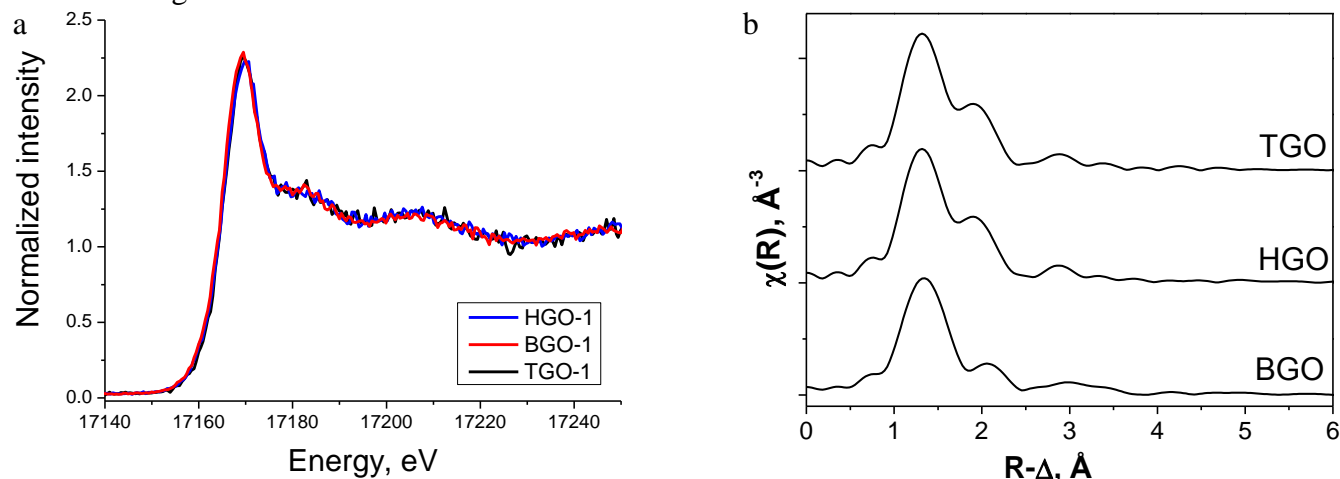

Figure 1. The U (a) HERFD and (b) EXAFS spectra of U(VI) sorbed onto different GO samples at pH 4.7

EXAFS spectra fitting and extraction structural information for disodered systems is quiet complicated procedure. To overcome difficulties of traditional EXAFS fitting procedure we employed Reverse Monte Carlo modeling scheme to fit experimental data [6]. Coordination numbers, interatomic distances were varied during the minimization of the difference between experimental spectra and calculated one. Comparison of EXAFS fitting for BGO sample is shown on the Fig.2. Radial density of oxygen atoms near U was obtained as a result of the fitting. Three distinct peaks are seen in radial density of oxygen atoms, at 1.8 Å, 2.25 Å and 2.4 Å. Oxygens at 2.25 Å corresponds to atoms which are considered like a bridge between U and graphene flakes.
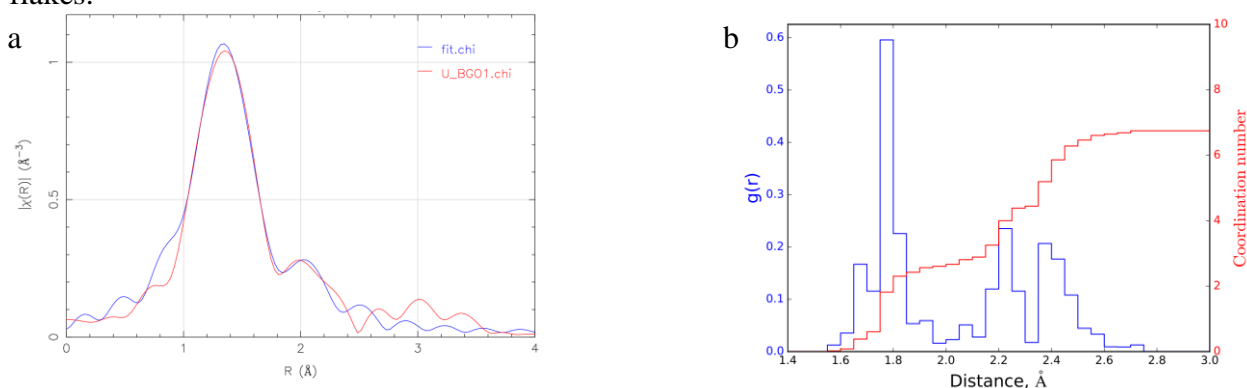

Figure 2. (a) – comparison of the absolute value Fourier transformation of the experimental spectra and fitted one. (b) – radial density of oxygen atoms and its coordination number.

2) Eu(III) and Cs(I) sorbed onto BGO, TGO and HGO at different pH values were studied. Eu L_2 edge and Cs K edge EXAFS were measured (EXAFS results are shown in Figure 3). EXAFS spectra are very similar in case of U sorption on TGO and Eu sorption on HGO, while results for BGO indicate that local atomic distribution are changed.

The detail comparison of the experimental results with the modelling will give an answer about predominant mechanism of cations interaction with GO.
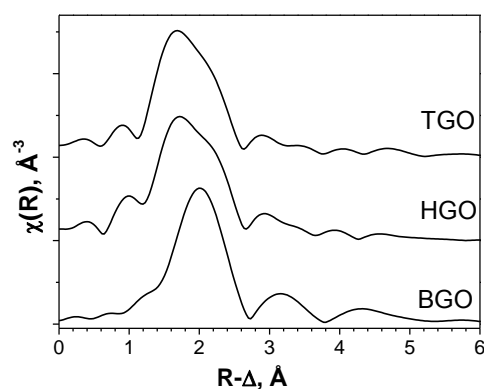

Figure 3. EXAFS spectra of Eu(III) sorbed onto different GO at pH 3.0

Literature:

1. Hummers, W., Offeman. J. Am. Chem. Soc. 1958, 80, 1339-1339.
2. Talyzin, A.V. Mercier, G., Klechikov, A. et al. Carbon, 2017, 115, 430-440.
3. Marcano, D.C.; Kosynkin, D.V.; Berlin, J.M.et al. ACS Nano, 2010, 4(8), 4806-4814.
4. Brodie, B.C. Ann Chim Phys, 1860, 59, 466-72.
5. Ravel, B., and Newville, M. J. Synch. Rad., 2005, 12, 537-541.
6.Rossberg, A., Scheinost, A.C. Anal. Bioanal. Chem. 2005, 383, 56.