
Rabchinskii M.K¹

Ryzhkov S.A.¹, Baidakova M.V.^{1,2}, Shnitov V.V.¹, Kirilenko D.A.^{1,2}, Pavlov S.I.¹,
Chumakov R.G.³, Dideikin A.T.¹, Besedina N.A.⁴, Vul A.Ya.¹

¹ Ioffe Institute, 26 Politekhnikeskaya, Saint-Petersburg 194021, Russia

² ITMO University, 49 Kronverksky Pr., Saint-Petersburg 197101, Russia

³ NRC Kurchatov Institute, 1, Akademika Kurchatova pl., Moscow, 123182, Russia

⁴ St. Petersburg Academic University, Khlopina st., Sankt-Peterburg, 194021, Russia

rabchinskii@mail.ioffe.ru

Graphene chemical derivatives: from synthesis to applications

The increasing progress in the study of pristine and chemically derived graphenes led to arising of new subclass of graphene materials, functionalized graphenes (FGs). These are the conductive graphene layers decorated with the certain types and amounts of functional groups. Owing to the presence of these functionalities, FGs exhibit new electronic properties and can be easily grafted with various moieties. All this makes FGs to be perfect candidates for a large field of applications: gas sensing, biosensing, formation of photovoltaic and optoelectronic devices. In this study we present our results on the synthesis, physical properties and application of three different FGs. Carboxylated (C-xy) graphene was synthesized via photochemical modification of graphene oxide (GO) films in argon atmosphere using soft UV radiation [1]. By the means of various spectroscopy methods and electron microscopy it is demonstrated that C-xy graphene is presented by perforated graphene layers grafted with up to 11 at.% of carboxyl groups (Fig. 1) [2]. The valence band structure and work function of C-xy graphene is determined to significantly differ from the ones in pristine graphene. Particularly, the presence of high number of carboxyl groups leads to significant changes in the structure of the valence band with appearance of prominent peaks at 5.1, 13.5 and 25.1 eV, corresponding to the π - and σ -orbitals of carboxyl groups as was demonstrated by further comparison of the experimental data to the results of DFT calculations. Of high interest is that the feature at 5.1 eV is sensitive to the substitution of hydrogen ion in carboxyl groups to earth metal, demonstrating significant increase if sodium cations are introduced. Owing to the presence of chemically reactive carboxyl groups, covalent grafting of C-xy graphene with aptamers can be performed, allowing manufacturing of viral electrochemical biosensors of multiple use with high sensitivity and selectivity. The second FG, carbonylated (C-ny) graphene with up to 11 at.% of carbonyl groups was synthesized via wet-chemistry GO modification [3]. This FG exhibits low conductivity and highly defective structure. Nevertheless, C-ny graphene is determined to be an efficient frame for obtaining luminescent films by non-covalent bonding with lanthanide β -diketonate complexes. The following studies of C-ny graphene demonstrated that presence of carbonyl groups also regulates the structure of the valence band around 9.6 eV. Collectively, these results demonstrate the graphene density of states in the valence band is sensitive to the edge-located oxygen-containing functional groups. The further study of GO, C-xy graphene, C-ny graphene and pristine graphene work functions also showed dependence of this parameter on the concentration and type of edge moieties. C-xy_graphene and C-ny_graphene are determined to exhibit higher work function compared to graphene with its reversible decrease after the elimination of carboxyl and carbonyl groups. Aminated graphene (Am) is a third reviewed member of CFs family obtained via the two-step liquid phase GO reduction using hydrobromic acid and ammonia solution. The obtained material contains up to 7 at.% of amine groups and exhibit C/O ratio of 11 with conductivity of 290 S*m⁻¹ (Fig. 2). Images of transmission electron microscopy demonstrated that despite other modification and reduction approaches the applied amination procedure does not introduce defects into graphene plane. On the other hand, the presence of amine groups revealed to result in strong bending of graphene layers, leading to formation of graphene mesoporous structures with high specific area. Lyophilization of Am graphene dioxane suspensions resulted in formation of highly-conductive aerogels with specific surface area of 600-800 m²/g. Further experiments showed that the attached amine groups are chemically active allowing to covalently bond various functionalities and nanoparticle, in particular fullerenes and organic dyes. This fact in combination of high electrical conductivity makes Am graphene to be a perfect candidate for formation of various optoelectronic devices and photovoltaic

systems. As a net result, FGs appears to be a versatile platform for the formation of graphene-based structures and rigorous study of graphene physical properties. At the same time, only the initial steps are done in this field and synthesis of new types of FGs is of a high interest nowadays.

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Figures

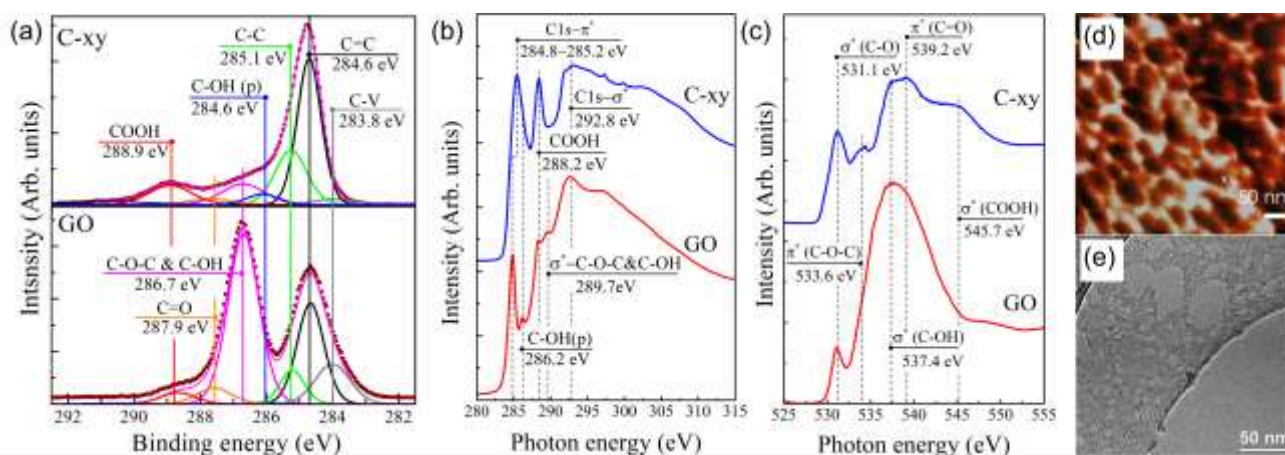


Figure 1: (a) C 1s XPS spectra, (b) C-K Edge and (c) O-K Edge XAS spectra of the initial GO and C-xy graphene, demonstrating dominant character of carboxyl groups and absence of other moieties in the C-xy graphene. (d) Atomic-force microscopy and (e) transmission electron microscopy images of C-xy graphene.

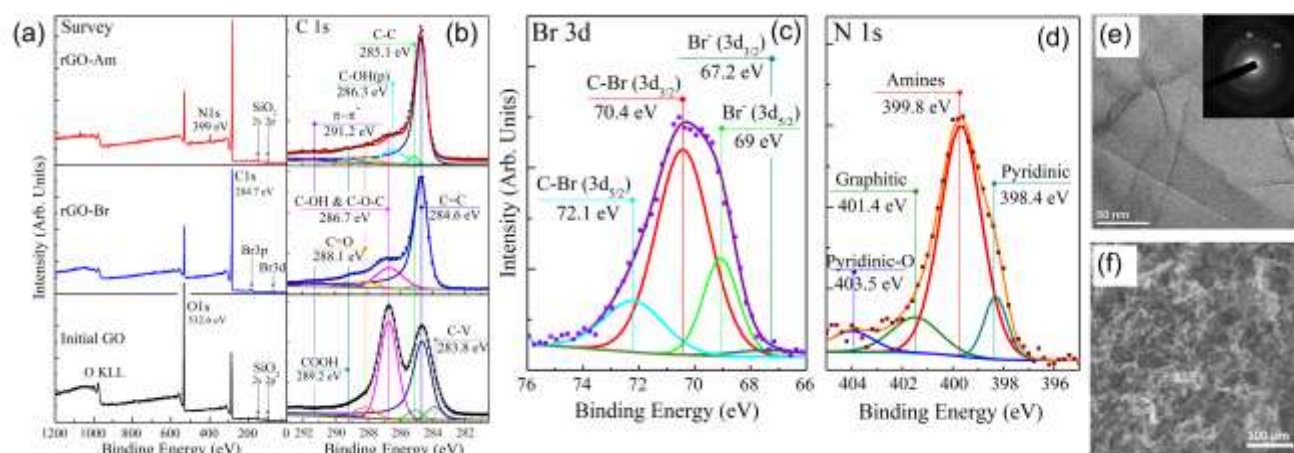


Figure 2: (a) Survey and (b) C 1s XPS spectra of the initial GO, GO after bromination (rGO-Br) and Am graphene. (c) Br 3d and (d) N 1s XPS spectra of the rGO-Br and Am graphene, respectively. (e) Transmission electron microscopy image of the Am graphene layer. (f) Scanning electron microscopy image of the aerogel obtained from Am graphene suspension.