

Graphene chemical derivatives: from synthesis to applications

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In this work we present our results on the synthesis, study, and application of a set of chemically modified graphenes (CMGs): conductive graphene layers controllably grafted with various organic functionalities: carboxyls (C-xy), carbonyls (C-ny), and primary amines (Am). We demonstrate that UV irradiation and chemical treatment of GO using silicates results in the formation of C-xy and C-ny graphenes, containing up to 11 at.% of carboxyls and carbonyls, respectively [1,2]. It is further shown that the provided graphene derivatization also leads to the perforation of the graphene network and holey structure of these CMGs [2,3]. However, despite the presence of a large number of nanoscale holes, C-xy graphene demonstrates the electronic and optical properties analogous to ones in pristine graphene. Given this fact and the presence of chemically reactive carboxyl groups, electrochemical biosensors have been developed on the base of the C-xy graphene films, demonstrating high selectivity of detecting viral proteins. Oppositely, higher density and smaller size of the formed holes in the C-ny graphene result in high resistivity of the material of several MΩ. Although this value is too high for the application in electronic devices it was found out that gas sensing chips with sensitivity of up to tens of ppm, which operates and are able to regenerate at room temperature can be manufactured on the base of C-ny graphene layers. In comparison, the conventional metal oxide gas sensors require heating to 300-400 °C while operating. Furthermore, the precise study of C-xy and C-ny graphene also revealed that the carried out functionalization resulted in substantial changes in the graphene electronic structure. Particularly new local states related to the molecular orbitals of the covalently attached carboxyls and carbonyls appears in the graphene valence band near the Fermi level as is demonstrated by the ultraviolet photoelectron spectroscopy and theoretical modeling. Aminated graphene (Am) is a third reviewed member of CMGs family which is obtained via the two-step liquid phase GO reduction and contains up to 4 at.% of primary amines. The presence of amine groups is revealed to result in strong twisting of graphene layers, leading to the formation of graphene mesoporous structures with high specific area. Lyophilization of Am graphene dioxane suspensions has allowed us to obtain conductive aerogels with specific surface area of 800 m²/g and conductivities of 300 S·m⁻¹. Attached amine groups are chemically active allowing to covalently bond various functionalities, fullerenes, and organic dyes. As a net result, the obtained CMGs appears to be a versatile platform for both the formation of graphene-based structures and rigorous study of graphene physical properties. The presented work was financially supported by the Russian Foundation for Basic Research (grant no. 18-29-19172).

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