REVIEW OF GRAPHENE PROPERTIES IN VIEW OF ITS USE AS A SUBSTRATE FOR MATRIX-FREE MASS SPECTROMETRY

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Short review of the graphene basic properties is given. This material is discussed, in particular, as a possible ionization support for mass spectrometry. The attention is paid to the possible role of intrinsic and deliberately induced structural defects in electronic and chemical properties of graphene substrates.

Carbon is one of the most abundant elements in the Universe (the fourth most abundant element by mass in the Universe and the 15th most abundant element by mass in the Earth's crust) and the basic constituent of the biosphere. Nevertheless, last and current centuries demonstrated that carbon abilities to generate condensed matter phases are far from be exhaustedly studied. The richness of the carbon own allotropes and different kinds of derivatives was even used to call carbon "the king of the elements" [1].

Graphene, an allotrope of carbon, turned out to be among spectacular materials of modern solid matter science. Graphene inherent crystalline structure ensures new peculiar mechanical, electrical and optical properties of this material. It was the last carbon allotrope to be discovered. While fullerenes were known in the 1980's and nanotubes in the 1990's, graphene was discovered only in 2004 by the group lead by Andre Geim at Manchester University in England [2]. The chronology of relevant events is shown in Fig. 1.
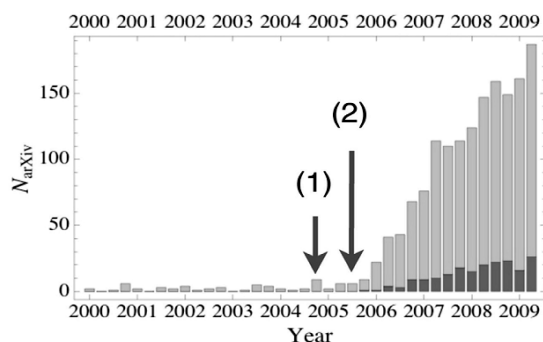

Fig. 1. Number of articles posted on graphene. (*1*) Discovery of graphene. (*2*) Anomalous QHE measurement [3]

Actually, graphene was discovered by exfoliation (or peeling) of graphite using what nowadays is called "scotch tape technique". After its discovery there was a short period of time when graphene was not taken seriously, since it was believed that such a material could not exist in crystalline form. The field of graphene research began to flourish only after the measurements of the anomalous Hall effect by Geim's [3] and Philip Kim's group at Columbia University in the USA [4] had been carried out. Graphene is a graphite layer being a pure carbon formed from flat stacked layers of atoms. The tiered structure of graphite was discerned centuries ago and so it was natural for physicists and materials scientists to try splitting the mineral into its constituent sheets to study a substance with an extremely simple geometry. Graphene is made up of atoms bound together in a network of repeating hexagons within a single plane just one atom thick.
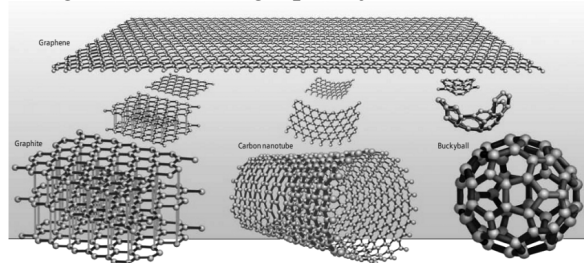

Fig. 2. The graphite family[5]

As is easily seen from Fig. 1, graphene serves as a basis for all other allotropes of graphite. Graphite, buckyballs and carbon nanotubes consist of graphene units merged in different ways. Graphene properties are not only unique in the case of the perfect crystal structure. The graphene surface with artificial or natural defects might be also useful. These defects can change certain material properties and allow to use graphene for wider spectrum of scientifical tasks [6, 7]. In particular, chemical applications are among those tasks. Indeed, it is easy to understand that any defect in strictly two-dimensional graphene should drastically modify its electronic properties [8].

We would like to emphasize here that graphene due to variety of possible structural defects can find a promising application in mass spectrometry. Matrix-free laser-desorption mass spectrometry using various inert surfaces to promote ion formation has been widely investigated during last years [9]. The technique was applied to get rid of drawbacks appropriate to MALDI mass spectrometry, e.g., a miscibility problem for the matrix selection, the appearance of hot spots, and difficulties while measuring low-weight analytes. In the latter case, interference between matrix ions and analyte ones obscures the results. It is evident that this phenomenon can be totally avoided when analytes are located on inert surfaces. Porous silicon and carbon powders are among successful ionization supports used in matrix-free mass spectrometry [10]. Nevertheless, it is always desirable to have a number of supports as wide as possible to study all kinds of organic analytes. Hence, we propose graphene as such a support instead of silicon bearing in mind its specific properties. Namely, graphene (two-dimensional carbon) flakes [11] are no more the exotics and might be produced in the nearest future in industrial quantities. Thus, we hope graphene ionization supports to become cheap enough. On the other hand, such a substrate is universal enough to adsorb various classes of analytes.

Various kinds of defects, which seriously modify electron properties, strongly scatter charge carriers being of no surprise in view of the indicated above two-dimensional peculiar electron spectrum of graphene [8]. These very defects may be good sites for organic molecules to be later desorbed by laser irradiation. The more so, topological defects, vacancies and adatoms have been experimentally shown to be stable at least under electron irradiation [8]. What is extremely important, defects of graphene flakes should be centers of chemical activity [12] which is crucial for our purposes. This was directly proved by functionalizing graphene with large aromatic donor and acceptor molecules [13]. In Fig. 3 and Fig. 4 two types of defects are shown to demonstrate their powerful influence on the graphene single layer.

One can hope that filled with organic molecules the existing defects will become centers of laser-induced evaporation. Such a behavior of carbon planes might be an extrapolation of carbon nanotube properties which serve as hosts for different particles, thus being a material for numerous useful applications [15].
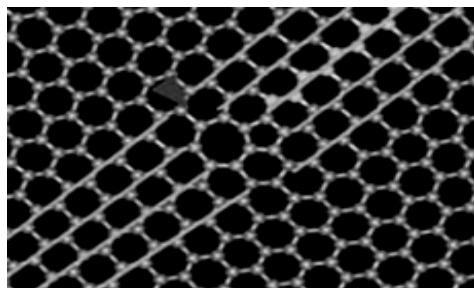

Fig. 3. An atomistic model of the pentagon–heptagon pair in the graphitic network [12]
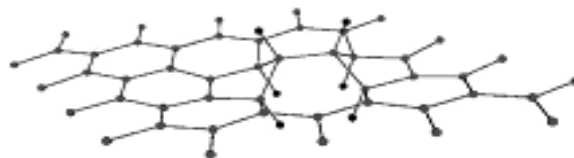

Fig. 4. Optimized geometric structures for the Stone-Wales defect functionalized by 6 (out-of-plane) hydrogen atoms [14]

All those speculations can be checked in our subsequent experimental work where we are going to solve several problems. Specifically, we hope to obtain answers to such questions as: (i) how practically effective is graphene as a support for LDI; (ii) is graphene suitable as a substitute of the NALDI^{tm} substrate; (iii) can it effectively separate small molecules and fragments due to its structural defects of different kinds.

One should bear in mind that the closer is the substrate structure to that of graphene the easier is the ionization process. Ionized fragments become heavier and mass spectrum gets richer for the same molecular probe. To be specific, we have considered bi-nuclear copper complexes. Graphenes are preferable in the sense that the ionization point (i.e. the substrate area influenced by laser radiation) is controllable. This is not the case for other carbon-involving substrates, the substrates of which is to a great extent chaotic so that the actual structure may affect ion formation in various points in a different way.

In our subsequent studies we should solve the following problems. First, what are the peculiarities of the ion formation on different kinds of graphite substrates? What is the origin of those peculiarities? Second, are those effects the plane surface ones or sharp step edges are dominant? Third, we shall make choice among probe molecules which are of practical interest.

We are going to ascertain correlations between properties of single layer and bi-layer graphenes including those related to point and ex-

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tended defects and their electronic structure on the one hand and the corresponding ion formation on the other hand.

Selected probes coupled with graphenes should be promising for various electronic devices including storage ones. Biologically active molecules interacting with the graphite and graphene are also interesting in view of possible medical applications.

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Огляд властивостей графену в зв'язку з його використанням як підкладки для безматричної мас-спектрометрії

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Представлено короткий огляд основних властивостей графену. Цей матеріал розглядається з точки зору можливого використання як підкладки для мас-спектрометричних досліджень. Також розглянуто вплив природних та штучно створених дефектів на електронні та хімічні властивості графенових структур.

Обзор свойств графена в связи с его использованием как подложки для безматричной масс-спектрометрии

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Представлен краткий обзор основных свойств графена. Этот материал рассматривается с точки зрения возможного использования в качестве подложки при масс-спектрометрических исследованиях. Также рассмотрена роль естественных и искусственно созданных дефектов в электронных и химических свойствах графеновых структур.