

Computer Simulations and Experimental Study of Graphane-Like Materials Produced by Electrolytic Hydrogenation

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ABSTRACT

Computer modeling and quantum-mechanical calculations were used for computational characterization of the energetic and structural properties of the graphane and graphane-like structures. Graphane-like fragments with various levels of hydrogenation were experimentally produced by mechanical exfoliation of multilayer highly oriented pyrolytic graphite preliminary doped electrolytically. Raman spectra showed the essential contribution of hydrogenated state and the correlation between the time of hydrogenation and the amplitudes of the peaks, related to “graphane-like” state.

Keywords: graphene, graphane-like materials, computer simulation.

1 INTRODUCTION

Composite of graphene and hydrogen associated with its surface [1], was theoretically predicted few years ago [2] and named as graphane. At the present time several conformations of graphane are being predicted theoretically [3] but our paper will not focus on peculiarities of all these structures. In contrast to graphene, graphane’s electronic structure shows considerable contribution of sp^3 states, which makes it a dielectric material with energy gap dependent on degree of hydrogenation. In this relation it should be noticed, that the term graphane commonly used for graphene structures having all bonds saturated with hydrogen. All graphene-hydrogen systems with partly covered surface of graphene are usually named as “graphane-like” structures. It can be noticed, that since recent time “graphane-like” structures are objects of greater interest than graphane itself for many researches. The graphane and graphane-like systems was also considered as a possible safe and capacious carrier of hydrogen, that can be important for hydrogen energetic. But this area of application demands developing of technology of economical production of graphane-like materials in large amounts. The aim of this work is to draw attention to the new method of formation of graphane and graphane-like materials, using preliminary electrolytic treatment of thin and ultra-thin graphite [4] and afterwards mechanical exfoliation of graphane or

graphane-like fragments in order to avoid the use of much more expensive and long-term ion-plasma methods [1,5].

2 COMPUTER SIMULATION

Here and down we use the wide spread term graphane for configurations, where all graphene’s bonds are fully saturated with hydrogen atoms. For example, the earlier predicted in the paper [2] conformations of graphane (“chair” and “boat”) are presented in Figure 1.

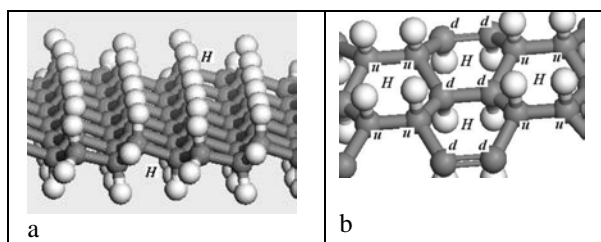


Fig.1. a) “Chair”-graphane conformation ; b) “boat”-graphane conformation

One can see that “chair” conformation results in rising up the three C atoms of hexagon (marked as u) and alternatively falling three C atoms down (marked as d) within the area of graphane structure on the surface. The “boat” conformation results in rising up a pair of C atoms and alternatively falling down a pair of C atoms. All configurations with partly covered with hydrogen surface of graphene will be named as “graphane-like” structures.

Obviously, energetic characteristics of graphane and graphane-like configurations are being very important for possible applications, particularly, in hydrogen-fueled engines. Theoretical values for the hydrogen binding energies, obtained by quantum-mechanical calculations for graphane structures are usually in the interval 5.0 -6.5 eV. But it is too large for effective cars hydrogen fuel applications. Therefore we focused on computer simulation and DFT calculations of graphane-like structures. Some results of our

calculations of possible structures forming due electrolytic hydrogenation are presented in Fig.2 (a,b).

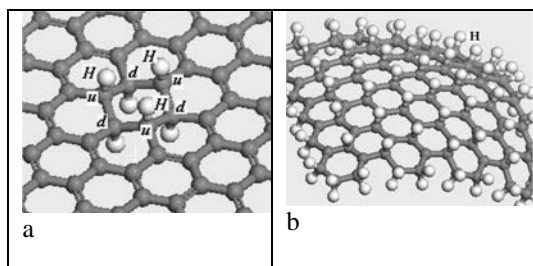


Fig.2. a) two-sided “chair”-graphane-like cluster. A C – C bond length within the cluster is 1.52 Å. b) one-sided “chair –graphane-like” cap; The binding energies: $E_b =$: a) 5.2 eV, b) 1.8 eV

For example, Fig.2,a presents a “chair”- graphane-like cluster structure. One can see that it results in rising up the three C atoms of hexagon (marked as u) and alternatively falling three C atoms down (marked as d) within the area of graphane cluster on the surface. We also found that there is a narrow transition structure zone between graphane cluster and the origin of graphene area. We taken into account that in a real process of low-energy electrolytic hydrogenation one-sided reaction with formation a peculiar graphane-like configuration is very likely. The binding energy of the hydrogen atoms placed on the outside surface of the “chair-graphane – like cap” (see Figure 2,b) was obtained as large as 1.8 eV. This value is rather acceptable for hydrogen fuel engine applications. It should be noticed, that for inside-cap arrangement the binding energy of H-atoms was equal to 4.5 eV.

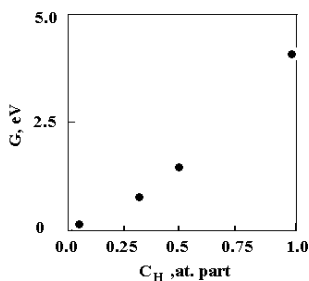


Fig. 3. The dependence of the band-gap of graphane-like structure on hydrogen concentration.

Fig.3 presents results of DFT calculations for the dependence of the band-gap of graphane-like structure on hydrogen concentration on the surface of graphene hydrogenated.

3 EXPERIMENTAL RESULTS

On the first stage thin graphite pieces were produced from multilayer high-oriented pyrolytic graphite by

mechanical exfoliation and afterwards they were hydrogenated by electrolytic techniques at room temperature. The electrolytic hydrogenation was performed in a cell with a Pd anode in distilled water by $U=40-100$ V, $I = (2\div 5) 10^{-3}$ A, at the room temperature. In typical case the distance between anode and specimen was nearly 1-2 mm. Raman spectra were obtained by NT-MDT NTegra Spectra spectrometer, using laser irradiation with $\lambda= 473$ nm in backscattering geometry. The features of spectra for the pristine state of multilayer graphite specimens are well known and characterized by the two intense peaks G (1580 cm^{-1}) and 2D (2744 cm^{-1}) (Figure 4,a).

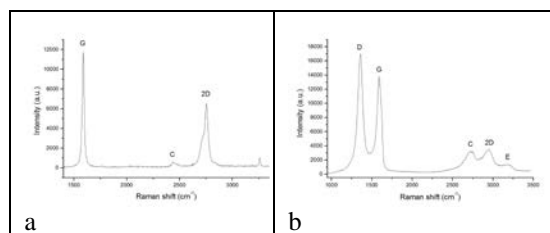


Fig.4. Typical Raman-spectra of multilayer specimens: a) - pristine state, b) a hydrogenated state.

After hydrogenation all Raman spectra essentially changed (Figure 4,b). The three new peaks appeared in all spectra of the hydrogenated multilayer specimens: D (1350 cm^{-1}), C (2430 cm^{-1}), E (2940 cm^{-1}). They all are in a good accordance with recent results, which were obtained with using the hydrogen plasma techniques [1,5]. It is known well, that the peak D at ~ 1350 cm^{-1} is linked to disordered structure of graphite or graphene. On the second stage the graphane and graphane-like pieces were exfoliated from above mentioned ultra-thin hydrogenated flakes by simple technique of “drawing” on glass substrates.

Specimens exfoliated were investigated by the optical microscopy and Raman spectroscopy. Figure 5 presents typical optical images of few layer graphene surfaces after hydrogenation with different regimes. Figures 5,a illustrates the typical optical microscopy surface structure with clusters, which formed during 5-30 min expositions by the current equals $2-3 10^{-3}$ A. Figure 5,b shows a typical surface after more long and intensive hydrogenation (60 min, $4 10^{-3}$ A). This surface displays morphology features that are obviously relating to formation of small blisters.

Figure 6 presents typical Raman spectra of these specimens. All spectra show the relation between G and 2D peaks which characterized them as one- or two-layer specimens [1]. Moreover, our spectra display in hydrogenated specimens well distinguished peak E at ~ 2950 cm^{-1} . It is quite reasonable to suppose that E-peak characterized C-H bond in these nanostructures.

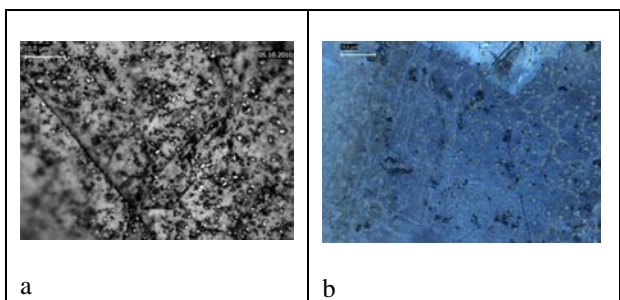


Fig.5. Typical optical images of surfaces after hydrogenation: (a)- a surface after short time hydrogenation in electrolytic cell (10 min), displaying structure with small clusters; (b) - surface after long hydrogenation (60 min) with obvious blistering.

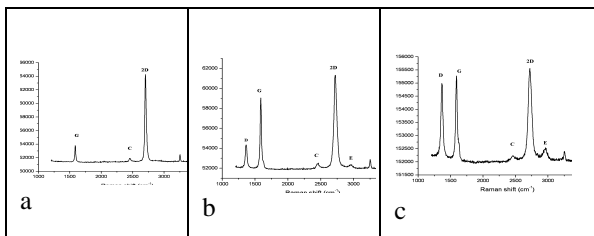


Fig.6. Typical Raman-spectra of one- and two-layer specimens, containing hydrogen. a) - a pristine state one layer graphene; b) a pristine state of two layer graphene; c) hydrogenated two layer graphene.

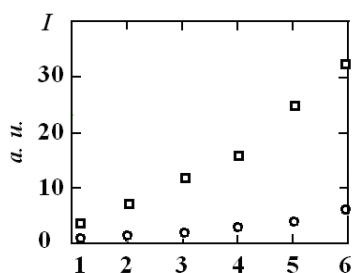


Fig.7. Correlation between the amplitudes of D- and E - peaks.

In Fig.7 one can see nearly linear correlation between D and E peaks, that was revealed for a set of specimens with different time of hydrogenation.

CONCLUSION

Computer simulation and quantum mechanical calculations of structural and energetic characteristics of some possible configurations of hydrogenated graphene was performed. Graphane-like fragments were obtained experimentally by using mechanical exfoliation from the highly oriented pyrolytic graphite preliminary hydrogenated in electrolytic cell. Data of the Raman spectroscopy have confirmed the existence of graphane-like structures with different levels of hydrogenation. The linear correlation between D and E peaks in Raman spectra was revealed for a group of specimens with different level of hydrogenation.

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