Статья поступила в редакцию 28.10.15. Ред. рег. № 2391 The article has entered in publishing office 28.10.15. Ed. reg. No. 2391

УДК 541.67:541.142 doi: 10.15518/isjaee.2015.21.008

ЭКСТРАОРДИНАРНОЕ ПРОЯВЛЕНИЕ ЭФФЕКТОВ ТИПА ЭФФЕКТА КУРДЮМОВА И ВОДОРОДНОГО СПИЛЛОВЕР ЭФФЕКТА В СВЯЗИ С ПРОБЛЕМОЙ ЭФФЕКТИВНОГО ХРАНЕНИЯ ВОДОРОДА В ГРАФИТОВЫХ НАНОВОЛОКНАХ

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Заключение совета рецензентов: 01.11.15 Заключение совета экспертов: 05.11.15 Принято к публикации: 09.11.15

Рассматриваются термодинамические стимулы и энергетика интеркаляции нанофазы молекулярного водорода высокой плотности в углеродные наноструктуры. Обсуждается физика экстраординарного проявления эффектов типа эффекта Курдюмова и водородного спилловер эффекта в связи с проблемой эффективного хранения водорода в графитовых нановолокнах.

Ключевые слова: обработка атомным водородом, высоко ориентированный пиролитический графит, эпитаксиальные графены, графитовые нановолокна, интеркаляция твердого H_2, эффект Курдюмова, водородный спилловер эффект, хранение водорода на борту автомобиля.

EXTRAORDINARY MANIFESTATION OF THE KURDJUMOV-LIKE EFFECT AND THE SPILLOVER-LIKE ONE, RELEVANCE TO THE PROBLEM OF THE EFFICIENT HYDROGEN STORAGE IN GRAPHITE NANOFIBERS

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Referred: 01.11.15 Expertise: 05.11.15 Accepted: 09.11.15

Thermodynamic stimuli and energetics of intercalation of H_2 nanophase of a high density into carbon-based nanostructures are considered. The physics of the extraordinary manifestation of the Kurdjumov-like effect and the hydrogen spillover-like one, relevance to the problem of the efficient hydrogen storage in graphite nanofibers are discussed.

Keywords: atomic hydrogen treatment, HOPG, epitaxial graphenes, graphite nanofibers, solid H_2 intercalation, hydrogen spillover effect, the Kurdjumov effect, hydrogen on-board storage.

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Область научных интересов: физическое материаловедение.

Публикации: www.scopus.com.scopeesprx.elsevier.com/results (Scopus – Results: AU-ID (“Nechaev,Yu.S.”7005536791).

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Publications: www.scopus.com.scopeesprx.elsevier.com/results (Scopus – Results: AU-ID (“Nechaev,Yu.S.”7005536791).

1. Introduction

Over the past 20 years, many scientists have reported that hydrogen spillover is a viable technique to achieve more hydrogen storage on different carbon-based materials and nanomaterials, even at ambient conditions [1-25]. However, as noted, for instance, in [1], the veracity of these results and the efficiency of such graphitic structures to store hydrogen are still questionable. In addition, the spillover mechanism and energetics of molecular hydrogen on different carbon-based materials and nanomaterials, in the presence of metallic catalysts, has not been satisfactory understood up to nowadays [1].

These open questions are considered in the present study, which is a further development of results [26] and the previous results [27] (of an open access). The present study is related to the extraordinary data on molecular gaseous hydrogen interactions with graphite nanofibers (with metallic catalysts), when, as is shown in this study, a unique manifestation of both the spillover effect [1-25] and the Kurdjumov-like [28, 29] extraordinary effect occur. The mechanism and energetics of such two effects are revealed, particularly, by comparing with data on atomic gaseous hydrogen interactions with highly oriented pyrolytic graphites (without any catalysts) and epitaxial graphenes (also without any catalysts).

2. Experimental methodology

In this study, thermodynamic analysis approach [26, 27] of the related experimental data (including some figures from [27]) have been used.

3. Results and discussion

3.1. The physics of intercalation of H_2 gaseous nanophase of high density into graphene nanoblisters in HOPG and epitaxial graphenes (under atomic hydrogen treatment)

Fig. 1, 2 (Fig. 19, 20 from [27]) show the two steps ((*a*) and (*b*)) of hydrogenation (at 300 K and the atomic hydrogen flux, formally corresponding to pressure $P_{(\mathrm{Hgas})} \approx 1\cdot10^{-4}$ Pa, without any catalyst) of surface graphene layers of a highly oriented pyrolytic graphite (HOPG) resulted in intercalation of H_2 gaseous nanophase of a high density into surface graphene nanoblisters.

Approximating the nanoblister to be of a semi-ellipse form, results in the blister area of $S_b \approx 2.0\cdot10^{-11}$ cm^2 and its volume $V_b \approx 8.4\cdot10^{-19}$ cm^3. The amount of retained hydrogen in this sample becomes $Q \approx 2.8\cdot10^{14}$ $\mathrm{H_2/cm^2}$, and the number of hydrogen molecules captured inside the blister becomes $n \approx (QS_b) \approx 5.5\cdot10^3$. Thus, within the ideal gas approximation and accuracy of one order of the magnitude, the internal pressure of molecular hydrogen in a single nanoblister at near-room temperature ($T \approx 300$ K) becomes $P_{\mathrm{H2}} \approx \{k_{\mathrm{B}}(QS_b)T/V_b\} \approx 1\cdot10^8$ Pa. The hydrogen molecular gas density in the blisters (at $T \approx 300$ K and $P_{\mathrm{H2}} \approx 1\cdot10^8$ Pa) can be estimated as $\rho \approx \{(QM_{\mathrm{H2}}S_b)/V_b\} \approx 0.045$ g/cm^3, where M_{H2} is the hydrogen molecule mass.

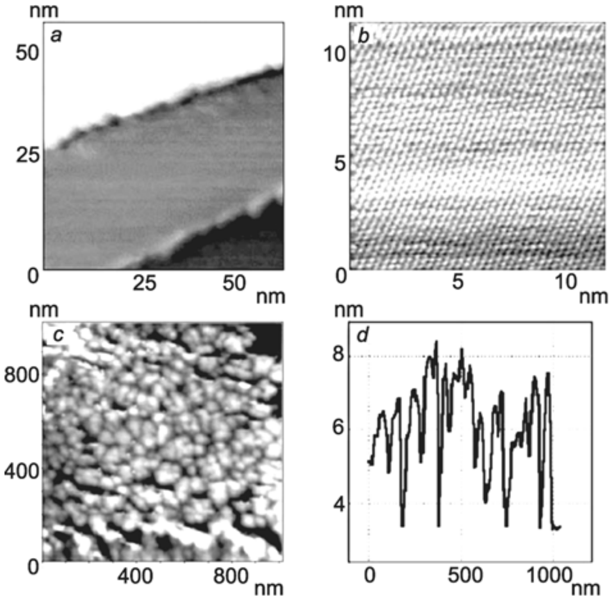

Рис. 1 (рис. 19 из [27]). STM данные (Waqar, 2007) для исходного (не обработанного атомным водородом) образца высоко ориентированного пиролитического графита (HOPG): (*a*) площадь поверхности 60,8x60,8 нм; (*b*) площадь поверхности 10,9x10,9 нм. (*c*) Площадь поверхности 1x1 нм, для образца, подвергнутого обработке атомным водородом дозой *D* = 1,8·10^{16} H$^{\mathrm{O}}$/см^2. (*d*) Профиль поверхности для обработанного образца (*c*)
Fig. 1 (Fig. 19 from [27]). STM images of the untreated HOPG sample (Waqar, 2007) taken from areas of (*a*) 60.8 x60.8 nm and (*b*) 10.9x10.9 nm. (*c*) AFM image (area of 1x1 nm) of the HOPG sample subjected to atomic hydrogen dose (*D*) of 1.8·10^{16} H$^{\mathrm{O}}$/cm^2. (*d*) Surface height profile obtained from the AFM image reported in (*c*)

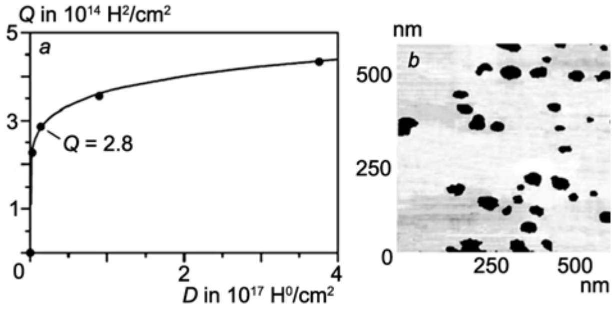

Рис. 2 (рис. 20 из [27]). (*a*) Эффективность аккумулирования водорода в HOPG образцах (Waqar, 2007): зависимость количества десорбированного молекулярного водорода (*Q*) от дозы (*D*) атомного водорода. (*b*) STM данные для площади поверхности 600x600 нм для HOPG образца, подвергнутого обработке атомным водородом дозой 1,8·10^{16} H$^{\mathrm{O}}$/см^2 и последующему термодесорбционному нагреву
Fig. 2 (Fig. 20 from [27]). (*a*) Hydrogen storage efficiency of HOPG samples (Waqar, 2007): quantity of desorbed molecular hydrogen (*Q*) versus dose (*D*) of atomic hydrogen exposure. (*b*) STM image for 600x600 nm area of the HOPG sample subjected to atomic hydrogen dose of 1.8·10^{16} H$^{\mathrm{O}}$/cm^2, followed by hydrogen thermal desorption

The data in Fig. 1, 2 (Fig.19-20 from [27]) can be quantitatively described, with an accuracy of one order of magnitude, and interpreted within the thermodynamic approach [26, 27], by using the condition of the thermal-elastic equilibrium of two phases (the Kurdjumov-like effect) for the process of ($H_{(gas)} \rightarrow$ ½ $H_{2(gas\_in\_blisters)}$), as follows:

$$P_{H_2}/P^0_{H_2} = \left(P_H/P^0_H\right)^2 \exp\left\{\left[\Delta H_{dis} - P^*_{H_2}\Delta V\right]/k_B T\right\}, \quad (1)$$

where $P^*_{H_2}$ is related to the blister "wall" back pressure (caused by P_{H_2}) the so called surface pressure ($P^*_{H_2} \approx$ $\approx P_{H_2} \approx 1{\cdot}10^8$ Pa), P_H is the atomic hydrogen pressure corresponding (formally) to the atomic hydrogen flux ($P_H \approx 1{\cdot}10^{-4}$ Pa), $P^0_{H_2}$ = P^0_H = 1 Pa is the standard pressure, ΔH_{dis} = 4.6 eV is the dissociation energy (enthalpy) of one molecule of gaseous hydrogen (at room temperatures), ΔS_{dis} = 11.8 k_B is the dissociation entropy, $\Delta V \approx (S_b r_b/n)$ is the apparent volume change, r_b is the radius of curvature of nanoblisters at the nanoblister edge ($r_b \approx 30$ nm, Fig. 1), N_A is the Avogadro number, and T is the temperature ($T \approx 300$ K). The quantity of ($P^*_{H_2}\Delta V$) is related to the work of the nanoblister surface increasing with an intercalation of 1 molecule of hydrogen.

It is necessary to emphasize that the process ($H_{(gas)} \rightarrow$ $\rightarrow$ ½ $H_{2(gas\_in\_blisters)}$) is one directional, and the process ends when the thermo-elastic equilibrium of the two gas phases ($H_{(gas)}$ and $H_{2(gas\_in\_blisters)}$) is reached (Fig. 20 (*a*) in [27], Equation (1)). This is a typical situation of the Kurdjumov effect. But in the case under the consideration, there is an unusually high energetics (at the expense of the free energy of association of penetrating (in the graphene nanoblisters) hydrogen atoms to the "captured" hydrogen molecules).

The value of the tensile stresses σ_b (caused by $P^*_{H_2}$) in the graphene nanoblister "walls" with a thickness of d_b and a radius of curvature r_b can be evaluated from another condition (equation) of the thermal-elastic equilibrium of the system in question, as follows:

$$\sigma_b \approx P^*_{H_2}(r_b/2d_b) \approx (\varepsilon_b E_b), \quad (2)$$

where ε_b is a degree of elastic deformation of the graphene nanoblister walls, and E_b is the Young's modulus of the graphene nanoblister walls.

Substituting in the first part of Equation (2) the quantities of $P^*_{H_2}$ $\approx 1{\cdot}10^8$ Pa, $r_b \approx 30$ nm and $d_b \approx 0.15$ nm, results in the value of $\sigma_b \approx 1{\cdot}10^{10}$ Pa.

The degree of the elastic deformation of the graphene nanoblister walls, apparently reaches $\varepsilon_b \approx 0.1$ (Fig. 21, 19 in [27]). Hence, with Hooke's law of approximation, using the second part of Equation (2), one can estimate, with the accuracy of one order of the magnitude, the value of the Young's modulus of the graphene nanoblister walls: $E_b \approx (\sigma_b/\varepsilon_b) \approx 0.1$ TPa. The calculated quantity of E_b is of one order lower than that considered in [27] experimental value (Lee et al., 2008; Pinto and Leszczynski, 2014) of the Young's modulus of graphene ($E_{graphene} \approx 1.0$ TPa). This difference may be related to a possible higher defect level of the graphene nanoblister walls, and/or to a possible internal side hydrogenation of the walls.

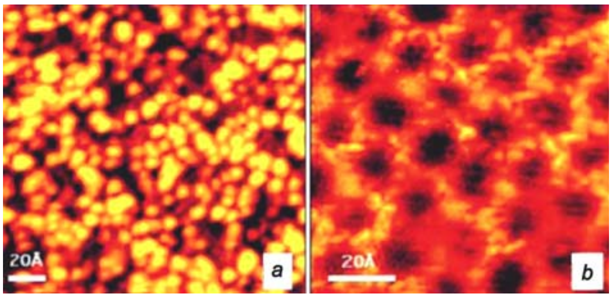

Рис. 3 (рис. 14 из [27]). (*a*) STM данные (Balog et al., 2009) для поверхности эпитаксиального графена, подвергнутого водородной обработке. Наблюдаемые яркие наноблистеры (нановспучивания поверхностного слоя) отвечают водородным кластерам. Температура водородного пучка составляла T = 1600 K, время воздействия t = 90 с, интенсивность потока атомов водорода $F = 10^{12}$-10^{13} ат./см^2·с, что отвечало давлению атомарного водорода $P_H \approx 10^{-4}$ Па [26]. (*b*) Наблюдаются большие области дегидрированного графена, образующиеся при нагреве (отжиге) материала до 1073 K

Fig. 3 (Fig. 14 from [27]). (*a*) STM image of the graphene surface after extended hydrogen exposure (Balog et al., 2009). The bright protrusions visible in the image are hydrogen clusters. Hydrogen dose at T = 1600 K, t = 90 s, $F = 10^{12}$-10^{13} atoms/cm^2·s, it corresponds to $P_H \approx 10^{-4}$ Pa [26]. (*b*) Large graphene area recovered from hydrogenation by annealing to 1073 K

Similar STM, AFM and other data of different researchers for the epitaxial graphenes (for instance, Fig. 3 (Fig. 14 in [27]) can be analyzed and interpreted in a similar manner [26, 27], within the same physical concept (Equations 1 and 2, the Kurdjumov-like extraordinary effect). As is noted in [27], a number of researchers (Waqar, 2007; Watcharinyanon et al., 2011; Wojtaszek et al., 2011; Castellanos-Gomezet al., 2012; Bocquet et al., 2012; Hornekaer et al., 2006; Luo et al., 2009; Balog et al., 2009; Waqar et al., 2010) have not sufficiently considered the "thermodynamic forces" and/or energetics of forming (under the atomic hydrogen treatment) graphene nanoblisters in the surface HOPG layers and epitaxial graphenes. Particularly, they have not taken into account a possibility of the Kurdjumov-like effect manifestation. It is also expedient to note that the recent experimental data [30] {Geim et al. (2014)} show that a hydrogen atom can not pass through a perfect graphene network. On the other hand, the analysis [27] of a number of experimental data (including Fig. 19-21, 13, 14, 22, 24 in [27]) shows that a hydrogen atom can pass through permeable defects in graphene, for instance, through triple junctions of grain boundaries. In Fig. 20(*b*), 13(*a*) and 13(*b*) in [27], one can imagine some grain boundary network decorated (obviously, in some nanoregions at grain boundaries) by some nanoprotrusions.

3.2. The physics of intercalation of the solid H_2 nanophase into hydrogenated graphite nanofibers (with metallic catalysts)

The physics of intercalation of solid molecular hydrogen of high density ($\rho_{H2} \approx 0.5$ g/cm^3, Fig. 4 (Fig. 22 in [27]) into closed (in the definite sense) nanoregions in hydrogenated GNFs (Fig. 5 (Fig. 24 in [27]) is related to the same concept (Equations of type 1 and 2, the Kurdjumov-like effect).

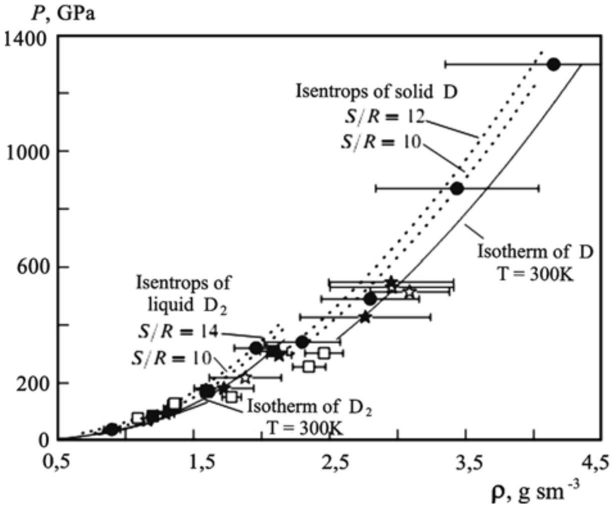

Рис. 4 (рис. 22 из [27]). Литературные данные {Trunin et al. (2010)} об изоэнтропах ((*S*/*R*) = const) и изотермах (*T* = 300 K) для дейтерия и протия (водорода). Плотность (ρ) протия (H_2, H) увеличена вдвое (по масштабным соображениям). Экспериментальные и теоретические изотермы показывают, что при *T* = 300 K и внешнем сжимающем давлении *P* = 50 ГПА водород существует в твердом молекулярном состоянии с плотностью $\rho_{H2} \approx 0{,}5$ г/см^3

Fig. 4 (Fig. 22 from [27]). Literary data {Trunin et al. (2010)} on isentropes ((*S*/*R*) = const) and isotherms (*T* = 300 K) of deuterium and protium. The density (ρ) of protium (H_2, H) is increased by a factor of two (for the scale reasons). The experimental and theoretical isotherms show that at *T* = 300 K and the external compression pressure of *P* = 50 GPa hydrogen exists in the solid molecular state of a high density $\rho_{H2} \approx 0.5$ g/cm^3

The comparison with the previous results (presented in Item 3.1) shows that there is a unique manifestation of the spillover effect (particularly, in Fig. 24 in [27]), as related to providing of the necessary one direction flux of atomic hydrogen from Pd-catalyst to the nanopores (when the material hydrogenation at initial molecular hydrogen pressure P_{H2} = 8 MPa).

The atomic hydrogen, obviously, forms at the expense of the energy of the surroundings, for instance, by heat conducting from it to the Pd-catalyst system, which provides the dissociative dissolving of H_2 in Pd and some other related processes. It seems that this is not a violation of the Second Law of thermodynamics, since there should be some difference in temperatures of the surroundings and the Pd-catalyst system (due to the hydrogen spillover effect). Also, the thermal-elastic self-compression (the Kurdjumov-like effect) of the "captured" H_2 in the nanopores occurs at the expense of the association energy of the penetrating hydrogen atoms (as considered in Item 3.1).

The recent related data [31, 32] can be taken into account in further studies.

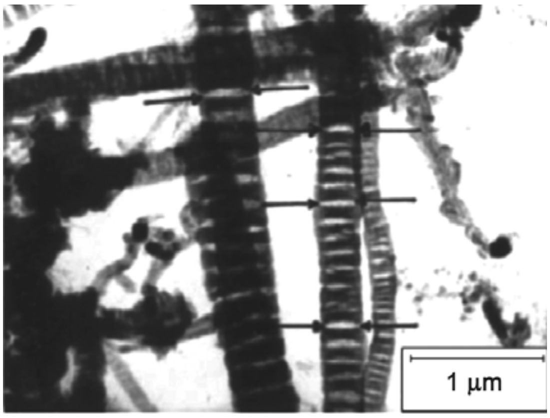

Рис. 5 (рис. 24 из [27]). Микрофотография {Gupta et al. (2004)} графитовых нановолокон (ГНВ) с Pd-катализатором, гидрированных при 300 K и начальном давлении молекулярного водорода $P_{H2} \approx 8$ МПа, после удаления из них (при 300 K, за 10 мин {Park et al. (1999)}) интеркалированной нанофазы твердого H_2 (17 масс. %) высокой плотности ~0,5 г/см^3 (анализ [26, 27]). Стрелки на рисунке указывают на щелеподобные закрытые нанопоры линзообразной формы, где находилась интеркалированная нанофаза твердого H_2 (под давлением ~50 ГПа) [26, 27]. Такую же величину давления можно получить [26, 27], рассматривая деформацию материала и напряжения, необходимые для образования закрытых нанопор линзообразной формы

Fig. 5 (Fig. 24 from [27]). Micrograph {Gupta et al. (2004)} of hydrogenated graphite nanofibers (GNFs), with Pd-catalyst (hydrogenated at 300 K and initial pressure of molecular hydrogen $P_{H2} \approx 8$ MPa, after release from them, at 300 K, for 10 min {Park et al. (1999)}, of the intercalated solid H_2 nanophase (17 mass. %) of a high density of $\rho_{H2} \approx 0.5$ g/cm^3 (analysis [26, 27]). The arrows in the picture indicate some of the slit-like closed nanopores of the lens shape, where the solid H_2 intercalated nanophase (under pressure of ~50 GPa) was localized [26, 27]. Such a pressure level can be also evaluated [26, 27] by the consideration of the material deformation and the necessary stresses for forming the lens shape closed nanopores

4. Conclusions

1. The "thermodynamic forces" and energetics of forming of graphene nanoblisters (under atomic hydrogen treatment, without catalysts) in the surface HOPG layers (Figs. 19-21 in [27]) and epitaxial graphenes (Figs. 13, 14 in [27]) are quantitatively described, particularly, two conditions of the thermal-elastic thermodynamic equilibrium of the two gaseous phases (Equations 1 and 2, the Kurdjumov-like effect) are considered.

2. The physics of intercalation of gaseous H_2 nanophase of a high density ($\rho_{H2} \approx 0.045$ g/cm^3) into graphene nanoblisters (Figs. 19-21 in [27]) is considered (Equations 1 and 2). The hydrogen self-compression effect of 12 orders (from $P_{(Hgas)} \approx 1 \cdot 10^{-4}$ Pa to $P_{(H2gas)} \approx$ $\approx 1 \cdot 10^{8}$ Pa), at the expense of the free energy of association of the penetrating hydrogen atoms to the "captured" hydrogen molecules, is shown (the Kurdjumov-like effect extraordinary manifestation).

3. The physics of intercalation of the solid H_2 nanophase of a high density ($\rho_{H2} \approx 0.5$ g/cm^3) into hydrogenated graphite nanofibers with Pd-catalyst (Figs. 22, 24 in [27]) is considered.

4. In the light of analysis [26, 27], both the spillover effect and the Kurjumov-like effect are obviously manifested in the extraordinary data {Gupta et al. (2001, 2004)} (Fig. 24 in [27]) and the extraordinary data {Park et al. (1999)} considered in [27].

5. These results can be used for solving of the current problem of the efficient and safe hydrogen on-board storage [33].

Acknowledgements

The author is grateful to Alp Yürüm, Adem Tekin, Nilgün Karatepe Yavuz and Yuda Yürüm, participants of the joint RFBR-TUBIBAK project, and especially to T. Nejat Veziroglu, for helpful and fruitful discussions.

This work has been supported by the RFBR Project #14-08-91376 CT and the TUBITAK Project # 213M523.

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