

Mechanism and Energetics of the Unique Spillover Effect Manifestation, Relevance to the Efficient Hydrogen Storage in Graphite Nanofibers

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Abstract

The “thermodynamic forces” and energetics of intercalation of H₂ nanophase of a high density into carbon-based nanostructures are considered. The hydrogen self-compression effect, at the expense of the free energy of association of the penetrating hydrogen atoms to the “captured” hydrogen molecules, is shown. The mechanisms of the extraordinary manifestation of both the hydrogen spillover effect, and the Kurdjumov-like effect are discussed.

Keywords: atomic hydrogen treatment, HOPG, epitaxial graphenes, graphite nanofibers, solid H₂ intercalation, spillover effect, the Kurdjumov effect, hydrogen on-board storage

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. However, as noted, for instance, in (Juarez-Mosqueda, Mavrandonakis, Kuc, Pettersson & Heine, 2015), 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 satisfactorily understood up to nowadays (Juarez-Mosqueda et al., 2015).

These open questions are considered in the present study, which is a further development of results (Nechaev & Veziroglu, 2015) 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 (Juarez-Mosqueda et al., 2015) and the Kurdjumov-like extraordinary effect (Koval, 2005) 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 of the related experimental data (including Figures 1-7 from (Nechaev & Veziroglu, 2015)) has been used.

3. Results and Discussion

3.1 The Physics of Intercalation of H₂ Gaseous Nanophase of High Density into Graphene Nanoblister in HOPG and Epitaxial Graphenes (Under Atomic Hydrogen Treatment)

Figures 1-3 shows the two steps ((a) and (b)) of hydrogenation (at 300 K and the atomic hydrogen flux, formally corresponding to pressure $P_{(\text{Hgas})} \approx 1 \times 10^{-4}$ Pa, without any catalyst) of surface graphene layers of a highly oriented pyrolytic graphite (HOPG) resulted in intercalation of H₂ gaseous nanophase of a high density into surface graphene nanoblister.

Approximating the nanoblister to be of a semi-ellipse form, results in the blister area of $S_b \approx 2.0 \times 10^{-11} \text{ cm}^2$ and its volume $V_b \approx 8.4 \times 10^{-19} \text{ cm}^3$. The amount of retained hydrogen in this sample becomes $Q \approx 2.8 \times 10^{14} \text{ H}_2/\text{cm}^2$, and the number of hydrogen molecules captured inside the blister becomes $n \approx (Q S_b) \approx 5.5 \times 10^3$. 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 ($T \approx 300 \text{ K}$) becomes $P_{\text{H}_2} \approx \{k_B (Q S_b) T / V_b\} \approx 1 \times 10^8 \text{ Pa}$. The hydrogen molecular gas density in the blisters (at $T \approx 300 \text{ K}$ and $P_{\text{H}_2} \approx 1 \times 10^8 \text{ Pa}$) can be estimated as $\rho_{\text{H}_2} \approx \{(QM_{\text{H}_2}S_b)/V_b\} \approx 0.045 \text{ g/cm}^3$, where M_{H_2} is the hydrogen molecule mass.

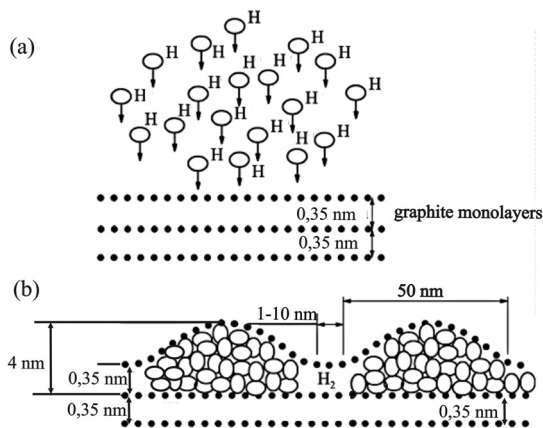


Figure 1. Model (from STM and AFM data (Figures 2, 3)) showing the hydrogen accumulation (intercalation) in HOPG, with forming blister-like surface nanostructures; hydrogenation was done at 300 K and the atomic hydrogen flux, formally corresponding to pressure $P_{(\text{H}_{\text{gas}})} \approx 1 \times 10^{-4} \text{ Pa}$, without any catalyst. (a) Pre-atomic hydrogen penetration (intercalation) step. (b) Molecular gaseous hydrogen, “captured” inside the surface graphene nanoblister (at $P_{(\text{H}_2\text{gas})} \approx 1 \times 10^8 \text{ Pa}$), after the intercalation step. Sizes are not drawn exactly in scale. The hydrogen self-compression effect is of 12 orders (from $P_{(\text{H}_{\text{gas}})} \approx 1 \times 10^{-4} \text{ Pa}$ to $P_{(\text{H}_2\text{gas})} \approx 1 \times 10^8 \text{ Pa}$). According to analysis (Nechaev & Veziroglu, 2015), it occurs at the expense of the free energy of association of the penetrating hydrogen atoms to the “captured” hydrogen molecules (Equations 1 and 2, the Kurdjumov-like effect extraordinary manifestation).

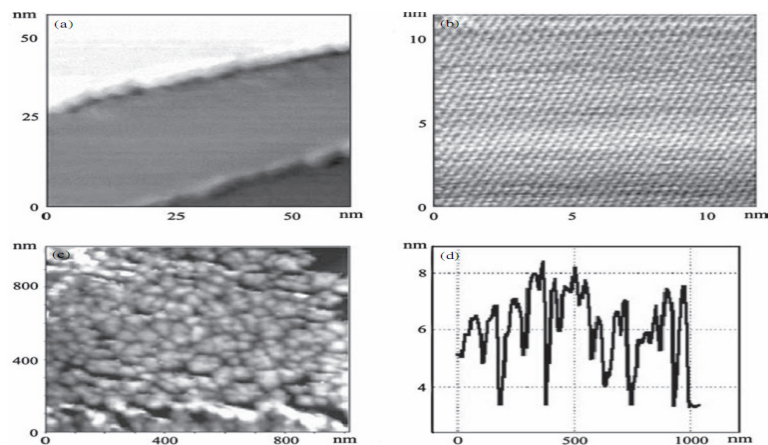


Figure 2. STM images of the untreated HOPG sample (under ambient conditions) taken from areas of (a) 60.8 x 60.8 nm and (b) 10.9 x 10.9 nm (high resolution image of the square in image (a)). (c). AFM image (area of 1 x 1 nm) of the HOPG sample subjected to atomic hydrogen dose (D) of $1.8 \cdot 10^{16} \text{ H}^0/\text{cm}^2$. (d) Surface height profile obtained from the AFM image reported in (c). The STM tunnel V_{bias} and current are 50-100 mV and 1-1.5 mA, respectively. (It may be the Kurdjumov-like effect extraordinary manifestation).

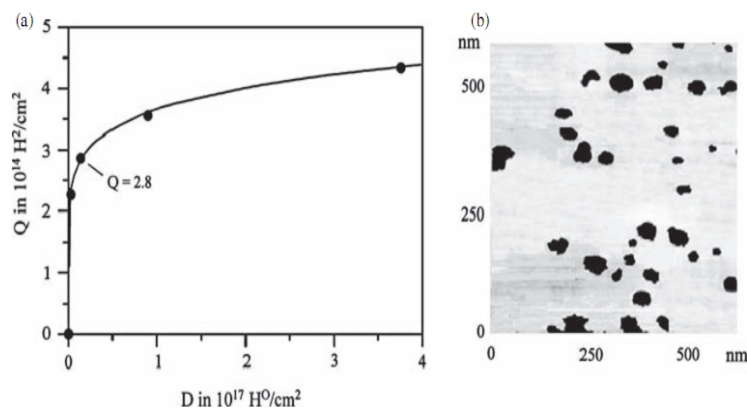


Figure 3. (a) Hydrogen storage efficiency of HOPG samples, desorbed molecular hydrogen (Q) versus dose (D) of atomic hydrogen exposure. (b) STM image for 600x600 nm area of the HOPG sample subjected to atomic hydrogen dose of $1.8 \cdot 10^{16} \text{ H}^0/\text{cm}^2$, followed by hydrogen thermal desorption. (It may be the Kurdjumov-like effect extraordinary manifestation).

These data (Figures 1-3) can be quantitatively described, with an accuracy of one order of magnitude, and interpreted within the thermodynamic approach (Nechaev & Veziroglu, 2015), by using the condition of the thermal-elastic equilibrium of two phases (the Kurdjumov-like effect) for the process of $(2\text{H}_{(\text{gas})} \rightarrow \text{H}_{2(\text{gas_in_blisters})})$, as follows:

$$(P_{\text{H}_2} / P_{\text{H}_2}^0) = (P_{\text{H}} / P_{\text{H}}^0)^2 \exp\{[\Delta H_{\text{dis}} - P_{\text{H}_2}^* \Delta V] / k_{\text{B}} T\} \quad (1)$$

where $P_{\text{H}_2}^*$ is related to the blister “wall” back pressure (caused by P_{H_2}) the so called surface pressure ($P_{\text{H}_2}^* \approx P_{\text{H}_2} \approx 1 \times 10^8 \text{ Pa}$), P_{H} is the atomic hydrogen pressure corresponding (formally) to the atomic hydrogen flux ($P_{\text{H}} \approx 1 \times 10^{-4} \text{ Pa}$), $P_{\text{H}_2}^0 = P_{\text{H}}^0 = 1 \text{ Pa}$ is the standard pressure, $\Delta H_{\text{dis}} = 4.6 \text{ eV}$ is the dissociation energy (enthalpy) of one molecule of gaseous hydrogen (at room temperatures), $\Delta S_{\text{dis}} = 11.8 k_{\text{B}}$ is the dissociation entropy, $\Delta V \approx (S_{\text{b}} r_{\text{b}} / n)$ is the apparent volume change, r_{b} is the radius of curvature of nanoblister walls at the nanoblister edge ($r_{\text{b}} \approx 30 \text{ nm}$, Figure 1), N_{A} is the Avogadro number, and T is the temperature ($T \approx 300 \text{ K}$). The quantity of $(P_{\text{H}_2}^* \Delta V)$ 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 $(2\text{H}_{(\text{gas})} \rightarrow \text{H}_{2(\text{gas_in_blisters})})$ is one directional, and the process ends when the thermo-elastic equilibrium of the two gas phases ($\text{H}_{(\text{gas})}$ and $\text{H}_{2(\text{gas_in_blisters})}$) is reached (Figure 3(a), 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 nanoblister walls) hydrogen atoms to the “captured” hydrogen molecules).

The value of the tensile stresses σ_{b} (caused by $P_{\text{H}_2}^*$) 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:

$$\sigma_{\text{b}} \approx P_{\text{H}_2}^* (r_{\text{b}} / 2 d_{\text{b}}) \approx (\varepsilon_{\text{b}} E_{\text{b}}) \quad (2)$$

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 $P_{\text{H}_2}^* \approx 1 \times 10^8 \text{ Pa}$, $r_{\text{b}} \approx 30 \text{ nm}$ and $d_{\text{b}} \approx 0.15 \text{ nm}$, results in the value of $\sigma_{\text{b}} \approx 1 \times 10^{10} \text{ Pa}$.

The degree of the elastic deformation of the graphene nanoblister walls, apparently reaches $\varepsilon_{\text{b}} \approx 0.1$ (Figures 1, 2). 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: $E_{\text{b}} \approx (\sigma_{\text{b}} / \varepsilon_{\text{b}}) \approx 0.1 \text{ TPa}$. The calculated quantity of E_{b} is of one order lower than that considered in (Nechaev & Veziroglu, 2015) experimental value of the Young’s modulus of graphene ($E_{\text{graphene}} \approx 1.0 \text{ TPa}$). 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.

Similar STM, AFM and other data of different researchers for the epitaxial graphenes (for instance, Figures 4, 5) can be analyzed and interpreted in a similar manner, within the same physical concept (Equations 1 and 2, the Kurdjumov-like extraordinary effect). As is noted in (Nechaev & Veziroglu, 2015), a number of researchers have not sufficiently considered the “thermodynamic forces” and/or energetics of forming (under the atomic hydrogen treatment) graphene nanoblister walls 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 (Hu et al., 2014) show that a hydrogen atom can not pass through a perfect graphene network. On the other hand, the analysis (Nechaev & Veziroglu, 2015) of a number of experimental data (including Figures 1 - 7) shows that a hydrogen atom can pass through permeable defects in graphene, for instance, through triple junctions of grain boundaries. In Figures 3(b), 4(a) and 4(b), one can imagine some grain boundary network decorated (obviously, in some nanoregions at grain boundaries) by some nanoprotusions.

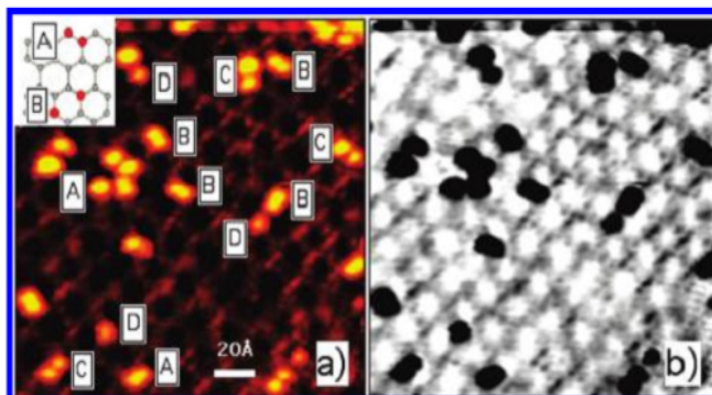


Figure 4. (a) STM image of hydrogenated graphene/SiC. (b) Same image as in (a) with inverted color scheme, giving emphasis to preferential hydrogen adsorption on the SiC surface. Hydrogen dose at $T_{(\text{beam})} = 1600$ K, $t = 5$ s, $F = 10^{12} - 10^{13}$ atoms/cm²s ($P_{(\text{Hgas})} \approx 1 \times 10^{-4}$ Pa (Nechaev & Veziroglu, 2015)). (It may be the Kurdjumov-like effect extraordinary manifestation).

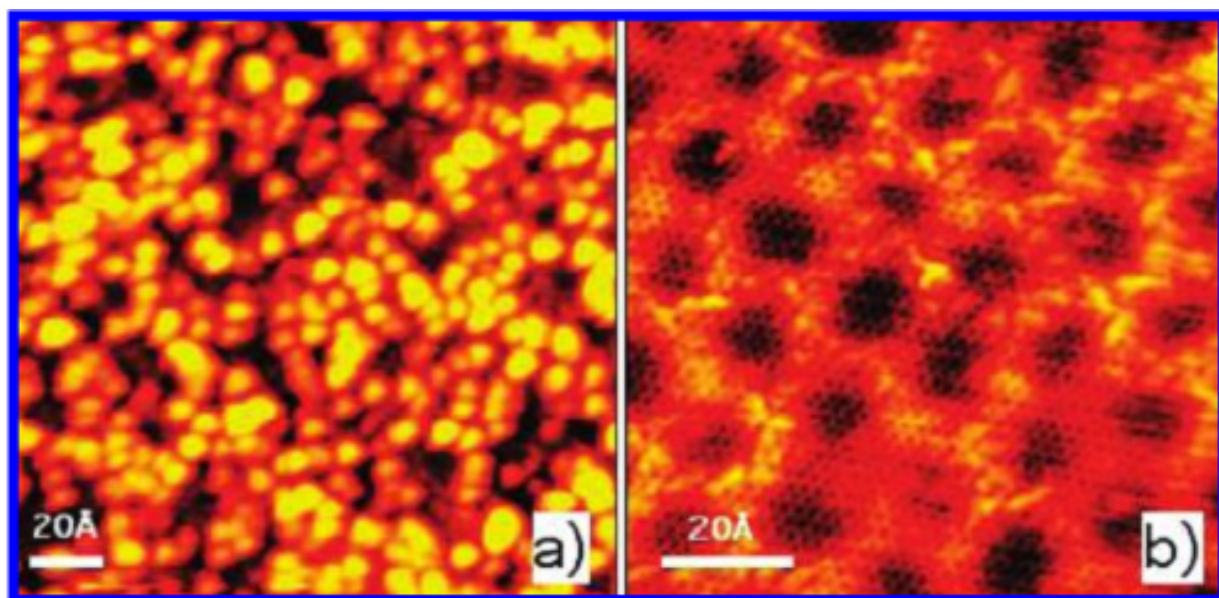


Figure 5. (a) STM image of the graphene surface after extended hydrogen exposure. The bright protrusions visible in the image are atomic hydrogen clusters (imaging parameters: $V_t = -0.36$ V, $I_t = -0.32$ nA). Hydrogen dose at $T = 1600$ K, $t = 90$ s, $F = 10^{12} - 10^{13}$ atoms/cm² s. (b) Large graphene area recovered from hydrogenation by annealing to 1073 K (imaging parameters: $V_t = -0.38$ V, $I_t = -0.41$ nA). (It may be the Kurdjumov-like effect extraordinary manifestation).

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 ($\rho_{H_2} \approx 0.5$ g/cm³, Figure 6) into closed (in the definite sense) nanoregions in hydrogenated GNFs (Figure 7) is related to the same concept (Equations of type 1 and 2, the Kurdjumov-like effect).

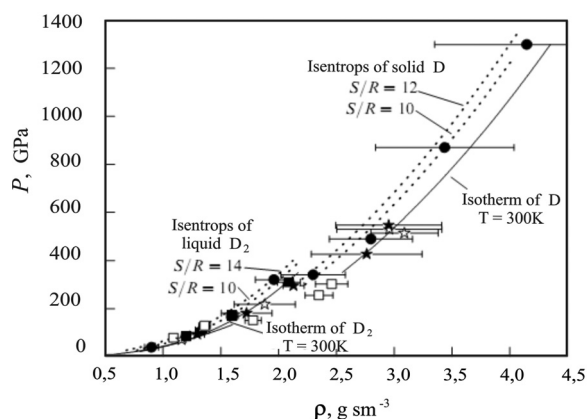


Figure 6. Literary data on isentropes (S/R) and isotherms of deuterium and protium. The density (ρ) of protium (H_2 , H) is increased by a factor of two (for the scale reasons). The experimental and theoretical isotherms show that at $T = 300$ K and the external compression pressure of $P = 50$ GPa hydrogen exists in the solid molecular state of a high density $\rho_{H_2} \approx 0.5$ g/cm³.

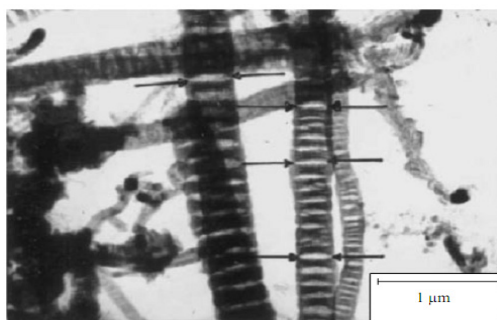


Figure 7. Micrograph of hydrogenated graphite nanofibers (GNFs), with Pd-catalyst (hydrogenated at 300 K and initial pressure of $P_{(H_2\text{gas})} \approx 8$ MPa), after release from them, at 300 K, for 10 min, of the intercalated solid H_2 nanophase (17 mass. %) of a high density of $\rho_{H_2} \approx 0.5$ g/cm³ (analysis (Nechaev & Veziroglu, 2015)). 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, according to data on Fig. 6) was localized. Such a pressure level can be also evaluated by the consideration of the material deformation and the necessary stresses for forming the lens shape closed nanopores (at the expense of the energy of association of penetrating (into the nanopores) hydrogen atoms to molecules “captured” inside the nanopores (Equations of type 1 and 2). (It may be an extraordinary manifestation of both the Kurdjumov-like effect, and the spillover effect).

The comparison with the previous results (presented in Item 3.1) shows that there is a unique manifestation of the spillover effect (particularly, in Figure 7), 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 $P_{H_2} = 8$ MPa).

The atomic hydrogen, obviously, forms at the expense of the energy of the surroundings, 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 a small 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 ((Naumov & Hemley, 2014), (Ting et al., in press)) can be taken into account in further studies.

4. Conclusions

1. The “thermodynamic forces” and energetics of forming of graphene nanoblusters (under atomic hydrogen treatment, without catalysts) in the surface HOPG layers (Figures 1-3) and epitaxial graphenes (Figures 4, 5) 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 H₂ nanophase of a high density ($\rho_{\text{H}_2} \approx 0.045 \text{ g/cm}^3$) into graphene nanoblusters (Figures 1-3) is considered (Equations 1 and 2). The hydrogen self-compression effect of 12 orders (from $P_{(\text{H}_{2\text{gas}})} \approx 1 \times 10^{-4} \text{ Pa}$ to $P_{(\text{H}_{2\text{gas}})} \approx 1 \times 10^8 \text{ Pa}$), 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 H₂ nanophase of a high density ($\rho_{\text{H}_2} \approx 0.5 \text{ g/cm}^3$) into hydrogenated graphite nanofibers with Pd-catalyst (Figures 6, 7) is considered. Both the spillover effect and the Kurdjumov-like effect are obviously manifested in the extraordinary data considered in (Nechaev & Veziroglu, 2015).

4. These results can be used for solving of the current problem of the efficient and safe hydrogen on-board storage (Nechaev et al., 2014).

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