Physics of the Solid State, 2022, Vol. 64, No. 12

13,18

To the theory of organic macromolecules adhesion on the single-layer graphene: Dangling bonds model

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Received August 3, 2022
Revised August 3, 2022
Accepted August 9, 2022

A model is proposed in which the interaction of a macromolecule (MM) with a single-layer graphene (SLG) is carried out by dangling interfacial molecular bonds. To estimate the energy of MM−SLG stitching, or adsorption energy (the index i numbers the broken bonds), a simple theoretical scheme, permitting to obtain analytical results, was used. The adhesion energy is defined as the sum of the terms $E_i^{ads}N_i$, where N_i is the concentration of i-type dangling bonds. The obtained results are compared with experimental data on adhesion for various heterostructures

Keywords: macromolecule, graphene, charge transfer, adsorption, adhesion.

DOI: 10.21883/PSS.2022.12.54400.452

1. Introduction

Among the various unique properties of graphene, its ability to detect (in the undoped state) the adsorption of a single gas molecule, demonstrated for the first time in [1], has apparently attracted the greatest interest of researchers. This interest has produced theoretical suggestions (with subsequent technological implementation) of different variants of chemical gas sensors [2–7]. Further developments in this area were biosensors [2,8–18]. From the theoretical viewpoint, the value of charge transfer between the adsorbed object and the substrate must be known in order to describe sensor operation; from the technological viewpoint the energy of bond between the studied object and the substrate (adsorption energy) has to be known. As regards gas molecules (like other microscopic objects), researchers developed many variants of ab initio calculations (mainly based on the density functional theory (DFT)) and model approaches in order to answer these questions [19–21]. DFT-methods in case of bioobjects, which are macromolecules (MMs), are extremely labor-intensive. Indeed (see [22]), the typical MM structures are plaques formed, for instance, by beta-amyloid peptide (Aβ) which have a molecular mass of $4 \cdot 10^3$ hydrogen masses and linear dimensions of about 40 amino acid residues (one unstructured amino acid residue has the length of 0.36 nm). Moreover, both the geometry of this plaque and area of its contact with the substrate are not only unknown, but also are not fixed, they rather are random values. Therefore, radically simplified schemes are required for a model description of a macromolecule−substrate system. (It should be noted that such a situation occurred during consideration of the thermodynamics of free macromolecules [23]). In the present paper, to the author's knowledge, the first attempt is made for describing the MM bond to a solid-state substrate (here graphene) at the microscopic level within the framework of a simple model.

It is assumed in the proposed dangling bond model that MM interaction with single layer graphene (SLG) is performed by cross-links of these interface orbitals to graphene atoms [24,25] (Fig. 1, 2). Such multicenter adsorption should be more logically called MM adhesion to SLG.

2. Model

Let us represent the Hamiltonian of the MM−SLG system as

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathrm{SLG}}(\mathbf{k}) c_{\mathbf{k}}^{+} c_{\mathbf{k}} + \sum_i \varepsilon_i a_i^{+} a_i + \sum_{i,\mathbf{k}} \frac{V_i^2 (c_{\mathbf{k}}^{+} a_i + a_i^{+} c_{\mathbf{k}})}{\omega - \varepsilon_{\mathrm{SLG}}(\mathbf{k}) + i0^{+}}, \tag{1}$$

where ω is the energy variable, $\varepsilon_{\mathrm{SLG}}(\mathbf{k})$ is the SLG dispersion law, ε_i is the energy of i-th dangling MM bond (p-orbitals, which contained one electron before interaction with graphene), V_i is the energy of interaction of i-th MM bond with the SLG electronic spectrum, $c_{\mathbf{k}}^{+}(c_{\mathbf{k}})$ is the operator of creation (annihilation) of the SLG electron in state $|\mathbf{k}\rangle$, $a_i^{+}(a_i)$ are similar operators for i-th dangling

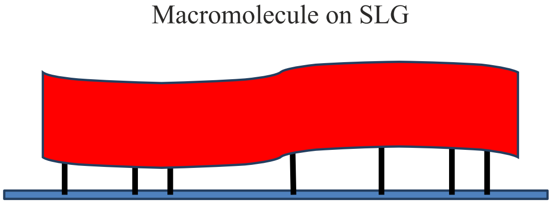

Figure 1. Diagram of macromolecule contact with single-layer graphene. Vertical lines show the cross-links of MM to SLG.

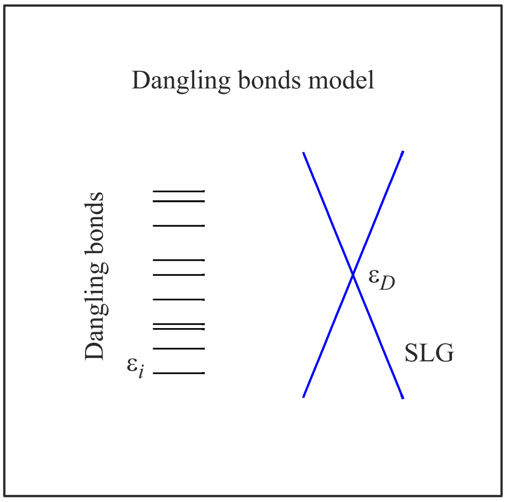

Figure 2. Energy diagram of MM adhesion to SLG (ε_i is the energy of dangling bond, ε_D is the energy of Dirac point).

MM bond. It is easy to show [20,21,26] that, due to adsorption, the density of states (DOS) of an electron on an i-th bond (for one spin projection) is equal to

$$\rho_i(\omega) = \frac{1}{\pi}\,\frac{\Gamma_i(\omega)}{\left(\omega - \varepsilon_i - \Lambda(\omega)\right)^2 + \Gamma_i^2(\omega)}, \tag{2}$$

where the functions of half-width and shift of an i-th quasi-level are respectively equal to

$$\Gamma_i(\omega) = \pi V_i^2 \rho_{\mathrm{SLG}}(\omega), \quad \Lambda_i(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\Gamma_i(\omega')d\omega'}{\omega-\omega'} \tag{3}$$

and $\rho_{\mathrm{SLG}}(\omega)$ is the density of states of SLG. Within the framework of a low-energy approximation, the SLG spectrum has the form $\varepsilon^{\pm}_{\mathrm{SLG}}(\mathbf{k}) = \pm(3t/2)|\mathbf{k}|a$, [27], where $t \sim 2.7\,\mathrm{eV}$ is the electron hopping energy between the nearest neighbors in SLG, located at distance a, $\mathbf{k}$ is the wave vector counted from the Dirac point, to which energy $\varepsilon_D = 0$ is ascribed [27]. This spectrum in the low-energy region (i.e. near the Dirac point) corresponds to DOS of the form

$$\rho_{\mathrm{SLG}}(\omega) = |\omega|/\xi^2, \quad |\omega| < \xi, \tag{4}$$

where $\xi = \sqrt{\pi\sqrt{3}/4t} \sim t \sim 3\,\mathrm{eV}$ [27]. Then the functions of half-width and shift of MM quasi-levels can be represented as follows [28]:

$$\Gamma_i(\omega) = \pi V_i^2 \rho_{\mathrm{SLG}}(\omega),$$

$$\Lambda_i(\omega) = \frac{V_i^2\omega}{\xi^2}\ln[\omega^2/(\xi^2-\omega^2)]. \tag{5}$$

Using the approximation, often applied in the adsorption theory [21], and assuming that $V_i^2/\xi^2 \ll 1$, let us represent DOS (2) as

$$\rho_i(\omega) \approx \frac{1}{\pi}\,\frac{\bar{\Gamma}_i}{(\omega-\bar{\varepsilon}_i)^2 + \bar{\Gamma}_i^2}, \tag{6}$$

where $\bar{\varepsilon}_i = \varepsilon_i + \Lambda_i(\varepsilon_i)$, $\bar{\Gamma}_i = \pi V_i^2\rho_{\mathrm{SLG}}(\varepsilon_i)$. Since the occupation number of an i-th (initially broken) bond at zero temperature is

$$n_i = 2\int_{-\infty}^{0}\rho_i(\omega)d\omega, \tag{7}$$

where the Fermi level of undoped graphene $E_F = \varepsilon_D = 0$, the charge of bond is $Z_i = 1 - n_i$ is approximately equal to

$$Z_i \approx \frac{2}{\pi}\arctan\frac{\bar{\varepsilon}_i}{\bar{\Gamma}_i}. \tag{8}$$

The total charge transfered from MM to SLG is equal to $Z_{\mathrm{SLG}} = -\sum_i Z_i$, so that charge carriers with concentration $n_{\mathrm{SLG}} = |Z_{\mathrm{SLG}}|/S$ originates in the initially undoped graphene, where $S = 3\sqrt{3}a^2/2$ is the graphene unit cell area ($a = 1.42\,\text{Å}$ is the distance between the nearest neighbors in graphene). Thus, SLG conductivity becomes equal to

$$\sigma_{\mathrm{SLG}} = e n_{\mathrm{SLG}}\mu_{\mathrm{SLG}}, \tag{9}$$

where μ_{SLG} is carrier mobility. Charge carriers at $Z_{\mathrm{SLG}} < 0$ are electrons, at $Z_{\mathrm{SLG}} > 0$ are holes. Relation (9) was written down assuming that carrier mobility does not greatly depend on adsorption (see [29] and the references therein).

Similarly to adsorption energy [21,26], let us represent adhesion energy as a sum of ionic E^{ion}_{adh} and metallic E^{met}_{ads} components. Quantity E^{ion}_{adh} can be estimated as electrostatic energy of the form

$$E^{ion}_{adh} = \sum_i E^{ion}_i N_i, \quad E^{ion}_i = e^2 Z_i^2/4\varepsilon_{st}d_i, \tag{10}$$

where e is the elementary charge, d_i is absorption bond length, ε_{st} is the static dielectric function of SLG, $N_i = m_i/S$ is concentration of m_i dangling bonds per a graphene unit cell.

Let us estimate the metallic component E^{met}_{ads} taking into account the uncertainty principle. In the absence of contact with SLG, uncertainty of position of electron Δr^i_a, localize on bond i, is of the order of radius r_{ai} of the atom via which the bond to graphene is provided. Thereat, electron kinetic energy E^i_{kin} is of the order of $\hbar/2m_0 r^2_{ai}$, where m_0 is the free electron mass, $\hbar$ is the reduced Planck constant. If we assume complete delocalization of an electron upon a transfer from bond i into SLG, the contribution of such electrons to adhesion energy, equal to a decrease of kinetic energy, is

$$E^{met}_{i1} = |Z_i|(h^2/2m_0 r^2_{ai}). \tag{11}$$

Uncertainty of coordinate Δr^i_a for the remaining electrons $1-|Z_i|$ is of the order of d_i, so that a gain in kinetic energy is equal to

$$E^{met}_{i2} = 2(1-|Z_i|)(h^2/m_0 d_i^2)(1 - r^2_{ai}/d_i^2). \tag{12}$$

Thus, the total adsorption energy for i-th bond is $E^{ads}_i = E^{ion}_i + E^{met}_i$, where $E^{met}_i = E^{met}_{i1} + E^{met}_{i2}$. energy of MM adhesion to SLG is equal to

$$E_{adh} = \sum_i E^{ads}_i N_i. \tag{13}$$

In the absence of a charge transfer,

$$E_{ads} = (h^2/m_0 d^2)M/a^2\sqrt{3},$$

where $M = \sum_i m_i$. It should be noted that the accepted proportionality of adhesion energy to N_i is true at $m_i \ll 1$, when the interaction dangling bonds need not be taken into account.

The cases of MM adhesion on doped graphene and gapped graphene are discussed in the Appendix.

3. Numerical estimates

MMs consist of different molecular combinations of H, C, N and O atoms. Dangling bonds of C, N and O atoms, bordering with SLG, are considered as i-bonds. In order to estimate energy ε_i, counted from the graphene Dirac point, we assume $\varepsilon_i = \phi_{\text{SLG}} - (I_i + A_i)/2$ (ϕ_{SLG} is the SLG work function, I_i and A_i are energies of ionization and electron affinity for a molecule). It is taken into consideration that intra-atomic Coulomb repulsion of electrons with opposite spins is $U_i = I_i - A_i$. The work function is $\phi_{\text{SLG}} = 4.50\,\text{eV}$ [30,31], the values of I_i and A_i for a number of gas molecules were taken from [32]. The obtained values of ε_i are given in the table.

Let us note one additional circumstance: real energies ε_i of dangling bonds for one and the same molecule depend on the MM fragment to which the given molecule is bound. Indeed, let us imagine a dimer composed of an „atom" with orbital energy ε_*, which models a MM fragment, and an „atom" with orbital energy ε_i which models a molecule. If the states of ε_* and ε_i are bound by matrix element t_*, we obtain a bonding state (the minus sign) and an antibonding state (the plus sign)

$$\varepsilon_{\pm} = \left[\varepsilon_* + \varepsilon_i \pm \sqrt{(\varepsilon_* - \varepsilon_i)^2 + 4t_*^2}\right] \Big/ 2.$$

Thus, energies of dangling bonds of the same molecule, which is in contact with graphene, will differ.

According to the numerical calculations [33–35], values d_i for the gas molecules C, N and O lie in the interval of $\sim 2-3\,\text{Å}$. For the σ-bond of dangling p-orbitals of MM with the p_z-orbital of SLG we have $V_i = V_{pp\sigma} = 2.22(\hbar^2/m_0 d_i^2)$ [36], which for the average bond length value of $d \approx 2.5\,\text{Å}$ gives the average energy of $V \approx 3\,\text{eV}$. Thus, $V^2/\xi^2 \sim 1$. It should be noted that the possibility of such averaging is based on the closeness of atomic radii r_{ai} of C, N and O atoms, respectively equal to 0.77, 0.71 and 0.74 Å [32].

The values of $\bar{\varepsilon}_i$, found from expression $\bar{\varepsilon}_i = \varepsilon_i + \Lambda(\varepsilon_i)$, and Z_i are given in the table. The obtained charge values considerably exceed the results in the numerical calculations [37,38], but they are of the same order as in [39] (in [37,38] the adsorption bond lengths are significantly greater than herein). It should be noted that the signs even for the same molecule, depending on its orientation in relation to a graphene sheet, may differ [37]. As a consequence, values of $Z_{\text{SLG}} = -\sum_i Z_i$ and σ_{SLG} can be close to zero, although $Z_i \neq 0$.

Energies of dangling bonds ε_i, values of charges Z_i and energies E_i^{ion}, E_{i1}^{met}, E_{i2}^{met}, E_i^{ads}

Fragment MM	ε_i, eV	Z_i	E_i^{ion}, eV	E_{i1}^{met}, eV	E_{i2}^{met}, eV	E_i^{ads}, eV
O_2	−1.78	−0.12	0.01	0.29	1.61	1.91
NO	−0.47	0.67	0.43	1.64	0.60	2.67
NH	−0.32	0.53	0.27	1.15	0.85	2.27
CH_2	−1.02	0.20	0.04	0.49	1.46	1.99
NH_2	−0.96	0.23	0.05	0.56	1.42	2.03
CH_3	−0.96	0.23	0.05	0.56	1.42	2.03

When estimating the components of adhesion energy (8)–(10), let us assume (for simplicity) $r_{ai} = d_i/2 = d/2$, from where $E_i^{ion} = (eZ_i)^2/2\varepsilon_{st}d$, $E_{i1}^{met} = 2|Z_i|(\hbar^2/m_0 d^2)$, $E_{i2}^{met} = (3/2)(1-|Z_i|)(\hbar^2/m_0 d^2)$, so that

$$E_{adh}^{ion} = (e^2/2\varepsilon_{st}d)\sum_i Z_i^2 N_i,$$

$$E_{adh}^{met} = (3h^2/2m_0 d^2)\sum_i [1 + |Z_i|]N_i. \tag{14}$$

The estimation results are given in the table; we have calculated E_i^{ion} assuming that$\varepsilon_{st} = 3$ [40,41].

When estimating the components of adhesion energy (10)–(12) let us assume (for simplicity) $r_{ai} = d_i/2 = d/2$, from where $E_i^{ion} = (eZ_i)^2/2\varepsilon_{st}d$, $E_{i1}^{met} = 2|Z_i|(\hbar^2/m_0 d^2)$, $E_{i2}^{met} = (3/2)(1 - |Z_i|)(\hbar^2/m_0 d^2)$ and $E_i^{met} = (3\hbar/2m_0 d^2)\sum_i (1 + |Z_i|)$. The estimation results are given in the table (we have calculated E_i^{ion} assuming that $\varepsilon_{st} = 3$ [40,41]).

In the absence of a charge transfer

$$E_{adh}(Z_i = 0)/M = (h^2/m_0 d^2)/a^2\sqrt{3}$$

$$= 0.35\,\text{eV/Å}^2 = 5.6\,\text{J/m}^2, \tag{15}$$

where $M = \sum_i m_i$. The experimental values of interplanar adhesion energy in layered structures of graphite and hexagonal boron nitride are $0.33\,\text{J/m}^2$, in the structures composed of MoS_2 layers — $0.48\,\text{J/m}^2$ [42]. A considerable spread in the experimental data should be noted: for graphite, e.g, E_{adh} is within $0.15-0.72\,\text{J/m}^2$; for heterostructures formed by SLG and MoS_2 on the SiO_x substrate. E_{adh} is estimated as $0.14-0.90\,\text{J/m}^2$ and $0.17-0.48\,\text{J/m}^2$ respectively [42]. For mica we have $E_{adh} \approx 0.22\,\text{J/m}^2$ [43]. For a series of van der Waals vertical heterostructures, paper [44] gives values from several units to $\sim 20\,\text{meV/Å}^2$. The adhesion energies of solvent liquids on Pt (111) and Ni (111) vary from 0.15 to $0.60\,\text{J/m}^2$, increasing towards CH_3OH < HCOOH < H_2O < benzene ≈ phenol [45]. E_{adh}

for adhesion of various polymers on the surface of a stiff-chain polymer has the value of $40-70\,\mathrm{mJ/m^2}$ [46]. Applying formula (15) purely formally to the given experimental results, we come to the conclusion that the value of multiplier M must not exceed $0.01-0.1$.

4. Conclusion

In the present paper we proposed a model where the contact between MM and SLG is conditioned by dangling bonds and presented a simple theoretical scheme for estimating the corresponding bond energies. This approach made it possible to obtain analytical expressions for the adhesion energy. The calculation results were compared with the available experimental data.

While dealing with biological systems, it should be noted that information about intercellular and intercellular-matrix adhesion is very important and of crucial importance not only for fundamental research, but also for technological applications [47–49]. It should be noted, however, that quantitative studies of adhesion are evidently insufficient, though such papers are sometimes published [10,50]. Moreover, adhesion issues are not considered at all in papers on biosensors [2,8–18].

The proposed adhesion model is considerably simplified, but even in this case additional information is required for an adequate estimation of parameters. That's why experimental studies are required to develop the theory of macromolecule adhesion on graphene.

Funding

The work was supported by the grant from Russian Science foundation 22-12-00134.

Conflict of interest

The author declares that he has no conflict of interest.

Appendix

1. Undoped graphene has been considered so far. Let us find out how doping changes the MM adhesion on SLG, by substituting the upper limit of integration $E_F = 0$ in expression (7) with $E_F = \delta E_F$. Then the numerator of equation (8) is equal to $\bar{\varepsilon}_i - \delta E_F$. Assuming (for simplicity) $|\delta E_F| \ll \Gamma_i$, instead of (8), we obtain

$$\tilde{Z}_i = Z_i - \pi\rho_i(\bar{\varepsilon}_i)\delta E_F, \tag{A1}$$

where DOS $\rho_i(\bar{\varepsilon}_i)$ is determined by expression (6). Then, when the Fermi level is shifted upwards from the Dirac point of SLG, values of negative charges on dangling bonds increase and those of positive charges decrease. Thus, the charge value of a dangling O_2 bond increases, while that of the other molecules decreases for the considered cases at $\delta E_F > -0$ (see the table). A reverse situation takes place upon a downward shift of the Fermi level from the Dirac point. The total doping effect depends on specific values of positive and negative charges and their concentrations, i.e. coefficients m_i. It should be noted that, according to (14), the ionic and metallic components of adhesion energy increase with an increase of $|Z_i|$.

2. Let us now consider the influence of a gap with width 2Δ in the SLG electronic spectrum on adhesion. In this case, DOS of SLG near the gap can be represented as

$$\rho_{\mathrm{SLG}}(\omega) = \begin{cases} |\omega|/\xi^2, & |\omega| > \Delta, \\ 0, & |\omega| \le \Delta, \end{cases} \tag{A2}$$

assuming that the gap center coincides with the Dirac point, $\varepsilon_D = 0$. Then we obtain the following expression instead of shift function (5) [27]:

$$\Lambda_i(\omega) = \frac{V_i^2\omega}{\xi^2}\ln\left|\frac{\Delta^2-\omega^2}{\xi^2+\Delta^2-\omega^2}\right|. \tag{A3}$$

When the level of dangling bond ε_i overlap with the continuous spectrum of gapped graphene, the situation described above for gapless graphene takes place. Therefore, let us consider a case when level ε_i is in the gap. As shown in [27], the occupation number of this level is equal to

$$n_i^{loc} = \left|1 - \frac{\partial\Lambda_i(\omega)}{\partial\omega}\right|^{-1}_{\bar{\varepsilon}_i^{loc}}, \tag{A4}$$

where $\bar{\varepsilon}_i^{loc} = \varepsilon_i + \Lambda_i(\varepsilon_i)$ is the energy of the local level in the gap ($|\bar{\varepsilon}_i^{loc}| < \Delta$). The analytical expression for $\partial\Lambda_i(\omega)/\partial\omega$ is given in [27]. Having determined the value of $\bar{\varepsilon}_i^{loc}$ and calculated n_i^{loc}, let us find the local-level charge $Z_i^{loc} = 1 - n_i^{loc}$, which will be substituted in equations (11)–(13).

The following circumstance should be noted. In the present paper we have determined DOS (4) and (A2) using parameter $\xi = \sqrt{\pi\sqrt{3}/4}t$, which adequately describes the derivative $\partial\rho_{\mathrm{SLG}}(\omega)/\partial\omega \propto \xi^{-2}$ at $|\omega| \ll \xi$. On the other hand, quantity $\xi^2/2$, where $\xi = \sqrt{2\pi\sqrt{3}}t \sim 3t$, is used instead of ξ^2 when calculating the occupation numbers of graphene [51]. That's why parameter ξ is used in [27]. Here we do not calculate the SLG charge directly, but, based on a maintained number of electrons, we take it equal to — $\sum_i Z_i$, while parameter ξ should be used when calculating charge Z_i for estimating the values of $\bar{\varepsilon}_i$ and $\bar{\Gamma}_i$ included in formula (8).

References

[1] F. Schedin, A.K. Geim, S.V. Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov. Nature Mater. **6**, 652 (2007).

[2] C.I. Justino, A.R. Gomes, A.C. Freitas, A.C. Duarte, T.A. Rocha-Santos. Trends Anal. Chem. **91**, 53 (2017).

[3] L. Ge, X. Mu, G. Tian, Q. Huang, J. Ahmed, Z. Hu. Front. Chem. **7**, 839 (2019).

[4] D.J. Buckley, N.C.G. Black, E.G. Castanon, C. Melios, M. Hardman. O. Kazakova. 2D Mater. **7**, 032002 (2020).

[5] S.Z.N. Demon, A.I. Kamisan, N. Abdullah, S.A.M. Noor, O.K. Khim, N.A.M. Kasim, M.Z.A. Yahya, N.A.A. Manaf, A.F.M. Azmi, N.A. Halim. Sens. Mater. **32**, 759 (2020).

[6] U. Yaqoob, M.I. Younis. Sensors **21**, 2877 (2021).

[7] S. Dhall, B.R. Mehta, A.K. Tyagi, K. Sood. Sensors Int. **2**, 100116 (2021).

[8] J. Pena-Bahamonde, H.N. Nguyen, S.K. Fanourakis, D.F. Rodrigues. J. Nanobiotechnology **16**, 75 (2018).

[9] S. Szunerits, R. Boukherroub. Interface Focus **8**, 20160132 (2018).

[10] A.F. Behbahani, G.H. Motlagh, S.M.V. Allaei, V.A. Harmandaris. Macromolecules **52**, 3825 (2019).

[11] S.K. Krishnan, E. Singh, P. Singh, M. Meyyappan, H.S. Nalwa. RSC Adv. **9**, 8778 (2019).

[12] Y. Bai, T. Xu, X. Zhang. Micromachines **11**, 60 (2020).

[13] M. Coros, S. Pruneanu, R.-I. Stefan-van Staden. J. Electrochem. Soc. **167**, 037528 (2020).

[14] A.A. Lebedev, S.Yu. Davydov, I.A. Eliseyev, A.D. Roenkov, O. Avdeev, S.P. Lebedev, Y. Makarov, M. Puzyk, S. Klotchenko, A.S. Usikov. Materials **14**, 590 (2021).

[15] V. Naresh, N. Lee. Sensors **21**, 1109 (2021).

[16] S. Shahriari, M. Sastry. S. Panjikar, R.K. Singh Raman. Nanotechnol. Sci. Appl. **14**, 197 (2021).

[17] Laxmi, B. Mahapatra, R.V. Krishna, P.K. Patel. AIP Conf. Proc. **2327**, 020011 (2021).

[18] S. Wang, X. Qi, D. Hao, R. Moro, Y. Ma, L. Ma. J. Electrochem. Soc. **169**, 027509 (2022).

[19] O.M. Braun, V.K. Medvedev. UFN **157**, 631 (1989).

[20] S.Yu. Davydov, S.V. Troshin. Phys. Solid State **49**, 1583 (2007).

[21] S.Yu. Davydov. Teoriya adsorbtsii: metod modelnykh gamiltonianov. Izd-vo SPbGETU „LETI“, SPb (2013). 235 p. (in Russian). twirpx.com/file/1596114/.

[22] O.G. Tatarnikova, M.A. Orlov, N.V. Bobkova. Uspekhi biologicheskoy khimii **55**, 351 (2015) (in Russian).

[23] J. Ziman. Modeli besporyadka. Mir, M. (1982) (in Russian). Ch. 7.

[24] H. Ji, P.-G. de Gemnes. Macromolecules **26**, 52M25 (1993).

[25] C.-A. Palma, P. Samorí. Nature Chem. **3**, 431 (2011).

[26] S.Yu. Davydov, A.A. Lebedev, O.V. Posrednik. Elementarnoye vvedeniye v teoriyu nanosistem. Izd-vo „Lan“, SPb (2014). Ch. 9.

[27] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim. Rev. Mod. Phys. **81**, 109 (2009).

[28] S.Yu. Davydov. Semiconductors **51**, 217 (2017).

[29] S.Yu. Davydov, O.V. Posrednik. Technical Physics **87**, 656 (2017).

[30] J.-H. Kim, J.H. Hwang, J. Suh, S. Tongay, S. Kwon, C.C. Hwang, J. Wu, J.Y. Park. Appl. Phys. Lett. **103**, 171604 (2013).

[31] D. Niesner, T. Fauster. J. Phys.: Condens. Matter 26, 393001 (2014).

[32] Fizicheskiye velichiny. Spravochnik. Ed. by E.S. Grigoriyev, E.Z. Meylikhov. Energoatomizdat, M. (1991) (in Russian).

[33] J. Ni, N. Yang, Q. Liang, J. Jiang, X. Chen. 16th International Conference on Electronic Packaging Technology (ICEPT) — Changsha, China (2015). DOI: 1109/ICEPT.2015.7236745.

[34] T.Y. Mi, D.M. Triet, N.T. Tien. Phys. Open **2**, 100014 (2020).

[35] T. Xie, P. Wang, C. Tian, G. Zhao, J. Jia, C. He, C. Zhao, H. Wu. Molecules **27**, 2315 (2022).

[36] W.A. Harrison. Phys. Rev. B **27**, 3592 (1983).

[37] O. Leenaerts, B. Partoens, F.M. Peeters. Phys. Rev. B **77**, 125416 (2008).

[38] S. Kumar, M. Malhotra, H. Sharma. Mater. Res. Express **5**, 105007 (2018).

[39] B. Huang, Z. Li, Z. Liu, G. Zhou, S. Hao, J. Wu, B.-L. Gu, W. Duan. J. Phys. Chem. C **112**, 13442 (2008).

[40] D.C. Elias, R.V. Gorbachev, A.S. Mayorov, S.V. Morozov, A.A. Zhukov, P. Blake, L.A. Ponomarenko, I.V. Grigorieva, K.S. Novoselov, F. Guinea, A.K. Geim. Nature Phys. **7**, 701 (2011).

[41] E.J.G. Santos, E. Kaxiras. Nano Lett. **13**, 898 (2013).

[42] H. Rokni, W. Lu. Nature Commun. **11**, 5607— (2020).

[43] B. Yu, L. Hou, S. Wang, H. Huang. Adv. Mater. Interfaces **6**, 1801552 (2018).

[44] E. Blundo, T. Yildirim, G. Pettinari, A. Polimeni. Phys. Rev. Lett. **127**, 046101 (2021).

[45] J.R. Rumptz, C.T. Campbell. ACS Catal. **9**, 11819 (2019).

[46] A.E. Chalykh, V.Yu. Stepanenko, A.D. Aliev. Polymers **12**, 2956 (2020).

[47] R. Ungai-Salánki, B. Peter, T. Gerecsei, N. Orgovan, R. Horvath, B. Szabó. Adv. Colloid Interface Sci. **269**, 309 (2019).

[48] S. Cai, C. Wu, W. Yang, W. Liang, H. Yu, L. Liu. Nanotechnol. Rev. **9**, 971 (2020).

[49] D. El Arawi, C. Vezy, R. Déturche, M. Lehmann, H. Kessler, M. Dontenwill, R. Jaffiol. Biophys. Rep. **1**, 100021 (2021).

[50] C. Meng, K. Gao, S. Tang, L. Zhou, W. Lai, L. Luo, X. Wang, Y. Liu, K. Wang, Y. Chen, X. Liu. J. Colloid Interface Sci. **599**, 12 (2021).

[51] N.M.R. Peres, F. Guinea, A.H. Castro Neto. Phys. Rev. B **73**, 125411 (2006).