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Organic macromolecule on free-standing and epitaxial graphene: HOMO–LUMO model

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A two-level model of an organic macromolecule is proposed, initially containing completely filled (HOMO) and empty (LUMO) levels. The interaction of these levels with free-standing and epitaxial graphene is considered within the framework of the standard adsorption approach. sp- and d-metal and a semiconductor (dielectric) are considered as a substrate. In the latter case, these are silicon carbide polytypes. Estimates have shown that the maximum transition of electrons to graphene takes place for the 3*C*-SiC substrate.

Keywords: a two-level model of a macromolecule, single-layer graphene, metal and semiconductor substrates.

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1. The unique ability of graphene to detect absorption of individual molecule found in [1] made graphene one of the most attractive material for resistive gas sensors [2–5], and most recently for biosensors as well [6–10]. Typical objects for studying in the latter case are macromolecules (MM), which are systems (plaques) with large number of atoms and linear dimensions about hundreds of Å. And neither geometry of such a plaque nor the area of its contact with the substrate are known, yet are strictly fixed. It is clear that direct application of DFT (density functional theory) methods is difficult in this case. Therefore, in [11], to describe the energy of interaction (adhesion) of a MM with a single-layer graphene (SLG) a dangling bonds model (DBM) was suggested with these bonds considered responsible for the stitching of the MM with the SLG. Under framework of DBM and thanks to the simplified scheme of the problem consideration, the author succeeded in obtaining analytical expressions for the charge and the energy of adhesion transfer. In this paper for the same purposes we propose a two-level model of a macromolecule, the lower completely filled level of which is designated as HOMO (higher occupied molecular orbital), and the empty upper level is designated as LUMO (lower unoccupied molecular orbital) [12–15]. Hereinafter we will call such model as HLM (HOMO–LUMO model).

2. Let us first consider, within the framework of HLM, the adsorption of MM on SLG. Let us denote as ε_-^0 and ε_+^0 the HOMO and LUMO energies of the free MM, their occupation numbers at zero temperature are by definition equal to $n_-^0 = 2$ and $n_+^0 = 0$. For MM adsorbed on SLG with work function ϕ_{SLG}, we set HOMO and LUMO energies equal to $\varepsilon_\mp = \varepsilon_\mp^0 + \phi_{SLG}$. The gap between LUMO and HOMO is $\Delta_{LH} = \varepsilon_+ - \varepsilon_-$. In accordance with [11] the densities of states (DOSs) on HOMO and LUMO interacting with graphene per one spin projection are

$$\rho_{\rm m}(\omega) = \frac{1}{\pi} \frac{\Gamma_{\rm m}(\omega)}{(\omega - \varepsilon_{\rm m} - \Lambda_{\rm m}(\omega))^2 + \Gamma_{\rm m}^2(\omega)}. \qquad (1)$$

Here the broadening function $\Gamma_m(\omega) = \pi V_m^2 \rho_{SLG}(\omega)$, and the shift function $\Lambda_{\rm m}(\omega)$ is the Hilbert transform $\Gamma_{\rm m}(\omega)$, where ω is energy variable, $V_{\rm m}$ is matrix element of HOMO and LUMO coupling with the electronic spectrum of SLG. In the low-energy approximation $\rho_{SLG}(\omega) = |\omega|/\xi^2$ at $|\omega| < \xi$ and zero at $|\omega| \geq \xi$, where $\xi = \sqrt{\pi\sqrt{3}/4t}$ is cutoff energy and $t \sim 3\,\text{eV}$ is energy of electron transition between nearest neighbors in graphene. Then

$$\Gamma_{\rm m}(\omega) = \pi V_{\rm m}^2 \rho_{SLG}(\omega),$$

$$\Lambda_{\rm m}(\omega) = (V_{\rm m}^2 \omega/\xi^2) \ln\left[\omega^2/(\xi^2 - \omega^2)\right].$$

As in [11], we represent DOSs (1) in the form

$$\rho_\pm(\omega) \approx \frac{1}{\pi} \frac{\Gamma_{\rm m}}{(\omega - \bar{\varepsilon}_{\rm m})^2 + \Gamma_{\rm m}^2}, \qquad (2)$$

where

$$\bar{\varepsilon}_\mp = \varepsilon_\mp + \Lambda_\mp,$$

$$\Lambda_\mp = \bar{\varepsilon}_\mp (V_\mp/\xi)^2 \ln\left[\bar{\varepsilon}_\mp^2/(\xi^2 - \bar{\varepsilon}_\mp^2)\right]$$

and

$$\Gamma_{\rm m} = \pi V_{\rm m}^2 \rho_{SLG}(\bar{\varepsilon}_m)\ [11].$$

The equation $\omega - \varepsilon_\mp - \Lambda_\mp(\omega) = 0$ defines the values of $\bar{\varepsilon}_\mp$. Assuming $V_- = V_+ = V$, we can show that a sufficient condition for replacing (1) with (2) is the fulfillment of the inequality $|\varepsilon_\pm| < \xi/e$. At zero temperature the occupation numbers of HOMO and LUMO are determined by the expressions

$$n_\mp = \frac{2}{\pi} \operatorname{arccot} \frac{\operatorname{sgn}(\bar{\varepsilon}_\mp) - \varepsilon_F/|\bar{\varepsilon}_\mp|}{\pi (V_\mp/\xi)^2}. \qquad (3)$$

Here ε_F is Fermi level energy. At $\varepsilon_F = -\phi_{SLG} = 0$ (undoped SLG), where the energy of the Dirac point ε_D is taken as zero energy, we obtain the corresponding charges $Z_- = 2 - n_-$ and $Z_+ = -n_+$. For $\varepsilon \equiv \bar{\varepsilon}_+ = -\bar{\varepsilon}_-$ we have

$$Z_{\mp} = \pm\left[1 - (2/\pi)\arctan(\xi^2/\pi V^2)\right].$$

The total charge transferred from MM to SLG is equal to $Z_{SLG} = -(Z_- + Z_+)$, i.e. There is no charge transfer between MM and SLG. When $\phi_{SLG} > 0$the value Z_-increases, and $|Z_+|$decreases, as a result SLG is enriched in electrons and acquires n-type conductivity. At $\phi_{SLG} < 0$the picture is reversed, and SLG has p-type conductivity. The gap width at $e\varepsilon/\xi < 1$ is equal to

$$\bar{\Delta}_{LN} = \Delta_{LN}[1 + (V/\xi)^2 \ln(\varepsilon/\xi)] < \Delta_{LN} = 2\varepsilon.$$

In [11] molecular fragments O_2, NO, NH, CH_2, NH_2 and CH_3 were considered as sources of dangling bonds. If for the values ε_-^0 and ε_+^0 estimation we assume $\varepsilon_-^0 = \min\{I_{mol}\}$ and $\varepsilon_+^0 = \max\{A_{mol}\}$, where I_{mol} and A_{mol} — ionization energy and electron affinity (for the listed molecules, the values of these energies are given in [16]) and take into account that for free single-layer graphene $\phi_{SLG} = 4.5\,\text{eV}$ and $V/\xi \sim 1$ [11], then for NO and NH we obtain $\varepsilon_+/|\varepsilon_-| \sim \bar{\varepsilon}_+/|\bar{\varepsilon}_-| \sim 1$, so the equality $\varepsilon \equiv \bar{\varepsilon}_+ = -\bar{\varepsilon}_-$ used for the estimates is correct in order of magnitude. For the remaining molecules considered in [11] — $\varepsilon_+/|\varepsilon_-| \sim 0.6$.

3. Let us proceed to the discussion of MM adsorption on epigraphene, using the same approach as in the previous Section, and using the mode of weak bond of graphene with the substrate, when $\Gamma'_{\text{m}}(\omega)/t \ll 1$, i.e. quasi-free-standing graphene. This mode is implemented technologically and ensures that the unique properties of free graphene are largely preserved. Then, using the same simplifications as above, we obtain the LUMO and HOMO occupation numbers of the form

$$\tilde{n}_{\mp} \approx \frac{2}{\pi}\,\text{arccot}\,\frac{\tilde{\varepsilon}_{\mp} - \varepsilon_F}{\tilde{\Gamma}_{\mp}}, \qquad (4)$$

where

$$\tilde{\varepsilon}_{\mp} = \bar{\varepsilon}_{\mp} + \Lambda'_{\mp}(\tilde{\varepsilon}_{\mp}), \quad \Gamma_{\text{m}}^{\%} = \pi V_{\text{m}}^2 \rho_{SLG}(\varepsilon_{\text{m}}^{\%}).$$

In the case of DOS semiconductor substrate with band gap E_g can be represented as $\rho_{sc}(\omega) = \bar{\rho}_{sc} = \text{const}$ at $|\Omega_{sc}| \geq E_g/2$ and $\rho_{sc}(\omega) = 0$ at $|\Omega_{sc}| < E_g/2$, where $\Omega_{sc} = \omega - \omega_{sc}$, ω_{sc} is band gap center [17], so

$$\bar{\Gamma}_{sc} = \pi V_{sc}^2 \bar{\rho}_{sc}$$

and

$$\Lambda_{sc}(\omega) = (\bar{\Gamma}_{sc}/\pi)\ln\left[(\Omega_{sc} - E_g/2)/(\Omega_{sc} + E_g/2)\right],$$

where V_{sc} is matrix element of interaction of the semiconductor and SLG. The occupation numbers of LUMO and HOMO are determined by equation (4). Case $\varepsilon_F = \varepsilon_D = 0$ corresponds to the doped SiC polytype SiC and undoped SLG, case $\varepsilon_F = \omega_{sc}$ — to the undoped polytype and doped SLG.

Degree of hexagonality of the polytype D and energy characteristics of the MM/SLG/SiC polytype structure: band gap E_g, electron affinity χ, $\omega_{sc} - \varepsilon_D$

Polytype	D	E_g, eV	χ, eV	$\omega_{sc} - \varepsilon_D$, eV
3*C*	0	2.40	4.00	−0.70
8*H*	0.25	2.86	3.58	−0.51
21*R*	0.29	2.96	3.52	−0.50
6*H*	0.33	3.00	3.45	−0.45
15*R*	0.40	3.06	3.33	−0.37
27*R*	0.44	3.13	3.27	−0.34
4*H*	0.50	3.23	3.17	−0.29

As an example, let us consider MM adsorption on SLG formed on polytypes of silicon carbide. The energy parameters of SiC polytypes and the degree of their hexagonality D were taken from the paper [18] and are presented in the table.

In the case of undoped polytypes ($\varepsilon_F = \omega_{sc}$), the values of $\tilde{n}_{\mp}$ in the series 3*C* → 4*H* increase, and the total charge $\tilde{Z} = 2 - \tilde{n}_- - \tilde{n}_+$ on the MM decreases. In this case, electrons move to SLG, which acquires a charge $-\tilde{Z}$. Thus, the SLG formed on 3*C*-SiC receives the greatest charge. Add that the charge transfer between MM and SLG/SiC polytype is influenced by the choice of polytype face. For example, for the SLG/6*H*-SiC structure the electron work functions for Si and C faces differ by ~ 1.5 eV [19]. A more rigorous approach to describing the adsorption of atoms and molecules on epitaxial graphene is presented in the paper [20]. However, in a situation where experimental information is extremely limited, the simplifications made seem to be quite acceptable for estimating the charge transition.

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Conflict of interest

The authors declare that they have no conflict of interest.

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