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# A new method for determining energetically favorable landing sites of carboxyl groups during the functionalization of graphene nanomesh

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In this paper, we propose a new method for the stepwise functionalization of graphene nanomesh (GNM) with carboxyl (COOH) groups. The key point of this method is the determination of landing sites for COOH groups. As a criterion for determining the most favorable arrangement of COOH groups, it is proposed to use the charge distribution over the GNM atoms. According to our idea, atoms with the largest negative charge will more easily form strong covalent bonds with functional groups. Testing of the proposed method is carried out on the example of GNM supercell with a circular hole 1.2 nm in diameter and 2.46 nm in the direction of zigzag edge and 2.55 nm in the direction of armchair edge. The self-consistent charge density functional tight-binding (SCC-DFTB) method is used to simulate the stepwise functionalization of GNM with a sequential increase in the number of COOH groups from 1 to 9. During landing, COOH groups are located at the GNM hole edges. The orbital charge distribution is analyzed according to the Mulliken. According to the binding energy calculations, the addition of COOH groups by selected GNM atoms is energetically favorable at each step of functionalization. In the course of functionalization, the energy gap of GNM practically does not change, and the Fermi level shifts downward by several tenths of electron volts. At the maximum saturation of the hole edge atoms with COOH groups, the Fermi level and the energy gap of the functionalized GNM take values close to the values of the non-functionalized GNM.

**Keywords:** graphene nanomesh, carboxyl groups, functionalization, energy gap, binding energy.

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# Новая методика определения энергетически выгодных мест посадки карбоксильных групп при функционализации наносетчатого графена

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В работе предложена новая методика пошаговой функционализации наносетчатого графена (НСГ) карбоксильными (COOH) группами. Ключевым моментом данной методики является выбор мест посадки для групп COOH. В качестве критерия для определения наиболее выгодного расположения групп COOH предлагается использовать распределение зарядов по атомам НСГ. Согласно нашей идее атомы с наибольшим по величине отрицательным зарядом будут легче образовывать прочные ковалентные связи с атомами функциональных групп. Тестирование предложенной методики проводилось на примере суперъячейки НСГ с круглым отверстием диаметром 1.2 нм и размерами 2.46 нм в направлении края зигзаг и 2.55 нм в направлении края кресло. Методом функционала плотности в приближении сильной связи с применением самосогласованного заряда (SCC-DFTB) моделировался процесс пошаговой функционализации НСГ при последовательном увеличении числа групп COOH от 1 до 9. Группы COOH при посадке располагались по краям отверстия НСГ. Анализ распределения заряда по орбиталям проводился согласно процедуре по Малликену. По результатам расчета энергии связывания установлено, что процесс присоединения групп COOH выбранными атомами НСГ является энергетически выгодным на каждом шаге функционализации.

Показано, что в ходе пошаговой функционализации энергетическая щель НСГ практически не меняется, а уровень Ферми смещается вниз по оси энергии вниз на несколько десятых электрон-вольт. При максимальном насыщении краевых атомов отверстия группами COOH уровень Ферми и энергетическая щель функционализированного НСГ принимают значения, близкие к значениям нефункционализированного НСГ.

**Ключевые слова:** наносетчатый графен, карбоксильные группы, функционализация, энергетическая щель, энергия связывания.

## 1. Introduction

In recent years, GNM has attracted considerable attention of researchers due to its promising properties and a wide range of potential applications [1–3]. GNM possesses an adjustable band gap, a high specific surface area, a unique porous structure, and also contains a large number of abundant superficial and border active sites [4]. GNM-based structures are widely used as filter membranes, in catalysis, in energy storage/conversion devices, as well as in electronics and nanosensorics [5–9]. An important key to controlling and adjusting GNM properties is functionalization. To date, there are numerous examples of successful functionalization of GNM for its subsequent application in nanoelectronics and sensorics. For example, DNA-decorated graphene nanomesh based sensor devices with fast response and recovery have been developed to detect various types of vapors, including carboxylic acids, aldehydes, organophosphates, and explosives [10]. A high-performance nitrogen-doped GNM electrochemical sensor for determination of methyl parathion has been successfully developed [11]. Amine-functionalized GNM has been used as a metal-free catalyst for the oxygen reduction reaction [12]. Functionalization with silicon or nitrogen makes GNM a promising material for the manufacture of electrodes for lithium-ion batteries and supercapacitors. Kung et al. showed that the binder-free Si-GNM composite electrode demonstrates reversible capacities of 3200 mAh/g at 1 A/g and 1100 mAh/g at 8 A/g [13]. Xu et al. found that the performance characteristics of nitrogen-doped GNM electrodes were significantly improved compared to pure GNM. In particular, the discharge/charge capacities of the electrode were as high as 3056/990 mAh/g at 0.1 A/g, and the battery with such an electrode demonstrates stable operation while maintaining capacity for 6000 cycles [14]. The most common in practice is the functionalization of GNM with oxygen-containing groups. There are quite a few works describing the prospects for using GNM functionalized with oxygen-containing groups as a material for electrochemical energy storage [15–19]. One of them [19] clearly showed that the presence of oxygen-containing groups leads to an improvement in the specific capacity of GNM due to additional faradaic charges. In this case, the samples of the functionalized GNM retain capacitance better than the original GNM at both higher voltage scan rates and current densities [19]. The use of GNM with oxygen-containing groups for sensors seems to be no less promising. It has previously been shown that oxidized graphene exhibits excellent sensitivity to numerous gases, including $NO_2$, $NH_3$, CO, ethanol, $H_2O$, trimethylamine, HCN, and dimethyl methylphosphonate [20], and also has great potential for use in chemoreistors [21]. When functionalizing graphene with oxygen-containing groups, it is important to correctly determine the site of the atoms of oxygen functional groups. For the GNM, no effective method has yet been proposed for determining the sites for landing oxygen-containing functional groups. This paper is devoted to the development of such a method using computer modeling tools.

## 2. Computational details

The search for equilibrium states of the objects under consideration was carried out within the framework of the SCC-DFTB method [22]. Using the tight binding approximation within the DFTB method, the total energy of a polyatomic system was given by:

$$E_{TOT} = E_{OCC} + E_{SCC} + E_{REP} \quad (1)$$

The components of Eq. (1) were responsible for the energy of occupied electronic states ($E_{OCC}$), the energy of interaction of electrons ($E_{SCC}$) and the repulsive energy of atomic nuclei ($E_{REP}$), respectively. The terms $E_{OCC}$ and $E_{SCC}$ were calculated in the course of a self-consistent procedure, since the Hamiltonian of the system depends on the magnitude of the Mulliken charges. The Mulliken charges were expressed in terms of the overlap matrix $S$ and the expansion coefficients $c_i$, $c_j$ of one-electron wave functions in atomic orbitals. Expansion coefficients can be obtained in the course of finding the eigenvalues of the Hamiltonian.

The binding energy $E_b$ for GNM with COOH groups was calculated using the following formula:

$$E_b = E_{GNM+nCOOH} - E_{GNM} - E_{nCOOH}, \quad (2)$$

where $E_b = E_{GNM+nCOOH}$ is the energy of GNM functionalized with COOH groups, $n$ is the number of COOH, $E_{GNM}$ and $E_{nCOOH}$ groups are the energies of isolated GNM and COOH groups, respectively.

## 3. Results and discussion

We have developed a method for the functionalization of edge atoms of the hole in GNM with COOH groups. The key point in the development of the methodology was the choice of the criterion for determining the landing site of functional groups. As such a criterion, the value of the charge per atom of the GNM was chosen. According to our idea, atoms with the highest negative charge will more readily form strong covalent bonds with atoms of functional groups. We will describe the principles of the method using the example of a GNM supercell with a circular hole of 1.2 nm in diameter and dimensions of 2.46 nm in the direction of the zigzag edge and 2.55 nm in the direction of the armchair edge. This GNM supercell had already been obtained and described by the authors of this work [23]. At the initial stage, we calculated

the charge distribution over the atoms of the GNM supercell (see Fig. 1a). Based on the obtained distribution, the hole edge atom with the largest negative charge was determined. Then, the COOH group was placed on this edge atom, and the atomic structure of the GNM supercell was reoptimized. For the reoptimized supercell, the charge distribution was calculated again. Analysis of the charge distribution over the supercell atoms showed that the COOH group took most of the GNM charge (see Fig. 1b). This suggests that carboxyl groups are the most reactive. Based on the charge distribution shown in Fig. 1b, the next hole atom for the landing of one more COOH group was determined. As a result of optimization of the atomic structure of GNM with two COOH groups, it was found that COOH groups formed covalent bonds with edge atoms adjacent to the landing site (see Fig. 1c). The presence of such covalent bonds can reduce the sensitivity of the functionalized GNM, which is extremely undesirable for a potential GNM based sensor.

In order to avoid the formation of unnecessary covalent bonds, it was decided to return to the initial GNM supercell without COOH groups and saturate the hole atoms with hydrogen to the left and right of the landing site of the COOH groups. The landing site was chosen according to the charge distribution, as described above. After optimizing the structure of the GNM supercell with already placed functional groups, the charge distribution was calculated and the landing site for the next COOH group was determined. The stepwise functionalization of the edge atoms of the hole in the GNM supercell with an increase in the COOH groups from 1 to 9 was carried out in the manner described above. Fig. 2 clearly illustrates this stepwise process and how our method works. As a result of the functionalization of the GNM with nine COOH groups, a holey graphene structure with completely occupied atoms of the hole was obtained (see Fig. 2i).

To check whether the process of addition of each subsequent COOH group is beneficial from an energy point of view, the binding energy $E_b$ was calculated at each stage of functionalization. The obtained calculation results are presented in Table 1. The data in Table 1 show that the configurations of GNM supercells with different numbers of COOH groups are characterized by a negative value of $E_b$. Therefore, the process of functionalization is energetically beneficial for them.

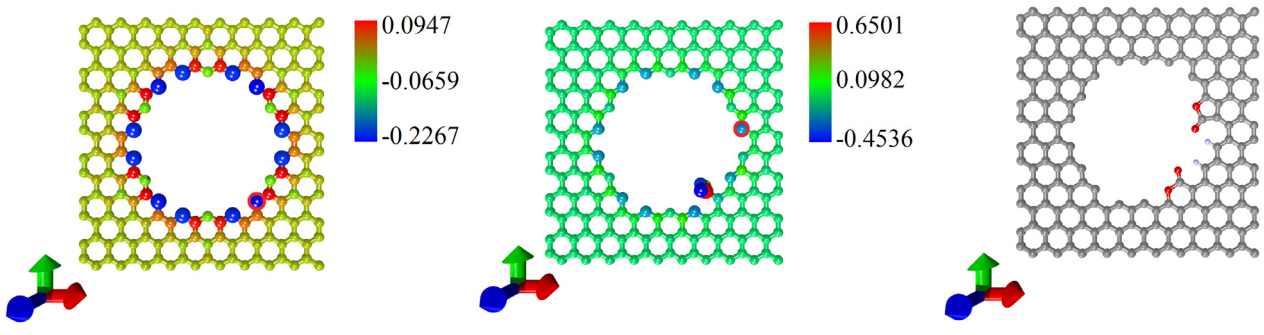
Along with the calculation of the binding energy $E_b$, we were also interested in how the electronic and energy characteristics of GNM, namely the Fermi level ($E_F$) and the energy gap ($E_{gap}$), will change during functionalization. The calculated values of these characteristics are presented in Table 1. As can be seen from the data in Table 1, the energy gap of the GNM functionalized with COOH groups practically did not change in comparison with the non-functionalizedone, therefore the type of conductivity of the GNM was preserved. This result indicates that the presence of carboxyl groups did not affect the sensitivity of GNM to detected molecules during sensor operation. The Fermi level behaved differently. In the presence of only one COOH group, the GNM shifts downward immediately by 0.4 eV, which indicates the emerging rearrangement of the electronic structure of the GNM. However, with complete saturation of atoms at the edges of the GNM hole, the Fermi level approaches by 0.2 eV to its value in the absence of COOH groups, which means that the electronic structure of functionalized graphene is stabilized.

## 4. Conclusions

In the course of testing the proposed stepwise procedure for the functionalization of the GNM with carboxyl groups COOH, an energetically stable atomic structure of the GNM supercell with fully occupied edge atoms of the hole was obtained. It was found that the Fermi level of the energetically stable atomic configuration of the GNM with nine COOH groups was shifted down the energy axis by 0.2 eV compared

**Table 1.** Energy characteristics of functionalized GNM.

| Structure | $E_b$, eV/atom | $E_{gap}$, eV | $E_F$, eV |
|---|---|---|---|
| GNM | - | 0.06 | −4.73 |
| GNM+1COOH | −0.08 | 0.02 | −5.19 |
| GNM+2COOH | −0.08 | 0.06 | −5.18 |
| GNM+3COOH | −0.02 | 0.01 | −5.20 |
| GNM+4COOH | −0.05 | 0.01 | −5.16 |
| GNM+5COOH | −0.07 | 0.03 | −5.16 |
| GNM+6COOH | −0.02 | 0.06 | −5.17 |
| GNM+7COOH | −0.05 | 0 | −5.18 |
| GNM+8COOH | −0.05 | 0.04 | −5.16 |
| GNM+9COOH | −0.02 | 0.07 | −4.99 |




a b c

**Fig. 1.** (Color online) Map of charge distribution on the supercell of the non-functionalized GNM (the edge atom with the highest negative charge is circled in red) (a); GNM supercell with one COOH group (b); the case of the formation of covalent bonds between the COOH group and the edge atoms of the GNM hole (c).

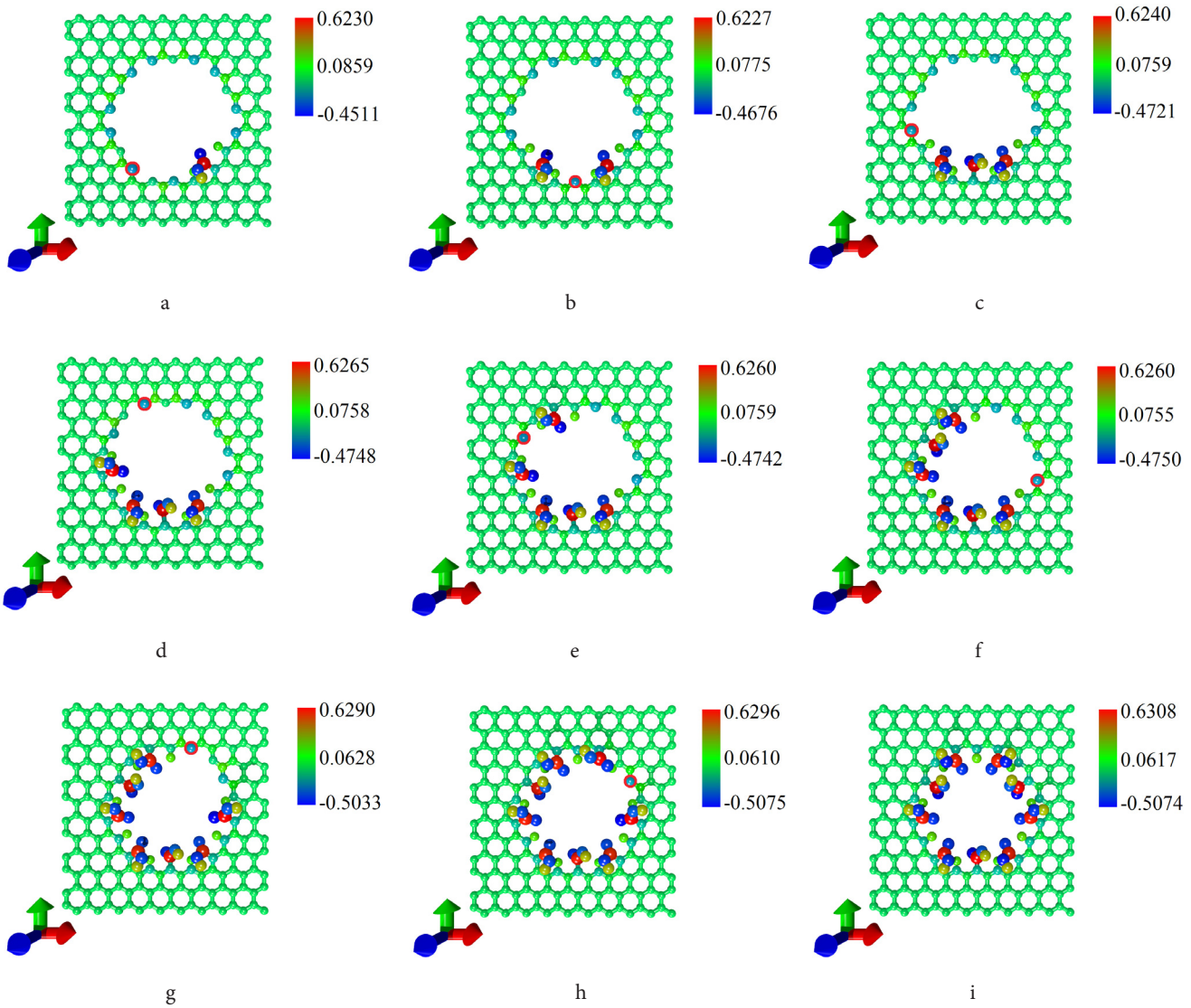



**Fig. 2.** (Color online) A phased process of the GNM functionalization with an increase in the number of COOH groups from 1 to 9 (a – i).

to the non-functionalized GNM. In this case, the energy gap practically does not change, which indicates the retention of the electrically conductive properties of the GNM after functionalization. Taking into account the energetically favorable nature of the covalent bonds of GNM with COOH groups and insignificant changes in the conducting properties of the functionalized GNM, it is possible to predict the prospects of using this configuration of GNM as a sensor for detecting various molecules.

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