On the stability and existence of nitro-graphene, nitro-graphane, and nitro-graphene oxide

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Abstract
Here, the possibility of the existence of nitro-graphene derivatives with undisturbed graphene backbone is considered. Based on the first-principles calculation, it is shown that while NO$_2$ is unable to form a covalent bond with bare graphene, it becomes possible in some structures of hydrogenated graphane, fluorographene, and graphene oxide. This paper presents, among others, an analysis of the surrounding influence on the C-NO$_2$ bond strength. The author believes that the potential prospects of these materials and discussion about possible synthesizing routes may help further research on graphene-based materials.

Keywords Graphene · NO$_2$ · Nitro graphene · Gas sensors · Graphene derivatives

Introduction
Functionalized graphene exhibits high potential for application in gas (Liu et al. 2017) and biosensors (Suvarnaphaet and Pechprasarn 2017); supercapacitors (Bakandritsos et al. 2019), solar cells (Liu et al. 2015), batteries (Lee et al. 2012), and other energy materials; catalysis (Haag and Kung 2014), electromechanical devices (Panahi-Sarmad et al. 2019), etc (Georgakilas et al. 2016). This diversity is due to a wide range of properties that can be adjusted depending on the type of functionalization, which can be divided into covalent (chemical) or non-covalent (physical) functionalization (Jeon et al. 2011). While there is an enormous number of composites and non-covalently bonded materials, the number of known covalently modified graphene materials with the original carbon backbone is limited (Chua and Pumera 2013). The three most studied primary graphene derivatives with a covalent chemical bond are hydrogenated graphene (HG), fluorinated graphene (FG), and graphene oxide (GO). In turn, the nucleophilic substitution of functional groups in FG and GO can lead to a number of additional derivatives (Whitener et al. 2015; Lai et al. 2011).

It was shown that various covalently bonded functional groups in GO, FG, and HG tend to form a unique pattern on graphene (Johns and Hersam 2013). Various distributions lead to differences in physical properties, which introduces an additional degree of freedom in the adjustment of characteristics of such materials (Yamaletdinov et al. 2020; Gargiulo et al. 2014). Their functional groups patterns are mainly determined by energy parameters, such as the efficiency of the C-X interaction, violation of geometry, disruption of the graphene $\pi$-system, non-covalent interaction with the nearest neighbors, etc (Neek-Amal and Peeters 2015). Based on this, the pattern of functionalized graphene with electron-withdrawing groups characterized by an extensive $\pi$ system should strongly differ from those known in FG, HG, GO, and therefore has a set of unique properties. NO$_2$ is one of the classic examples of such groups.

There are many studies dedicated to the interaction of NO$_2$ molecule with graphene-based material, in terms of application in gas-sensors (e.g. Wang et al. 2016). Such an application is possible due to a significant difference in the resistance of the initial material and the material bounded with the gas molecules. Numerous studies demonstrate the non-covalent interaction of the NO$_2$ with a plane of pristine or functionalized graphene with the binding energy 0-0.5 eV and distance 2-4 Å (Maity et al. 2017). Based on all these studies, it can be assumed that only edge atoms of graphene flakes and boundary atoms of sufficiently large vacancies can form a covalent C-NO$_2$ bond (You et al. 2017). The presence of nitro groups is also reported after the modification of highly oxidized GO with a high concentration of -COOH groups and holes (Satheesh et al. 2014; Pérez et al. 2011).
However, materials with such a damaged graphene backbone are poor conductors and are subjected to rapid degeneration. At the same time, the rich chemistry of nitro compounds (especially a large number of possible reduced forms) (Sassykova et al. 2019) encourages great potential in the RedOx applications of graphene with covalently bonded nitro groups.

Recently, based on an extensive density functional theory (DFT) data set, we concluded that the binding energy of a single CF is higher the more opposing fluorine atoms in the first coordination sphere and the fewer fluorine atoms in the second coordination sphere. Yamaletdinov et al. (2021) (see Fig. 1). Inspired by this fact, here the possibility of covalent bonding of the -NO$_2$ group with graphene and its derivatives is considered.

**DFT calculations details**

DFT calculations were carried out using the QUANTUM-espresso toolkit (Giannozzi et al. 2009, 2017) within Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional (Perdew et al. 1996). PAW potentials with nonlinear core correction for each atom from http://www.quantum-espresso.org and corresponded recommended cutoff parameters were used. In this work were evaluated small unit cells of $2 \times 2$ or $3 \times 3$ primitive graphene unit cells (Fig. 1, first column of Table 1).

**Results and discussions**

An unsuccessful attempt to find any stable covalently bounded nitrographene C(NO$_2$)$_X$ was performed. Single NO$_2$ group, pairs, alternating chains C$_4$NO$_2$, fully nitrated CNO$_2$, and any distributed systems (such as C$_4$F in Ref. Robinson et al. (2010)) do not converge in any stable covalently bonded

| Structure | E$_{CN}$ | C-N | C-X$_1$ | C-X$_2$ |
|-----------|---------|-----|---------|---------|
| HG:       | 0.27    | 1.83| 1.13    |         |
| FG:       | -0.25   | 1.74| 1.49    |         |
| GO:       | -0.17   | 1.73| 1.48    | 0.99    |

**Fig. 1** An example of a unit cell. Green and orange dashed circles correspond to first and second coordination spheres. Blue-colored atoms correspond to functional H- or F- or HO- groups. Red-colored atom corresponds to the -NO$_2$ group. Dot and cross notations correspond to up and down-oriented functional groups, respectively.
structures in our calculations. It seems that large NO$_2$ groups mutually destabilize being even in the second coordination spheres of each other. However, in the case of a single NO$_2$ molecule, it forms a relatively stable non-covalent bond with the graphene plane. Modeling of the C$_7$HNO$_2$ supercell gives distance $r$(Grp-NO$_2$) = 3.35 Å and binding energy $E_{\text{Grp-NO}_2} = 1.35$ eV, which agrees with other theoretical studies of NO$_2$ binding (You et al. 2017). For various derivatives of graphene, an estimate of the energy and bonding length of non-covalent interactions with NO$_2$ is also mentioned and varies enormously from tenths eV (e.g. 0.25 eV and 3 Å for FG (Sysoev et al. 2017)) to values more characteristic of covalent bonds (e.g. 2.2 eV and 2.2 Å for Ag-Gr (Li et al. 2021)).

As is known, the presence of a neighbor in the first coordination sphere stabilizes H- in HG and F- in FG (Neek-Amal and Peeters 2015; Yamaletdinov et al. 2021; Zhou et al. 2014). Based on this, simulation of structures with NO$_2$ group and one, two, or three oppositely directed X (X = H, F, OH) in the first coordination sphere was carried out (see Table 1, structures I-III). Since the NO$_2$ molecule is quite large and has a significant destabilizing sterical effect, all of the structures considered had an anti-orientation of the X with respect to NO$_2$. Obtained results are analyzed in terms of C-NO$_2$ bond dissociation energy and C-NO$_2$ and C-X$_{1,2}$ bond length. C-NO$_2$ bond dissociation energy ($E_{C-N}$) is calculated as a difference between the energy of the XG structure with ($E_{\text{XG-NO}_2}$) and without ($E_{\text{XG}}$) the nitro group: $E_{CN} = -[E_{\text{XG-NO}_2} - E_{\text{XG}}]$. It can be seen that the C-NO$_2$ and C-X bond changes as the number of neighbors in the first coordination sphere increases. Hydrogen has the strongest stabilizing effect, while hydroxyl and fluorine show almost the same influence, with a slight advantage for the hydroxyl group. Binding of NO$_2$ mutually leads to stabilization of C-X bond. This effect is manifested by a decrease in the C-X bond length. This is most significantly observed in the case of FG (change in bond length up to 0.1 Å) less for HG (up to 0.03 Å) and is negligible for GO (<0.01 Å). Based on the data obtained, we can conclude that structure I is unlikely to be detected experimentally. It is difficult to conclude about the experimental observability of structures II and III, but the stability of XG in them without NO$_2$ is rather low (Johns and Hersam 2013).

While neighbors in the first coordination sphere stabilize the structures, second neighbors obstruct them. Structures IV-VI was selected as one of the most stable for FG (Yamaletdinov et al. 2021). It is seen that only for HG the covalent C-N bond can be formed in all described structures IV - VI. In the case of FG and GO, only the alternated chain (IV) is stable. Hydroxyl and fluorine again have the same effect on structure stability, but hydroxyl has the greatest destabilizing effect among neighbors in the second coordination sphere, which can be explained by the largest group size among X. NO$_2$ binding results in a smaller change in bond length. In the first coordination sphere, the shrinkage is 0.02, 0.03, and 0.01 Å for HG, FG, and GO, respectively, and in the second, it is 0.01 Å or less for all structures. At the same time, the increase in structure saturation itself decreases the length of the C-X bond in the second sphere, which can be interpreted as the C-X bonding enhancement. The greater the destabilization of X, the stronger the C-X bond.

The binding of NO$_2$ to the vacant carbon of structure IV leads to a noticeable redistribution of electron density (Fig. 2). First of all, this binding leads to the polarization of NO$_2$ itself and to the destruction of the C = C π bond. A strong negative inductive effect of NO$_2$ affects the first coordination sphere, which manifests itself in a slight decrease of electron density on X. In addition, the Bader charges (Yu and Trinkle 2011) of the NO$_2$ group and the carbon atom bonded to it were calculated (Fig. 3). The charge on the NO$_2$ group directly correlates with the bonding energy (the lower the absolute charge, the greater the bonding energy (Tang and Cao 2011; Li et al. 2021)). In the series of structures I-III, there is a clear trend of increasing electron density on the NO$_2$ group, which is a consequence of the aforementioned strong negative inductive effect.

### Table 1 (continued)

| Structure | E$_{CN}$ | C-N | C-X$_1$ | C-X$_2$ |
|-----------|---------|-----|---------|---------|
| VI HG:    | 1.04    | 1.68| 1.11    | 1.10    |
| FG:       | 0.06    | 2.31| 1.40    | 1.40    |
| GO:       | 0.04    | 2.58| 1.44    | 1.43    |
|           |         |     | 1.00    | 1.00    |

C-X$_1$ and C-X$_2$ are the median C-X bond length in the first and second coordination sphere, respectively. The second line of GO is the length of the O-H bond of the first and second neighbors.
The most interesting effect appears on the X of the second coordination sphere. It looks like electron density is shifted towards the $\sigma$(C-H) orbital for $X = H$, $\rho$(F) orbital for $X = F$, and $sp^2$($O^+$/u$\pi$(OH) for $X = OH$. Since NO$_2$ is the only available source of electrons, we can conclude that substituents in the second coordination sphere pull the electron density from NO$_2$ toward their bonding orbitals. This effect also manifests itself in a significant decrease in the charge of the NO$_2$ group in fully functionalized structures (structure V, Fig. 3). The detailed mechanism of this effect requires further study.

Since the first mentions of fluorographene and graphane, they are qualified as two-dimensional Teflon (Nair et al. 2010) and hydrocarbon (Sofo et al. 2007), respectively. In this regard, the obtained C-NO$_2$ binding energy is compared with some nitroalkanes and fluoronitroalkanes (Fig. 4). Figure 4 shows that the C-N binding energy of the structures considered in this work is mainly lower than in one-dimensional analogs. From this point of view, structure III shows the greatest similarity with a difference of 0.33 eV (2.05 eV for structure III vs 2.38 eV for nitromethane and nitroethane).

Despite the relatively weak C-NO$_2$ bond, some of the considered structures are stable and, as expected, can be observed experimentally. However, no mention of this has been found. A possible explanation is the failure of the synthesis with conventional nitration methods and/or researchers may not pay enough attention to the type of binding when studying the characteristics of gas sensors. For example, it has been reported that the UV-assisted sensing performance of HG is several times higher than that of GO, without any analysis of the binding type (Park et al. 2017).

So, under what conditions can nitro derivatives of graphene be synthesized, while a mixture of nitric and sulfuric acids is a commonly used method for graphene oxidizing (Jankovský et al. 2017)? A comparison of the energy required to release one NO$_2$ molecule with C-NO$_2$ bond energy is carried out. The following precursors of NO$_2$ are considered (green dashed lines in Fig. 4): HNO$_3$, NO$_2$F (for FG only), N$_2$O$_4$, NO$_2$. Gas-phase radical nitration can lead to nitro-graphane due to the great similarity of graphane with alkanes. However, the low stability of the C-NO$_2$ bond can prevent this even for HG. In the case of plasma synthesis of HG, FG, and GO, a few unsaturated reactive centers remain on the structure (Yamaletdinov et al. 2021). These centers can form C-NO$_2$ bonds under a large excess of NO$_2$ or N$_2$O$_4$. However, this nitration method is unlikely to result in a structure with a high NO$_2$ concentration. The most promising method is the binding of NO$_2$ during synthesis when there are a large number of reactive centers. In the case of plasma modification of graphene, this can be achieved by adding NO$_2$ to the gas mixture. Liquid phase modification can be performed by autoclaving with a functionalizing agent (e.g. NO$_2$F for nitrofluorination) at room temperature with a N$_2$O$_4$ solvent.

**Conclusion**

For now, it is difficult to predict the real-life stability of materials based on nitro-graphene derivatives. Nevertheless, this study shows the possibility of their existence, as well as the first initial analysis of factors, that influenced nitro group stability, and proposes a possible synthesis approach. The
study shows that the NO$_2$ group can form not only a strong noncovalent binding to graphene, but can also form weak covalent bonds with its derivatives. The stability of such binding is primarily affected by the functionalization of the surrounding atoms, and the formation of such binding is to be expected with highly active carbon atoms with a localized unpaired electron. The strong inductive effect as well as the size of the NO$_2$ group leads to a destabilizing effect of neighboring groups (especially with strongly electronegative atoms) aligned with the NO$_2$ group. The ability to create graphene-based materials with such a RedOx variable group may have great potential in electrochemical applications.

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Declarations

Conflict of interest The author declares that there is no conflict of interest.

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