Porous graphene structures, also termed graphene nanomeshes (GNMs), are garnering increasing interest due to their potential application to important technologies such as chemical sensing, ion-filtration, and nanoelectronics. Semiconducting GNMs designed to have fractional eV band gaps are good candidates for graphene-based electronics, provided that a mechanism for their stable and controlled doping is developed. Recent work has shown that controlled passivation of the edges of sub-nanometer pores and subsequent doping by atoms or molecules gives rise to $p$- and $n$-doped GNM structures. However, these structures are difficult to fabricate at the nanoscale. Here, we use first principle calculations to study the effect of the pore size on the doping physics of GNM structures with larger pores that can potentially host more than a single dopant. We show that such doping mechanism is effective even for pores with relatively large radii. We also study the effect of the number of dopants per pore on doping stability. We find that stable rigid band $n$- and $p$-doping emerges in such structures even if the dopants form a nano-cluster in the pore.
band doping is achieved in all \( n \)- and \( p \)-doping studied. Such doped large-pore GNM structures have potential applications as field effect transistors, and as transparent conducting electrodes.

I. INTRODUCTION

Over the last 13 years since its experimental realization, graphene has captured the interest of both theoretical and experimental researchers due to its unique physical and chemical properties, leading to a host of potential application to many technological niches including chemical separation, nanocatalysis, RF amplifiers, and nanoelectronics. Despite its high electronic mobility, graphene lacks an electronic gap, which limits its potential as a substitute for silicon in the transistor world.

Graphene nanomeshes (GNM’s, also called porous graphene) are formed by creating a super-lattice of pores in a graphene sheet. Depending on the super-lattice constant and the pore geometry, these structures can inherit graphene’s semimetallicity, or can be semiconducting with a fractional eV gap. If such semiconducting structures could be controllably and stably doped, they could be used to fabricate graphene-based computer logic switches and spintronic devices.

Controlled, stable, chemical doping of pore-edge passivated GNM’s has been recently proposed: A neutral dopant undergoes a charge transfer reaction with the GNM of specific pore edge passivation, ionizes, and is then electrostatically trapped in the pore by the local dipole moments of the edge functional groups. The charge so transferred dopes the GNM, moving the Fermi level into the valence or the conduction bands (see Fig.). The GNM band structure is essentially not affected by the doping process, and the dopant state involved in the charge transfer is far from the Fermi level. In this way, a stable controlled rigid band doping of semiconducting GNM can be achieved.

GNMs have been fabricated by several groups, with pore-size distributions in the 3-200 nm range. A study of the I-V characteristics of \( p \)-doped GNM-based transistors indicated that their ON-OFF ratio is an order of magnitude larger than that of pristine graphene, but with lower electrical conductivity. Most recently, sub-nanometer pores were fabricated, albeit without the periodicity necessary for transport application. Since fabrication techniques are likely to yield GNM’s with nanometer-sized pores which can host more than one
FIG. 1: A conceptual sketch of multiple-ion chelation doping of a GNM. Chelant atoms are successively brought close to pore, where some or all of them become ionized, thus doping the GNM. Here, $n$-doping is shown; $p$-doping simply replaces the electron with a hole. In principle, partial charge transfer can occur, where the HOMO/LUMO of the chelants can move relative to the GNM spectrum.\cite{18,20}

dopant atom, a question arises regarding the dopant stability in the pores. How would multiple dopants behave in a large pore? Would they uniformly distribute around the pore edge, or would they cluster together, with obvious impact on the dopants binding energy? In addition, how would the distribution/clustering of the dopants in the pore affect the rigid band doping picture?

In this work, we address the aforementioned questions through the study of the electronic properties of a representative set of GNM structures with varying pore sizes, dopant loads, and pore edge passivations, for both $n$- and $p$-doping. Using first principles calculations, we will calculate the binding energy as well as the maximum number of dopants bound per pore. We will also explore the effect of multiple small dopants on the band structure of the doped GNMs to determine whether or not the rigid band picture is applicable.

II. DESCRIPTION OF THE PHYSICAL SYSTEM

Since $n$- and $p$-type FET’s are required for digital electronics, the adoption of GNM’s for post-CMOS technologies relies heavily on a thorough understanding of their properties, including doping. Experimental work on GNM’s currently achieves pore diameters as small as 3 nm.\cite{23} Therefore, we have to consider multiple dopants per pore, studying the details of their packing and stability for near term applications. These studies also provide a
framework for understanding the behavior of dopant ionic complexes for chemical separation applications.

We have recently suggested a novel approach [17] to dope GNM’s based on a concept from chemistry - ion chelation. Here, the pore perimeter is passivated by a species with an electronegativity different from carbon, which results in the formation of local radial dipoles at the pore perimeter creating a favorable environment to host ions. A neutral atom is ionized by the sheet through a charge transfer reaction in which the electrostatic energy gain is higher than the charge transfer cost. This results in the tight electrostatic binding of the ion, and the rigid band doping of the GNM sheet. This is consistent with the behavior predicted by the Newns-Anderson and Norskov-type models. [19, 26, 27] The pore lattice strictly controls dopant concentration. In the following, we build on this basic physics.

In GNM’s with nanometer-sized pores, electrostatic dopant binding is expected to decrease due to four effects: 1- A weaker interaction between a dopant and the pore dipoles. 2- The increase in the charge transfer to the sheet, and hence its energy cost. 3- The repulsion between ionized dopants. 4- The introduction of more dopants in large pores can lead to the clustering of dopant atoms. This implies that chemical binding, well known in metals, may occur between the dopant atoms which may affect the doping physics observed with single dopants (Fig. 1).

In order to understand the implications of these effects on the doping of GNM’s, we study the doping produced by multiple dopants in n- and p-doped GNM systems: For n-type, we consider an oxygen passivated GNM, for two supercells, and two pore sizes. We study the loading of this GNM and hence n-doping with multiple lithium and sodium atoms. For p-type, we consider a hydrogen passivated GNM, also for two supercells, and two pore sizes. The dopants studied here are multiple fluorine and chlorine atoms.

We use density functional theory within the generalized gradient approximation to describe the systems of interest as verified in Ref. [17]. We introduce the nomenclature nX@Y–GNM to denote a GNM structure with a supercell size of c graphene unit cells, with its pore edges passivated by species ”Y”, and with n atoms of species ”X” hosted in the pore. Therefore, our parameter space is constructed by X = \{Li,Na\}, n = 1, 2, ..7, and c = 9, 12 for the O–GNM systems, and X = \{F,Cl\}, n = 1, 2, ..6, and c = 9, 12 for the H–GNM systems. We will cover points in this parameter space that are sufficient to unravel the doping physics.
III. RESULTS AND DISCUSSION

We begin by presenting the electronic properties of our undoped GNM systems. Figure 2(a,b) shows an oxygen- and a hydrogen-passivated GNM (insets), with supercell size of $9 \times 9$ graphene unit cells ($O$–GNM9 and $H$–GNM9), as well as their density of states (DOS). The two GNMs have a pore size of about 0.8 nm, and are chemically stable as the passivation saturates all bonds. Both GNMs are semiconducting, with a gap of about 0.5 eV for the oxygen case, and 0.7 eV for the hydrogen case. Projection of the electronic states on the atomic orbitals (PDOS) shows that the states of the passivating species are located far from the top/bottom of the valence/conduction bands, and are therefore not expected to induce resonant scattering.

![Figure 2: DOS and PDOS of the pristine (a) O–GNM9, (b) H–GNM9, (c) O–GNM12, and (d) H–GNM12 systems. The insets show the unit cells of the relaxed structures.](image)

Two GNMs with larger pores are shown in Fig 2(c,d) - the oxygen passivated GNM,
O–GNM12, has a pore diameter of \( \sim 1.6 \text{ nm} \), while the hydrogen-passivated GNM, H–
GNM12, has a pore diameter of \( \sim 1.3 \text{ nm} \). The DOS of both systems indicate that they are
intrinsically semiconducting, with gap sizes of 0.8 eV and 0.4 eV for the oxygen-passivated
and hydrogen-passivated systems, respectively.

The chemical stability of the studied systems is estimated through a calculation of the
zero temperature binding energy \( (E_b) \) of the doped crown GNM system using:

\[
E_b = E_{nX@Y\text{-}GNMc} - E_{Y\text{-}GNMc} - E_{Xn},
\]

where \( E_{nX@Y\text{-}GNMc} \) is the energy of the \( n \)X-chelated \( Y \)-passivated GNM system with a \( c \times c \)
supercell size, \( E_{Y\text{-}GNMc} \) is the energy of the \( Y \)-passivated GNM, and \( E_{Xn} \) is the energy of
the most stable molecular cluster of \( n \) atoms of species \( X \).

A. \( n \)-doping

In this section, we consider \( n \)-doping cases of O–GNM for 22 physical embodiments and
two dopants: Li and Na, and 2 pore sizes. This allows us to study cases with multiple
dopants in each pore.

We first consider the cases of O–GNM9, with pore diameter 0.8 nm. A lithium atom
brought close to the edge of the pore (inset of Fig. 3a) loses its electron to the graphene
skeleton, thereby ionizing and becoming electrostatically trapped in the field of the edge
dipoles, forming a Li@O–GNM9, with a binding energy of 1.29 eV. The average distance
between the Li ion and the closest two oxygen atoms is 2.19 Å.

The DOS and PDOS for that system is shown in Fig. 3a. The Fermi level indicates
that the O–GNM9 is \( n \)-doped. The O–GNM9 perturbs the Li state such that it raises its
2s state by about 1.1 eV above the Fermi level. The Li 2s state is therefore too far up in
the spectrum to obstruct low energy electronic transport. By integrating the DOS from the
conduction band edge to the Fermi level, we find that one electron has been transferred to
the O–GNM9.
FIG. 3: Density of states of the (a) Li@O–GNM9, (b) 2Li@O–GNM9, (c) 3Li@O–GNM9, and (d) Na@O–GNM9, (e) 2Na@O–GNM9, (f) 3Na@O–GNM9 systems (DOS). The bottom insets refer to the relaxed structures. In (b), (c), (e), and (f) the top insets show the Li/Na states within the corresponding O–GNM9 system, as compared to those of the isolated Li/Na clusters. The locations of the Li/Na states are marked on the energy axis. The DOS of the pristine O–GNM9 (GNM) is shown for comparison.
We now place another lithium atom close to the pore edge. After structural relaxation, the second atom docks at the pore edge opposite to the first one (inset of Fig. 3b), with a Li-Li separation of 5.28 Å, and in the same plane of the GNM. The average Li distance to the closest oxygen atoms is 2.10 Å. The binding energy of the two lithium atoms in the pore is found to be 0.79 eV. This in-pore configuration is about 0.50 eV higher than the binding energy of the system with the second lithium atom atop the sheet carbon atoms, whether far from the pore, or close to it.

The DOS and PDOS of the 2Li@O–GNM9 system are shown in Fig. 3b. The shift in the Fermi energy indicates the increase in the doping level of the 2Li@O–GNM9 over the Li@O–GNM9 system. Calculations confirm a charge transfer of 2e between the two lithium atoms and the graphene lattice. The DOS shows that the two empty Li states are now raised above the Fermi level by 0.5 eV and 1.2 eV. These two states are the symmetric and antisymmetric linear combinations of the atomic 2s lithium states. Thus the two Li atoms double the doping level, and maintain the rigid band doping picture, but with a smaller binding energy.

Adding a third lithium atom to the pore introduces a qualitative change. Whereas the states of the single and double Li doping are far above the conduction band edge of the O–GNM9 (thus resulting in the spilling of one and two electrons to the O–GNM9, respectively), one of the states of the triple Li doping now falls in the conduction band of the O–GNM9. The O–GNM9 perturbs the Li and 2Li spectra in such a way so as to raise their atomic/molecular HOMO states, leading to the ionization of lithium atoms in both cases. In the 3Li case, the perturbation is such that the lowest lithium 2s-like state lies in the conduction band of the system below the Fermi level, and therefore two electrons occupy that state, while the third electron is donated to the O–GNM9, thus doping it to a level similar to that of the Li@O–GNM9 system. The binding energy in this case is 1.91 eV. The insets of Figs. 3b and 3c compare the spectra of the two and three Li atoms in the pore to those of the Li2 and Li3 clusters. This case is probably the least desirable for device engineers, as switching the device off would involve emptying the lowest Li state.

The difference in the binding energy of the Li atoms in the three above cases can be understood as follows: In the Li@O–GNM9 case, the cost to ionize the Li atom and to charge the O–GNM9 is compensated by the electrostatic energy gain, leading to a binding energy of 1.29 eV. The 2Li@O–GNM9 system can be thought of starting from a Li2 molecule
(dimer) placed in the center of the pore. The pore separates the Li$_2$ to a distance of 5.28 Å, twice its dimer equilibrium distance of 2.74A, and ionizes the two atoms. The energy cost thus includes the breaking of the Li$_2$ dimer as well as the electrostatic repulsion between the resulting Li$^+$–Li$^+$ structure. This decreases the binding energy of the 2Li@O–GNM9 to 0.79 eV. The case of Li$_3$ follows a similar logic, but since the final configuration in the pore has an average Li-Li distance of 3.26 Å, i.e. nearly the equilibrium distance of the trimer (2.82 Å), very little of the electrostatic gain has to be paid towards the trimer deformation. The lowest state of the Li$_3$ cluster lies below the Fermi level of the system, i.e the cluster is singly ionized (Li$^+_3$). Its positive charge is delocalized over the cluster, causing a stronger electrostatic interaction with the pore oxygen atoms compared to that between the Li$^+$ and its two neighboring oxygen atoms in the Li@O–GNM9 case, thus leading to a higher binding energy of 1.91 eV for the 3Li@O–GNM9 system.

To reach the maximum capacity of the pore, we add more lithium atoms, thus forming 4Li@O–GNM9, 5Li@O–GNM9, 6Li@O–GNM9, and 7Li@O–GNM9 systems (Fig. 4). The Li atoms cluster above the pore, with the fourth one sitting about 2.79 Å above the plane of the GNM. The DOS of these systems shows that the trend that started with small Li clusters continues; that the lowest Li$_n$ states get pushed deeper into the system spectrum, an indication that fewer Li atoms are ionized. One interesting feature is that in the 4Li@O–GNM9 the lowest Li$_4$ state is now below the valence band edge, with two electrons transferred from the cluster to the O–GNM. The binding energy of the 4Li@O–GNM9 is 1.59 eV. At higher doping, a Li state always persists in the conduction band of the system. The charge transfer to the O–GNM9 is 1, 2, and 3 electrons, and the binding energy is 1.43, 0.73, and 0.44 eV, for the 5Li@O–GNM9, 6Li@O–GNM9, and 7Li@O–GNM9, respectively. This makes the 4Li@O–GNM9 system the most favorable from a device perspective. Table I summarizes our results for various O–GNM9 systems.

The situation for the Na-doping case is qualitatively similar to that of the Li-doping. Figures 3(d, e, and f) show the structure and DOS of the three systems Na@O–GNM9, 2Na@O–GNM9, and 3Na@O–GNM9. In the case of the Na@O-GNM9 and 2Na@O-GNM9 systems, the 2s Na states are located above the Fermi level, and the systems are $n$-doped with a charge transfer of 1 and 2 electrons, respectively. The binding energies are 1.62 and 1.57 eV, respectively. As in the Li case, the binding energy of the 2Na@O–GNM9 system decreases compared to the Na@O-GNM9 system, due to the extra charging of the GNM and
FIG. 4: Density of states of the (a) 4Li@O–GNM9, (b) 5Li@O–GNM9, (c) 6Li@O–GNM9 (d) 7Li@O–GNM9, (e) 4Na@O–GNM9, (f) 5Na@O–GNM9, (g) 6Na@O–GNM9, and (h) 7Na@O–GNM9 systems (DOS). The insets refer to the relaxed structures. The DOS of the pristine O–GNM9 (GNM) is shown for comparison.
the electrostatic repulsion between the two Na\(^+\) ions. For the 3Na@O–GNM9 system, the lowest Na\(_3\) state lies below the Fermi energy, and hosts two of the three Na\(_3\) electrons, while the third electron is transferred to the GNM. The Na cluster is thus singly ionized (Na\(_3^+\)), with a binding energy of 2.79 eV. As in the Li case, the delocalized positive charge interacts with all pore oxygen atoms, leading to a higher binding energy compared to that of the Na@O–GNM9 system. Furthermore, the Na-doped systems have higher binding energies than the Li ones due to the higher ionization energy cost of lithium. The effect of the O–GNM9 on the spectra of the Na\(_2\) and Na\(_3\) clusters is sketched in the insets of Figs. 3e and 3f. As with its Li version, the 3Na@O–GNM is the least desirable for device applications.

The higher Na-doping scenarios, 4Na@O–GNM9, 5Na@O–GNM9, 6Na@O–GNM9, and 7Na@O–GNM9, follow a trend similar to that of the Li systems (Fig. 4e,f,g,h). The main difference here is two fold: (1) the Na clusters adopt structures that are more symmetric than those of Li, and (2) the decrease of the binding energy with the cluster size is much slower than in the case of Li. The largest binding energy is that of the 4Na@O–GNM9, 2.94 eV, with only one Na state below the Fermi energy in the valence band of the system. Higher Na-doped systems have two Na states below the Fermi level, one of them is in the conduction band. Therefore, the 4Na@O–GNM9 system is the most favorable from a device perspective.

Now that we have understood the effect of the dopants on the electronic structure of all n-doped systems, we compute the free energy differences for various reactions forming them. This is needed as the entropic cost for forming these systems may not be negligible. We will assume that our systems are formed according to:

\[
2 \ (n-1)X@O–GNM + X_2 \rightarrow \ 2 \ nX@O–GNM, \quad (2)
\]

where \(n = 1, 2, \ldots, 7\) and \(X=\text{Li,Na}\). Table 1 shows the free energy difference,

\[
\Delta A = A_{\text{reactants}} - A_{\text{products}} \quad (3)
\]

for the formation of all systems. We notice that \(\Delta A\) is positive for all Li systems, suggesting that they are all experimentally achievable. For the Na case, the situation is different as the last stable structure is the 4Na@O–GNM9. This could be an advantage for Na doping, as the 4Na@O–GNM9 has no Na states below the Fermi energy in the conduction band, which confirms that Na is more favorable for doping GNM-based transistor devices.
We now turn to \(n\)-doping of the larger pore systems. We first consider \(\text{Li}\@\text{O–GNM12},\) \(2\text{Li}\@\text{O–GNM12},\) and \(3\text{Li}\@\text{O–GNM12}.\) Figure 5 shows the structure and DOS of the three systems. The average \(\text{Li}^+–\text{O}^–\) distance in the three cases is close to the case of the smaller pore. The \(\text{Li}^+–\text{Li}^+\) distances in the \(2\text{Li}\@\text{O–GNM12}\) and \(3\text{Li}\@\text{O–GNM12}\) systems are 13.52 and 11.79 Å, respectively. The DOS of the three systems (Fig. 5) suggests that the doping level increases with the number of dopants. Indeed, calculations indicate that the charge transfer in the three cases is 1, 2, and 3 electrons, respectively. This is similar to the small pore case for the \(\text{Li}\) and \(\text{Li}_2\), but different for the \(\text{Li}_3\). Here, the \(3\text{Li}\) atoms are ionized. The \(\text{Li}\@\text{O–GNM12}\) has a binding energy similar to the \(\text{Li}\@\text{O–GNM9}\) case. The \(2\text{Li}\@\text{O–GNM12}\) has a binding energy of 1.07 eV (\(\sim\) 0.54 eV/dopant), higher than the \(2\text{Li}\@\text{O–GNM9},\) which can be mainly attributed to the smaller repulsive interaction between the two \(\text{Li}^+\) ions, now \(\sim\) 13.52 Å apart. The \(3\text{Li}\@\text{O–GNM12}\) system has a binding energy of 1.39 eV (\(\sim\) 0.46 eV/dopant). The repulsive interaction between the \(3\text{Li}^+\) ions, with a \(\text{Li}^+–\text{Li}^+\) distance of \(\sim\) 11.79 Å explains the lower energy per dopant compared to the \(2\text{Li}\@\text{O–GNM12}\) case.

To study the effect of increasing the doping load further, we study three \(\text{Na}\)-doped systems; \(2\text{Na}\@\text{O–GNM12},\) \(4\text{Na}\@\text{O–GNM12},\) and \(6\text{Na}\@\text{O–GNM12}\) (Figs. 5(d, e, and f)). Two \(\text{Na}\) atoms dope the \(\text{O–GNM12}\) with two electrons as in the \(\text{O–GNM9}\) case. Due to the weaker electrostatic repulsion between the two \(\text{Na}^+\) ions, now 13.11 Å apart, the binding energy of the \(2\text{Na}\@\text{O–GNM12}\) system is slightly higher (1.83 eV) than that of the \(2\text{Na}\@\text{O–GNM9}.\) Adding two more \(\text{Na}\) atoms (\(4\text{Na}\@\text{O–GNM12}\)) to the pore leads to their ionization, and hence to the doping of the \(\text{O–GNM12}.\) Calculations show that 4 electrons are transferred to the GNM. As we see in Figs. 5(e, the \(\text{O–GNM12}\) pulls down the lowest two states of the \(4\text{Na}\) atoms, but they are still above the Fermi level of the system. Adding two more \(\text{Na}\) atoms (\(6\text{Na}\@\text{O–GNM12}\)) leads to the lowering of one of the \(\text{Na}\) states below the Fermi level, thus achieving a doping level similar to the \(4\text{Na}\@\text{O–GNM12}\) case. The free energy for the \(\text{O–GNM12}\) reactions is shown in Table I. All scenarios seem plausible, except for the \(6\text{Na}\@\text{O–GNM12}.\)
FIG. 5: Density of states of the (a) Li@O–GNM12, (b) 2Li@O–GNM12, (c) 3Li@O–GNM12, (d) 2Na@O–GNM12, (e) 4Na@O–GNM12, and (f) 6Na@O–GNM12 systems (DOS). The bottom insets refer to the relaxed structures. In (d), (e), and (f) the top insets show the Na states within the corresponding O–GNM12 system, as compared to those of the isolated Na clusters. The DOS of the pristine O–GNM12 (GNM) is shown for comparison.
FIG. 6: Electronic band structures of (a) 3Li@O–GNM9, and (b) 3Li@O–GNM12 systems. A Li state lies just below the Fermi energy in the 3Li@O–GNM9 case. The band structure of graphene, pristine O–GNM9, and O–GNM12 are shown for comparison.

To confirm the rigid band nature of the doping, we show the band structures of two n-doped systems; 3Li@O–GNM9 (Fig.6a), and 3Li@O–GNM12 (Fig.6b). Compared to the undoped O–GNMs, there is no significant change in the band curvatures in the Fermi level/gap region. The pristine graphene is also shown for comparison. The bands are linear in the vicinity of the Fermi energy, with a group velocity of about half/quarter that of graphene for the O–GNM9/O–GNM12, respectively.
TABLE I: Binding energies per dopant ($E_b/n$, eV), free energy difference ($\Delta A$, eV), charge transferred ($q$, electrons), average distance between two dopants in the pore ($nX$, Å), average distance between two dopants in the dopant cluster ($X_n$, Å), and average distance between a dopant and the nearest oxygen atoms ($X-O$, Å), of various $n$-doping systems.

| GNM9 | $E_b/n : \Delta A$ | $q$ | $nX : X_n : X-O$ | GNM9 | $E_b/n : \Delta A$ | $q$ | $nX : X_n : X-O$ |
|------|---------------------|-----|------------------|------|---------------------|-----|------------------|
| Li   | 1.29 : 0.99         | 1   | $-$ : $-$ : 2.19 | Na   | 1.62 : 1.27         | 1   | $-$ : $-$ : 2.36 |
| 2Li  | 0.40 : 0.18         | 2   | 5.28 : 2.74 : 2.10 | 2Na  | 0.79 : 0.83         | 2   | 4.41 : 3.10 : 2.33 |
| 3Li  | 0.64 : 0.73         | 3   | 3.26 : 2.82 : 2.08 | 3Na  | 0.93 : 0.82         | 3   | 3.51 : 3.43 : 2.44 |
| 4Li  | 0.40 : 1.07         | 2   | 3.35 : 3.04 : 1.97 | 4Na  | 0.74 : 0.97         | 2   | 3.65 : 3.44 : 2.39 |
| 5Li  | 0.29 : 0.10         | 1   | 3.23 : 2.93 : 2.09 | 5Na  | 0.55 : 0.06         | 1   | 3.59 : 3.47 : 2.40 |
| 6Li  | 0.12 : 0.05         | 2   | 3.23 : 2.93 : 2.09 | 6Na  | 0.41 : (0.31)       | 2   | 3.59 : 3.49 : 2.40 |
| 7Li  | 0.06 : 0.31         | 3   | 3.23 : 2.93 : 2.09 | 7Na  | 0.31 : (0.32)       | 3   | 3.59 : 3.50 : 2.40 |

| GNM12 | $E_b/n : \Delta A$ | $q$ | $nX : X_n : X-O$ | GNM12 | $E_b/n : \Delta A$ | $q$ | $nX : X_n : X-O$ |
|-------|---------------------|-----|------------------|-------|---------------------|-----|------------------|
| Li    | 1.23 : 0.93         | 1   | $-$ : $-$ : 2.2  | 2Na   | 0.90 : 1.11         | 2   | 13.11 : 3.10 : 2.33 |
| 2Li   | 0.54 : 0.46         | 2   | 13.52 : 2.74 : 2.18 | 4Na  | 0.61 : 0.28         | 4   | 9.17 : 3.44 : 2.30 |
| 3Li   | 0.46 : 0.27         | 3   | 11.79 : 2.82 : 2.17 | 6Na  | 0.38 : 0.08         | 4   | 6.50 : 3.49 : 2.36 |

B. $p$-doping

We now examine $p$-doping of large pore GNM systems. We consider 6 doped H–GNM9 systems (pore size 0.9 nm), and 4 doped H–GNM12 systems (pore size 1.2 nm), using F and Cl. The reported binding energies are calculated from the energies of the most stable form of the dopants (F$_2$ and Cl$_2$ molecules).

A fluorine atom brought close to the edge of the H–GNM9 pore will have its spectrum perturbed by the pore dipoles, resulting in the LUMO of the F falling below the valence band edge of the GNM. This will cause an electron to spill from the GNM skeleton to occupy the F LUMO, thus ionizing it, and $p$-doping the GNM. The electrostatic attraction with the nearby hydrogen atoms creates an ultra stable environment for the F anion. Figure 7a shows the structure of the F@H–GNM9. The average F–H distance with the nearest two hydrogen atoms is 1.70 Å. The binding energy of F@H–GNM9 is found to be 1.07 eV. The
H–GNM causes the F 2p\textsubscript{z} state to be pinned about 0.3 eV below the valence band edge of the H–GNM, and 0.1 eV below the Fermi level. Integrating the DOS from the valence band edge to the Fermi level indicates that one electron has been transferred to H–GNM\textsubscript{9}.

Adding another F atom to the system leads to a similar picture, with the second F atom pinned across the pore from the first one (Fig. 7b, inset), with an average F–H distance of 1.72 Å. The binding energy of the 2F@H–GNM\textsubscript{9} system is found to be 1.72 eV. The decrease in the binding energy per dopant can be partially attributed to the electrostatic repulsion between the two fluorine anions.

The DOS of the 2F@H–GNM\textsubscript{9} system is shown in Fig. 7b. The GNM is p-doped, with the Fermi energy located \(\sim\) 0.3 eV below the valence band edge. The two F atoms are now ionized, with their 2p\textsubscript{z} states full, and located \(\sim\) 0.2 eV below the Fermi level, and therefore will not interfere with electronic transport of a 2F@H–GNM\textsubscript{9}-based device.

To reach the maximum pore capacity of the H–GNM\textsubscript{9}, we add two more fluorine atoms, one at a time. Figure 7c shows the structure and DOS of the 3F@H–GNM\textsubscript{9} system. The average F–H distance decreases to 1.38 Å, as the three F atoms form a triangular structure, with an average F–F distance of 4.53 Å. The DOS of the system shows that the three fluorine 2p\textsubscript{z} states are filled, and the Fermi energy is \(\sim\) 0.3 eV below the edge of the valence band. A calculation of the charge transfer shows that three electrons are removed from the H–GNM. The binding energy of the 3F@H–GNM\textsubscript{9} system is 1.97 eV, giving a yet smaller binding energy per dopant than the 2F@H–GNM\textsubscript{9} case due to the repulsion between the three F anions.

Upon introducing the fourth fluorine atom, the system finds its minimum energy by having two of its fluorine atoms form an elongated fluorine molecule that protrudes out of the pore plane (Fig. 7d), F\textsubscript{2}*, with a bond length of 1.68 Å (an F\textsubscript{2} molecule has a bond length of 1.43 Å). The F\textsubscript{2}* is positioned close to the corresponding location of the third fluorine dopant of the 3F@H–GNM\textsubscript{9} system, with a distance of 2.21 Å from the closest pore-edge hydrogen.

The DOS of the 4F@H–GNM\textsubscript{9} system shows that there is one fluorine state just above the Fermi energy. Inspection of this state indicates that it is a superposition of the 2p\textsubscript{z} states of the two fluorine atoms forming the elongated molecule. These two fluorine atoms are not ionized. This is confirmed by the Löwdin charge analysis, which also shows that the other two fluorine atoms are each singly ionized. The binding energy of the 4F@H–GNM\textsubscript{9}
FIG. 7: Density of states of the (a) F@H–GNM9, (b) 2F@H–GNM9, (c) 3F@H–GNM9, (d) 4F@H–GNM9, (e) Cl@H–GNM9, and (f) 2Cl@H–GNM9 systems (DOS). The inset figures refer to the relaxed structures. In (d) and (f), the insets show a side view of the 4F@H–GNM9 and 2Cl@H–GNM9 systems, indicating the off-plane structures of the 4F and 2Cl dopants, respectively. The DOS of the pristine H–GNM9 (GNM) is shown for comparison.
system is 2.02 eV, which is only $\sim 0.10$ eV higher than that of the 3F@H–GNM9 system, suggesting that 3F@H–GNM9 is the maximally-doped and most stable fluorine doped H-GNM9 structure, and hence best suited for a p-doped H–GNM9-based device.

The situation with the second p-dopant, chlorine, is slightly different. Doping with one Cl atom leads to qualitatively similar results. A Cl@H–GNM9 has a Cl–H distance of 2.44 Å, with a small binding energy of 0.10 eV (Fig. 7e). The DOS of the system shows that the now-filled 3p$_z$ state of the Cl is located 0.1 eV below the Fermi level, which is pinned 0.2 eV below the edge of the valence band. Upon adding another Cl atom, the system favors the formation of an elongated Cl$_2$ molecule (Cl$^*_2$), which sticks out of the plane of the GNM (Fig. 7f). The Cl$^*_2$ molecule has a Cl–Cl distance of 2.28 Å, larger than the Cl$_2$ molecular distance of 2.00 Å. The system has a small binding energy of 0.19 eV. The DOS of the system shows that the GNM is slightly doped and that the Cl 3p$_z$ states are only partially full. The Löwdin charge analysis confirms this picture showing that the Cl$^*_2$ structure carries a small negative charge of about 0.2e. Adding more Cl dopants does not lead to stable structures. The small binding energies of the Cl-doped H–GNM9 systems shows that chlorine should not be considered for p-doping H–GNM9 systems.

As in the n-doping case, we take into account the entropic cost of forming our p-doped systems. We calculate the free energy for the reaction forming the structure $(n + 1)X@H–GNM$ from the lesser doped structure $(n − 1)X@H–GNM$:

\[
(n − 1)X@H–GNM + X \rightarrow (n + 1)X@H–GNM,
\]

(4)

where $n = 1, 2, 3, 4, 6$ for X=F, $n = 1, 2$ for X=Cl. Table III shows that the 3F@H–GNM9 system is the most likely to occur for p-doping the H–GNM9 with fluorine, while chlorine should not be considered.

Next we describe our p-doping results for larger pores. We form a hydrogen doped GNM with a pore radius of about 1.3 nm, H–GNM12. Since the pore is large, and three fluorine atoms can stably dope the smaller pore system, we begin with 3F@H–GNM12 (Fig. 8a). The average distance between the fluorine and the closest two hydrogen atoms in the structurally relaxed system is 1.67 Å. The average F–F distance is 8.62 Å. The DOS of the system shows that the GNM12 is p-doped, with the Fermi energy placed $\sim 0.1$ eV below the valence band edge. The fluorine 2p$_z$ states are all full, and are located at least 0.3 eV below the Fermi level, indicating the full ionization of the three fluorine dopants. The integrated DOS shows
that the GNM lost three electrons. The binding energy of the 3F@H–GNM12 is 2.72 eV.

FIG. 8: Density of states of the (a) 3F@H–GNM12, (b) 4F@H–GNM12, (c) 6F@H–GNM12, and (d) 2Cl@H–GNM12 systems (DOS). The inset figures show to the relaxed structures. The DOS of the pristine H–GNM12 (GNM) is shown for comparison.

Adding more fluorine atoms leads to similar physics. For the 4F@H–GNM12 case (Fig. 8b), doping occurs with 4 electrons. The average F–F distance is 7.15 Å. The Fermi level sinks deeper in the valence band, 0.2 eV from the band edge. The fluorine 2p$_z$ states are all populated, and the closest one to the Fermi level is 0.2 eV away. The binding energy of the 4F@H–GNM12 system is 3.08 eV. For the 6F@H–GNM12 system, the average F–F distance drops to 5.05 Å. The highest filled fluorine 2p$_z$ state is $\sim$ 0.5 eV away from the Fermi level, which is pinned 0.3 eV below the valence band edge. The binding energy of the 6F@H–GNM12 is decreased to 2.76 eV. Calculations show that the charge transfer from the GNM to the fluorine atoms is 4e for the 4F@H–GNM12 and 6e for the 6F@H–GNM12, confirming the full ionization of the fluorine atoms in both systems. The average F–H distance in the
4F@H–GNM12 system is 1.23 Å, while it is 1.67 Å in the 3F@H–GNM12 and 1.61 Å the 6F@H–GNM12 systems. This difference can be attributed to the breaking of the rotational symmetry of the pore by the 4F dopants structure, where each fluorine atom faces one hydrogen. In the other two cases, each fluorine atom faces two hydrogen atoms.

Replacing F by Cl in the large pore leads to different physics. Studying the 2Cl@H–GNM12 system shows that a stable structure can be achieved with the 2Cl atoms docked at opposite sides of the pore at 8.46 Å apart (Fig. 8d). The DOS shows that the system is $p$-doped, with the Fermi level 0.1 eV below the band edge, and that the filled Cl 3$p_z$ states are right below the Fermi energy, indicating the full ionization of the Cl atoms. Although the system is stable, the configuration with the separated Cl$_2$ molecule and H–GNM12 is energetically favorable by 0.07 eV. The lesser binding energies of the Cl-doped GNMs compared to the F-doped ones are due to the higher binding energy of the Cl$_2$ molecule (2.52 eV for Cl$_2$ vs 1.64 eV for F$_2$).

![Diagram](image)

**FIG. 9:** Electronic band structures of (a) 2Cl@H–GNM9, and (b) 2Cl@H–GNM12. The band structure of graphene, pristine H–GNM9, and H–GNM12 are shown for comparison.

Chelation $p$-doping of GNMs occurs in a rigid band manner, as is demonstrated by the band structure of the doped systems. In Fig. 9 we show the band structures of the 2Cl@H–GNM9 and 2Cl@H–GNM12 systems. Band curvatures are very similar to those of the pristine GNM systems. In addition, they are linear in the neighborhood of the Fermi level, with an electronic group velocity half/quarter that of graphene for the H–GNM9/H–GNM12.
As with the smaller pore, we compute the free energy for reactions forming the considered systems. As we see in Table II, the most stable fluorine-doped systems and most likely to occur for the large pore is the 4F@H–GNM12.

| GNM9 | $E_b/n : \Delta A$ | $q$ | nX : X$_n$ : X-H | GNM9 | $E_b/n : \Delta A$ | $q$ | nX : X$_n$ : X-H |
|------|------------------|----|------------------|------|------------------|----|------------------|
| F    | 1.07 : 0.75      | 1  | $-$ : $-$ : 1.70 | Cl   | 0.10 : (0.24)    | 1  | $-$ : $-$ : 2.46 |
| 2F   | 0.86 : 1.09      | 2  | 4.95 : 1.43 : 1.72 | 2Cl  | 0.09 : (0.51)    | 0.2| 2.28 : 2.00 : 3.07 |
| 3F   | 0.64 : 0.27      | 3  | 4.53 : 1.60 : 1.38 |      |                  |    |                  |
| 4F   | 0.51 : (0.33)    | 2  | 3.55 : 2.00 : 1.78 |      |                  |    |                  |
|      |                  |    |                  | GNM12|                 |    |                  |
| 3F   | 0.91 : 1.77      | 3  | 8.62 : 1.60 : 1.67 | Cl   | (0.03) : (0.76)  | 2  | 8.46 : 2.00 : 2.37 |
| 4F   | 0.77 : 1.82      | 4  | 7.15 : 2.00 : 1.56 |      |                  |    |                  |
| 6F   | 0.46 : (0.95)    | 6  | 5.05 : 1.74 : 1.61 |      |                  |    |                  |

**TABLE II:** Binding energies per dopant ($E_b/n$, eV), free energy difference ($\Delta A$, eV), charge transferred ($q$, electrons), average distance between two dopants in the pore (nX, Å), average distance between two dopants in the dopant cluster (X$_n$, Å), and average distance between a dopant and the nearest hydrogen atoms (X-H, Å), of various $p$-doping systems.

The use of GNMs in microelectronic applications requires controlled doping of the sheets. Thus the pores, post fabrication, must be filled with the desired number of dopants, no more, no fewer. To achieve this result, it is convenient to select the binding energy dopant level with the lowest free energy such that sufficient thermal annealing, for instance, will allow the GNM/dopant system to relax to the correct number of dopants per pore. This approach avoids difficult stoichiometric control and other problems associated with achieving a doping state that is not the most thermodynamically stable. There are two caveats. First, it may be the case, as in Li doping, that the lowest free energy state is not a good fit for microelectronics, in which case, another dopant such as Na must be selected. Second, the free energy of the next most stable dopant should be well separated from the lowest stable (large free energy gap) such that the thermal anneal will be effective.
IV. CONCLUSION

Graphene nanomeshes (GNM’s) with easily-fabricated pores (∼ 1 nm) have band gaps and electronic mobilities that are attractive for nanoelectronic applications. We use first-principles calculations to show that it is possible to achieve stable controlled doping of large-pore GNM’s using multiple ion chelation. Selective passivation of the pore edges allows for the hosting of negative and positive ions. Stable $n$-doping of a 0.8 nm pore GNM using multiple dopants is possible using Li$_n$, and Na$_n$ clusters, $n = 1..4$, with a binding energy that is higher than 50$k_B T$ at room temperature. The most energetically favorable scenario is that of doping with four sodium atoms, which is also the best from a device perspective as no dopant states exist in the conduction band below the Fermi energy. For larger pores (∼ 1.3 nm), more dopants can be hosted, with a binding energy of the same order. The doping level increases with the number of dopants, and occurs in a rigid band way.

For the case of $p$-doping, we find that stable rigid band doping occurs with up to four F atoms in the first hydrogen-passivated pore, with the three F case being the most energetically favorable. Chlorine doping does not lead to stable doped structures. The larger pore systems also favor Fluorine as a dopant, where 6 F$^-$ ions can be stably hosted, while chlorine doped systems remain unstable. Our results satisfy the need to study relatively large systems with bigger pores, and more ions per pore. This renders GNM’s closer to an experimentally realizable device in terms of length scale, with many potential applications, such as field effect transistors and transparent electrodes.

V. COMPUTATIONAL METHODS

Electronic structure calculations were performed with the Quantum Espresso software package®. Minimum energy configurations were obtained by relaxing the X@Y–GNM$c$ systems with forces less than 0.001 Ry/Bohr. The calculations were performed on up to 16 nodes of the Bibliotheca Alexandrina supercomputer using the generalized gradient approximation PBE functional, with an energy cutoff of 45 Ry, a $12 \times 12 \times 1$ Monkhorst-Pack k-point grid for the X@Y–GNM9 systems, and a $6 \times 6 \times 1$ k-point grid for the larger X@Y–GNM12 ones. A vacuum distance of 12 Å has been used for an image separation in the direction perpendicular to the plane of the GNM. Charge transfer is calculated by integrat-
ing the total density of states.

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[1] H. Du, J. Li, J. Zhang, G. Su, X. Li, and Y. Zhao, The Journal of Physical Chemistry C 115, 23261 (2011).
[2] B. F. Machado and P. Serp, Catal. Sci. Technol. 2, 54 (2012).
[3] Y. Wu, Y.-M. Lin, A. A. Bol, K. A. Jenkins, F. Xia, D. B. Farmer, Y. Zhu, and P. Avouris, Nature 472, 74 (2011).
[4] C. Sire, F. Ardiaca, S. Lepilliet, J.-W. T. Seo, M. C. Hersam, G. Dambrine, H. Happy, and V. Derycke, Nano Letters 12, 1184 (2012).
[5] Y.-M. Lin, K. A. Jenkins, A. Valdes-Garcia, J. P. Small, D. B. Farmer, and P. Avouris, Nano Letters 9, 422 (2009).
[6] Y. M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H. Y. Chiu, A. Grill, and P. Avouris, Science 327, 662 (2010).
[7] K. Bolotin, K. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. Stormer, 146, 351 (2008).
[8] J. A. Fürst, J. G. Pedersen, C. Flindt, N. A. Mortensen, M. Brandbyge, T. G. Pedersen, and A.-P. Jauho, New Journal of Physics 11, 095020 (2009).
[9] T. Pedersen, C. Flindt, J. Pedersen, N. Mortensen, A.-P. Jauho, and K. Pedersen, Phys. Rev. Lett. 100, 1 (2008).
[10] W. Liu, Z. F. Wang, Q. W. Shi, J. Yang, and F. Liu, Phys. Rev. B 80, 2 (2009).
[11] R. Petersen and T. Pedersen, Phys. Rev. B 80, 113404 (2009).
[12] M. Vanević, V. Stojanović, and M. Kindermann, Phys. Rev. B 80, 045410 (2009).
[13] R. Martinazzo, S. Casolo, and G. Tantardini, Phys. Rev. B 81, 1 (2010).
[14] A. Baskin and P. Král, Scientific Reports 1, 36 (2011).
[15] R. Petersen, T. G. Pedersen, and A.-P. Jauho, ACS Nano 5, 523 (2010).
[16] M. M. Fadlallah, A. A. Maarouf, U. Schwingenschlgl, and U. Eckern, Journal of Physics: Condensed Matter 29, 055301 (2017).
[17] A. A. Maarouf, R. A. Nistor, A. Afzali-Ardakani, M. A. Kuroda, D. M. Newns, and G. J. Martyna, Journal of Chemical Theory and Computation 9, 2398 (2013).
[18] R. A. Nistor, D. M. Newns, and G. J. Martyna, ACS nano 5, 3096 (2011).
[19] D. M. Newns, Phys. Rev. 178, 1123 (1969).
[20] A. C. Hewson and D. M. Newns, Japanese Journal of Applied Physics 282, 121 (1974).
[21] J. Bai, X. Zhong, S. Jiang, Y. Huang, and X. Duan, Nature nanotechnology 5, 190 (2010).
[22] J. Ding, K. Du, I. Wathuthanthri, C.-H. Choi, F. T. Fisher, and E.-H. Yang, Journal of Vacuum Science & Technology B 32, 06FF01 (2014).
[23] J. Zhang, H. Song, D. Zeng, H. Wang, Z. Qin, K. Xu, A. Pang, and C. Xie, Scientific Reports 6 (2016).
[24] M. König, G. Ruhl, J.-M. Batke, and M. C. Lemme, Nanoscale 8, 15490 (2016).
[25] J. Guo, J. Lee, C. I. Contescu, N. C. Gallego, S. T. Pantelides, S. J. Pennycook, B. A. Moyer, M. F. Chisholm, C. J. Pedersen, Z. Grote, et al., Nature Communications 5, 5389 (2014).
[26] P. W. Anderson, Phys. Rev. 124, 41 (1961).
[27] B. Hammer and J. K. Norskov, Nature 376, 238 (1995).
[28] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).