Enhancement of quantum capacitance by chemical modification of graphene supercapacitor electrodes: a study by first principles

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Abstract.   In this paper, we specify a powerful way to boost quantum capacitance of graphene-based electrode materials by density functional theory calculations. We performed functionalization of graphene to manifest high-quantum capacitance. A marked quantum capacitance of above $420\,\mu\mathrm{F\,cm^{-2}}$ has been observed. Our calculations show that quantum capacitance of graphene enhances with nitrogen concentration. We have also scrutinized effect on the increase of graphene quantum capacitance due to the variation of doping concentration, configuration change as well as co-doping with nitrogen and oxygen ad-atoms in pristine graphene sheets. A significant increase in quantum capacitance was theoretically detected in functionalized graphene, mainly because of the generation of new electronic states near the Dirac point and the shift of Fermi level caused by ad-atom adsorption.

Keywords.   Supercapacitor; quantum capacitance; density functional theory.

1. Introduction

Production of sufficient energy from renewable energy sources, bypassing the use of fossil fuels, natural gas and coal is one of the biggest challenges to suppress climate change. In tropical developing countries such as India with increasingly high demand of energy, one must have to find efficient ways to produce renewable energies from sustainable sources such as wind and sunlight. However, renewable energies cannot be produced uniformly all the time. Therefore, efficiently storing and transporting of generated energy is an integral part of energy production processes, which can be achieved by using supercapacitors. Designing of efficient supercapacitors for this purpose is a major challenge because of the lack of suitable electrode materials. Supercapacitors should have extremely fast charging and discharging capabilities with long life time. Total capacitance (C_{Total}) of supercapacitors is given by $1/C_{\mathrm{Total}} = 1/C_{\mathrm{D}} + 1/C_{\mathrm{Q}}$, where C_{Total} is the total capacitance, C_{D} is the double-layer capacitance and C_{Q} is the quantum capacitance. Insufficiency in either double-layer capacitance or quantum capacitance may weaken total capacitance of a device. Thus, electrode materials with sufficiently large quantum capacitance are important to obtain high-energy density. Quantum capacitance mainly relies on the electronic properties of supercapacitor electrode materials. Being two-dimensional in nature, graphene could be realized as an ideal electrode material for supercapacitor applications [1–3]. Tuning the electronic structure of graphene by means of doping with ad-atoms from different groups in the periodic table may enhance quantum capacitance [4]. In the

present study, we performed density functional theory (DFT) calculations to investigate quantum capacitance of functionalized graphene by means of electronic structure calculations [5]. We explored the impact of increasing nitrogen and oxygen doping concentration as well as the combinational effect of co-doping on the quantum capacitance of graphene [6]. Availability of the density of states (DOS) close to the Fermi energy is one of the key factors in enhancing quantum capacitance in material [7]. Therefore, our main aim in this study was to investigate how the modified electronic structure of the doped graphene increases the DOS near the Fermi energy region and influences the nature of quantum capacitance in systems [8]. The functionalization of graphene may change the position of the Fermi level with respect to the Dirac point or destroy linear dispersion due to a change in correlation between the conducting charge carriers [9]. Quantum capacitance (C_{Q}) originates from the change in chemical potential (μ) of the electrons with respect to the change in carrier density, and is therefore directly proportional to the change in electron DOS near the Fermi energy.

Pristine graphene shows a very low-quantum capacitance due to a limited DOS near the Fermi level. Previous study predicted the enhancement of quantum capacitance value in nitrogenated graphene and nitrogenated graphene oxide. In this work, we systematically study the variation of quantum capacitance in functionalized graphene by varying the concentration and sublattice position of O and N ad-atoms. Our study suggests that two-dimensional functionalized graphene with proper functionalization could be

used as a promising electrode material for supercapacitor applications.

2. Methodology and simulation details

We have employed DFT formalism as implemented in the VASP package to perform atomic structure optimization and subsequently electronic structure calculations. Generalized-gradient approximation with Perdew–Burke–Ernzerhof (PBE) parameterization was used to describe exchange correlation energy [10]. Calculations were performed with a cutoff kinetic energy of 400 eV. In order to investigate the result of chemical modification on quantum capacitance, calculations were performed by making use of 3×3 and 5×5 in-plane supercells (each graphene sheet has 18 and 50 carbon atoms, respectively) of graphene. Adequate vacuum of 6 Å has been considered in the z direction of a graphene sheet. We have used a $6 \times 6 \times 1$ Γ-centred k-point for the Brillouin zone sampling to optimize the geometric structure. A denser k-point grid $12 \times 12 \times 1$ was used for the precise extraction of electron DOS $D(E)$ and projected density of states (PDOS). Energy optimizations were performed for different ad-atoms on graphene. The stability of the functionalized system was predicted by the adsorption energy of the ad-atom on the graphene surface. Functionalization of graphene has performed with the elements from different groups in the periodic table such as S, B, Ca, Sn, O and N. The variation in the electronic DOS and consequently the change in quantum capacitance were examined. The method for calculating quantum capacitance is based on the DOS obtained from the DFT-VASP calculation. From $D(E)$, we can readily calculate quantum capacitance from [11]:

$$C_{\mathrm{Q}} = \frac{\mathrm{d}Q}{\mathrm{d}\phi} = \frac{e^2}{4kT} \int_{-\infty}^{+\infty} D(E)\mathrm{sech}^2 \left(\frac{E - e\phi}{2kT} \right) \mathrm{d}E,$$

(1)

where Q is the excessive charge on the electrode, $D(E)$ is the DOS, $F(E)$ is the Fermi–Dirac distribution function, E represents the energy with respect to the Fermi level and e is the electron charge (1.6×10^{-19} C).

3. Results and discussion

Functionalization alters the electronic structure of graphene. Dirac cones get reshaped due to strong interactions which changes the electronic density near the Fermi energy, and consequently the quantum capacitance (C_{Q}) gets modified [12]. Therefore, we have carried out our investigation in two different stages. To start with, we have studied the change in electronic structure of the functionalized graphene with various ad-atoms and subsequently we have calculated total quantum capacitance and identified the most favourable ad-atom for the maximum enhancement of C_{Q} [13]. In the second

Table 1. Adsorption energy of ad-atoms adsorbed on the pristine graphene surface.

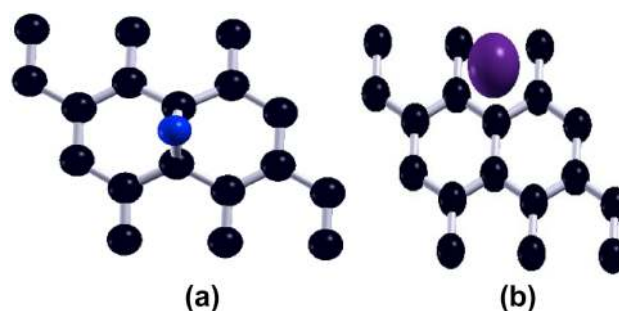| Ad-atom	Adsorption energy (in eV)	Ad-atom	Adsorption energy (in eV)
Ac	−1.416	Si	−1.244
B	−1.268	Ge	−1.015
Ca	−0.346	Sn	−0.983
La	−1.537	N	−2.372

Figure 1. Optimized geometric structure for (**a**) FG–N and (**b**) FG–Sn. The black balls represent C atoms in the graphene sheet; blue and indigo balls represent the doped N and Sn atoms, respectively.
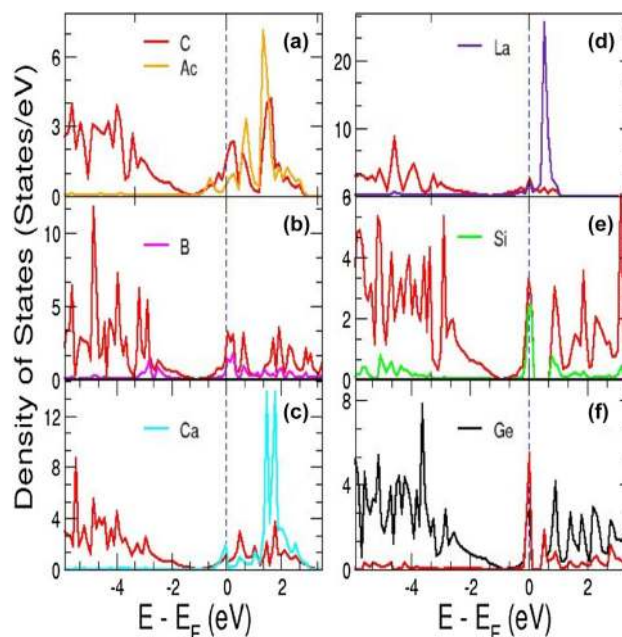

Figure 2. Atom PDOS for functionalized graphene with (**a**) Ac, (**b**) B, (**c**) Ca, (**d**) La, (**e**) Si and (**f**) Ge atoms. Coloured curve represents DOS from the doped atom. Vertical blue dashed line is the Fermi energy set at $E = 0$.

stage, we have performed a similar study by varying the doping concentration of the favourable ad-atoms as well as the combinational effect of co-doping on graphene.
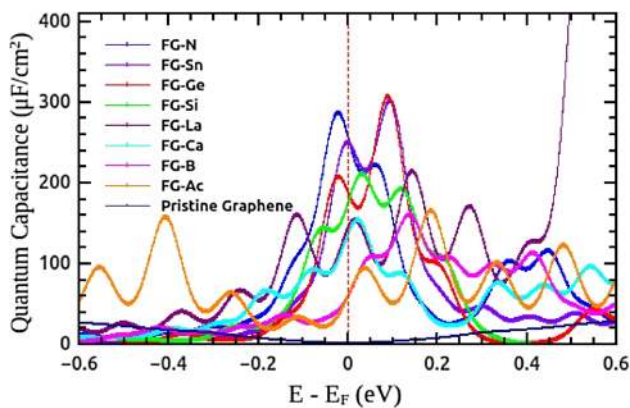
Figure 3. The different colour curves represent the energy variations of quantum capacitance for graphene functionalized with various ad-atoms.

Table 2. Details of C_Q values calculated at the Fermi level for various ad-atom-functionalized graphene.

Configuration	C_Q (μF cm^{-2})	Configuration	C_Q (μF cm^{-2})
FG–Ac	60.319	FG–Si	174.825
FG–B	60.847	FG–Ge	253.457
FG–Ca	137.200	FG–Sn	255.716
FG–La	145.131	FG–N	256.420

3.1 *Functionalization of graphene with various ad-atoms*

The type and concentration of charge carriers in graphene can be controlled effectively by functionalization. The carrier density at the band edges varies with dopant types and concentration. However, stability of the functionalized graphene totally depends on the adsorbing capacity of the ad-atoms. Therefore, we first verify the proper adsorption of ad-atoms by calculating the adsorption energy using the equation:

$$E_{ads} = E_{tot} - E_{gr} - nE_{at},$$

where E_{tot} is the total ground-state energy of the adsorb system, E_{gr} is the ground-state total energy of the graphene sheet, E_{at} is the ground-state energy of the ad-atoms and n is the number of ad-atoms present in the system. The negative values of E_{ads} for different ad-atoms shown in table 1 confirm the stable adsorption of ad-atoms on the graphene sheet.

There could be three different sites for adsorption on the graphene lattice namely, the top (on vertically top of the graphene C atoms), hollow (at the centre of the hexagon in the sheet) and bridge site (in between two graphene C atoms). The stable adsorption position of ad-atoms on graphene is found by comparing ground-state energies. Our calculation shows that the bridge site is the most favourable position for nitrogen adsorption and the top configuration for all other ad-atoms.
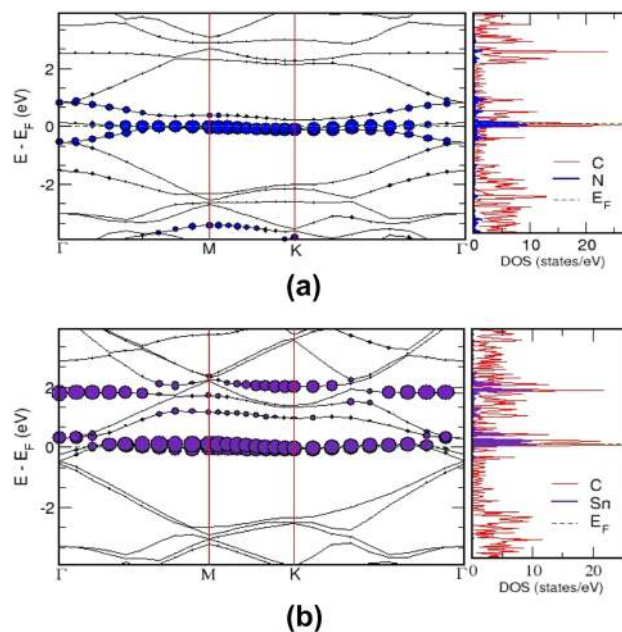

Figure 4. Electronic band and DOS for (**a**) FG–N and (**b**) FG–Sn. Coloured curve in the DOS and circle in the band structure represents contribution from doped atoms. Horizontal red dashed line is the Fermi energy set at $E = 0$.

Table 3. Details of charge transferred for various ad-atom-functionalized graphene.

System	Charge transferred (e)
FG–B	0.3645
FG–Si	0.5248
FG–Ge	0.3792
FG–Sn	0.3166
FG–N	-0.4138

Table 4. Details of C_Q calculated at the Fermi level for nitrogenated graphene with different N/C ratios.

N/C ratio	C_Q (μF cm^{-2})	N/C ratio	C_Q (μF cm^{-2})
10:50 (0.20)	94.689	2:50 (0.04)	239.093
9:50 (0.18)	137.629	1:50 (0.02)	279.385

The optimized structures of functionalized graphene with N and Sn ad-atoms are shown in figure 1a and b.

The nature of the charge carrier in the functionalized-graphene configurations can be predicted through its DOS and electronic band structure. Conduction in pristine graphene is contributed purely by the delocalized π cloud from the p$_z$ orbitals of carbon. Whereas in the functionalized graphene the DOS near the Fermi level is mainly contributed by ad-atoms as shown in figure 2. Since the quantum capacitance is directly proportional to this high-electron density near the Fermi level
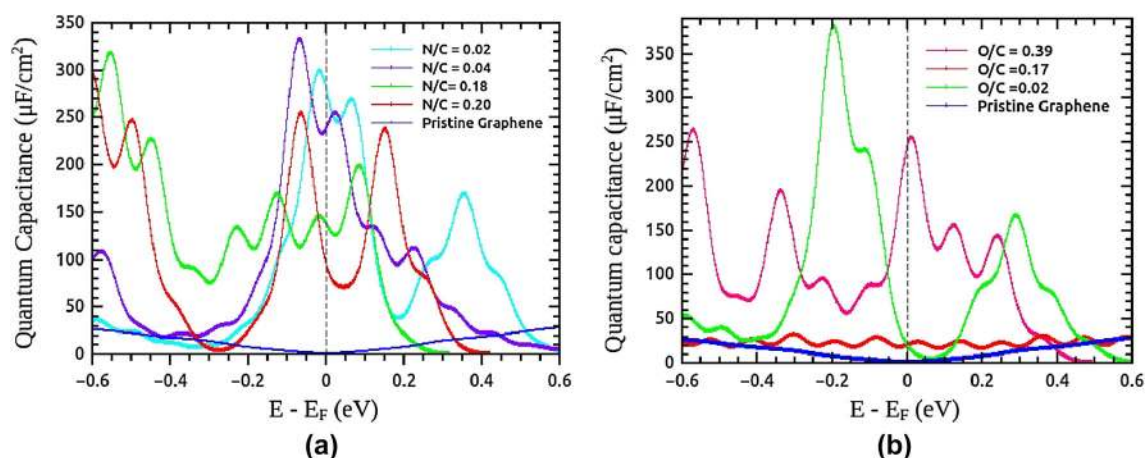
Figure 5. Quantum capacitance for graphene functionalized with an increase in (**a**) nitrogen ad-atom and (**b**) oxygen ad-atom concentration.

as shown in equation (1), tuning of the electronic structure near the Fermi energy may lead to a significant enhancement in C_Q.

The calculated C_Q for various ad-atom-doped graphene are plotted in figure 3 and the values are shown in table 2. For Sn- and N-functionalized graphene, a large amount of DOS gets accumulate near the Fermi level as shown in figure 4a and b; as a result high-quantum capacitance values of 255.72 and 256.42 $\mu F\,cm^{-2}$ for Sn and N, respectively, were observed in these systems. The calculated values of C_Q in Si- and Ge-doped graphene are 174.82 and 253.46 $\mu F\,cm^{-2}$, respectively. On the other hand, oxygen doping significantly reduces the value.

An increase in C_Q is due to these localized DOS at the Fermi level, which is maximum for Ge, Sn and N compared to other ad-atoms as depicted in figure 2. One possibility for obtaining a high C_Q value is that a significant charge reorganization occurs due to functionalization of graphene. Therefore, we investigated the charge redistribution in the functionalized graphene using Bader charge analysis and observed a large amount of charge transfer between graphene and the ad-atoms. We found 0.4e charge transfer to N and 0.5e charge transfer from Si to graphene, where N and Si are the most and the least electronegative ad-atoms in our study as shown in table 3.

3.2 *Variation of doping concentration and its impact on quantum capacitance*

Next, we varied the doping concentration and examined its effect on electronic structure and subsequently on C_Q of graphene. We found that doping concentration can enhance quantum capacitance due to the corresponding change in the total DOS near the band edges. In the case of nitrogenated graphene, there is a significant charge transfer from graphene to the N site, resulting in a Fermi level shift towards the valence band. The system shows a metallic behaviour.

Table 5. Details of C_Q calculated at the Fermi level for oxygenated graphene with varying O/C ratios.

O/C ratio	C_Q ($\mu F\,cm^{-2}$)
1:50 (0.02)	19.997
3:18 (0.17)	20.722
7:18 (0.39)	247.379

Table 6. Details of C_Q values calculated at the Fermi level for graphene co-doped with nitrogen and oxygen in different concentrations.

C:O:N ratio	C_Q ($\mu F\,cm^{-2}$)	C:O:N ratio	C_Q ($\mu F\,cm^{-2}$)
50:8:2	103.327	50:8:3	189.767
50:8:1	132.915	50:8:4	423.73

The electronic structures of graphene has been changed considerably due to the presence of nitrogen, oxygen and other functional groups. The electronic structure of N-doped graphene is shown in figure 4a, which clearly indicates the shift of the Fermi level due to electron injection into the π^* band. The nitrogenated graphene with 2% doping gives a maximum value of C_Q of 279.385 $\mu F\,cm^{-2}$. Our studies show a significant reduction in the quantum capacitance value on increasing of doping concentration for most of the ad-atoms.

One possibility for the reduced C_Q value is due to the interaction between the ad-atoms in the functionalized graphene. The interactions between the ad-atoms become much more strong when the ad-atom concentration crosses the optimal value. These interactions have an effect on the localized states near the Fermi level. As a result, we observed a reduction in the C_Q value as shown in table 4. However, in the case of
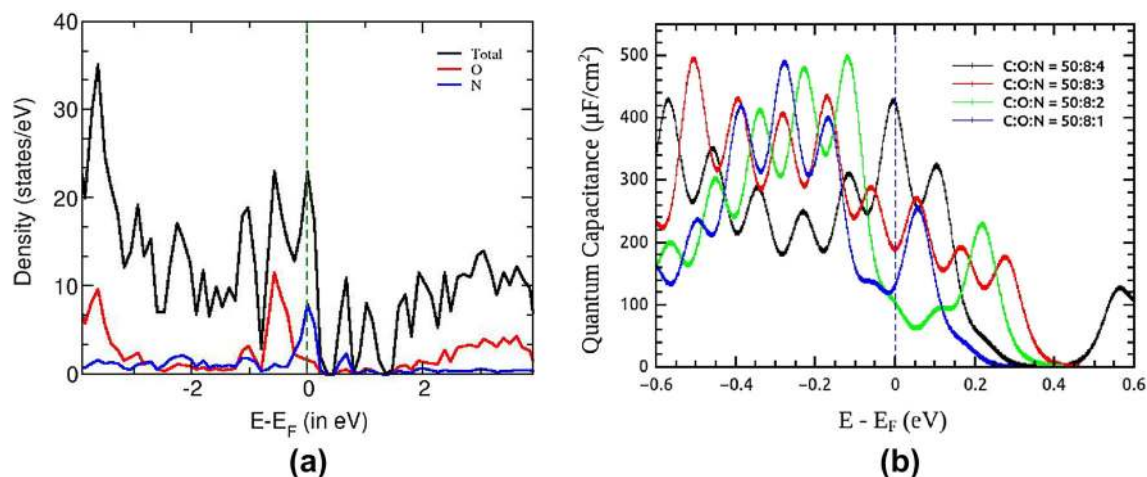
Figure 6. (**a**) Atom PDOS and (**b**) quantum capacitance for N, O dual-doped graphene.

N-doped system there is a steady increment of C_Q up to a certain concentration where the N–C ratio is 1:50 as shown in figure 5a and listed in table 4, where 2% is the critical doping concentration for the N ad-atom. We observed a similar behaviour in the case of Sn ad-atom.

We also observed the enhancement of quantum capacitance with an increase in oxygen concentration as show in figure 5b. A quantum capacitance of $247.379 \, \mu F \, cm^{-2}$ has been observed for oxygenated graphene with an O–C ratio of 7:18 as listed in table 5.

3.2a   *Change in C_Q due to a co-doping with nitrogen and oxygen*:   The enhanced quantum capacitance can be obtained from reduced graphene oxide when functionalized with ad-atoms as predicted by Ce *et al* [14]. Therefore, we explored the combined effect using N and O ad-atoms. A clear enhancement of quantum capacitance in nitrogenated graphene is observed in the presence of oxygen. We then simultaneously varied the O and N concentration and found that the increment in C_Q is maximum when the C:O:N ratio is 50:8:4 as listed in table 6 and the variation of C_Q in different N and O doping concentrations are shown in figure 6b.

We have studied the variation of quantum capacitance in functionalized graphene by varying the concentration and sublattice positions of O and N ad-atoms. We found that the C_Q in nitrogenated graphene increases two-fold ($423.73 \, \mu F \, cm^{-2}$) in the presence of O in the above mentioned concentration. The enhancement in C_Q can be realized as there is a significant charge transfer from the graphene sheet to the O atom, which in turn reduces the hybridization between the graphene carbon atom and the doped N atoms. As a result, the band widths of the impurity bands due to N atoms became narrower and extended only in a very small energy range near the Fermi level. Figure 6a clearly shows the localization effect of nitrogen DOS near the Fermi level, which effectively helps increasing the charge carrier density and hence the quantum capacitance.

4.   Conclusions

Our DFT calculations show that chemical modification of graphene-based electrodes enhances quantum capacitance. The enhancement is due to the generation of new electronic states close to the Dirac point and a shift of Fermi level caused by the ad-atom doping. In this work, we have investigated the effect of doping on electronic properties and quantum capacitance of graphene. We observed that doping with ad-atom creates new states near the Fermi level, which in turn helps accumulating greater amounts of charge carriers in functionalized graphene in comparison with pristine graphene and hence the quantum capacitance of the functionalized graphene enhanced significantly. Based on the obtained results, a quantum capacitance of $249.477 \, \mu F \, cm^{-2}$ was observed for Sn-functionalized graphene. The nitrogenated graphene gives a relatively high-quantum capacitance of $279.385 \, \mu F \, cm^{-2}$ which was further increased to $423.73 \, \mu F \, cm^{-2}$ in the presence of oxygen atoms in the system.

Acknowledgements

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