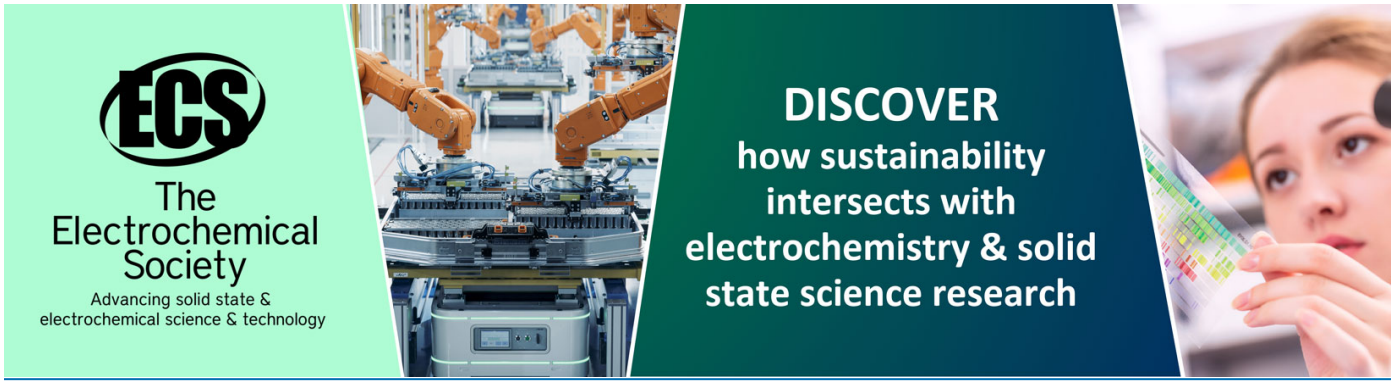
Computational insights into the electronic structure of functionalized monolayer hBN supercapacitor electrodes



Computational insights into the electronic structure of functionalized monolayer hBN supercapacitor electrodes

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Abstract. In this study, we examined a collection of functionalized hBN monolayers' electronic structure and quantum capacitance. Different ad-atom adsorption techniques have been used to functionalize the hBN monolayer. Density functional theory calculations are performed to precisely determine the electrical structure of an ad-atom doped hBN monolayer with a range of doping concentrations. The quantum capacitance of every functionalized system was then calculated. Above 500 $\mu F/cm^2$, a noticeable quantum capacitance has been seen. Our calculations demonstrate that ad-atom doping at hollow position of hBN honeycomb lattice greatly increases the quantum capacitance of hBN monolayer. The microscopic cause of this system's increased quantum capacitance has been investigated. Our DFT-based calculation shows that the system has a very large quantum capacitance due to the creation of new electronic states in the vicinity of the band edge and the Fermi level shift caused by the ad-atom adsorption.

Introduction

One of the biggest obstacles to halting climate change is the process of producing enough energy without using fossil fuels by using renewable sources instead. Thus, it is imperative in the current context to generate green energy on a large scale using sustainable energy sources. However, technology must be created that can effectively transform and preserve the energy produced. Supercapacitors, fuel cells, and batteries are the three main types of modern technology used to convert and store energy. Supercapacitors have many advantages, including a high power density, long lifespan, greater stability, and the ability to be used in a wide range of temperatures[1, 2]. Large amounts of electrical energy can be temporarily stored by supercapacitors and released as needed. Their high production costs and low energy density, however, impede their development[3]. To increase the use of supercapacitors in more complex applications, these issues must be resolved. Research is being done extensively to alter the electrode material of supercapacitors in an effort to solve the problem of poor energy density[4-6]. A noticeably high ion density in the electrode material is one of the fundamental conditions for a highly effective supercapacitor. The ideal alternative for supercapacitor electrode applications may consequently be two-dimensional materials because they often have a large specific area. Graphene is a 2D substance that is one atom thick and composed of carbon atoms organised in a honeycomb lattice. It exhibits exceptional electrical and mechanical capabilities. Studies have been done using graphene, graphene that has undergone chemical modification, and composites based on

graphene as electrode materials for supercapacitors[7–10]. Its limited scalability [11, 12] hinders its broad application, necessitating the search for substitute, suitable two-dimensional materials for supercapacitor electrodes.

Due to its insufficiently large bandgap (5.95 eV), hexagonal boron nitride (h-BN), a 2D material, has not been thought to be an appropriate material for supercapacitor electrodes (Cassabois et al. 2016).Chemical modification changes h-BN from a broad bandgap semiconductor to a metallic system with DOS at the Fermi level. So, in an effort to make these materials viable for supercapacitor applications, I functionalized them with the appropriate adatoms.

Methodology

The structural optimisation and electronic structure information of different functionalized systems are obtained using first-principle DFT calculations, which are included into the Vienna ab initio simulation(VASP) software[13,14]. The exchange-correlation energy was described by the generalized-gradient approximation with the Perdew-Burke-Ernzerhof parameterization [15]. For accurate results, the energy cut-off value (>400 eV) was considered to be extremely high. Calculations were performed using 3×3×1 supercells of hBN unit cells, which are composed of nine nitrogen and nine boron atoms, to examine the effects of different ad-atom doping on the quantum capacitance[16-18]. Comparison of ground-state energies reveals the stable adsorption location of ad-atoms on hBN monolayer. The stable configurations chosen for doping are hollow position in hBN monolayer. To avoid interaction with the layers of hBN unit cells' periodic pictures, a huge empty space (height>10Å) was taken into consideration along the out of the plane direction. The maximum energy tolerance for convergence was 10^{-6} H for geometrical optimisation. We employed a 6×6×1 Monkhorst-Pack grid to sample the Brillouin zone. To obtain the accurate D(E), and atom projected density of states (PDOS), a denser 20×20×1 Monkhorst-Pack grid was utilised. An electrical double-layer capacitor's total capacitance, C_T, is represented by the following formula:

$$\frac{1}{C_T} = \frac{1}{C_Q} + \frac{1}{C_D} \tag{1}$$

where C_D and C_Q denote, respectively, double-layer and quantum capacitance. Materials' quantum capacitance is determined by measuring the pace at which excessive charges (ions) shift when the applied voltage changes [31]. It is therefore directly related to the electronic energy configuration of the electrode materials and can be defined as the derivative of the net excess charge on the electrode or substrate with respect to the electrostatic potential. i.e.

$$C_Q = \frac{dQ}{d\phi} \tag{2}$$

where ϕ is the electrode's chemical potential and Q is the electrode's excessive charge. An electronic DOS weighted average up to the Fermi level, or E_F, is used to determine the overall charge. Therefore, the excessive charge on the electrode (Q) can be explained by an integral term related to the Fermi-Dirac distribution function f(E) and the electronic density of state D(E). So we can express Q as

$$Q = e\int_{-\infty}^{+\infty} D(E)[f(E) - f(E-\phi)]dE \tag{3}$$

Therefore, if the DOS is known, the channel's C_Q at a given temperature T may be

$$C_Q = \frac{dQ}{d\phi} = \frac{e^2}{4kT}\int_{-\infty}^{+\infty} D(E)sech^2\frac{E-e\phi}{2kT}dE \tag{4}$$

Chemical potential, electron charge, and Boltzmann constant are represented by the symbols ϕ, e and k, respectively.

Results and discussions

It is proven that equation (4) includes the DOS which is found close to the Fermi energy. As the single-layer hBN has no states near the Fermi level and has a large band gap semiconductor [32], it displays zero quantum capacitance (Figure 1). Ad-atom doping can be used to modify a material's electrical structure. The production of quantum capacitance by monolayer hBN could occur if the alteration in electronic structure leads to the collection of states at the Fermi level.

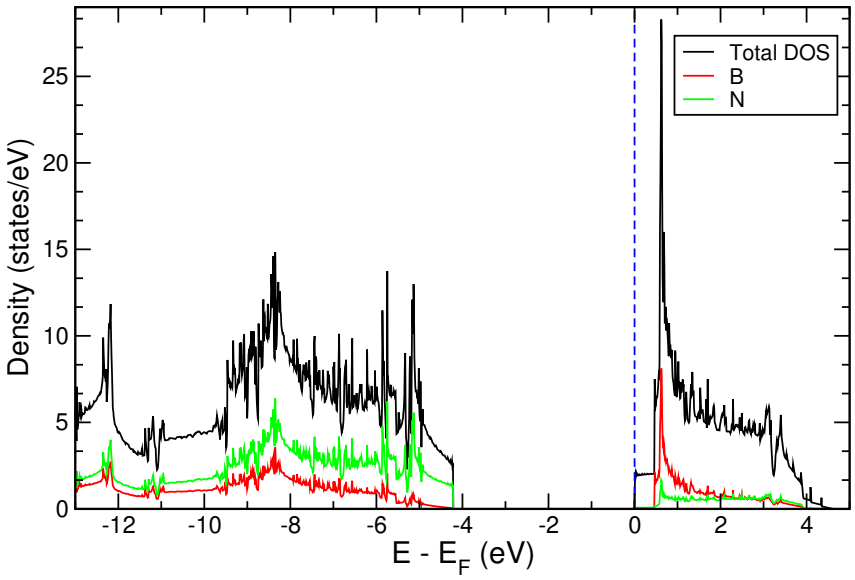

Figure 1. (color online) Atom projected density of states for monolayer hBN. The doped atom's DOS is represented by the coloured curve. E=0 is the Fermi energy represented by the vertical blue dashed line.

Chemical modification of monolayer hBN at Hollow position

On the hBN lattice, there may be three possible adsorption sites: the top (on the vertical top of the B and N atoms), hollow (in the sheet's hexagonal middle), and bridge site (between the B and N atoms). By contrasting ground-state energies, ad-atoms' stable adsorption position on monolayer hBN is found. According to our calculations, the hollow sites are the best places for ad-atom adsorption.

The average adsorption energy E_{ad} has been determined using the equation to investigate the stability of doped hBN structures.The stability of doped hBN structures has been examined by calculating the average adsorption energy E_{ad} utilising the equation.

$$E_{ad} = \frac{1}{n}[E_{tot} - E_{hBN} - nE_{at}] \tag{5}$$

where n is the unit cell's ad-atom count, E_{at} is the ad-atom's energy per atom. E_{tot} is the functionalized hBN unit cell's total energy, and the entire energy of pure hBN within a single unit cell is E_{hBN}. The adsorption energies for the different functionalized hBN are listed in Table 1. These atoms can readily bind to the pure hBN surface, according to the relatively high adsorption energies.

Table 1. Energy of adsorption per atom that adsorbs on monolayer hBN.

ad-atom	**E_{ad}(eV)**	**ad-atom**	**E_{ad}(eV)**
Br	-2.019	Li	-2.042
Si	-2.120	P	-0.202

We have studied how doping different atoms at the hollow position affects the quantum capacitance of monolayer hBN. The optimized geometric structure of configurations is shown in figure 2.

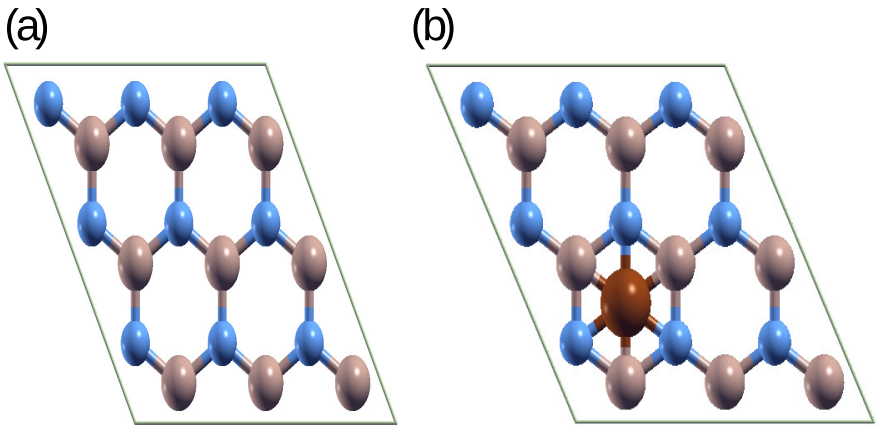

Figure 2. (color online) Structure of (a) Pristine hBN monolayer and (b)Br functionalized hBN at hollow site. Light brown balls and blue balls represent B and N atoms respectively. Dark brown ball represent the bromin atom which doped at hollow site.

The DOS and electronic band structure of the charge carrier in the functionalized-hBN configurations can be used to predict its characteristics. The electrical structure's tuning could result in a significant improvement in C_Q.

Figure 3 plots the computed C_Q for various ad-atom doped hBN monolayers, and table 2 lists the values. As illustrated in figure 3 for Br-functionalized hBN, significant amounts of DOS build up close to the Fermi level. As a result, high-quantum capacitance values of 1341.71 was found in this system. These localised DOS at the Fermi level cause a rise in C_Q, which is greatest for Br, Si, Li and P when compared to other ad-atoms.

Table 2. C_Q value computed at Fermi energy for different ad-atom doped hBN monolayer.

Configuration	**C_Q (μF/cm^2)**	**Configuration**	**C_Q (μF/cm^2)**
Br−hBN	1341.71	Li−hBN	643.90
Si−hBN	852.12	P−hBN	601.10

A considerable charge reorganisation caused by chemical modification is one way to achieve a high C_Q value. As a result, we used Bader charge analysis to examine the charge redistribution

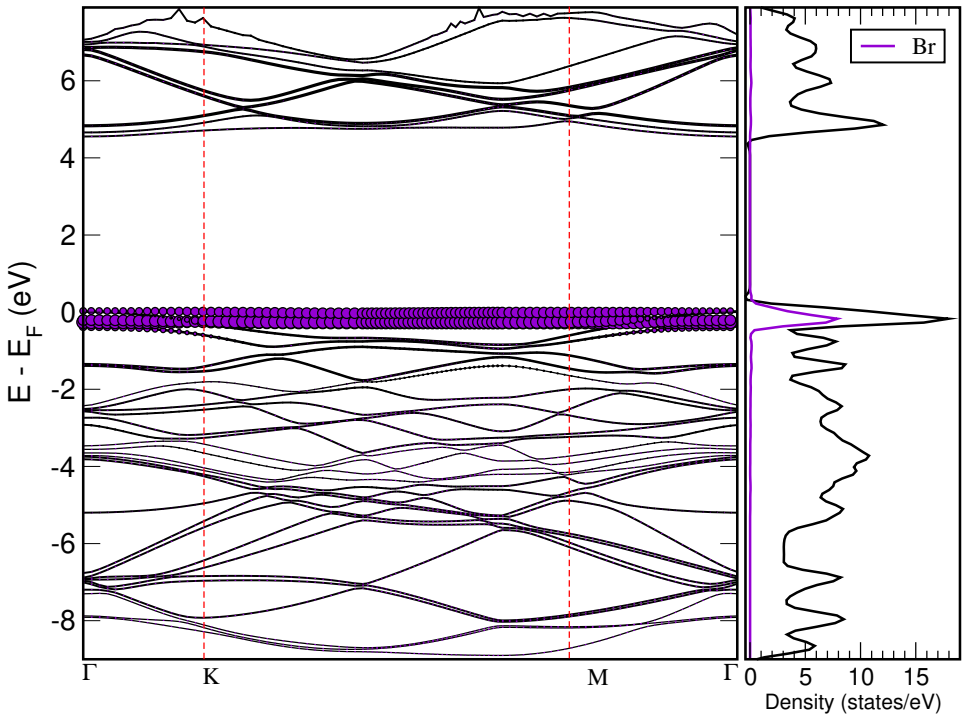

Figure 3. (color online) The coloured curve in the DOS and the circle in the band structure represent the electronic band and DOS for Br doped hBN at the hollow site, respectively. Doped atom contributions are displayed.

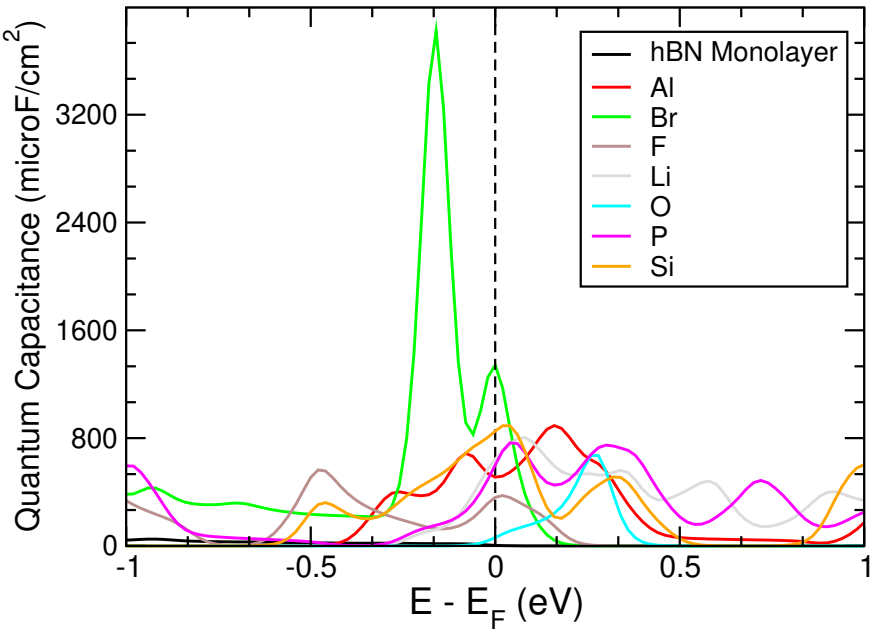

Figure 4. (color online) The energy variations in quantum capacitance for hBN functionalized with various ad-atoms at the Hollow site are shown by the varied colour trends.

in the chemically altered hBN. As shown in table 3, we discovered that there was a considerable quantity of charge transfer between the ad-atoms and the hBN monolayer.

Table 3. Charge transfer data for different ad-atom functionalized monolayer hBNs.

System	Transferred charge (e)
Br−hBN	-0.3075
Si−hBN	+2.3639
Li−hBN	-1.2576
P−hBN	+0.5672

Conclusion

We have investigated the functionalized hBN monolayer monolayer's quantum capacitance. Our theoretical analysis demonstrates that adding ad-atoms to the monolayer hBN sheet can greatly increase the quantum capacitance (C_Q) of hBN electrodes. The results demonstrate the improvement in quantum capacitance caused by altering the hBN monolayer's electrically insulating behaviour to a metallic one. These adatoms form a strong connection with the hBN monolayer, and the optimised shape exhibits metallic behaviour.

Above 500 $\mu F/cm^2$, a noticeable quantum capacitance has been observed. These calculations demonstrate that doping the honeycomb lattice's hollow site with various adatoms increases the quantum capacitance of the hBN monolayer. The functionalized hBN monolayer showed a large increase in quantum capacitance, which is mostly due to the doping effect's creation of new electronic states close to the Fermi level. In ad-atom doped monolayer hBN, a significant charge transfer and redistribution occurs. Ad-atoms' extra charge carriers alter the monolayer hBN's carrier concentration, shifting the Fermi level as a result.

Acknowledgments

Authors acknowledge the computing facility of Central University of Kerala. I am thankful for the post doctoral fellowship granted by the Kerala State Council for Science, Technology and Environment (KSCSTE).

References

[1] Kresse G and Furthmüller J 1996 *Phys. Rev. B* 54 11169
[2] Sruthi T and Kartick T 2019 *Bulletin of Materials Science* 42 257
[3] Choi B G, Hong J, Hong W H, Hammond P T and Park H 2011 *ACS Nano* 5 7205–13
[4] Sruthi T and Kartick T 2021 *Physica B: Condensed Matter* 604 412676
[5] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* 6 15–50
[6] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* 77 3865
[7] Huang X, Qi X, Boey F and Zhang H 2012 *Chem. Soc. Rev.* 41 666–86
[8] Sruthi T and Kartick T 2019 *J. Phys.: Condens. Matter* 31 475502
[9] Hirunsit P, Liangruksa M and Khanchaitit P 2016 *Carbon* 108 7–20
[10] Yang X, Cheng C, Wang Y, Qiu L and Li D 2013 *Science* 341 534–7
[11] Kim T Y, Lee H W, Stoller M, Dreyer D R, Bielawski C W, Ruoff R S and Suh K S 2011 *ACS Nano* 5 436–42
[12] Zhu Y et al 2011 Science 332 1537–41
[13] Wang G, Zhang L and Zhang J 2012 *Chem. Soc. Rev.* 41 797–828
[14] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 *Nano Lett.* 9 30–5
[15] Xu Q, Yang G M, Fan X and Zheng W T 2019 *Phys. Chem. Chem. Phys.* 21 4276–85
[16] Stoller M D, Park S, Zhu Y, An J and Ruoff R S 2008 *Nano Lett.* 8 3498–502

[17] Sruthi T, Nayana Devaraj and Kartick T 2021 *Electronic Structure* 3
[18] Simon P and Gogotsi Y 2008 *Nature Materials* 7 845–54