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Electronic structures and quantum capacitance of monolayer and multilayer graphenes influenced by Al, B, N and P doping, and monovacancy: Theoretical study

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ABSTRACT

Graphene has been extensively explored as an electrode material in supercapacitors because of its large surface area and high electronic conductivity. By designing diverse morphologies and doping graphene with certain elements, the properties of graphene can be efficiently modified. We present the influence of Al, B, N and P doping, monovacancy and multilayer graphene structures on stability, electronic structures and quantum capacitance, by applying density functional theory calculations. The electrode quantum capacitances are substantially modified due to doping, the presence of monovacancy, and interaction between layers occurred in multilayer structures. Our calculations suggest that the monolayer graphene with monovacancy, the monolayer and multilayer graphene structures with nitrogen doped around the monovacancy, and multilayer graphene structure with aluminum doped could provide substantial change of quantum capacitance. However, the structure stability could be challenging. The interaction between layers could lower quantum capacitances compared to those of the monolayer structures with the same dopant elements. Moreover, the association of monovacancy and nitrogen doping of a single layer structure could lead to as high quantum capacitance as ~80 μF/cm^2. This work suggests the possibility to enhance quantum capacitance of the graphene-based electrodes using the combination effect of doping, vacancy defect and stacking layers.

1. Introduction

Electrochemical capacitors, also known as ultracapacitors or supercapacitors, have gained much attention as electrical energy storage using either ion adsorption or fast surface redox reactions. Because of their high charge-discharge rate capabilities and long life cycle, they have become one of the most promising energy storage devices. Yet, a major drawback of supercapacitors is low energy density. The main parts of supercapacitors are electrolyte and electrodes. Many attempts are being made to extensively investigate new electrode materials which can enhance the capacitor performance and increase energy density. Carbon-based materials, such as, graphene, carbon nanotubes, and porous carbon have been considered as the promising materials for supercapacitor electrodes due to their high specific surface area, good electrical conductivity and good stability [1–5].

A key to achieve high capacitance requires electronically conducting electrodes with high specific surface area. Several studies have confirmed that graphitic carbon satisfies this condition providing high conductivity, electrochemical stability and high porosity. However, during the graphene electrodes preparation, the raw material graphene oxide easily gets agglomerated leading to the decrease of specific surface area. Thus, graphene-based materials performance can be limited by poor volumetric surface area and poor electrolyte accessibility which results in low capacitance [6,7]. Several approaches can improve the graphene electrodes performance such as the design of diverse morphologies and the incorporation of heteroatoms in the carbon matrix [8,9].

Many works have shown success to synthesize graphene with various morphologies, for instance, zero-dimensional graphene quantum dots, one-dimensional graphene nanoribbons, and two-dimensional graphene nanosheets [8,10,11]. They were also found to be the encouraging electrodes for supercapacitors. Among a variety of graphene-based structures, a multilayer graphene has been theoretically and experimentally explored in recent years for electrochemical sensing and biosensing for its large surface area

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and large 2D electrical conductivity [12–15]. In addition, the previous studies have reported the dependence of the electronic structures and quantum capacitance (C_Q) on the number of layers of pristine graphene [16–19]. It is found that the density of states (DOS) alters with an increase of the layer numbers, *n* [18], and C_Q changes accordingly. Therefore, it is important to elucidate the role of stacking graphene sheets which can either increase or decrease specific surface area and capacitance.

Besides the morphology design, the other effective technique to improve the supercapacitor performance is introducing fillers or dopants to graphene. Specifically, adding transition metal oxides [20–22], conducting polymers [23–26], carbon nanotubes [27,28], and heteroatoms [29] are reported to increase the capacitance. For example, the addition of the carbon nanotubes [30] could prevent restacking and serve as spacers to separate the neighboring graphene sheets, thus enhancing its effective surface area and a supercapacitor performance. Nitrogen-doped graphene has especially gained much interest more than other dopants as it has a comparable size and contains five valence electrons to form strong valence bonds with carbon atoms. Moreover, nitrogen-doping is easy to manipulate local electronic structures [31,32]. Jeong et al. reported that the capacitance of nitrogen-doped graphene electrode was significantly increased [33]. Also, sulfur and boron atoms are among other commonly used dopants [34–37]. The previous study reported that doping graphite with boron atoms is to achieve the better crystallinity and graphitization [35]. In this case, boron atoms replace some carbon atoms in the graphene sheet generating *p-type* semiconductor, where the electronic structure contains electronic holes. The introduction of halogen atoms to carbon nanotubes leads to the superconducting behavior of carbon nanotubes due to the high density of states around the hole [38,39]. Additionally, Garcia et al. modified the electronic and structural properties of a graphene layer by doping with sulfur or phosphorus atoms at different concentrations to enhance the electrical conductivity and chemical reactivity [40].

The electrode capacitance or quantum capacitance (C_Q) is one of the key parameters to indicate the supercapacitors performance. The total interfacial capacitance (C_T) is strongly dependent on the electrochemical double-layer capacitance (C_D) and the electrode quantum capacitance (C_Q) [41–43]. C_D is relevant to the electrolyte structure at the interface with electrode. The C_Q is proportional to the electronic density of states (DOS) [44–46], which can be altered by electrode materials. Together, C_D and C_Q are connected to one another in series, which the total capacitance C_T can be expressed as $1/C_T = 1/C_D + 1/C_Q$. The effect of C_Q is prominent in a low dimensional system, thus C_Q is particularly significant in such system.

The real mechanism of how the dopants and the morphologies of graphene play a role in the supercapacitor capacitance (C_T) enhancement is still ambiguous. The C_Q is proportional to DOS, and it is plausible that other dopants, functional groups, and defects, can substantially modify the C_Q. In this study, DFT calculations were performed to investigate the effects of doping, vacancy defects and interaction between layers of graphene structures on their quantum capacitances. We considered two commonly observed doping configurations of monolayer and multilayer graphene structures from experimental characterization [33,47]: (1) substitutional doping in which a C atom is replaced with a dopant, and (2) three atom doping around the single vacancy of a graphene she et. We analyzed geometries, structural stability, electronic properties and quantum capacitance of those configurations doped with Al, B, N, and P. The results reveals that with the dopants of Al and N combined with the presence of monovacancy or the interaction between layers could lead to significant quantum capacitance enhancement of graphene-based electrodes.

2. Simulation models and methods

The simulation systems, as illustrated in Fig. 1, are i) (Fig. 1(a)) graphene doped with Al, B, N and P elements by substitution, the X_1 system (Al_1, B_1, N_1 and P_1), which corresponds to 6.25% of impurity, by means of supercells, defined in terms of pristine graphene and ii) (Fig. 1(b)) graphene doped around monovacancy defect, the X_3V system (Al_3V, B_3V, N_3V, and P_3V), which corresponds to 6.25% of vacancy concentration and 18.75% of impurity. These systems are also investigated as a single layer (non-stacking) structure and multilayer (stacking) structure, denoted by $(X_1)_s$ and $(X_3V)_s$, respectively. The doping systems were carried out using a 3×2 supercells of graphene sheet. The vacuum region of 18 Å was expanded in the vertical z-direction of the non-stacking structure unit cell to avoid interaction between images in adjacent periodic cells (Fig. 1(c)). For the non-stacking structure, the initial trial structures of dopant atom locate in- and out-of the graphene planes are investigated. The vacuum region ~7 Å was initially expanded in the z-direction for the stacking structure unit cell (Fig. 1(d)). For the stacking structure, the initial trial structures of dopant atoms stay either offset or on top of one another are investigated. For the non-stacking structure, the shape of the unit cell was allowed to change while the volume was kept constant during structure relaxation. For the stacking structure, both the shape of the unit cell and the cell volume were allowed to change during structure relaxation which results in the change of interlayer spacing due to dopants and monovacancy.

The DFT calculations, as implemented in the Vienna *ab initio* Simulation Program [48,49] were applied for electronic structure calculations and atomic structure optimization. The calculations used the GGA-PBE functional [50] and the Projector Augmented Wavefunction (PAW) [51,52] method for representing the non-valence core electrons. For the inclusion of long-range dispersion, the semi-empirical dispersion potential correction method described by Grimme (DFT-D2 method) [53] was applied. The dispersion correction methods described by Grimme (DFT-D3 method) [54] and by Tkatchenko-Scheffler (DFT-TS) [55] were also performed on multilayer structures. The geometric parameters obtained from DFT-D3 and DFT-TS methods are reported in Table S2 of supporting information. The three different dispersion corrections yield different geometric parameter results and underestimate the inter sheet distance of layered graphene compared to the experiment (~3.35 Å). We chose to report the results obtained from the DFT-D2 method because it also gave reasonable results in the previous studies of graphene systems [56,57]. For all geometry relaxation calculations reported herein, we used a 500 eV cutoff for the kinetic energy of the plane-wave basis-set. The Gaussian broadening with a smearing width of 0.02 eV was employed. The surface Brillouin zone was sampled with a $15 \times 15 \times 1$ (non-stacking) and $15 \times 15 \times 15$ (stacking) Monkhorst-Pack k-point mesh [58] for structure optimization. The results were checked for convergence with respect to energy cutoff and number of k-points. The convergence criterion for electronic self-consistent iteration was set to 10^{-7} eV and the ionic relaxation loop was limited for all forces smaller than 0.01 eVÅÅ for free atoms. The self-consistent calculations were performed by means of a Monkhorst-Pack $45 \times 45 \times 1$ (non-stacking) and $45 \times 45 \times 45$ (stacking) k-point mesh for density of state (DOS) calculations. The Bader charge analysis was performed using VASP-VTST [59–61].

The formation energies, ΔE_f, are calculated from Eq. (1)

$$\Delta E_f = E_{X_1/X_3V} - n_C \cdot \mu_C - n_X \cdot \mu_X \quad (1)$$

where E_{X_1/X_3V} is the total energy of the system X_1 or X_3V, n_C is the number of carbon atoms, n_X is the number of doping atoms X, μ_C is