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Defect and functionalized graphene for supercapacitor electrodes

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ABSTRACT

The structural, electronic and transport properties of defected (single vacancy and double vacancy) and nitrogen functionalized graphene sheets have been analysed within the framework of Density Functional Theory (DFT) and non-equilibrium Green's function (NEGF) formalism for their possible application as supercapacitor electrodes. Formation energy calculations reveal the increasing stability of defect with nitrogen functional doping concentration at its edges. The extracted electronic properties reveal the presence of acceptor-type energy levels at Fermi level in the defected and functionalized sheets. Transport studies portray remarkable increase in electrical conductivity of graphene sheet after the formation of single vacancy defect and its functionalization. Especially, the Single Vacancy Trimerized pyridine-type defect (SVT) configuration has demonstrated superior thermodynamic stability as well as electrical conductance in comparison to all the other configurations.

1. Introduction

The demand for energy storage is on the peak these days in view of increasing energy consumption and declining fossil fuel resources. Recent surge in power generation through intermittent energy sources (wind and solar) stipulate the need for new generation electrochemical energy storage devices. High-performance Supercapacitor is one such a device with the potential to meet future energy storage demands. Electrochemical Double Layer Capacitor (EDLC) is a kind of supercapacitor with high power density that can enable fast charging and discharging along with high capacitance, long cycle life, superior electrochemical reversibility, rate capability and high energy density than the normal capacitors [1]. However, the energy density of supercapacitor is observed to be less than the conventional batteries (5 Wh/kg for carbon-based supercapacitor and 100–150 Wh/kg for convention Li-ion battery [2]), and is insufficient for many important applications. As EDLCs Store energy through adsorption of ions at the electrode and electrolyte interface; high surface area along with good electrical conductivity are the necessary requirements to attain high energy densities. Thus, besides the developing the advanced electrolytes, the researchers have also focused on optimizing the electrode material. Graphene is regarded as one of the best electrodes owing to its fascinating physical and chemical properties such as high electrical

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conductivity, remarkable surface area, low contact resistance etc. [3–5]. Furthermore, a graphene based material can store energy at seven times the density of commercial carbon-based products. Hence, the graphene sheets are viewed as most suitable candidates for electrodes in supercapacitors [6]. The single atomic layer of graphene can also be used as electrodes [7,8], however the limitations such as weak accessibility to electrolyte and insufficient capacitance pose hindrances [9,10]. It has been reported theoretically and experimentally, functionalization of graphene honeycombs can increase electrical conductivity, capacitance, electrolyte wettability and electrode accessibility [11,12]. Particularly, nitrogen doped graphene regarded as one of the promising material in terms of electrical conductance, power density, energy storage, catalysis adsorption as well as life cycle [13–17]. Nitrogen substitution in pristine graphene normally yields donor states in the electronic structure, however several reports states that, the type of conductivity (p-type or n-type) can be tuned through different ways [18,19]. Further, the substitution of nitrogen in graphene was reported to increases surface properties of carbon such as surface polarity and electron donor affinity [20]. Similar nitrogen functionalization of defected carbon nanotubes (CNTs) by Rocha et al. [21] reported increasing stability with nitrogen functionalization and high reactivity of such structures for ammonia sensing.

In this work, we have incorporated defects (Single Vacancy (SV) and Double Vacancy defect (DV)) and functionalized them with nitrogen to form Single Vacancy Monomeric Pyridine-type Defect (SVM), Single Vacancy Dimerized Pyridine-type Defect (SVD), Single Vacancy Trimerized Pyridine-type Defect (SVT), Double Vacancy Monomeric Pyridine-type Defect (DVM), Double Vacancy Dimerized Pyridine-type Defect (DVD), Double Vacancy Trimerized Pyridine-type Defect (DVT) and Porphyrin-type defect. Analysed the influence of these defects and functionalization on stability, electronic nature and electrical conductivity of the graphene for their possible application in supercapacitor electrodes.

2. Theoretical approach

The calculations have been performed using Density Functional Theory (DFT) [21,22] and Non-Equilibrium Green's Function (NEGF) [23] based Ab-initio package Atomistix Toolkit–Virtual NanoLab (ATK-VNL) [24]. ATK-VNL is a further development of Tran-SIESTA-C [25] and hence is based on methodology, models and algorithms developed in the academic code Trans-SIESTA and in part McDCal [26], employing localized basis sets as developed in SIESTA [27]. We used Generalized gradient approximation (GGA) exchange-correlation functional with Perdew Burke Ernzerhoff (PBE) [28,29] type parameterization for ground state calculations. The valence electrons are described by norm-conserving pseudopotentials with localized pseudo-atomic orbital's (PAOs) [30], with double-ζ single polarized basis set. A large plane wave mesh cut-off of 150Ryd considered throughout the calculations, which is sufficient for convergence of plane wave function. $7 \times 7 \times 1$ and $1 \times 1 \times 100$ k-point mesh were used to sample the Brillouin zone in the x, y, z-directions through the Monkhorst-pack scheme [31] for electronic and transport properties, respectively.

The convergence criterion for the Hamiltonian, charge density and band-structure energy is 10^{-4} via the mixture of the Hamiltonian. For optimization, self-consistent force optimization has been performed until Hellmann and Feynman force per unit between the atoms become less than 0.002 eV/Å. The further increment of k-points or cut off energy is observed to have very small impact on the computational results. Transport properties of the functionalized graphene sheets calculated using thekeldysh non-equilibrium green's (NEGF) formalism [32] and quasi-Newton method [33] until the absolute value of force acting on each atom is less than 0.05 eV/Å.

3. Results and discussion

3.1. Structural and stability analysis

The stability, electronic nature and electrical conducting ability of different Graphene configurations have been analysed for pristine, SV and DV defect with varying nitrogen substitutional doping concentrations depicted in Figs. 1 and 2. The defect vacancy is created in a $5 \times 5 \times 1$ repeated graphene basis and the under-coordinated atoms at the vacancy are substitutionally doped with nitrogens (N) to obtain functionalized defects pyridine-type and porphyrin-type. Nitrogen as a dopant has been preferred as it was reported earlier by some researchers to increases the energy storage capacity of graphene supercapacitors [11,12,14–16]. The measured bond lengths at the defect edges are tabulated in Table 1 and depicted in Figs. 1 and 2 for a clear vision of bond length variations. The variations in the bond length are mostly witnessed at the dopant positions. The C–N bond length is observed to be relatively smaller than the C–C bond length despite the fact that all atoms have undergone SP^2 hybridization; this might be due to the high electronegativity of dopant Nitrogen. SVM configuration has shown the strongest C–N bond of all the functional doping configurations owing to its smaller C–N bond length. In DV defect, the carbon atoms surrounding the vacancy come closer giving a pentagon–octagon-pentagon like formation and surrounding C–C bond lengths increased by a small amount of 0.05 Å when compared with the pristine graphene bond length of 1.420 Å.

Thermodynamic stability, a critical factor in opting the defected and functionalized graphene sheets for supercapacitor electrode applications, has been assessed through formation energy calculations. The stability of defect edges in each configuration has been evaluated by calculating the formation energy per unit length of the edge (E_F) using eq. (1) [34].