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Evaluation of the Performance of Graphene-Based Supercapacitors and the Impact of Boron Doping and Structural Defects on its Efficiency: a Theoretical Assessment

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Introduction

Supercapacitors are considered as the electrical energy storage device. Graphene-based materials are widely used in the manufacture of supercapacitor electrodes [1]. The importance of electronic structure in controlling the area-specific capacitance of an graphene-based supercapacitors has been recommended in the past [2]. In fact, the total capacity is considered as sum of the two series capacitance of the quantum capacitance and the double layer capacitance, which the quantum capacitance is known as the limiting factor. Thus, with enhancing the quantum capacitance, the total capacity will be improved. The quantum capacitance is given by equation (1): $C_Q(V) = e^2 \int_{-\infty}^{+\infty} D(E) F_T(E-\mu) dE$ (1)

Where D(E) is the electron density of state (DOS), $F_T(E)$ is the thermal broadening function, E is the relative energy with respect to the Fermi level E_F, and e is the elementary charge [3]. In this paper, we try to calculate the quantum capacitance of some graphene derivatives materials for use as supercapacitor electrodes.

Methods

Density functional theory (DFT) calculations were accomplished within the plane wave pseudopotential approach, as employed in the Quantum-ESPRESSO code. For the exchange correlation density functional, the generalized gradient approximation (GGA-PW91) was used. Periodic boundary conditions with a vacuum gap of 25Å in the z direction were imposed to avoid interaction with its periodic image. The integral of equation (1) was solved by Gaussian Quadrature method.

Results and Discussion

Two different configurations of graphene doped with boron atoms have considered. In one of

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them, a carbon atom is replaced by a boron atom (B). In another, four carbon atoms are replaced by three atoms of boron and a hole (B_3V). Three structural defects and the combination of B-doping and structural defects are considered as well. Structural defects were considered in this work include stone-wales defect [SW(55-77)], single vacancy [SV(5-9)] and double vacancy [DV(5-8-5)]. B has one electron less than C. Thus with each substitution of B instead of C, provides an electron deficiency. As a result, the Fermi level moves down inside the valence band of pristine graphene and gives rise the density of states at the negative energy respect to Fermi level. The occurrence of the topological defects disrupts the π system of graphene that gives rise the additional p_z states near the Fermi level. The optimized structure of combination of B-doped graphene and graphene with structural defect of DV(5-8-5) and also the results of the integrated quantum capacitance calculations for them are given in the Fig. 1. As can be seen, at the positive base, the capacity of boron-doped graphene significantly increased in comparison with pristine graphene. However, at potentials lower than -0.7 V, this configuration shows a smaller capacity in respect of the pristine graphene. The configuration of graphene with DV(5-8-5) structural defect also provides a better capacity in respect of the pristine graphene. The configurations that composed of DV(5-8-5) structural defect and B-doping show a higher capacity than pristine graphene and B-doped graphene. Other configurations (the combination of B-doping and SV(5-9) and the combination of B-doping and SW(55-77)) show good results as well. Indeed the increasing of capacity is a direct result of arising the Impurity state near the Fermi level.

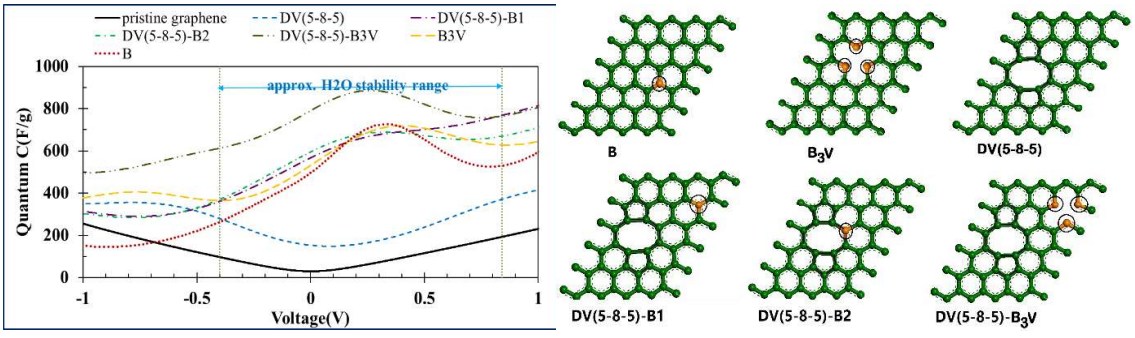

Fig. 1. Quantum capacitance of pristine graphene, boron doped graphene (B & B_3V) and three configuration of combination of di-vacancies structural defect [DV(5-8-5)] and boron doped graphene. Each considered pristine graphene sheet contained of 4×5 hexagonal supercells (60 carbon atoms). The case of DV(5-8-5)-B2 illustrates that the boron atom is replaced with carbon atom in defect site.

Conclusions

We have evaluated strategies for enhancing the efficiency of graphene-derived supercapacitors. Obtained results suggest that the presence of defects in sufficient concentrations into the graphene structure can significantly improve the capacitance. In addition, the B-doped graphene and its derivatives provide greater capacity with respect to pristine graphene too. However, they will be more effective at positive electrode.

References

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