Enhancing the capacity of graphene-based supercapacitors by functionalization of graphene with monovalent functional group (-CH_3, -H, -OH, -NH_2 and –COOH): a theoretical study

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Abstract

Supercapacitors is one of the most promising energy storage devices in the field of electrical energy. Graphene and its derivatives are the most commonly used materials in Supercapacitors electrode. However, the major limitation of this type of electrodes is their low energy density. Recently, it has been found that limitation factor in total capacitance of graphene-based Supercapacitors is their finite quantum capacitance at conventional electrolyte stability voltage range. The total capacitance (C_t) at the electrode/ionic-liquid interface is given by

$\frac{1}{C_t} = \frac{1}{C_Q} + \frac{1}{C_D}$ (1)

Where C_D is the electric double layer capacitanceandC_Q is the quantum capacitance, which given by

$C_Q(V) = e^2 \int_{-\infty}^{+\infty} D(E) F_T(E-\mu) dE$ (2)

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. In this work, we used of density functional theory calculations to explore the effect of the functionalization of graphene with some substituted groups on the electronic structure and consequently on the quantum capacitance of graphene. Substituted groups that were used contain -CH_3, -H, -OH, -NH_2, and -COOH. The full geometry optimizations and density of state calculations were carried out by the ESPRESSO code. We consider the hexagonal 3×3 supercell with one functional group and 25 Å a vacuum gap in the vertical (z) direction to separate the graphene system from its periodic images. Obtained results show that this type of functionalization shows one peak near the Fermi level at the plot of DOS. The impurity DOS that arises around the Fermi level is a direct result of produced local sp^3 hybridization. Inspection of projected DOSs suggests that p_z orbital of carbon atom that substituted group connected to it, contributes to the impurity states near the Fermi level. Our results demonstrate that the quantum capacitance and consequently stored charge in functionalized graphene with each substituted groupshas increased compared to the pristine graphene. This enhancement in quantum capacitance is directly related to additional availability of states near the Fermi level. In this type of functionalization of graphene, the capacitance is symmetrical around zero voltage. In other word, the use of these materials in both positive and negative electrodes is suggested.

Keywords: Supercapacitors, Quantum capacitance, Functionalized graphene

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