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ORIGINAL ARTICLE

Electronic Structure of Various Shapes of Graphene Quantum Dot

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ABSTRACT – The study of the electronic structure of graphene in bulk structure and graphene quantum dot (GQD) using density functional theory (DFT) using the Quantum ESPRESSO package is reported. To simulate the realistic shape of GQD, a vacuum layer is set, in the a-direction to be 58.52 Å, in the b-direction to be 58.52 Å, and in the c-direction to be 29.26 Å, to avoid interaction between quantum dots in the periodic structure of the crystal. Various shapes of quantum dots, namely triangular, hexagonal, and parallelogram, were examined. The band gap is tunable by its shape, which opens up wide application of GQD. It is shown that the electronic structure of graphene can be tuned by tuning its structure. In bulk structure, graphene is a zero-gap semiconductor. On the other hand, the results on GQD showed that the discrete energy levels and different shapes of GQD have different energy levels and band gaps. The band gaps for parallelogram, hexagonal, and triangular shapes are 0.13 eV, 1.33 eV, and 1.95 eV, respectively.

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INTRODUCTION

The basic form of carbon material is graphene, which has sp2 hybridization and is arranged in hexagonal lattice. Graphene has unique electronic properties. It has a zero band gap in which the conduction and valence bands touch each other at the Dirac point. Graphene can be stacked to form graphite, such as in a pencil, which has poor mechanical properties. On the other hand, graphene is known to be stronger than steel. In addition to its mechanical properties, graphene is flexible and more conductive than copper, which shows that the structure of carbon material is strongly affected in both mechanical and electronic properties [1]–[3].

The dramatic properties of graphene changed when its size became 1–10 nm, which is known as a graphene quantum dot (GQD). The band gap strongly depends on the size and shape. The controllable electronic properties of GQD were caused by the accumulation of passivated atoms by hydrogen and the hybridization of sp^2 and sp^3. The band gap can be tuned by tuning its shape and size, which opens up wide applications [4]–[6]. The smaller its size, the bigger the band gap. Since producing GQD samples with high purity and good crystallinity is very difficult, theoretical study to predict their properties plays an important role as a complement to experimental studies. Density functional (DFT) calculation is adopted for our theoretical study of GQD. DFT is well-known and very successful in explaining the electronic and magnetic properties of a wide range of materials [2], [7]. The stability of GQD is affected by its shape and the passivated atom at the edge of GQD [8], [9]. The main challenge in the DFT study of quantum dots is how the realistic model of quantum dots is simulated, which makes it different from bulk materials. In that case, it is needed to set a quantum dot which consists carbon atom and an edge-passivated atom and put that inside a large supercell with a vacuum space. The vacuum space needs to be large enough to avoid the interaction between quantum dots. A previous study reported the study of penta-graphene quantum dots [9]. In this study, the electronic structure of GQD in three different shapes, namely parallelogram, hexagonal, and triangular, is reported.

CALCULATION METHOD

The density functional theory (DFT) calculation was done by the plane-wave approach, which was implemented in Quantum ESPRESSO [10], [11]. The graphene quantum dot (GQD) from hexagonal graphene is generalized, as shown in Figure 1. Three different shapes of GQD were studied, which are parallelogram, hexagonal, and triangular, as shown in Figure 2. The previous study showed that a 15 Å vacuum is good enough to avoid interaction between GQD in the periodic structure [12]–[15]. Then in the calculations, the vacuum, with 30–50 Å, is set in the crystal structure, as shown in Figure 3. The size of the supercell with vacuum layer is a = 36.95 Å, b = c = 50.44 Å, with size GQD ~10 Å, which was constructed using VESTA [16]. The various shapes of GQD, namely parallelogram, hexagonal, and

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triangular, were studied. The number of C-atoms is 50, 96, and 33 for parallelogram, hexagonal, and triangular, respectively.

The projected augmented wave (PAW) pseudopotential was employed in all our calculations. The electron configuration of C is '$1s^2$ $2s^2$ $2p^{2}$' with four outer electrons treated as valence electrons. The energy cut is optimized and its start convergence at 40 Ry as shown in Figure 4. Then, an energy cut off of 60 Ry is used for all calculations with a convergence threshold of 10^{-6}. Since GQD is confined in three dimensions, we use a 1×1×1 k-point grid. The GQD was passivated by the C-H bond [17]. Further study is needed to investigate the effect of the passivated agent on the electronic structure.

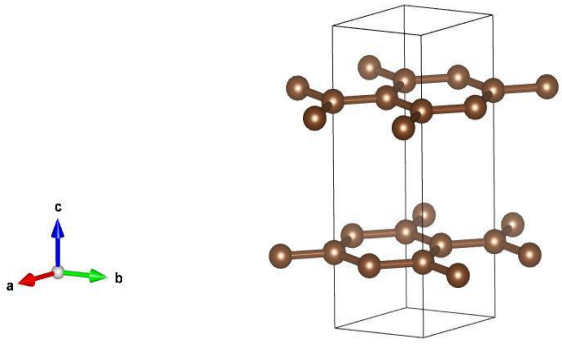
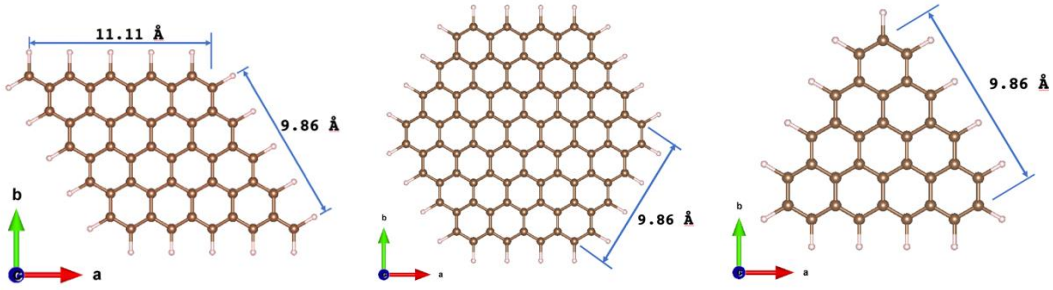


Figure 1. Crystal structure of graphene



(a) (b) (c)

Figure 2. Graphene quantum dots in various shapes: (a) parallelogram, (b) hexagonal, and (c) triangular

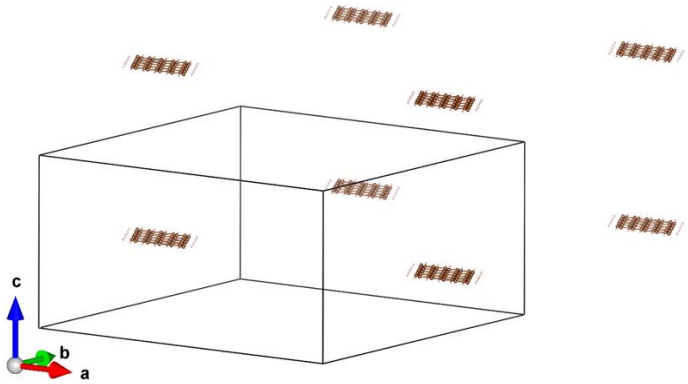


Figure 3. Vacuum layer between graphene quantum dot with a = 58.52000 Å; b = 58.52000 Å; c = 29.26000 Å

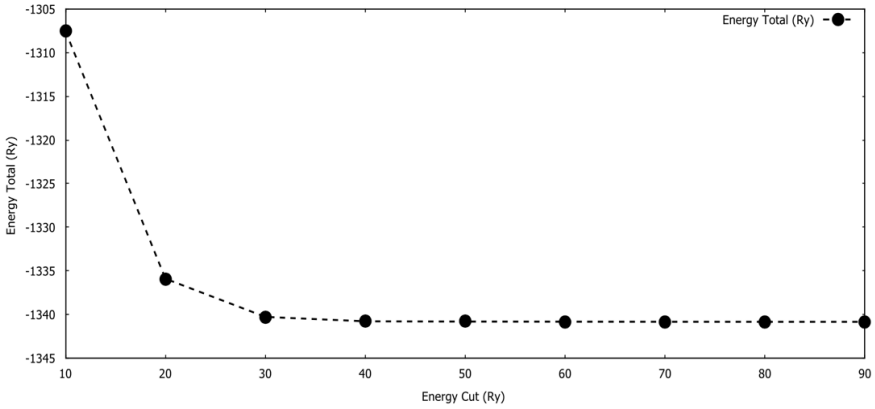


Figure 4. Energy cut optimalizations

RESULT AND DISCUSSION

In the first calculation, the electronic properties of graphene, which have been published in the previous study, are calculated. [18]. Its band structure and density of states are a gapless semiconductor. The Fermi energy is 5.2233 eV. The valence band and conduction band meet at the Dirac point (M-point). Due to this state, the threshold energy of energy to move from the filled band to the empty band is zero. Such properties are unique and very sensitive to any pressure and magnetic fields. At the Dirac point, an electronic excitation is induced, which is known as a Dirac fermion and behaves as a massless particle. The mobility of electrons is higher than in classical semiconductors [19], [20].

The calculation is continued to the graphene quantum dot (GQD), which has a size of nearly 1 nm. This size is assumed that be an image of the realistic quantum dots. The vacuum layer, which has a distance of 30~50 Å, was good enough to separate each quantum dot. The band structure of GQD is shown in Figure 5, Figure 6, and Figure 7. The energy level becomes discrete with the flat band, which is related to the atomic characteristic. Therefore, the vacuum layer, which has a distance of 30~50 Å, was good enough to separate each quantum dot, and the GQD model can be assumed as an artificial atom. The total energy of parallelogram, hexagonal, and triangular structures is -943.67 eV, 1796.63 eV, and -624.85 eV. The Fermi energies for parallelogram, hexagonal, and triangular structures are -4.09 eV, -3.90 eV, and -4.04 eV, respectively. The band gaps for parallelogram, hexagonal, and triangular are 0.13 eV, 1.33 eV, and 1.95 eV, respectively. These results indicate that the geometrical shape of GQD also plays an important role in determining the band gap, which directly relates to its electromagnetic absorption.

The geometrical shape is also reported to play an important role in magnetic systems [21]. The different shape of GQD has different zig-zag edge effects. The spin and electron polarization at the edge play the main role in determining the electronic state, namely the band gap. This band gap is the main characteristic of GQD, which can be tuned by changing its size and shape, which directly corresponds to the response of GQD to the electromagnetic radiation [22]–[25]. The discrete energy level can be explained by the quantum confinement effect in extremely small particles (less than 10 nm) comparable to the wavelength of the electron. It is also found that the confinement effect, which has a flat and discrete band, can be achieved by adding a hydrogen atom as a passivation of the edge of carbon [26]–[30]. From our calculation results, the band engineering of GQD can be achieved by shape modification, which can be done by controlling the synthesis parameters. The further investigation of electron distribution on each structure and the effect of the size of the quantum dot on the electronic structure will be reported in other publications.

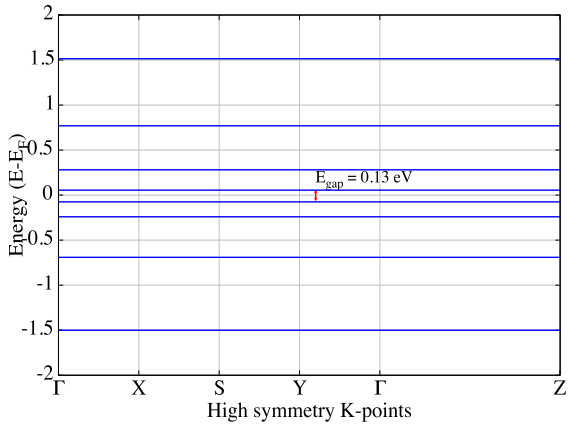


Figure 5. Density of states of GQD in a parallelogram with Fermi energy = -4.09 eV

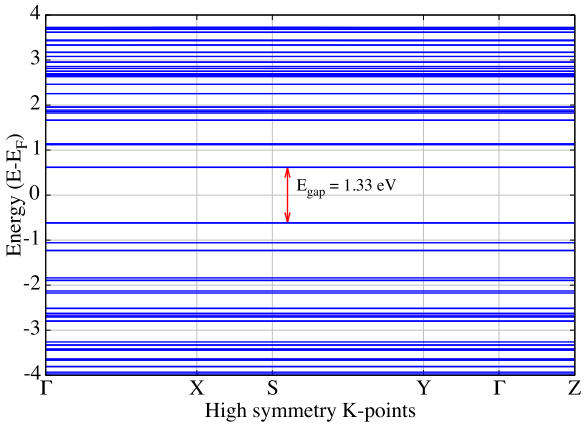


Figure 6. Density of states of GQD in hexagonal shapes with Fermi energy = -3.90 eV

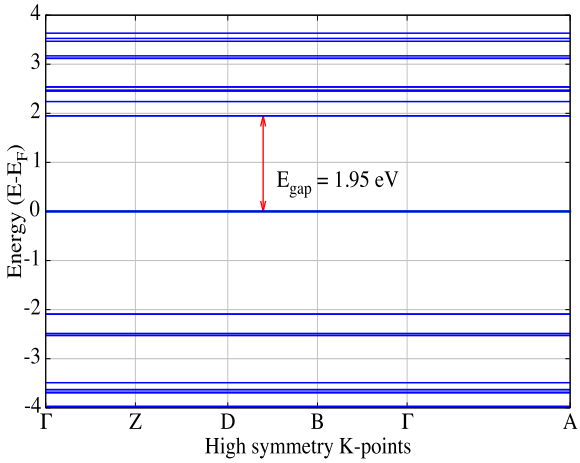


Figure 7. Density of states of GQD in triangular shapes with Fermi energy = -4.04 eV

CONCLUSION

The density functional theory (DFT) calculation was used to study the various shapes of quantum dots. The results showed that the band gap and the Fermi energy are strongly affected by the shape of the quantum dot. Further study of the effect of size in each shape and different functional groups in edge passivation is needed to give a complete description of band gap engineering in graphene quantum dot (GQD).

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