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Theoretical study on electronic properties of curved graphene quantum dots

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ABSTRACT

Electronic properties of curved graphene quantum dots (CGQDs) were studied using Density Functional Theory (DFT) method. Two shapes of the zigzag-edged CGQDs, i.e., rhomboidal (RGQDs) and hexagonal (HGQDs) graphene quantum dots, and each with five sizes were studied. For each GQD, its structure was curved along symmetry-unique folding axes at 2^0, 4^0, 6^0, 8^0, 10^0, 12^0, 14^0, and 16^0. There are four unique folding axes (FA1, FA2, FA3, and FA4) for RGQDS and only two axes for HGQDs (FA1 and FA2). The results showed that HOMO and LUMO energies of CGQDs depend on size, shape, folding axis, and folding degree. The band gap (HOMO-LUMO gap) at different folding degrees were monitored for all structures. For the folding at FA1, FA2, and FA4 of RGQDs and FA1 and FA2 of HGQDs, the narrowing of the band gap was observed, while only for the folding at FA3 of RGQDs the band gap widening was found. Orbital interactions can explain the narrowing/widening of the band gap of CGQDs. The energy used for curving GQDs (the deformation energy) depends on the size and folding axis but not their shape. The "armchair-like" folding has higher deformation energy than the "zigzag-like" one. The deformation energy is related to the folding strain and the number of the same-symmetry axis. The number of the same-symmetry axis is also related to the size of GQDs.

1. Introduction

Graphene is a two-dimensional monolayer of sp^2-hybridized carbons. Its hexagonal network, honeycomb lattice, is a primary building block for potential materials such as three-dimensional graphite, one-dimensional nanotubes, and zero-dimensional fullerenes [1–5]. Nowadays, graphene is applied to electronics and hi-technology devices. Because it has remarkable properties such as one-atom thinness, excellent transmittance and conductivity, extremely high stiffness, strong elasticity, and high thermal stability [6,7]. Bao et al. [8] using SEM and AFM techniques to study graphene membrane found that all graphene show periodic ripple. This is attributed to the strong in-plane (covalent bond) and weak out-of-plane (van der Waals) interactions of graphene [9]. Curved graphene has also been made. Several approaches such as mechanical exfoliation [10], AFM tip [11], chemical oxidation following by thermal treatment [12], printing or coating on a curved surface [8,13,14] have been reported to generate curved graphene. It has been shown that the deformation or curvature or ripple can change the optical and electronic properties of graphene [9–11,15–21]. From this behavior, we can make graphene into strain sensors [15,21] and novel electronic devices [13,22]. Graphene nanoribbons (GNRs) is the strip of graphene with the length of > 10 nm and the width of < 50 nm [23]. Zhang et al. [24] have reported that the curvature affects the electronic property of GNRs and found the band gap energy of GNRs to decrease at the increment of the curvature. Chang et al. [25] have studied the strain energy of curved GNRs and found it to become smaller for larger GNRs. Thus, the curvature influences the electronic and optical properties of graphene and GNRs.

Graphene quantum dots (GQDs) can be a single- or few-layer of graphene having dimensions in the range of a few nm to 100 nm in diameter, normally below 20 nm [26,27]. It can be prepared by top-down and bottom-up methods. In the top-down approach, GQD is generated from the decomposition and exfoliation of bulk graphene-based materials such as graphite. The process involves the use of concentrated acids, strong oxidizing agents, and high temperatures [28–33]. On the other hand, the bottom-up approach is achieved by the synthesis of aromatic molecules such as fullerenes, which often involves complicated reaction steps and specific organic reagents. However, this method can control the sizes and properties of the final products [28–33]. Recently, GQDs are being interested in bio-sensing, display, and energy applications. Because they have combined properties of graphene and quantum dots, such as high specific surface area, high mobility, good biocompatibility, strong luminescence,

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good hole transport ability, high solubility in various solvents, low toxicity, etc. [26,34–39]. Ritter et al. have found the decrease of the energy band gap when the size of GQD increases for both zigzag-edge and armchair-edge GQDs [40]. Apart from experimental evidence, there have been several theoretical studies on edge and size effects of GQDs [41–43]. Results from these theoretical works also support the finding of Ritter et al. Thus, the band gap of GQDs is tunable by modifying its size, edge, surface, and geometry [26,37,40,44] which leads to desired conductivity. Not only for flat GQDs, but electronic properties of curved GQDs (CGQDs) are also of interest. So far, there have been very limited numbers of studies on electronic properties of CGQDs. It has been reported that the electronic properties of GNRs can be affected by their sizes and edge similarly to GQDs [40]. Thus, we expect the curvature effect on electronic properties of GQDs to be the same as those of GNRs.

Unlike graphene, GQD is much smaller in size. Its properties depend on the size and locality, which make this material very interesting for applications. Since the electronic property such as the band gap energy is related to the optical property, it is then allowed GQD to be used as optical devices.

In this work, we focus on the effect of curvature deriving from folding axes and folding degrees as well as the shape and size of flat GQDs on their electronic properties. This understanding could then be applied to the design of GQDs-based electronic devices as well as strain sensors and optical devices.

2. Computational details

Two structural analogs of GQDs, i.e., rhomboidal- (RGQDs) and hexagonal- (HGQDs) shapes as shown in Fig. 1 were studied.

Initial GQD structures were created from a single layer of graphite taken from the library of the Material Studio 5.5 program [45]. Models of RGQDs denoted by anxn were generated from n x n hexagonal units, where n = 2–6. All dangling C atoms were terminated by H atom giving $C_{16}H_{10}$ (a2 × 2), $C_{30}H_{14}$ (a3 × 3), $C_{48}H_{18}$ (a4 × 4), $C_{70}H_{22}$ (a5 × 5), and $C_{96}H_{26}$ (a6 × 6), Fig. 1a. Three n x n rhombic structures can represent the hexagonal-shape. Models of HGQDs are denoted by bnxn for n = 2–6 and their terminal carbons were saturated by H atoms. Thus, they consist of $C_{24}H_{12}$ (b2 × 2), $C_{54}H_{18}$ (b3 × 3), $C_{96}H_{24}$ (b4 × 4), $C_{150}H_{30}$ (b5 × 5), and $C_{216}H_{36}$ (b6 × 6), Fig. 1b. Geometries of GQDs were fully optimized using DFT (Density Functional Theory) [46] with Perdew, Burke, and Ernzerhof (PBE) [47] functional and double numerical plus polarization (DNP) basis set [48,49] of DMol3 program in Material Studio 5.5 suite. To create CGQDs, geometrically optimized

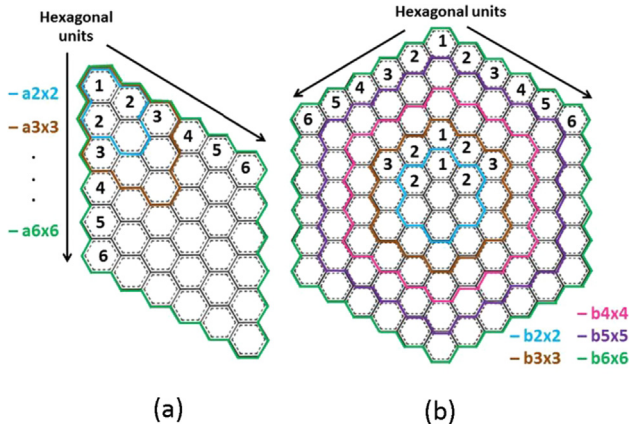

Fig. 1. (a) Rhomboidal-shape GQDs. (b) Hexagonal-shape GQDs.

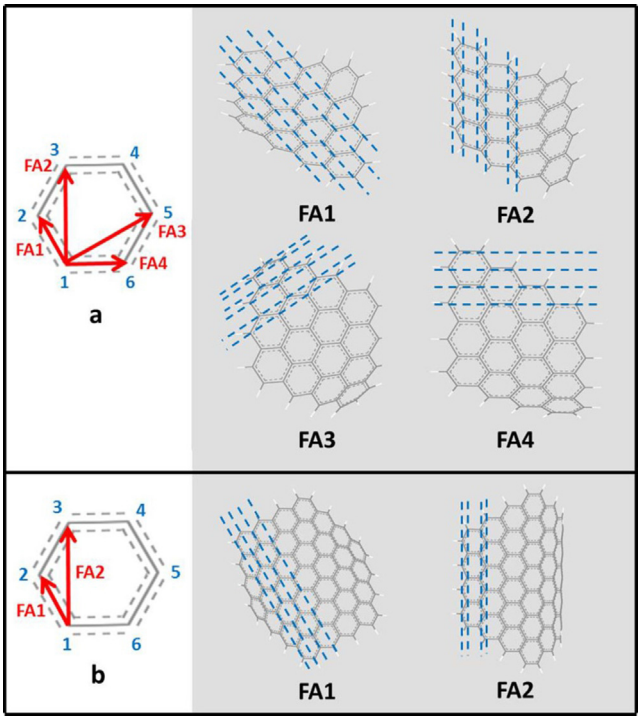

Fig. 2. Distinct folding axes of (a) RGQDs and (b) HGQDs.

GQDs were curved or folded along designated axes at the incremental of 2 to 16°.

Folding axes were defined from the unique atom-to-atom direction in the hexagonal unit (Fig. 2). There are four distinct folding axes, FA1, FA2, FA3, and FA4, for RGQDs and only two distinct folding axes, FA1 and FA2 for HGQDs (Fig. 2). However, it should be noticed that for a particular distinct folding axis there is more than one axis of the same symmetry or type. The number of "same-symmetry" axis depends on the folding axis and the size of GQDs. To curve the GQD to a certain degree along with a particular folding axis, all same-symmetry axes of that type will be folded simultaneously at the designated degree. It happens that for RGQDs the folding by FA1 and FA4 axes is through carbon atoms at the zigzag position ("zigzag" carbons), while the folding by FA2 and FA3 axes is through "armchair" carbons. We denoted the former by the "zigzag-like folding" and it has equal spacing between the same-symmetry axes. The latter is denoted by the "armchair-like folding" where it has the alternated short and long spacing between the same-symmetry axes. For HGQDs, the folding by FA1 belongs to the zigzag-like folding and by FA2 fits the armchair-like folding. This observation is also shared by Casabianca [50].

For CGQDs, only positions of hydrogen atoms were optimized at the same level of theory as those of GQDs. HOMO and LUMO energies of GQDs and CGQDs were also obtained at the same level of theory.

3. Results and discussion

3.1. HOMO-LUMO gaps

3.1.1. Rhomboidal-shape CGQDs

The reliance of HOMO-LUMO gaps of RGQDs on their sizes, folding axes, and folding angles was observed and displayed in Fig. 3. However,