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Exploring pentagon-heptagon pair defects in the triangular graphene quantum dots: A computational study

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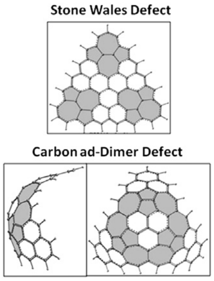
HIGHLIGHTS

- Defect formation energy depends on positions of SW defects.
- Defective GQDs with isolated SW defects are the most favorable.
- Introducing of CD defects induces a curvature leading to cone-like structure.
- Defect formation energies for CD defective GQDs are higher than those for SW ones.
- Electrophilicity: CD defective GQDs > SW defective GQDs > perfect GQDs.

GRAPHICAL ABSTRACT



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ABSTRACT

We have applied density functional calculations to investigate Stone Wales (SW) and carbon ad-dimer (CD) defect formation in triangular graphene quantum dots (GQDs). According to our results, defect formation energies depend on the positions of SW defects, such that the rotation of the C—C bond located near the vertex of triangular GQD is easier than the rotation of other C—C bonds. Therefore, the multiply defective GQDs with isolated SW defect sites are the most favorable while the formation of pentalene like structures in the connected SW defect sites costs larger formation energies. Introducing of carbon dimer defects on a triangular GQD induces a curvature at the defective sites, which leads to a more complex defect configuration with cone-like structure in the CD defective GQD with three defective sites. Then, formation energies for CD defective GQDs are higher than those for SW defective ones. The electrophilicity values calculated for SW and CD defective GQDs are greater than those for pristine GQDs. Moreover, perturbation of strong sp^2 bonding network of graphitic carbons on the GQD, leading to the formation of more localized C—C bonds, results in further electron deficiency of multiply SW and CD defective GQDs with increasing of electrophilicity values.

1. Introduction

Carbon-based nanostructures have attracted lots of interest in condensed matter physics and material science due to their unique mechanical, optical, and electronic properties [1–3]. Among these carbon-based nanostructures, the low-dimensional monolayer sheets such as graphene quantum dots (GQDs) [4,5], graphene nanoflakes (GNFs) [6], and one-dimensional graphene nanoribbons (GNRs) [7–9] become one of the most exciting topics in recent research. Many unconventional electronic properties of these graphene nanostructures, such as metallic ferromagnetism and magnetic moments, make those a promising material for future

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nanoelectronics and nanodevices such as spin memory, transistors, solid-state qubits, and perhaps optoelectronics applications [10–14]. Wang et al. [6] characterized arbitrarily shaped hydrogen-terminated graphene nanoflakes with large spin using benzenoid graph theory and first-principles calculations. They demonstrate that the spin of a GNF depends on its shape due to topological frustration of the π-bonds. First principle calculations have also been performed to investigate the electronic properties of rectangular shaped graphenes, finite length GNRs [15,16], and the calculated results reveal that, in addition to edge quantum entrapment from ribbon width, finite size effects along the ribbon length affect the electronic states. Several theoretical calculations have been carried out to study the electronic properties and magnetism for different shaped zero-dimensional GQDs [17]. For example, Yu et al. [18] investigated the electronic properties of N/B doped triangular GQDs with hydrogen passivated zigzag edges in order to explore how N/B doping influences the electronic properties of GQDs. Then, Anafcheh et al. [19] investigated the magnetic properties of N/B doped triangular GQDs by computing the grid distribution of nucleus independent chemical shift (NICS) in order to monitoring shielding effects around molecule. Triangular GQDs with zigzag edges have degenerate zero-energy states and show metallic ferromagnetism, in which the net spin increases linearly with its size, indicating that the net magnetic moments in triangular GQDs are usually satisfied with Lieb's theorem [20].

Defects have been proposed to play a major role in the growth and subsequent annealing down to the structurally ordered ground state of carbon nanostructures. In fact, it is the second law of thermodynamics that dictates the presence of a certain amount of disorder in crystalline materials [21,22]. On the other word, it is thermodynamically impossible for defect densities to go to zero, even in highly pure crystalline systems. One might imagine that the strong sp^2 bonding network of graphitic carbons would energetically preclude defect formation. But various studies have shown that atomic-scale intrinsic defects in carbon-based nanostructures can strongly influence the physical and chemical properties of such systems and can lead to interesting new applications [23–26]. The line and screw defects, interstitials, and bond rotation defects are all observed in carbon-based nanostructures in considerable numbers. Extensive literature has been developed around defects in carbon-based nanostructures, much of which is applicable to graphene-like structures [21,27,28]. It should be noted that in spite of the relevance theoretical works on GQDs so far, there has been no theoretical discussion on the defective GQDs in the literature. So, in the present work, we extend the study of the defects to triangular GQDs. A very important topological defect in carbon-based nanostructures is pentagon-heptagon pair, Stone-Wales (SW) [29] and carbon ad-dimer (CD) defect [30], leading to the formation of a 5-7-7-5 and 7-5-5-7 ring pattern, respectively, see Fig. 1. The formation of these pentagon-heptagon pairs with 5-7-7-5 arrangement, Stone-Wales defect, can be considered to emerge from the regular hexagonal lattice by a 90° rotation of a C–C bond which enables a pair of hexagons and pair of pentagons to switch places. In fact, it dates back to 1986, when Stone and Wales pointed out that there are many stable C_{60} isomers, which do not follow the well-known isolated pentagon rule, and which are related to the I_h form by transformations involving the rotation of two carbon atoms around the center of the bond connecting them [29]. In the 1999, Orlikowski et al. [30] introduced another pentagon-heptagon pair defect with the 7-5-5-7 arrangement, the carbon ad-dimer (CD) defect, which is obtained by the adsorption of a C_2 dimer to a strained carbon nanotube (CNT). They proposed a mechanism based on it for forming tube-tube junctions. Sternberg et al. [31] reveals that for an unstrained tube the barrier for formation of the 7-5-5-7 (CD) defect is much lower than that for the 5-7-7-5 (SW) defect, and the former is also thermodynamically more favorable than the latter for most CNT sizes.

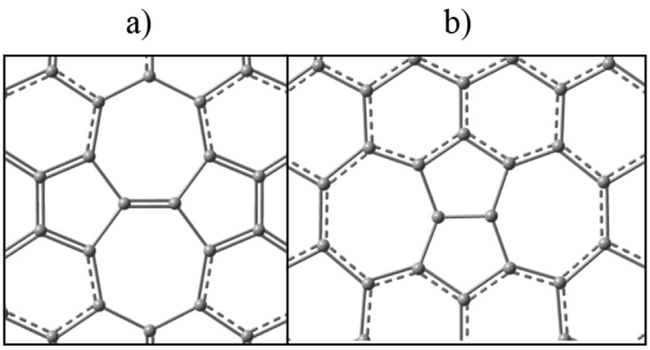

Fig. 1. Schematic structures of a) Stone-Wales (SW) and b) carbon ad-dimer (CD) defects, leading to the formation of a 5-7-7-5 and 7-5-5-7 ring patterns, respectively.

2. Computational method

All density functional theory (DFT) calculations are performed using GAMESS suite of programs [32]. First, a selected triangular GQD with hydrogen passivated zigzag edges with size $n = 6$ is considered as a starting point for the design of defective GQDs. A triangle representative patch (LMN) is considered on the surface of the triangular GQD as being the smallest structure unit which is equal to 1/6 of the total surface, see Fig. 2. In this representative model: C1 to C6 represent six different kinds of carbon atoms; b1 to b6 represent six distinct C–C bonds. Geometries of the perfect, SW and CD defective GQDs are optimized at the unrestricted Becke three-parameter LeeYang-Parr (UB3LYP) methods with the 6-31G* basis set [33–35]. The standard 6-31G* basis set is employed for being affordable and accurate enough for geometry optimization of even large molecules [36,37]. The optimized structures of SW and CD defective GQDs and their parent are subjected to the calculation

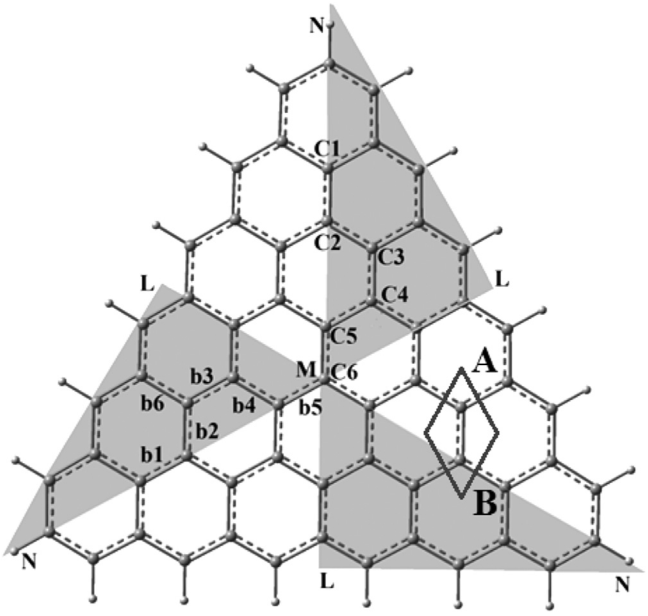

Fig. 2. The representative patch LMN and geometry of the triangular graphene quantum dots (GQDs).