Physica B: Condensed Matter 537 (2018) 77–86

Contents lists available at ScienceDirect

Physica B: Condensed Matter

journal homepage: www.elsevier.com/locate/physb

First principles study of edge carboxylated graphene quantum dots

Hazem Abdelsalam [a,*], Hanan Elhaes [b], Medhat A. Ibrahim [c]

[a] Department of Theoretical Physics, National Research Centre, Giza, 12622, Egypt
[b] Physics Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, 11757, Cairo, Egypt
[c] Spectroscopy Department, National Research Centre, Giza, 12622, Egypt

ARTICLE INFO

Keywords:
Graphene quantum dots
Density functional theory
COOH
Stability
Density of states
HOMO/LUMO

ABSTRACT

The structure stability and electronic properties of edge carboxylated hexagonal and triangular graphene quantum dots are investigated using density functional theory. The calculated binding energies show that the hexagonal clusters with armchair edges have the highest stability among all the quantum dots. The binding energy of carboxylated graphene quantum dots increases by increasing the number of carboxyl groups. Our study shows that the total dipole moment significantly increases by adding COOH with the highest value observed in triangular clusters. The edge states in triangular graphene quantum dots with zigzag edges produce completely different energy spectrum from other dots: (a) the energy gap in triangular zigzag is very small as compared to other clusters and (b) the highest occupied molecular orbital is localized at the edges which is in contrast to other clusters where it is distributed over the cluster surface. The enhanced reactivity and the controllable energy gap by shape and edge termination make graphene quantum dots ideal for various nanodevice applications such as sensors. The infrared spectra are presented to confirm the stability of the quantum dots.

1. Introduction

Flake-like graphene quantum dots (GQDs) have attracted much attention due to their unique electronic [1–5] and optical [6–10] properties. The distinguished properties of GQDs arise from the electron confinement in the finite size graphene cluster that leads to the opening of energy gap and quantization of electronic energy. Cutting graphene sheet into small clusters result in creation of GQDs with different shapes and edges. Energy gap strongly depends on shape, edges, and size of the GQDs. Moreover, new states (called edge states) appear in the low energy region that also depend on the size, shape (hexagonal and triangular), and edge termination (zigzag and armchair). Tight-binding (TB) calculations [1,2,5] show that there are two types of edge states in flakes with zigzag termination, zero energy states (ZES) that are degenerated and located exactly at the Fermi level and dispersed energy states (DES) that fill the low energy region and are symmetrically distributed around it [1,2,5,11,12]. ZES appear in triangular GQDs while DES appear in other shapes such as hexagonal and circular GQDs. Due to the inclusion of electron-electron interaction in the density functional theory (DFT) calculations, a tiny energy gap is opened between ZES [2,6,9]. In general, TB or DFT calculations confirmed the appearance of edge states in GQDs. Tuning the energy gap and edge states of GQDs paves the way toward numerous applications that are not possible for a bulk graphene [13–15].

The electronic and optical properties can be tuned by chemical functionalization of the GQDs. Al-Aqtash's and Vasiliev's investigations on the electronic properties and geometrical structure of carboxylated graphene have reported significant changes in the structure of GQDs after the attachment of the COOH group to the surface [16]. Mandal et al. have demonstrated that the nanohybrid GQD-porphyrin can be a potential candidate for application in solar cell [17]. Chen et al. have reported that the photoluminescence properties of GQDs can be tuned precisely by attaching chemical functionalities [18]. Moreover, different functional groups attached to the edge of hexagonal GQDs with zigzag termination have been studied by Y. Li et al. [19]. The authors provide a comparison between the effect of different functional groups on tuning the electronic and optical properties.

On the other hand, molecular modeling with different level of theory is an effective tool of studying the physical, chemical, and biological properties of carbon nanomaterials. It could be utilized for some of graphene-derivatives such as fullerene to test the functionality of its surface for gas sensing applications [20–22]. Molecular modeling could be also applied to study the effect of surface modification and biological activity for applications as anti-protease inhibitor [23,24]. Recently, the different functionalities of carbon nanomaterials have been reviewed [25]. It is noticed that substitution could affect the biological behavior [26] and electronic properties of fullerene [27,28].

* Corresponding author.
E-mail address: hazemabdelhameed@gmail.com (H. Abdelsalam).

https://doi.org/10.1016/j.physb.2018.02.001
Received 11 December 2017; Received in revised form 30 January 2018; Accepted 1 February 2018
Available online 6 February 2018
0921-4526/© 2018 Elsevier B.V. All rights reserved.

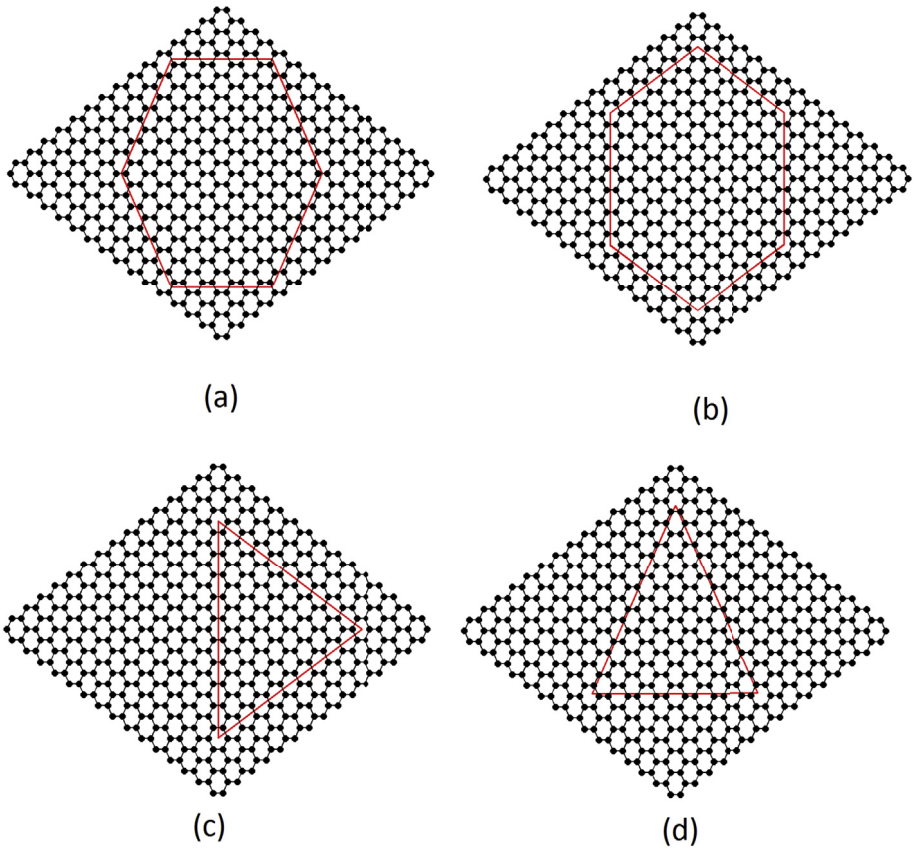

Fig. 1. Cutting graphene sheet into small clusters, (a) AHEX, (b) ZHEX, (c) ZTRI, and (d) ATRI.

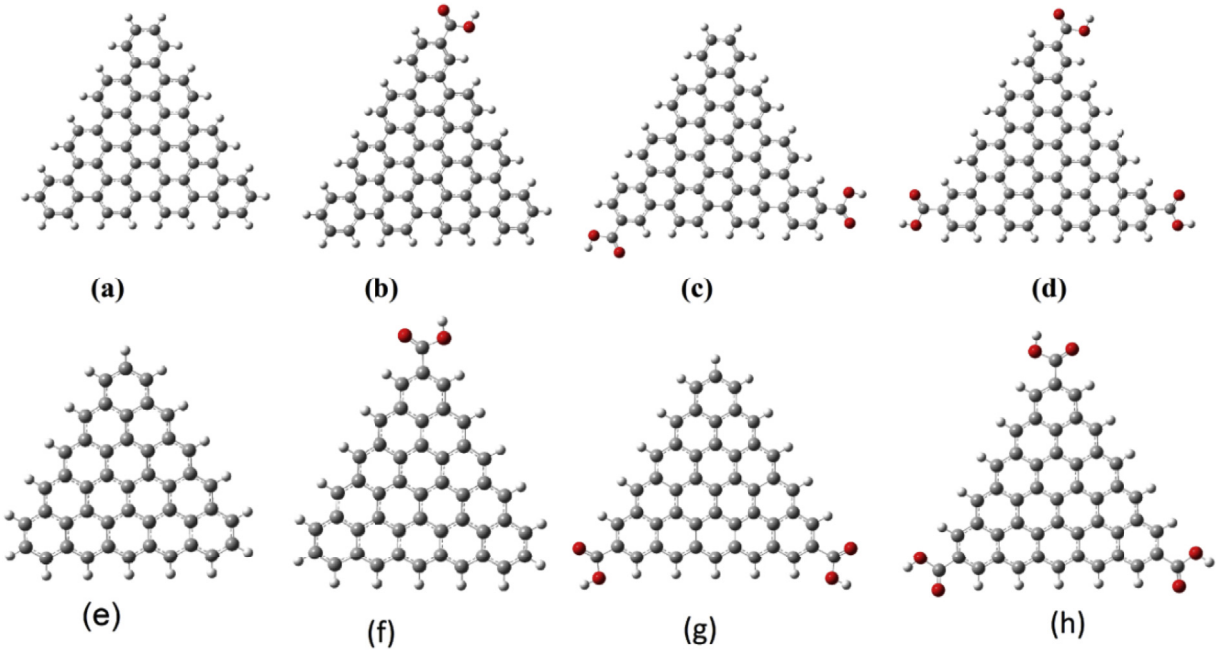

Fig. 2. The optimized structures of ATRI (a, b, c, d) and the optimized structure of ZTRI (e, f, g, h) without and with edge functionalization with carboxyl groups.

It is clear that carbon nanomaterials could be directed toward certain application with substitution and/or functionalization with certain functional group. Based upon the above considerations, the present work is conducted to investigate the structure stability and electronic properties of edge carboxylated GQDs. To the best of our knowledge no work has been done on edge functionalization of graphene quantum dots of hexagonal and triangular shapes with armchair and zigzag terminations. We study the effect of attaching different carboxyl groups to the edges of the GQDs on electronic density of states, energy gap, total dipole moment, and infrared (IR) spectra.

Download English Version:

https://daneshyari.com/en/article/8160787

Download Persian Version:

https://daneshyari.com/article/8160787

Daneshyari.com