Journal of Materials and Electronic Devices 6 (2021) 16-21

DFT calculations on the small zigzag C3N nanoribbons:

S. SENTURK DALGIC

[1]Trakya University, Department of Physics, Edirne, Turkey

In this work, the structural, electronic and Physico-chemical properties of small zigzag C3N nanoribbons have been investigated by density functional theory (DFT). The atomic structure of 1-D zigzag C3N nanoribbons have been created from the honeycomb structure of 2D- C3N monolayer, with carbon atoms in the centre and n=4 zigzag edges (Z4- C3N). The CCN edge atomic configuration of Z4-C3N nanoribbons has been studied without strain. The charge analysis, density of states (DOS) and projected density of states (PDOS) have been established with DFT/QE calculations. The results indicate that the presented atomic configuration of Z4-CCN- C3N nanoribbon exhibits metallic character with the indirect bandgap of 0.379 eV, which is consistent with the literature. The size effect on 4Z- C3N nanoribbons is strong. The carbon atoms in the centre of Z4- C3N nanoribbon improve the dimensional reduction of pristine 2D C3N compared to other configurations. The small band gap value contributes to the high conductivity for Z4-CCN- C3N nanoribbons. Thus, the obtained good electronic properties such as electrophilic and maximum electron flow parameters suggest that the presented Z4- C3N nanoribbons can be applied in Lithium-Ion Batteries (LiBs).

Keywords: C_3N*, zigzag nanoribbons, 1D-polyaniline, DFT, Quantum Espresso*

Submission Date: 20 June 2021
Acceptance Date: 24 October 2021

**Corresponding author: serapd@trakya.edu.tr , dserap@yahoo.com*

1. Introduction

Nowadays, the two dimensional (2D) materials have a great attention because of their unique properties which are different from their bulk structure in 3D [1,2].

Recently, 2D polyaniline nanosheet with stoichiometric formula C_3N has been synthesized [3]. To date, the tuneable structural, electronic and magnetic properties of C_3N nanostructures have been reported [4-8]. The C_3N nanostructures can be classified as: 2D- C_3N Nano sheet (NS) and 1D (one dimensional) nanoribbon. (NR) and nanotube (NT). It has been reported the adsorption behaviours of some molecules and nanoparticles on those C_3N surfaces [4,5].

On the other hand, the properties of nanomaterials are dependent on size, shape and dimension. By converting 2D Nano sheets to 1D nanoribbons, the fundamental changes occur in material properties due to the dimensional effect. When the size of material is reducing to quantum size, the quantum confinement effect is occurred with the finite width of the ribbon. The morphological effect in nanoribbons can

be defined as the difference in some material properties of different edge states or edge configurations.

Thus, the transport properties of ribbons are affected by cutting direction, nanoribbon width and the functionalizing of edge states [6-8].

Therefore, 1D nanoribbons are very important subject in developing new generation materials and their applications in nanotechnology.

On this line, the C_3N structure leads to interesting phenomena because of the existence of two different atoms which are absent in the structure of Graphene nanoribbons (GNR). The existence of nitrogen atoms causes the difference in their electronic properties. The single layer C_3N was first reported to be an indirect band gap semiconductor and three planar structure were suggested as known of allotropes of C_3N monolayer [7]. According to edge structure C_3N nanoribbons are classified as zigzag and armchair type nanoribbons by representing Z- C_3N and A-C_3N, respectively. The edge state effect on the material properties of C_3N nanoribbons, such as atomic, electronic and magnetic, have been studied by a number of researchers [6-8]. Tagani and co-workers have investigated the electronic and magnetic properties of n- C_3N nanoribbons with n=8-18 [6]. Bafekry and co-workers have also studied the atomic, structure and electronic properties of n- C_3N nanoribbons with n=4-11 which depend on the nanoribbon edge states and width [8]. Those reported results include the quantum size effect and edge effect (morphology effect) on n- C_3N nanoribbons. A very interesting point has been noted for Z- C_3N nanoribbons that they are magnetic materials when they are not terminated by hydrogen atoms [6].

The hydrogen terminated Z- C_3N nanoribbons show a transition from a metal to semiconductor when both edges have nitrogen atoms (CN-HZC_3N) in contrast to the hydrogen terminated zigzag graphene nanoribbons. The hydrogen terminated C_3N nanoribbons having carbon atoms in one edge (CCN-HZ C_3N) are metals. [6]. Therefore, CCN-HZ C_3N nanoribbons have small band gaps and high conductivity, which enables them to be used in Li-ion battery applications [7].

It has found that the zero band gaps for the largest hydrogen terminated Z-C_3N nanoribbons due to the size effect. Whereas, the electronic and magnetic properties of n-Z C_3N nanoribbons are affected by the strain rather than size and edge state morphology.

Bafekry and co-workers have demonstrated the band gap reduction with increasing width of the ribbon. The hydrogen terminated C_3N nanoribbons in the CCN edge state become metallic at the large widths. It is clear that, the size effect on 4Z- C_3N nanoribbons is strong. The dimensionality effect also could be seen clearly as a strain effect on 4Z- C_3N nanoribbons. With this in mind, we studied with 4Z- C_3N nanoribbons in the CCN edge state configuration with carbon atoms placed at the centre of nanoribbon, which are not investigated so far.

The results demonstrate that the presented small 4Z-C3N nanoribbon has small energy band gap. The carbon atoms at the centre of Z4- C_3N nanoribbon, improve the dimensionality reduction of pristine 2D C3N by comparing the other configurations without centre of carbon atoms. The obtained superior electronic properties of presented Z4-C3N nanoribbons with carbon atoms placed at the center can be applicable in LiBs.

2. Materials and Method

In this work, we have performed density functional theory (DFT) with Quantum Espresso codes, version 5.2.1. [9] The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) has been used for the exchange-correlation, and to deal with electron-ion core interactions the projected augmented wave method (PAW) has been employed. A cut-off energy of 45 Ry was selected for the plane waves used to expand the Kohn-Sham orbitals, and 350 Ry for the charge density. The automatic k point is used. van der Waals corrections has been taken into account using the Grimme-D3 method [9].

The 4Z- C_3N nanoribbons with CCN edge state used in this work have been created from honeycomb structure of 2D-C_3N monolayer with optimized lattice constant is 4.861Å, which agrees well the previous calculations [6-8].

The bond lengths of carbon atoms C-C (d_{CC}) and carbon-nitrogen atoms C-N (d_{NC}) are 1.403Å and 1.4029Å, in the optimized 2D- C_3N monolayer, respectively.

According to the three different edge profiles Z-C_3N nanoribbons can be investigated. The one edge is combined with the C atoms and the other edge with C and N atoms, as indicated C-CN. Secondly, there is C-C edge on both sides as CC. Third one is C-N atoms on both sides, namely CN. Here, the first type atomic structure is used

Another classification of the nanoribbons is characterized in terms of the number of C and N atoms as n number in the unit cell. Hence, n defines the number of C-N pairs in the studied unit cell along the nanoribbon axis. Thus, they can specify as n Z - C_3N and n A-- C_3N for zigzag and armchair edged nanoribbons, respectively. On the other hand, n denotes the number of zigzag C-C or C-N chains along the nanoribbon axis for zigzag nanoribbons, In this work, n=4 with zigzag edged C_3N nanoribbon is taking into account as Z4 - C_3N nanoribbon. Fig. 1 shows the hydrogen terminated zigzag C_3N nanoribbon with even number of n=4.

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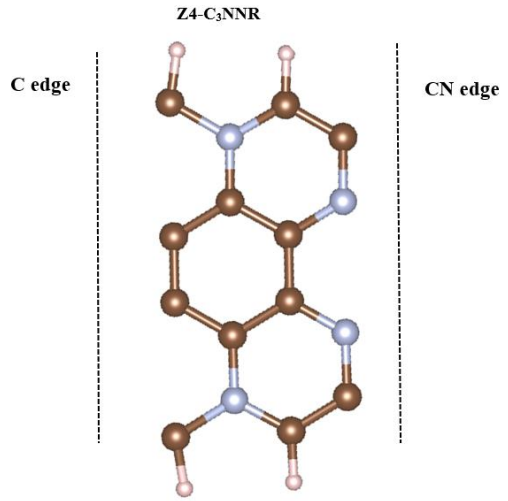

Fig.1. The top view of optimized atomic structure of Hydrogen terminated Zigzag- C_3N nanoribbon with n=4

The Chemical stability of the material was mainly influenced by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) where the HOMO and LUMO levels play an important role in its electrical properties. Band gap energy, E_g can be expressed in terms of E_{LUMO} and E_{HOMO} energies as follows:

$$E_g = E_{LUMO} - E_{HOMO} \quad (1)$$

The electrical conductivity of a material can be determined as:

$$\sigma \propto \exp\left(-\frac{E_g}{2k_bT}\right) \quad (2)$$

where E_g is the bandgap, T is the temperature, k_b is the Boltzmann constant.

Parameters related to E_{LUMO} and E_{HOMO} energies such as chemical potential (μ), hardness (η), electronegativity (ϰ), electrophility index (ω), nucleofugality (ΔE_n), electrofugality (ΔE_e), maximum electron flow (ΔN) were calculated using the following equations.

$$\mu = -\chi \cong \left(\frac{E_{HOMO}+E_{LUMO}}{2}\right) \quad (3)$$

$$\eta = \frac{E_{LUMO}-E_{HOMO}}{2} \quad (4)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

$$\Delta E_n = \frac{(\mu+\eta)^2}{2\eta} \quad (6)$$

$$\Delta E_e = \frac{(\mu-\eta)^2}{2\eta} \quad (7)$$

$$\Delta N = -\frac{\mu}{\eta} \quad (8)$$

In order to understand electronic properties of Z4- C_3N nanoribbon, the DOS and projected DOS (PDOS), fermi level E_f for the presented atomic configuration have obtained by DFT/ QE calculations

3. Results and Discussions

As indicated in previous section, the C_3N nanoribbon studied in this work was formed from a hexagonal hydrogen terminated C_3N nanosheet (C_3NNS) by cutting along the x directions. For this reason, the atomic structure of Z4- C_3N nanoribbon have different atomic profile of carbon and nitrogen atoms by comparing with others [6,8]. Results of the structural optimization of Z4- C_3N nanoribbon, the calculated energy contributions to the total energy are shown in Table 1. The calculated electronic and physicochemical properties are presented in Table2 and Table3, respectively.

Table 1. Contributions to total energy for Z4- C_3N nanoribbons calculated by GGA-PBE type pseudopotential

Structure	***Z4-* C_3N *nanoribbon***
Energies (Ry)	PBE-kjpaw
Total Energy	-337.5723
One-electron contribution	-1269.6087
Hartree contribution	642.980
xc contribution	-80.23865
Ewald contribution	475.22825
One-center paw contrib.	-105.93175

It is indicated in Table 1, the largest contribution to total energy is that of one-electron contribution energy. It has found the energy per atom is -16,878 Ryd for Z4- C_3N nanoribbon.

The charge analysis for nanoribbons is important issue to understand their electronic and optical properties. After the relax calculations, the charged values of each atom in Z4-C3N nanoribbon are presented in Fig. 2. Löwdin charges were calculated by the Löwdin atom and basis function population.

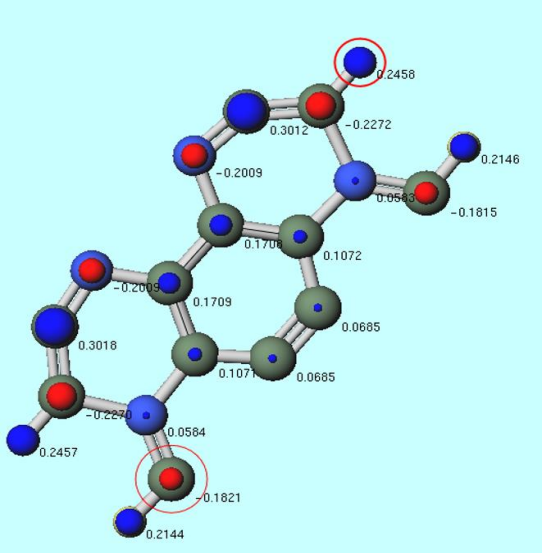

Fig.2. The Löwdin charges of optimized Z4- C_3N nanoribbon

In the stage as n is even number for n- C_3N nanoribbons, one edge is C atoms and the other edge is from C and N atoms, as a result the N edge and C edge are charged positively and negatively, respectively. Because of that polarization, the higher potential has been felt by electrons at the N edge, the lower one at the C edge which is contributes as a factor reducing the band gap, such that valence band maximum (VBM) and conduction band minimum (CBM) are localized on C edge and N edge, respectively.

However, in Fig. 2., the carbon atoms placed at the centre of nanoribbon have positively charged. The two C-N paired at CN edge side have negative and positive charges, respectively. On the side where all of the edge atoms are carbon, all carbon atoms except those bonded with hydrogen atoms are positively charged.

Thus, the main factor is here the charge of edge atoms. Thus, the band gap depends on the type of edge with the existence of nitrogen atoms. Therefore, the electronic properties of C3N nanoribbons could be modulated by controlling the energy band gap or atomic ordering in nanoribbons. The electronic properties of Z4-C3N are given in Table 2.

Table 2. E_{LUMO} and E_{HOMO} energies, Band gap energy, E_g and Fermi energy, E_F values for Z4-C3NNR. (All energies are in eV)

Properties	***Z4*- C_3N *nanoribbon*** **PBE-kjpaw**
E_{HOMO}	-4.7086
E_{LUMO}	-4.3296
E_g	0.379
E_F	-4.519

As indicated in Table 2, the energy gap of hydrogen terminated Z4- C_3N nanoribbon is about 0.379 e V, which is a very close to the those obtained in previous literature report as 0.39 e V (0.40 eV) for pristine non-hydrogenated 2D- C_3N nanosheet allotropes.

The hydrogen terminated C_3N nanoribbons exhibit both metallicity or semi conductivity depends on the type of edge state. Guo and co-workers [7] have reported the results for hydrogen terminated small zigzag C_3N nanoribbons 6-CC, 7CCN edges are metallicity where for CN edge on both side zigzag nanoribbons presents as semi conductivity.

In order to understand the electronic nature of the system, we have calculated the density of states (DOS) and projected density of states (PDOS) plots for the 4Z- C_3N nanoribbons with carbons placed at the centre. The total DOS plot for the studied C_3N nanoribbon illustrated in Fig.3.

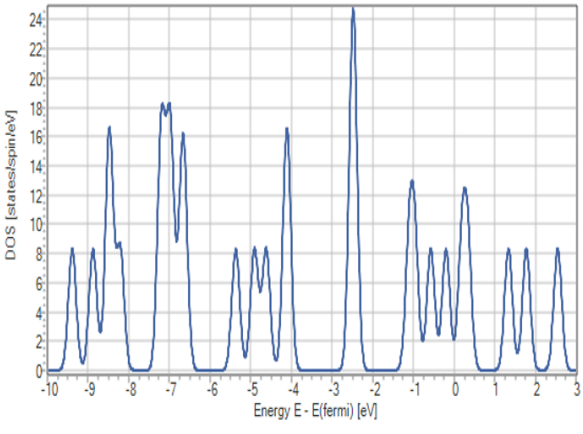

Fig.3. The calculated total DOS graph for of Z4- C_3N nanoribbon

The contribution of all atoms to the DOS as PDOS, the C-N pairs at the CN edge and C atoms at the C edge structure are illustrated, in Figs 4a-b-c, respectively.

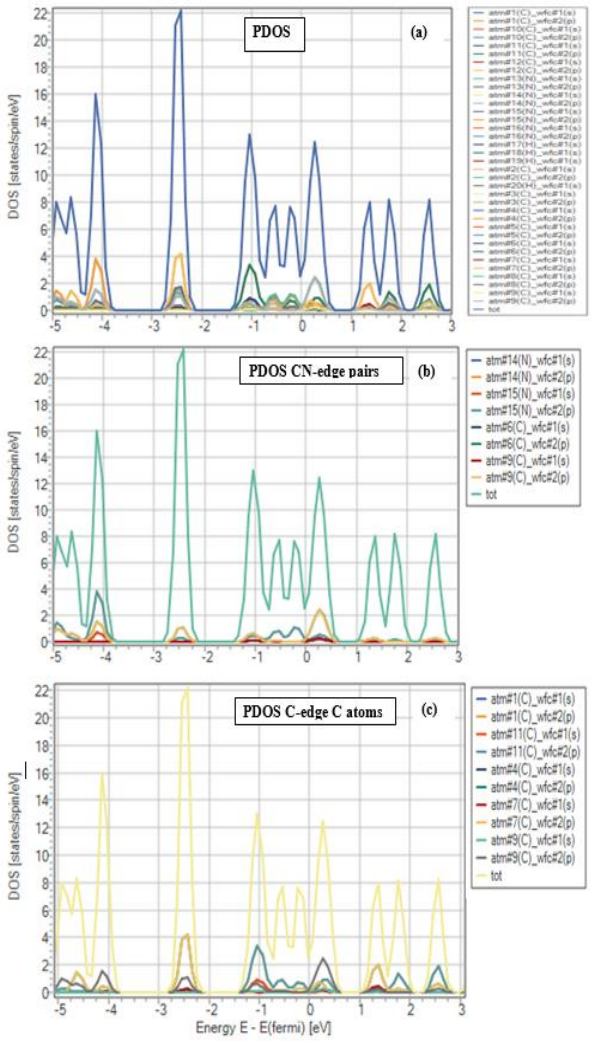

Fig.4. The calculated PDOS graphs for Z4- C_3N Nanoribbons (a) PDOS (b) CN edge atoms contribution (c) C edge atoms contribution to PDOS

The results given in Table 2 and calculated DOS and PDOS graphs illustrated in Figs.3-4 are completely consistent with the previous reports [6-8]. The presented atomic structure of the C_3N nanoribbon shows metallic character as indicated in Figs. 3-4. Our energy gap value is smaller than others because of the carbon atoms placed at the center. In Fig.3, the Z4- C_3N nanoribbon exhibits metallic behaviour because of the energy band gap is not around the Fermi level. However, it could be demonstrating an indirect band gap of 0.379 e V. Here, the 2p state of carbon atoms at the C edge side more affected than the nitrogen atoms placed at CN edge side.

Moreover, we have calculated some physicochemical properties based on HOMO and LUMO energies, given in Table 3.

Table 3. Physicochemical properties of Z4- C_3N nanoribbon

Properties	Z4- C_3N nanoribbon
$\boldsymbol{\mu}$	-4.519
$\boldsymbol{\eta}$	0.189
$\boldsymbol{\omega}$	53,884
$\boldsymbol{\Delta E_e}$	58,498
$\boldsymbol{\Delta E_n}$	49,460
$\boldsymbol{\Delta N_{max}}$	23,847

The results in Table 3 indicate the presented Z4-CCN- C_3N nanoribbon is metallicity. The calculated global hardness (η) value is 0.189 that the less hardness index shows more reactive system. The lower Eg values indicate higher electrical conductivity, reactivity and sensitivity that can be obtained Eq. 2.

With the electronic chemical potential of the nanoribbon, the direction of charge transfer is completely determined. The electrophile index (ω) exhibits the chemical type of the system that can accept electrons from the environment. The high electrophile index (ω) of 53.884 demonstrates that the electron accepting capability of the studied C3N nanoribbon is superior.

The calculated electrofugality (ΔE_e), and the nucleofugality (ΔE_n) and maximum electron flow (ΔN) values are also high which are completely consistent with other values given in Table 3 and literature. ΔN_{max} refers to the maximum charge transfer to the electrophile. . ΔN_{max} determines the ability of the system to obtain additional electronic charge from the medium that defines the charge capacity of the nanoribbon. The obtained value of ΔN_{max} is about 23.847.

4. Conclusion

In this work, the DFT calculations on the smallest zigzag C_3N nanoribbon (hydrogen terminated) with n=4 and carbon atoms placed at the center were first presented.

The C-CN edge state atomic structure was investigated for the zigzag 4Z- C_3N nanoribbon with the central carbon atoms. The charge, DOS and PDOS were also calculated and analyzed to understand the electronic properties of the system. The results indicate that the presented atomic configuration of Z4- C_3N nanoribbon exhibits metallic character with the indirect band gap of 0.379 eV which is consistent with literature. It has been found that the proposed atomic structure shows superior electronic and Physico chemical properties compared to those obtained in previous studies.

To sum up, the metallicity character and small band gap value contribute to the high conductivity for Z4-CCN- C_3N nanoribbons. Thus, its good electronic properties are beneficial for the application in Lithium Ion Batteries (LiBs).

The results for the width effect on the zigzag and armchair type C_3N nanoribbons with carbon atoms placed at the center, will presented in near future [10]

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