ELECTRONIC TRANSPORT PROPERTIES OF [6+Nx12]ANNULENE NETS

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Abstract

We analyzed electronic transport properties of graphene nanoribbons (GNR) patterned by [6+Nx12]annulene-like quantum antidots. We tried to simulate [18]annulene, [30]annulene and [42]annulene antidots placed on passivated graphene nanoribbon of appropriate width and length. Our results are predicting electronic transport properties similar to graphene. It is shown by analyzing the GNR transmissivities calculated by Extended Hückel self-consistent field model (EH-SCF). These structures can be used in future as a high precision molecular sieve for separation of almost any size of molecule because of its holes modifiable by using different [6+Nx12]annulenes. The sieving can be potentially controlled and/or measured by the changes of potential and/or current flow in chosen GNR layer of the sieve. These structures can be potentially usable for water desalinization, separation of industrially exhaled gases or for mining rare metals from ocean. It can be used as well as a totally new carbon-based nanomaterial with potentially interesting mechanical, optical or electronic transport properties and compatible with graphene. These structures can be prepared by the means of ion (or electron) beam lithography or by the bottom-up approach from chemical precursors in the future.

Keywords: annulene, graphene nanoribbon, transmission

1. INTRODUCTION

Graphene (and other two-dimensional materials) has attracted a big attention in recent years as a promising material for molecular electronic devices. Graphene is a polycyclic aromatic hydrocarbon, forming a single atomic layer of carbon atoms in infinite planar hexagonally orientated lattice. It has extraordinary electrical and mechanical properties, such as the high conductivity or very high spin transport coherence length [1]. In our work, we hypothesized a completely new nanomaterial based on graphene which we call annulene net. The single benzene molecule, which has six carbon and six hydrogen atoms can be treated as [6]annulene. Next similar molecule which is symmetrical, stable and aromatic is [18]annulene and further it can be extended infinitely to [6+Nx12]annulene, where N is natural number (e.g. on Fig. 1). If we treat graphene as infinite number of benzene molecules, let us assume annulene net as is some kind of extension of graphene where we are connecting together annulene molecules, in right way. By this idea, we can construct a thin layer, which has periodic structure somehow comparable with graphene. In our simulations we are trying to show, that this material is not even possible to construct (as it is a stable form of carbon) but also has similar properties as graphene himself. By checking the molecular dynamics, we can say, that at least [18]annulene, [30]annulene and [42]annulene can be used to form a carbon net with planar structure and minimal interatomic force involved. When confronted with this result, we tried to simulate the electronic transport properties (such as transmissivity, electron density and current pathways) and to compare with graphene. We are trying to prove, that annulene nets can be useful material for molecular sieves (with similar

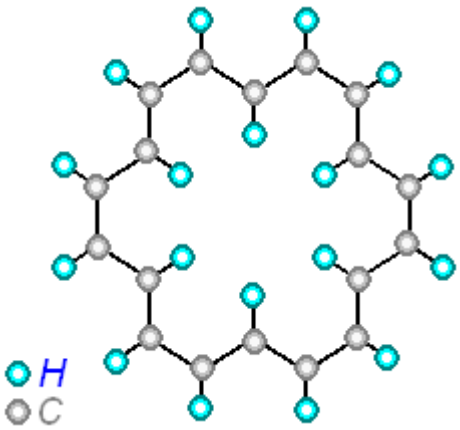


Fig. 1 Example of [6+Nx12]annulene, where N is equal to 1.

properties as zeolites) and for construction of lab-on-chip systems, where it can be used for precise electrically controlled flow of certain reactants. These nets can be as well used for desalinization or filtering of industrial exhalations in the future and for improvement of the graphene electronics, because it is presumed to be lighter than graphene (simply fewer atoms in same area) and it should have all the advantages of two-dimensional material, such as surface plasmon excitation or possible tunneling through it.

2. MODEL AND METHOD

We were approaching by same way as in our previous article. [2] We used the Atomistix ToolKit simulation software with Virtual NanoLab user environment from QuantumWise [3, 4, 5]. We selected the proper structure, placed the carbon atoms in the original positions and passivated all the free bonds with hydrogen atoms. In order to reach the thermodynamical equilibrium of the system, the optimized atom positions are computed by molecular dynamics technique. We used embedded Brenner`s quick optimizer to optimize geometry of the chemical bonds so as the maximal component of the interatomic force was less than 10^{-8} eV/Å in all cases after the optimization. For electrical properties calculations we used semi-empirical EH-SCF method for nanoscale devices with spin polarization considered [6]. As shown on the Fig. 2, the simulated system is divided in two electrodes (source and drain) and the central region. Due to the used method, we need to extend the electrodes into the structure. In order to consider the electrodes as a bulk region, there is need to have enough space in the central region for both electrode extensions. Depending on the structure, this length for extension should be at least about 5 to 10 Å. It is 10 Å for [18]annulene structure, 7.38 Å for [30]annulene and 7.5 Å for [42]annulene in our simulations. Atom in the electrode extension is identical to the one in the electrode (shown on the Fig. 2 as the red dots). Further details about the EH-SCF method can be obtained in [6]. We tried to attach the annulene net to graphene electrodes made of GNRs of appropriate width. In order to simulate the situation where electrodes are made of GNRs, we need to leave the atoms involved in electrodes without change. Thus the first three atoms from both sides of the structure are left without defects and they are only affected by dynamics of the whole system which mostly means small linear stretching over the z-axis.

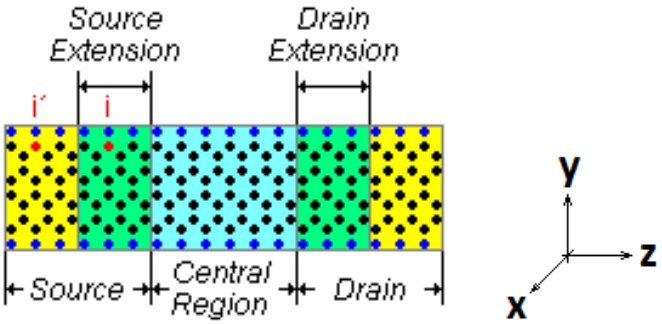
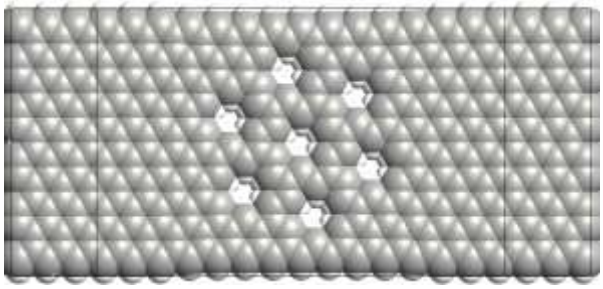


Fig. 2 General situation scheme of the simulated system [2].

3. NUMERICAL RESULTS

At first, we analyzed 10-ZGNR structure with 7 symmetrical deployed [18]annulene patches along 15 atoms wide central region as shown on the Fig. 3a. Van der Waals radiuses show that small pores becoming to emerge. Width of those pores should be around 3.9 Å and thus provide space for water molecules (~3 Å) to past thru. From the Fig. 3b we can see isosurface of electron difference density for value -10^{-5} Å^{-3}. We obtained transmission spectrum (Fig. 3c) with visible peak at Fermi level. Fig. 3d shows how the current is flowing in the ribbon at zero energy level $\varepsilon = 0$ eV.



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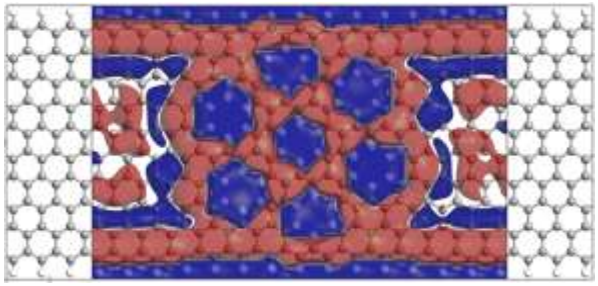

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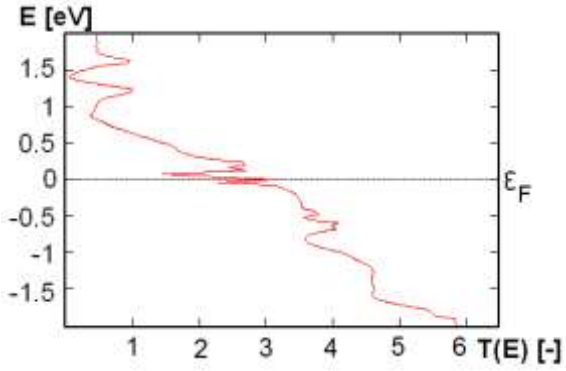
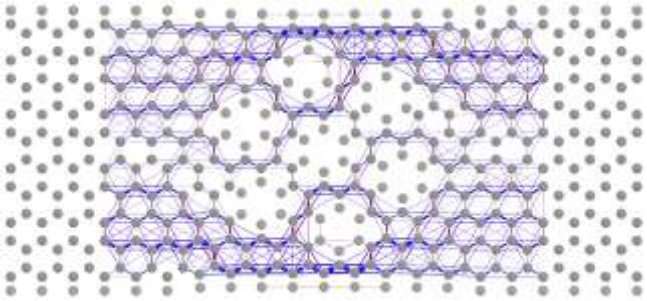


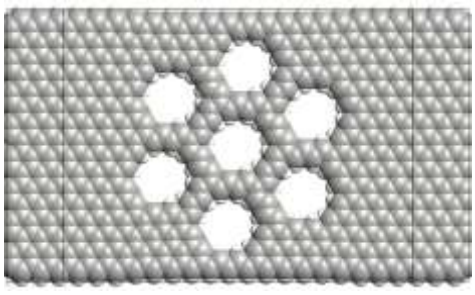
c)



d)

Fig. 3 a) Simulated system with visible Van der Waals radiuses. **b)** Electron difference density isosurface with value -10^{-5} Å^{-3}. **c)** Transmission spectrum for both spins (identical). **d)** Transmission pathways for zero energy level.

The second analyzed structure is the 16-ZGNR structure with 7 symmetrical deployed [30]annulene patches along 18 atoms wide central region as shown on the Fig. 4a. Van der Waals radiuses show much greater pores to emerge. Width of those pores should be around 8.46 Å and thus provide space for greater molecules to past thru. From the Fig. 4b we can see isosurface of electron difference density for value -10^{-5} Å^{-3}. We obtained transmission spectrum (Fig. 4c) with visible depression at Fermi level. Fig. 4d shows how the current is flowing in the ribbon at zero energy $\varepsilon = 0$ eV.



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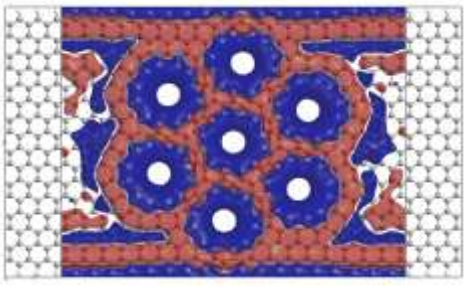

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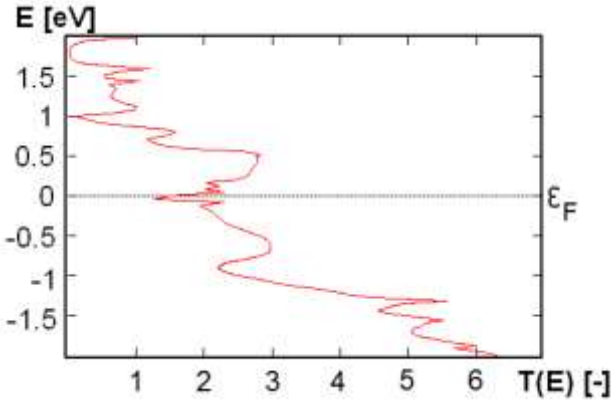
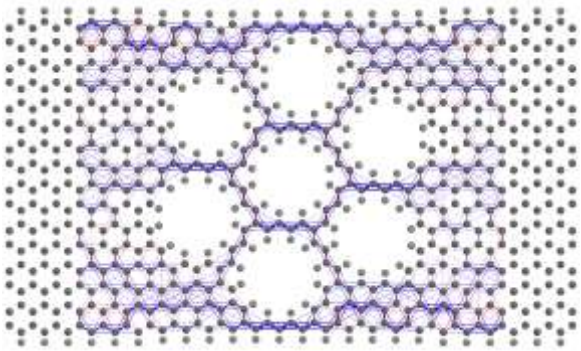
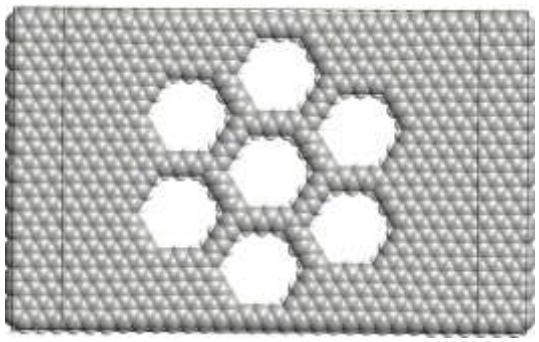


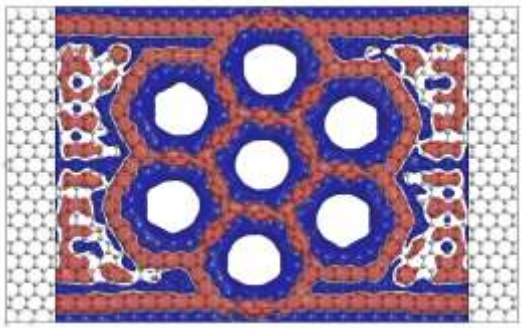


c) **d)**

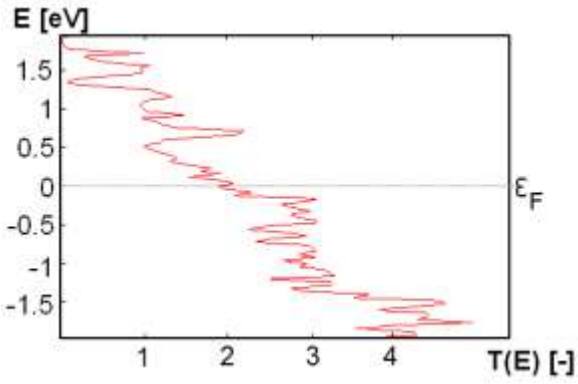
Fig. 4 a) Simulated system with visible Van der Waals radiuses. **b)** Electron difference density isosurface with value -10^{-5} Å^{-3}. **c)** Transmission spectrum for both spins (identical). **d)** Transmission pathways for zero energy level.

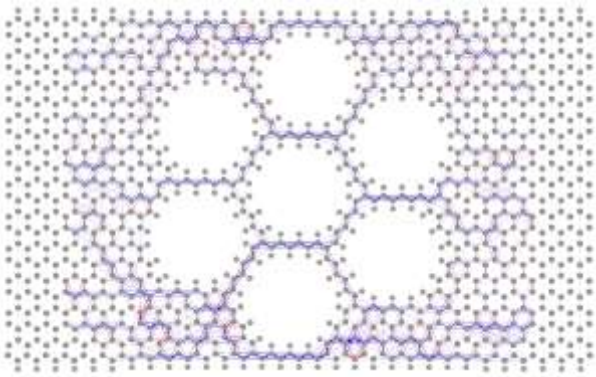
The third analyzed structure is the 22-ZGNR structure with 7 symmetrical deployed [42]annulene patches along 25 atoms wide central region as shown on the Fig. 5a. From the Fig. 5b we can see isosurface of electron difference density for value -10^{-5} Å^{-3}. We obtained transmission spectrum (Fig. 5c) Fig. 5d shows how the current is flowing in the ribbon at zero energy ε = 0 eV.





a) **b)**





c) **d)**

Fig. 5 a) Simulated system with visible Van der Waals radiuses. **b)** Electron difference density isosurface with value -10^{-5} Å^{-3}. **c)** Transmission spectrum for both spins (identical). **d)** Transmission pathways for zero energy level.

4. CONCLUSIONS

Although this work is only a brief insight in to annulene nets it shows that these are thermodynamically stable and can form greater structures as well as it shows similarity with graphene nanoribbons. This implies future use of these structures as molecular sieves usable in industry exhalation sanitation as well as in precise molecular lab-on-chip systems and for filtration of heavy metals from water and water desalinization. Possible applications are also improvements of graphene-based technology. These structures can be prepared by means of ion (electron) beam lithography or by growth from chemical precursors [7].

ACKNOWLEDGEMENTS

The work was supported by the grant of Grant Agency, Czech Republic No. P108/11/0894 and by the student grant of CTU No. SGS 13/207/OHK3/3T/13

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