

How does the porphyrin-like vacancy affect the spectral properties of graphene quantum dots? A theoretical study

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Abstract

By processing graphene quantum dot, an ideal semiconductor material with suitable band gap and higher electron mobility can be obtained. Thus, it has a broad prospect in the application of photoelectric response materials. Here, a graphene defect with porphyrin-like structure is selected to achieve the controllable light absorption. The double five-membered-ring parallel vacancy are based on self-healing properties of popular graphene defects. Aimed to separate exciton and hole more effectively and achieve higher photoelectric conversion efficiency, the occupied orbital and unoccupied orbital of the quantum dot with objected defect structure is taken as orderly dispersion to form an obvious charge separation state under the demonstration with first principles calculation. Most importantly, a real time real space charge separation is calculated by time-dependent ab-initio quantum dynamics based on numerical atomic basis sets. The result shows the specific graphene defects can form an efficient pure graphene photoelectric response medium like porphyrin skeleton, and the vacancy will induce to adjust and control the specific wavelength of the response light and charge separated state manipulably with odevity of number of peripheral carbon rings by the calculation of ultrafast process.

Keywords: graphene defects, time-dependent density functional theory, charge separation

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene [1], a fantastic material in hot interest, can be widely applied in electronic components [2, 3], luminescent materials [4] and solar cell components [5–7], based on its 2D carbon sp^2 hybrid hexagonal framework and π conjugated electron structure leading to a very unique electronic property of zero band gap and extremely high carrier mobility. In existing graphene based components, functional molecules are usually attached to the surface or edge of graphene to reach

performance improvement [6, 8–10]. This method is a convenient and efficient approach for trial, synthesis and processing. And the introduction of graphene materials improves the overall efficiency and function of the combinatorial systems [11]. While, in the preparation of functional materials, deflections or uneven distribution of dye molecules on graphene might present [12, 13]. The faultiness of graphene might limit photoelectric conversion efficiency of related components as well as the overall applicability and flexibility. The utilization of graphene for solving that problem and maintaining its soft

and sturdy skin-like material properties are sources of inspiration to our work.

In the past study on the properties of graphene, the main research direction is the properties of graphene linear nanoribbons [14–17], single point defect, mechanical reconfiguration and the influence of dopants [18–23]. While, it is rare for the study the role of vacancies in graphene. There are many types of stable defects that can be exploited and can be constructed in simple ways [24]. According to reports in the literature, some types of defects can self-healed under certain conditions in an appropriate size of graphene sheets [25, 26]. When there is even number of defective carbon atoms of graphene, the dangling bonds of those defects will form a stable topological vacancy to maintain a complete sp^2 hybrid orbital network. For example, a double vacancy (DV) will form a topological structure of pentagon–octagon–pentagon (5|8|5) or a cluster of two pentagons spacing with two heptagons (5–7–7–5) with Stone–Wales effect [27]. These vacancy structures can be calculated by density functional theory (DFT), and presented at the lowest stable point of global potential surface after self-healing of graphene defects.

Therefore, the property change caused by defect contour is a problem worthy of further study. The introduction of Stone–Wales defect will change the geometric structure of graphene, which will inevitably lead to changes in the electronic structure. Changes in electron structure may cause the charge separation of ground state and excited state, which is the desired property to be exploited. Carrying properties of the soft graphene sheet, smaller graphene quantum dots (GQD) can be selected to build defect structures with specific topological characters as showed in figure 1 [28, 29]. Energy band theory is used to analyze the electronic structures of 2D graphene usually. In this work, molecular orbital theory and detailed orbital characteristics were adopted to describe the electronic structures and properties based on the small-scale graphene quantum dots with defect structure. Because of the unique application of porphyrin structure in photophysical and photochemical processes, the porphyrin-like defect with good symmetry have aroused our interest. Porphyrin-like graphene vacancy structures with four five-membered-ring defects are also expected to have photo-absorption advantages like porphyrin [30]. Accordingly, the effects on the charge-dissociation state in porphyrin-like vacancy structural of graphene were studied by processing density-functional calculation and real-time *ab initio* approach. It provides a valuable basis for its application in photoelectric conversion materials. In this work, electron density distributions of ground state and excited state are used to evaluate the effect of carrier separation caused by defects in graphene quantum dots. In most cases, although the simple defects in graphene can lead to different electron density distribution, The results show that there is no effective distribution on HOMO and LUMO, and no acceptable separation effect [31]. Thus, we have started to explore whether complicated defect structure can lead to better carrier separation effect. In this work, we initially found that a porphyrin-like graphene vacancy structures can induce a good carrier separation effect, which is expected to inspire the related theoretical and experimental research.

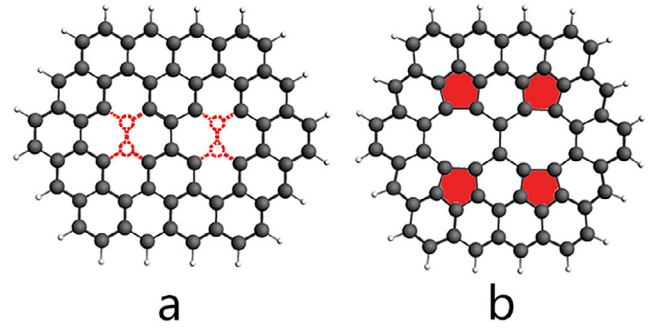


Figure 1. Assumed topological characters of build defect structures of graphene quantum dots, (a) parallel graphene defects without self-healing; (b) bivacancy defects of graphene quantum dots after self-healing.

2. Computational details

For non-dynamic calculations, we adopted the ADF calculation software to optimize the geometry of the ground state and excited state of molecules, choosing Perdew–Burke–Ernzerhof (PBE) of generalized gradient approximation (GGA) with a Slater type all-electron triple- ζ basis with polarizations (TZP) [32]. By optimizing the geometry of the ground state of the defect graphene, the stable structure of the lowest energy point was finally achieved, which can be used to simulate the formation of parallel double-vacancy defect structures. Then, we use the same method to calculate the molecular orbital, absorption spectrum, and electron density difference. The quantitative analysis of the transition behavior of electrons in molecular orbitals based on DFT should be appropriate and accurate depicted [33].

In order to more clearly describe the transmission process of electrons in the interface after excitation, the time-dependent *ab-initio* package (TDAP) calculation software was used to calculate the quantum dynamics of the excited state of the structure [34–37]. TDAP, a real-time Time-dependent density functional theory (TDDFT) calculation implemented in SIESTA [38], employs local atomic basis sets and real-time propagation of wave functions for solving the time-dependent Kohn–Sham (TDKS) equation as followings [39]

$$\dot{\varphi}_m(t) = -i\hat{H}[n(t)](t)\varphi_m(t), (m = 1, \dots, N) \quad (1)$$

where $(\dot{\varphi})$ is time derivative, $\hat{H}[n(t)](t)$ is the Kohn–Sham (KS) Hamiltonian, $\varphi \equiv \{\varphi_m\}_{m=1}^N$ are the KS orbital, N is the number of electrons, and n is the one-electron density, obtained from

$$n(\vec{r}, t) = \sum_{\sigma=\uparrow, \downarrow} \sum_{m=1}^N |\varphi_m(\vec{r}\sigma, t)|^2. \quad (2)$$

In the calculation, the GGA Pseudo-potential Database that obtained from Abinit's pseudo database and the adiabatic local density approximation for the exchange-correlation functional are used. When running the TDAP, the evolution time step was 0.5 fs for electrons in a microcanonical ensemble. After calculating the dynamics of electrons and analyzing the mul-ti-atomic distribution of atoms [40], the influence of porphyrin-like structure formed by parallel double-vacancy defect

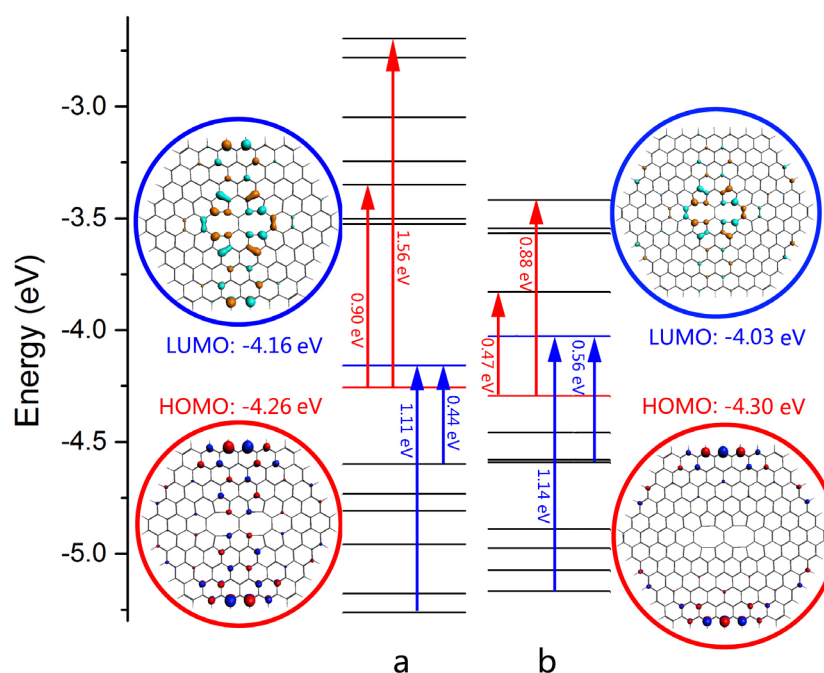


Figure 2. Molecular orbital energy levels and profiles of (a) the porphyrin-like vacancy in Triple-lapping GQD; (b) the porphyrin-like vacancy in Quadruple-lapping GQD. (Red arrows) electrons are excited to different higher energy levels after absorbing different energies, thus the holes are forming in HOMO. In the meanwhile, (blue arrows) the LUMO also receives excited electrons. Electrons and holes can form excitons instantaneously.

on the transmitting of excited electrons in graphene can be characterized.

3. Results and discussion

The length of the C-C bonds around the vacancy are stretched by the healing of the defects, which is 1.42 Å longer than the pristine GQD. The new formational C-C bonds in the (5|8|5) vacancy are also shorter than the original atomic distance of 2.46 Å, and this is different from Stone-Thrower-Wales defect (STW, 5-7-7-5) [41]. By analyzing the molecular orbitals, the separation of the highest occupied orbital and the lowest unoccupied orbital was obtained in figures 2 and S1 (stacks.iop.org/JPhysCM/32/155902/mmedia), while maintaining a small band gap of the 0.077 eV at least for a semiconductor. In general, the electron in highest occupied orbital in the ground state is excited most easily and firstly to unoccupied empty orbital after absorbing energy to reach excited state. Then, the hole formed in the original HOMO orbital by the excitation of electron and the excited electron already occupied in high energy can be separated by different orbital distribution. And after light absorption, the excitation of electrons occurs between different orbital with different symmetry, contributions and energy gap.

The separation of such orbitals can qualitatively reflect the charge separation of the excited state and the ground state of the molecule. An excellent charge-separated state can form a more movable current, and the reduced exciton combination that leads to a decrease in photo-generated current efficiency. Here we can deliberately control the specific position of graphene to form a double vacancy defect. On accordance

with the theory above, dangling bonds of the graphene will combine with each other to cause the self-heal of the defect, forming a double (5|8|5)-DV juxtaposition structure similar to the porphyrin.

The modified parallel double-vacancy (5|8|5) defects can be calculated to form a GAP of no more than 0.5 eV. The figure shows the orbital energy levels of the defects with different numbers of carbon chains around them. Such a small orbital difference makes it easier for electrons transition. But the profile of the molecular orbitals shows something different. The distribution of the highest occupied orbitals was in the longitudinal direction of the symmetry axis of the parallel bivacancy defect, and the distribution of the highest occupied orbitals was concentrated at the edge of the graphene sheet. This was because that the defective structure of graphene contributes to the formation of ground state molecular orbitals on the nanostrip at the zigzag edge of graphene [42].

From figures 2 and S2, It can be seen that as the number of peripheral carbon chains was $2n$, the lowest unoccupied orbital concentrates on the defect shape of the structure and its surroundings formed good separation of molecular orbitals. While, as the number of carbon chains on the periphery of the defect was $2n + 1$, the defect center although formed a lowest unoccupied orbital concentration area, the orbital distribution near the edge nanoribband still exists, but without a clear orbital separation.

The calculation of the CDD between the excited states and ground states verified the above analysis of orbital results (shown in figure 3). By calculating the Triple-lapping GQD and Quadruple-lapping GQD, it can be seen that Triple-lapping GQD of etching CDD electronic with no clear separation of the structure, but Quadruple-lapping GQD of etching

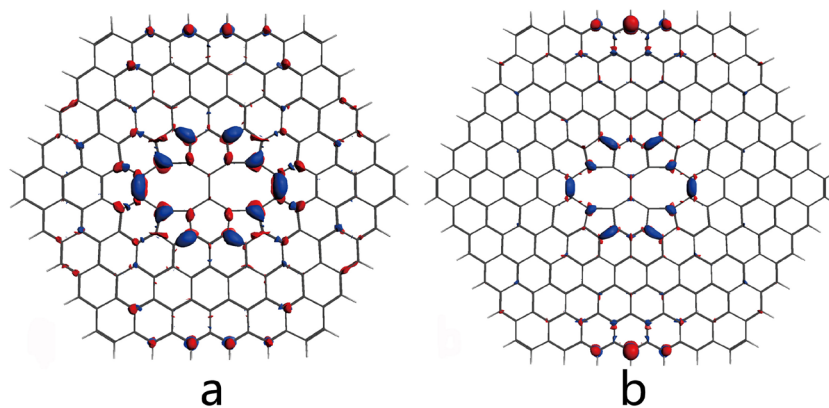


Figure 3. The charge different density (CDD) between the excited states and ground states; (a) CDD of the graphene vacancy in Triple-lapping GQD; (b) CDD of the graphene vacancy in Quadruple-lapping GQD.

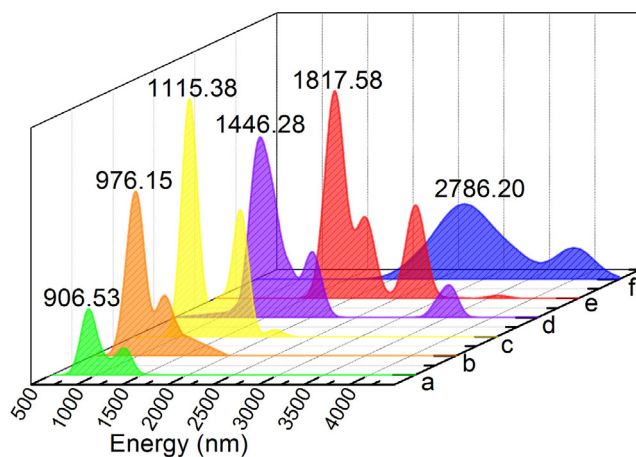


Figure 4. Absorption separation of porphyrin-like vacancy in double-lapping GQD (a), and in triple-lapping GQD (b), in quadruple-lapping GQD (c), in quintuple-lapping GQD(d), in sextuple-lapping GQD (e), in septuple-lapping GQD(f), respectively.

can be clearly seen the ground state electronic structure that was focused on the edge of excited electrons and pivot on the defect part at the same time. Moreover, compared with intact graphene, the electrons excited by graphene containing defects will migrate in a timely manner, thereby, reducing exciton recombination and making photoelectric current become the mainstream rather than increasing the internal energy of the system.

In order to determine the light absorption of porphyrin-like structure formed in graphene, we show the absorption transitions in figure 4. It can be found after calculation with the increase of the number of peripheral carbon chains, the light absorption peak of the whole structure will be red shifted, and the degree of red shift will gradually increase. Compared with zinc porphyrins, the absorption peak of graphene-like porphyrins was moved from the maximum solar radiation energy of 380 nm [30], which was relatively low, to the visible and infrared light with relatively high radiation energy, so as to achieve more effective absorption of light energy. Compared with the non-defect GQD, the smaller orbital energy gap makes the absorption spectrum more redshift to the infrared region [43]. This indicates that the porphyrin-like defect

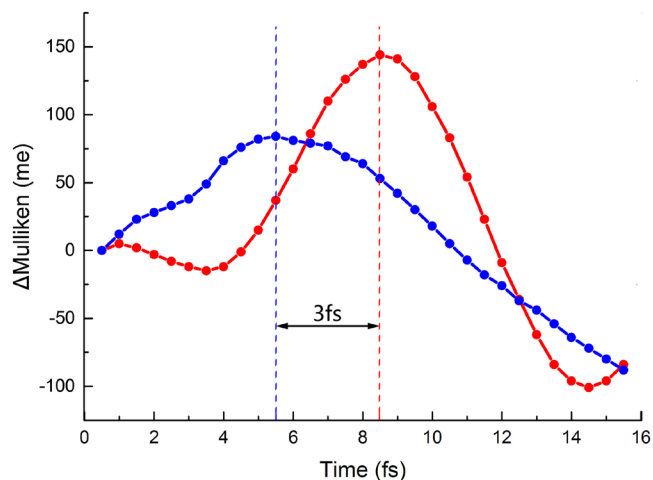


Figure 5. The mulliken charge distribution for the graphene vacancy in quadruple-lapping GQD from 0.5 fs to 15.5 fs; the red line represents the edge of the GQD structure and the blue represents the central region of the GQD.

structure constructed on a comparable small soft graphene sheet layer can absorb light closer to the infrared light region.

After a series of calculations about the ground state and excited state, it can be obtained that when the structure transitions from the ground state to the excited state, the electron flow direction was concentrated from the center to the edge. The center here refers to the edge of the constructed porphyrin-like structure. In order to clarify the process of electron migration, Quadruple-lapping GQD with better electron separation effect was selected for excitation state dynamics calculation. According to the calculation, the mulliken distribution of the central atom was at the highest point at 5.5 fs, and the mulliken distribution of the carbon chain at the edge was at the highest point around 8.5 fs (shown in figure 5). This means that the charge transfer from the center to the edge occurs over time within 3 fs after formation of vertical excited states.

4. Conclusions

According to the demonstration, the constructed double (51815) ring parallel vacancy breaks the conjugated π bond electron structure of graphene. The porphyrin-like structure

can regulate the charge separation of the excited states of the peripheral carbon chain in a few femtoseconds. When the peripheral carbon chain is even, the excited electrons can aggregate from the edge of the carbon chain to the central porphyrin-like region. By controlling the number of peripheral carbon rings, light absorption peaks in different regions can be subjectively adjusted. With progressing of precise etching techniques, graphene sheets with improved charge separation properties can be processed to form solar-sensitive molecule structures for light-responsive components under the accurate quantum dynamics calculation. It is expected that this properties of graphene will enable its porphyrin-like structure to be flexibly practicable and widely applicable than traditional GQD. More studies on the effects and applications of structural defects with different shapes in graphene quantum dots are under way. Moreover, we will carry out a further summary of the general rule of the defect structure and defect contour or combination of different types of simple defects for carrier separation, which will provide a theoretical reference for the influence of the defect structure of graphene in the application of photoelectric materials.

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