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Research paper

Optical response tuning in graphene nanoflakes: A computational study

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ABSTRACT

We use time dependent density functional theory to study the electronic and optical properties of rectangular graphene nanoflakes with mixed armchair and zigzag edges under uniaxial strain in order to determine the role of the size and aspect ratio. Both the HOMO-LUMO and optical bandgaps are found to exhibit strong variations under uniaxial strain, unlike two-dimensional graphene. A specific 140-atom nanoflake even is subject to a transition in the energetical order of the HOMO−1 and HOMO wavefunctions. The present work shows that through rational modifications in the aspect ratio and uniaxial strain, the electronic and optical properties of graphene nanoflakes can be favourably tuned.

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Graphene, a monolayer of carbon atoms arranged in a honeycomb lattice, has unique optical properties, including high frequency tunability, long-lived collective excitations and strong light confinement [1,2]. The elastic properties, in particular the stability under strain, can be investigated by means of nanoindentation in an atomic force microscope, showing that it is possible to deform graphene nanoflakes mechanically well beyond the linear regime [3]. Stability up to 13% uniaxial strain reflects a remarkable elasticity [3] and opens the door to strain engineering [4,5]. Nanostructures in general can sustain more strain than bulk materials, since plastic deformations and fracture are suppressed [6]. Nanoflakes can be synthesized by chemical routes with almost perfect crystalline quality and therefore are attracting considerable attention [7–9]. In contrast to the zero bandgap nature of graphene, a finite bandgap is present in graphene nanoribbons and nanoflakes (quantum dots). Numerous experimental studies have addressed the electronic and optical properties of graphene nanoflakes, see Refs. [10,11], for example.

From the theoretical point of view, Hartree-Fock based methods have been used to study the effect of edge functionalization [12] and self-consistent density functional tight binding theory has provided insight into the shape dependence of the absorption spectra [13]. Most of the optical calculations are based on semi-empirical approaches [13–15], as they require much less computation time than the more accurate ab initio methods. However, for low-dimensional systems the absorption spectra obtained by ab initio methods often agree much better with the experiment [16,17]. Neither semi-empirical nor ab initio studies so far have addressed the optical absorption as a function of strain. Therefore, this letter

aims at establishing insight into the strain dependence of the absorption spectra of graphene nanoflakes and the effects of their size and aspect ratio.

We use the DMol3 [18] implementation of density functional theory (DFT), employing a localized atom-centered basis set and the B3LYP [19,20] exchange correlation functional. The reliability of optical spectra obtained from time-dependent DFT depends strongly on the exchange correlation functional. We find for the B3LYP hybrid functional excellent agreement of our results (particularly the energetical positions of the two lowest absorption peaks) for an unstrained nanoflake with 140 carbon atoms with experiment [10]. It has been checked that accounting for polarization in the basis set gives no significant difference in the results. We used density functional semi-core pseudo-potential (DSPP) [18] with a global orbital cutoff of 4.5 Å. Since nanoflakes are non-periodic systems, the reciprocal space summations are restricted to the Γ point. Moreover, the Kohn-Sham energy levels are broadened by a Gaussian smearing of width 0.02 eV. The optical spectra are obtained by solving time-dependent Kohn-Sham equations using well-known Casida's method [21]. The poles of the frequency dependent dynamic polarization tensor and its response components are computed from the following eigenvalue problem,

$$\Omega F_I = \omega_I^2 F_I \tag{1}$$

where Ω is a matrix consisting of products of occupied-virtual Kohn-Sham orbitals and the eigenvalues ω_I^2 correspond to squared excitation energies while the oscillator strengths are extracted from the eigenvectors F_I. The number of dipole-allowed transitions (roots) should be high enough to cover the desired range in the absorption spectrum. Calculation of 1500 roots is found to be sufficient to generate absorption spectra up to 4.75 eV. All absorption

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spectra are broadened by a Gaussian smearing of width $\sigma = 0.1$ eV. Due to their closed-shell nature the nanoflakes are charge neutral.

We study nanoflakes with armchair edges along the strain direction and zigzag edges at the ends, see Fig. 1. The dangling bonds at the zigzag edges [22] are passivated by hydrogen atoms, which are not shown in the figure. Nanoflakes with opposite choice of edges (zigzag edges along the strain direction and armchair edges at the ends) show small bandgaps, typically below 0.4 eV, and therefore are not further considered in this study. Under uniaxial strain the bonds along the strain direction are stretched and those in other directions shrink, which results in the evolution of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital gaps and optical bandgaps shown in Fig. 1. We note that both the HOMO-LUMO and optical bandgaps can vary as a function of strain and the influence of the size and aspect ratio of the nanoflake is partially dramatic, as the quantum confinement due to the reduced dimensionality modifies the electron and hole wave functions.

Fig. 1 shows that nanoflakes (b) has distinct variations in the HOMO-LUMO and optical bandgaps as compared to the nanoflake (a) and (c). It is expected that a reduction of the quantum confinement will lower the bandgaps when the size of the nanoflake increases. We observe for nanoflake (b) a transition from increasing to decreasing bandgaps, which has a different origin and therefore will be studied in more detail in the following. The 1.3 eV HOMO-LUMO bandgap of nanoflake (b), which comprises 140 carbon atoms, without strain is in line with the value of 1.37 eV reported in Ref. [23] for a slightly larger nanoflake. 8% strain, for example, enhances the HOMO-LUMO bandgap to 1.7 eV. The fact that for increasing strain both the HOMO-LUMO and optical band-

gaps first increase and then decrease is similar to findings for two-dimensional C_2N crystals under biaxial strain [24], where it is also related to a reversal of the energetical order of the HOMO−1 (filled occupied molecular orbital closest in energy to the HOMO) and HOMO wavefunctions. The original value of the bandgap is almost reproduced for the maximal strain of 12%, see Fig. 2.

The strong variation of the bandgap is reflected by the density of states in Fig. 2. Both the valence band maximum and conduction band minimum shift down in energy as compared to the unstrained case, however, the former faster than the latter so that the bandgap increases. Above 8% strain the conduction band minimum continues to shift to lower energy but the trend for the valence band maximum is inverted, so that the bandgap decreases quickly. The reason for this behaviour is a transition between the HOMO−1 and HOMO wavefunctions around 8% strain, as shown in Fig. 3. Within the ranges of 0–6% and 8–12% strain the wavefunctions show no qualitative difference. Interestingly, no transition is observed for the other nanoflakes (see Fig. 1 in the supporting information). The transition has strong influence on the optical properties of nanoflake (b), as they are dominated by HOMO-to-LUMO transitions (for example, $\sim 70\%$ contribution to the first absorption peak). Therefore, the absorption spectra in Fig. 4 reveal moderate and systematic changes under strain from 0% to 6% and from 8% onwards, whereas the transition between the HOMO−1 and HOMO wavefunctions has significant consequences. For example, see the systematic blueshift and absorption intensity variations of the two low energy peaks (located in the energy range of 1.5–2.5 eV) and the higher energy peak (located in the energy range of 3.75–4.5 eV) for 0–6% strain. Interestingly, from 8% strain onwards, significant changes in the spectra begun to appear. Most importantly, the low energy peaks now redshift in energy together with significant redistribution in the absorption intensities (note the low energy peak around 2.5 eV getting stronger in intensity than higher energy peak around 4.5 eV). The reason for the significant changes in the spectra at the transition is that from 0% to 6% strain the HOMO wavefunction is dominated by vertical bonds and the HOMO-1 wavefunction by parallel bonds, which becomes interchanged for 8% strain. The swapping of the
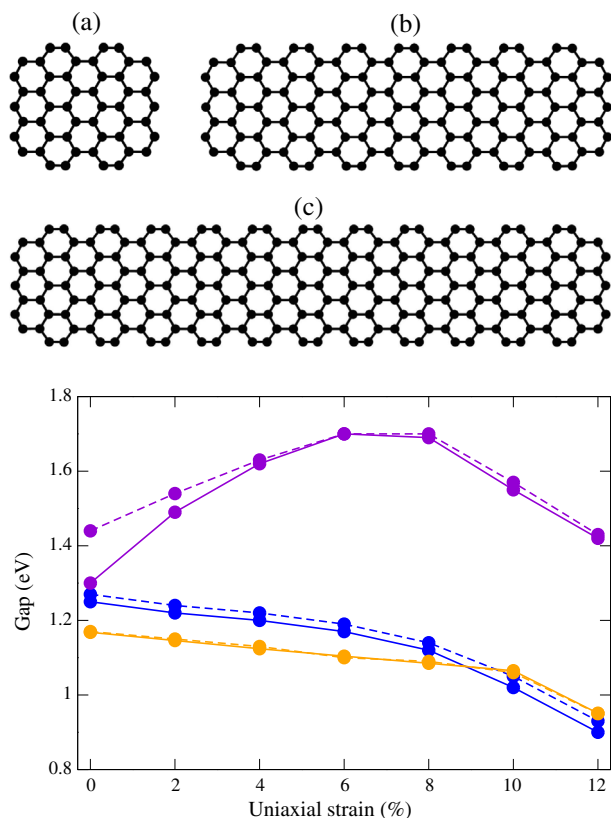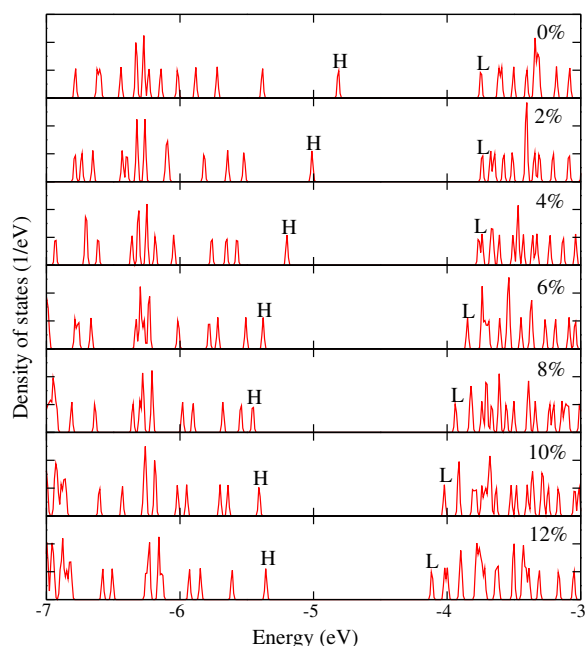

Fig. 1. Top: Nanoflakes of different sizes with armchair edges along the strain direction (horizontal) and zigzag edges at the ends. Bottom: Strain dependence of the HOMO-LUMO (full line) and optical (dashed line) bandgaps, using the color code (a) blue, (b) violet, and (c) orange. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Density of states of nanoflake (b) as function of the uniaxial strain. Letters H and L indicate the HOMO and LUMO, respectively.