Optical properties of graphene flakes from time-dependent density functional calculations

F. Marchesin[1,2,a)], P. Koval[1,2], D. Foerster[3], D. Sánchez-Portal[1,2]

[1]Centro de Física de Materiales CFM-MPC, Centro Mixto CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, E-20018 San Sebastián, Spain
[2]Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain
[3]CPMOH, University of Bordeaux 1, 351 Cours de la Liberation, 33405, Talence, France
[a)]Electronic mail: federico_marchesin1@ehu.es

Abstract

The unique properties of graphene[1], such as large conductivity, high mechanical strength, high thermal stability, tunable optical properties[2], have led to an intensive study since it was first isolated in 2004. It has become one of the most promising materials for applications such as optical signal processing and quantum information. Part of this interest stems from the possibility to control the properties of graphene by means of chemical and physical modifications. Apart from extended graphene structures, also graphene quantum dots, antidots, nanoribbons and moebius strips have attracted the interest of the scientific community.

In this work we focused our attention on the optical properties of hydrogen saturated and chemically modified graphene nanoflakes. We investigated in detail how the optical properties depend on the geometry and the size of the flakes. Although there are some previous works on similar subjects, they mainly use simple Tight-Binding (TB) models. In order to overcome restrictions of TB models we use ab-initio methods of electronic structure theory. We performed our calculation with an efficient Time-Dependent Density Functional Theory code[3] based on the use of basis set of localized functions (atomic orbitals). In conjunction with the ab-initio SIESTA package[4] this allows to study flakes containing more than a thousand atoms using much less severe approximations than those in the TB models.

We have chosen hydrogen-saturated hexagonal and rectangular planar flakes to characterize size and shape dependence of optical absorption. The spectra of all the flakes show two main groups of peaks, π peak and σ peak, which are blueshifted as the size of the flakes decreases. A typical spectrum can be seen in fig.1(a). At low frequency range the optical absorption is determined by the type of edges. In particular, we quantified the optical gap which is defined as the lowest-frequency resonance position. In fig.1(b) the dependence of the optical gap on the number of the valence electrons in the system for zigzag-hexagonal, armchair-hexagonal and rectangular flakes (which contain both edge types) can be observed. The optical gap is smaller for zigzag-hexagonal flakes than for the corresponding armchair flakes. However, we do not observe a complete closure of the gap for the explored sizes. In marked contrast, rectangular flakes with more than 250 valence electrons already show a negligible gap.

Moreover, we found that chemically functionalized edges affect the absorption spectrum. We saturated the carbon flakes with oxygen, fluorine and hydroxyl groups. The obtained results open the way for tuning optical properties by changing the edge functionalization. In fig.1(c) the shift of the first resonances as a function of the chemical modification of the flake. Oxygen functionalization provides clearly distinct optical response from hydrogen and fluorine. Hydrogen and fluorine functionalization show similar effects.

We also explored the spatial distribution of the density change induced by an external electric field with a given frequency. In particular, the plots of the imaginary part of that density change show which parts of the flake are responsible for an enhanced optical absorption. An example of a density change plot is gives in fig.1(d).

We hope that these results can improve our understanding of graphene optical properties and for future applications in the field of optical signal processing and quantum information.

References

[1]A. K. Geim, *SCIENCE* **5934**, (2009), 1530-1534
[2]Jianing Chen et al., *NATURE* **7405**, (2012), 77-81
[3]P. Koval, D. Foerster and O. Coulaud, *J. Chem. Theory Comput.,* **9**, (2010), 2654-2668
[4]José M. Soler, Emilio Artacho, Julian D. Gale, Alberto García, Javier Junquera, Pablo Ordejón and Daniel Sánchez- Portal, *J. Phys.: Condens. Matter*, **11**, (2002), 2745-2779

Figures

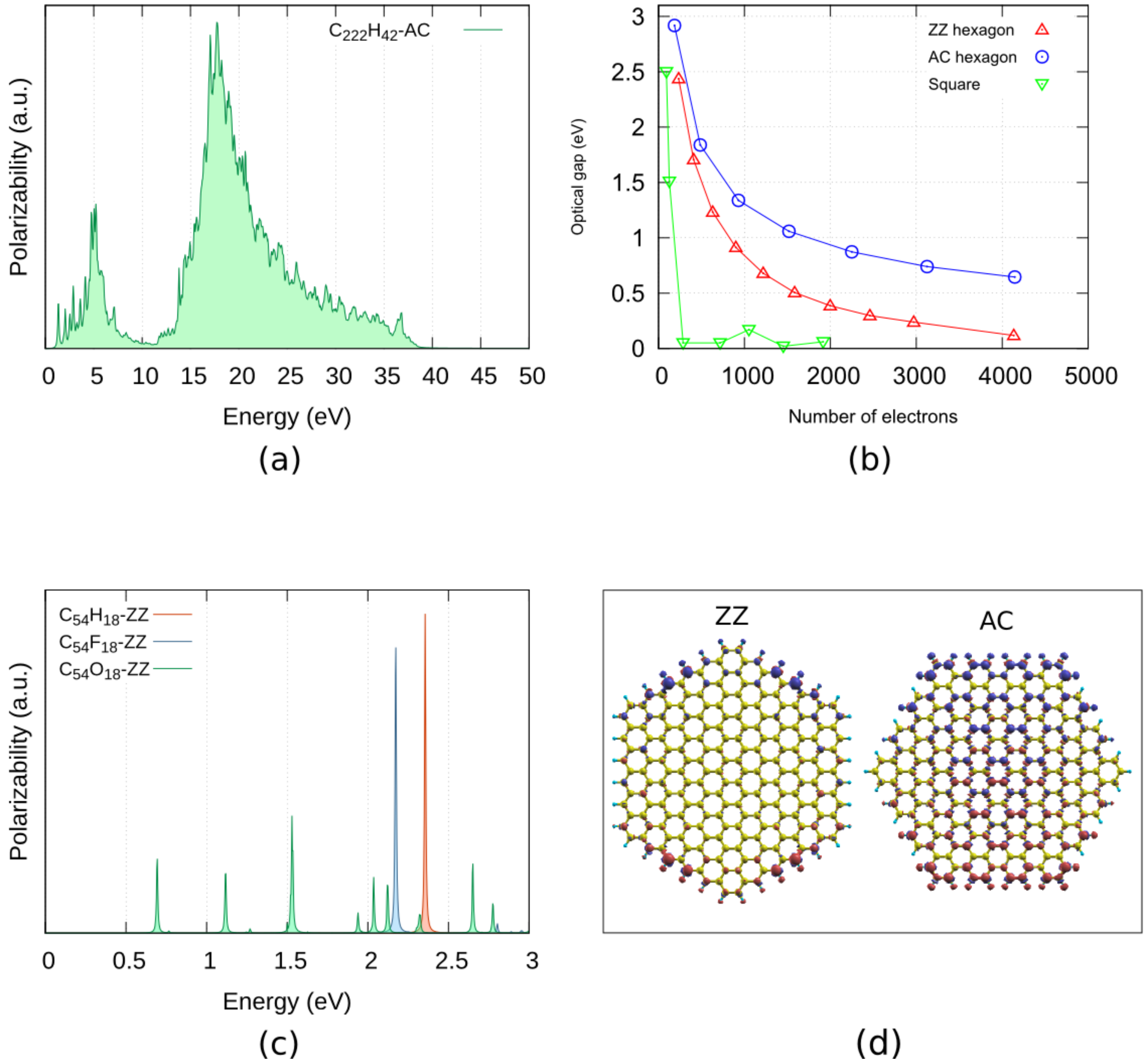

Figure 1: (a) Absorption spectrum of a hydrogen-saturated armchair (AC) graphene flake containing 222 carbon atoms. π and σ plasmonic features are characteristic for all grapheme flakes we studied. (b) Optical gap dependence on the number of valence electrons in the flake for different flake shapes. Optical gap of hexagonal flakes decreases steady, while optical gap of rectangular flakes quickly becomes negligible. (c) Absorption spectrum at low frequencies of hexagonal zigzag (ZZ) flakes saturated with hydrogen, oxygen and fluorine. Oxygen functionalization leads to a broader absorption which is weaker than in hydrogen- and fluorine-terminated flakes. (d) Example of density change plot which highlights the flake's parts with the highest absorption corresponding to an applied field with a frequency in the range 0-2eV for a ZZ-hexagonal and AC-hexagonal flake. Edges contribute stronger to the density change in case of ZZ flake.