



Ab initio study of the stability of H- and O-functionalized graphene as nanomaterial for electrical and optoelectronic applications

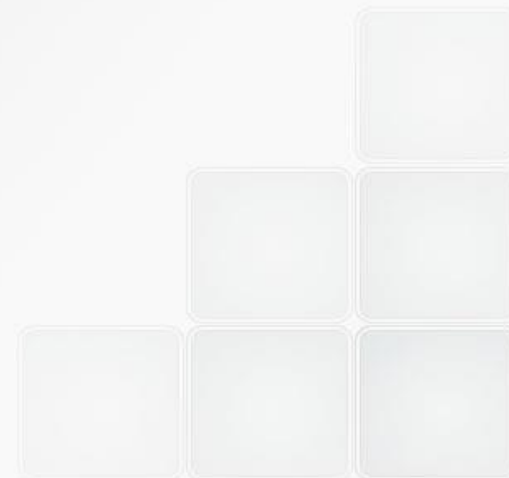
TS.II.E Simulation and Modeling for Nanotechnology

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2016 Innovation
Conference & Exhibition



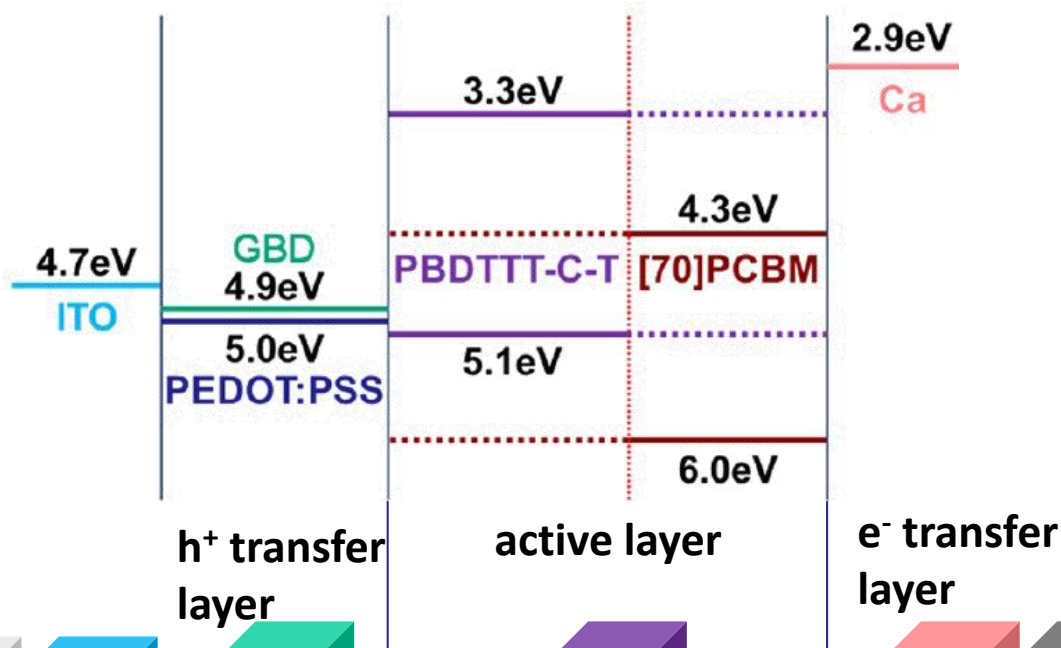
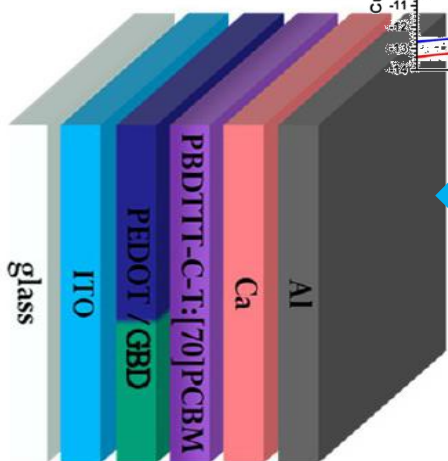
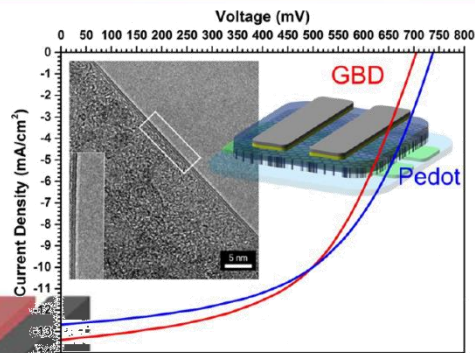
Summary



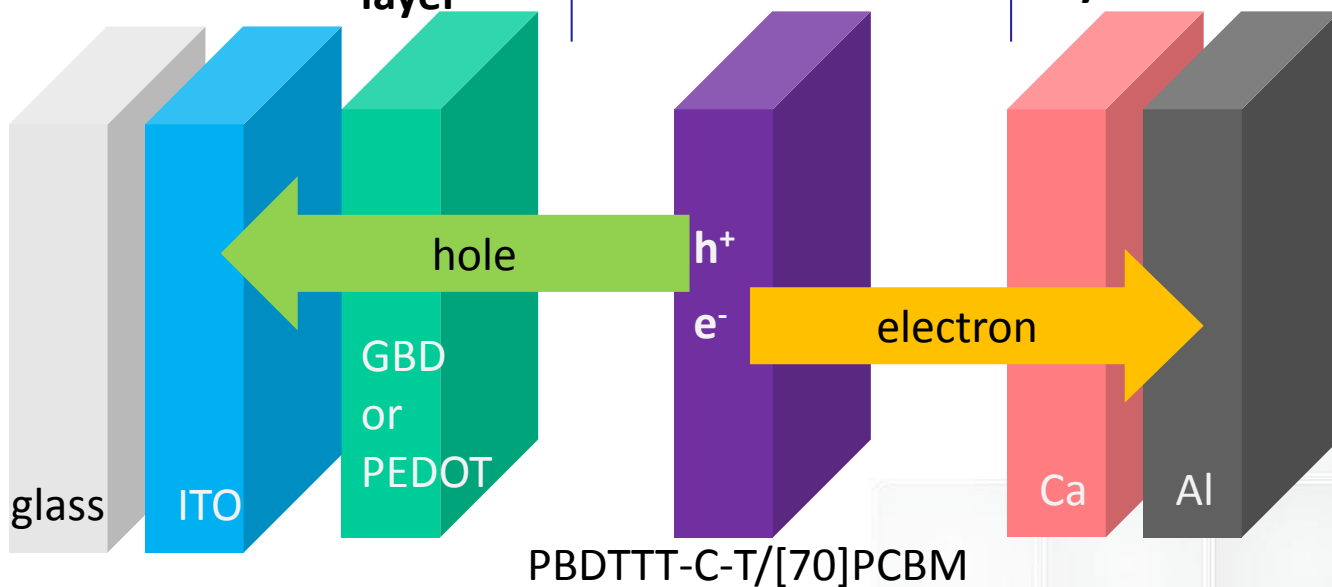
- Graphene based derivative as HTM for organic photovoltaics
- Theoretical Approach
 - Density Functional Theory
 - Computational Details
- Graphene (G)
- Graphene-derived nanomaterials
 - Graphane (GH)
 - Graphene Oxide (GO)
- Synthetic routes towards O- and H-functionalized graphene
- Phase Diagram of Graphene Oxide
- Phase Diagram of Hydrogenated Graphene Oxide (HGO)
- Conclusions



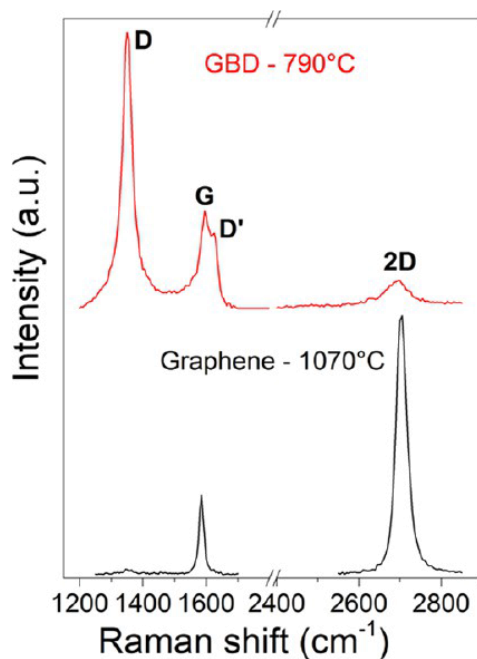
Graphene based derivative as HTM for organic photovoltaics: the solar cell



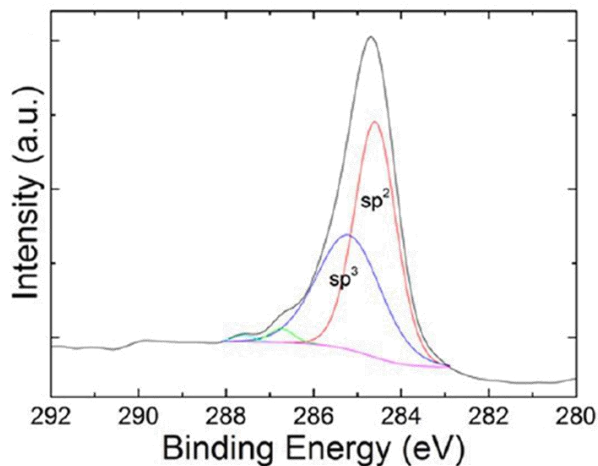
- The cells attained a maximum power conversion efficiency of 5%, matching reference cells made with state-of-the-art PEDOT:PSS as the hole transport layer
- The advantage is that GBD do not corrode the ITO electrode.



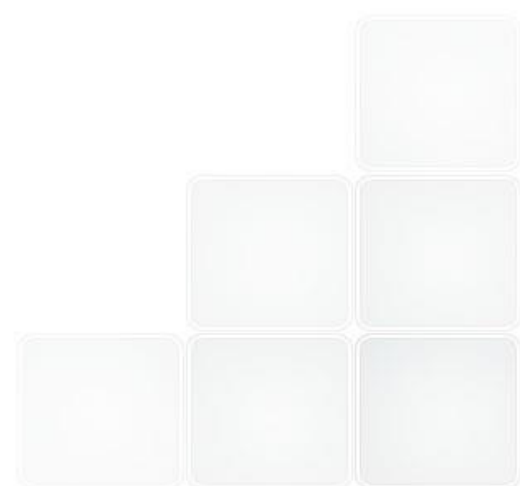
Graphene based derivative: characterization



- Raman spectra: CVD graphene film grown at 790° C (i.e., GBD) has shown features related to graphane, the fully-hydrogenated graphene (Elias DC, Science (2009))
- Raman, XPS and TEM analyses demonstrate that the GBD is made of an sp² carbon lattice with a large amount of carbon-containing groups in sp³ coordination.
- In this presentation we will see an ab initio study of O- and H-functionalized graphene structures and the growth conditions for the most stable related configurations.



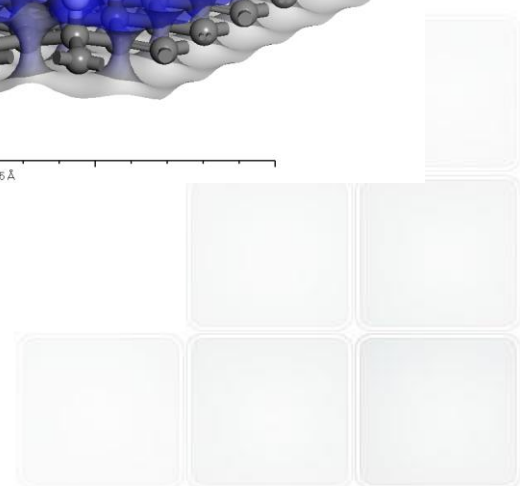
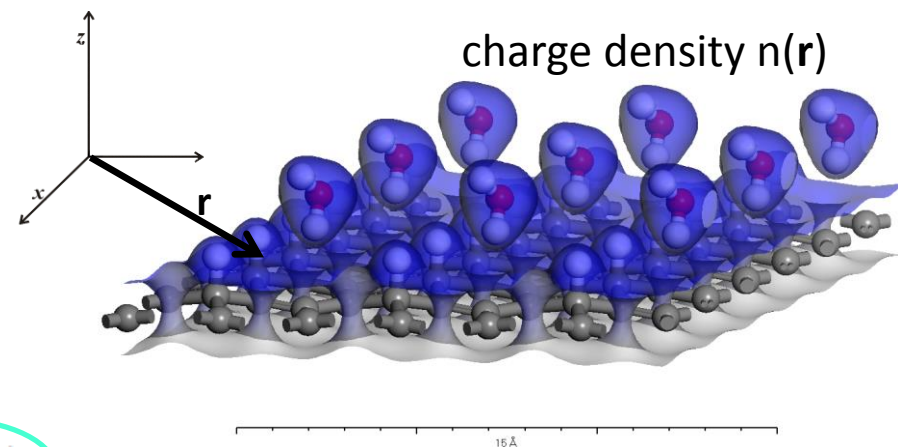
"Chemical Vapor Deposited Graphene-Based Derivative As High-Performance Hole Transport Material for Organic Photovoltaics" - A. Capasso et al ACS Appl. Mater. Interfaces (2016) DOI: 10.1021/acsami.6b06749



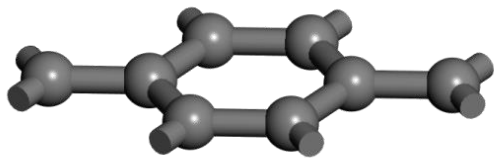
Density Functional Theory

- The ground state energy of a correlated system of many particles in an external potential is a functional of the density profile $n(\mathbf{r})$, so that all the static properties of a non-degenerate ground state of a quantum system can be described in terms of its density (Hohenberg and Kohn theorem, 1964).
- The many-particle system can be mapped onto a suited and fictitious non-interacting system of particles moving in an effective potential $V_{eff}(r)$ depending on the whole density distribution $n(r)$ everywhere, not just at position r , and including the bare potential energy and the exchange and correlation contribution $V_{xc}(r)$ (Kohn and Sham, 1965).

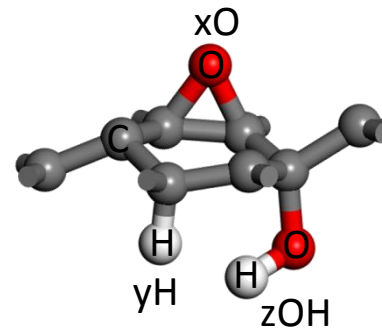
$$E_g[n(\mathbf{r})] = \underbrace{T[n(\mathbf{r})]}_{\text{kinetic energy of the ideal non-interacting system}} + \underbrace{\int V_e(\mathbf{r})n(\mathbf{r})d\mathbf{r}}_{\text{contribution of the external field}} + \underbrace{\frac{1}{2} \int d\mathbf{r}d\mathbf{r}'V(\mathbf{r},\mathbf{r}')n(\mathbf{r})n(\mathbf{r}')}_{\text{contribution of the potential energy between each pair of particles}} + \underbrace{E_{xc}[n(\mathbf{r})]}_{\text{the exchange and correlation contribution, defined as all what is to be added to the above terms to obtain the exact ground state energy}}$$



- We used the pseudo-potential plane-wave code PWSCF as implemented in the QUANTUM-ESPRESSO package [20]
- Generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [21], taking into account spin-polarisation
- The empirical correction of the long range forces (DFT-D, Grimme) are included for interactions with substrates
- We optimized the unit cell of graphene by imposing that the stress on the cell is less than 0.04 GPa, and we are here using the same cell for each of the functionalized graphene structures
- The final self-consistent calculations of the optimized structure properties made use of a cut-off for the wave functions and charge density of 60 and 600 Ry, respectively, allowing a convergence of the total energy below 0.002 eV/atom.
- In the GH/GO/HGO structures, we have added O and/or H atoms to the same carbon honeycomb supercell built by using the in-plane 2×2 unit cell of the graphene which contains 8 C atoms

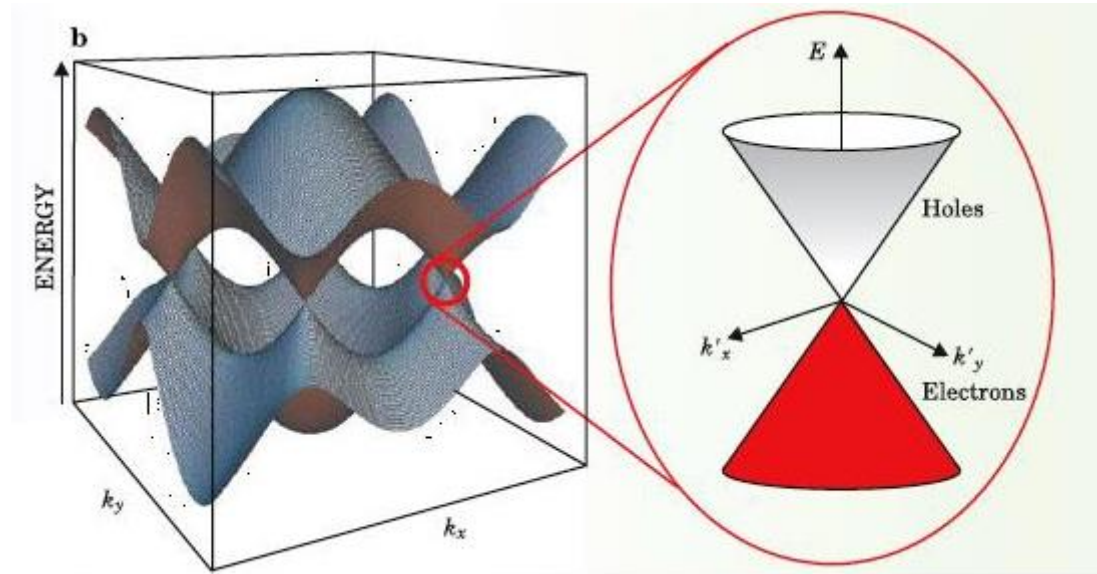
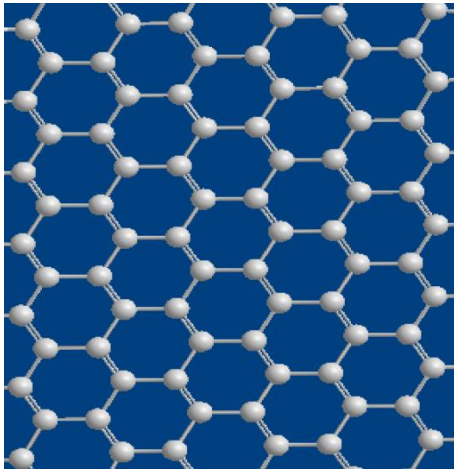


graphene



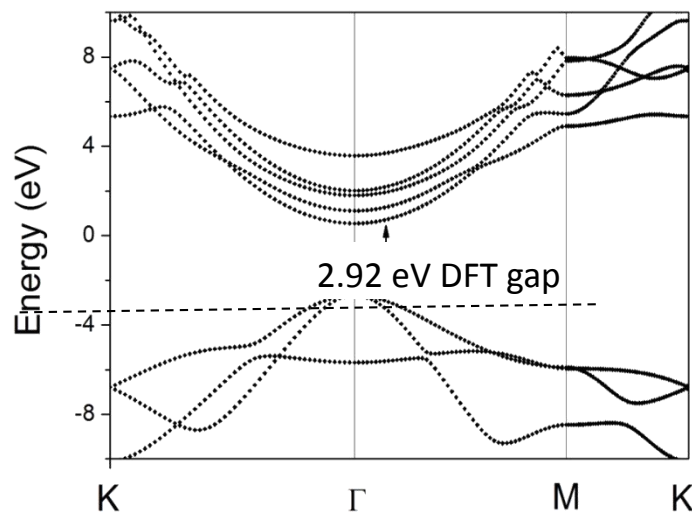
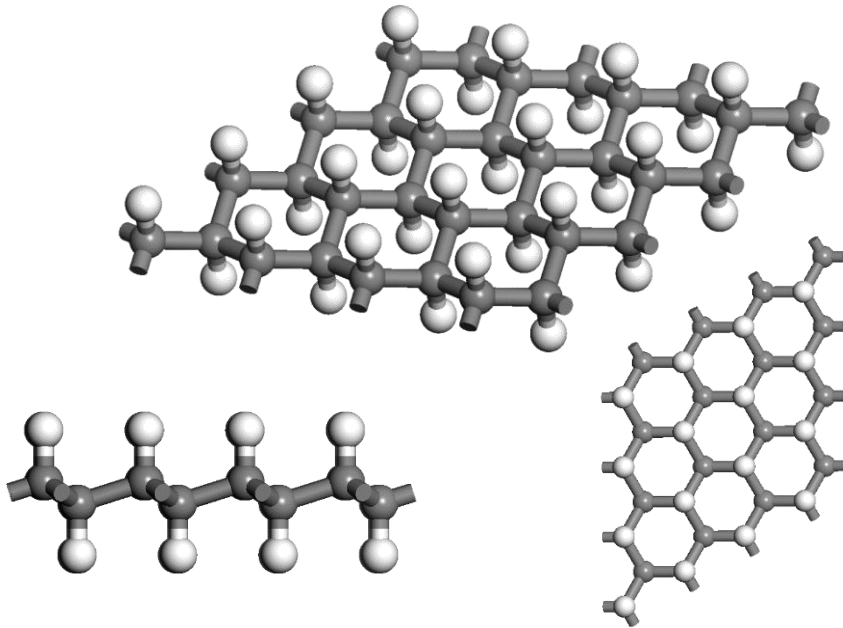
generic graphene oxide

Graphene (G)



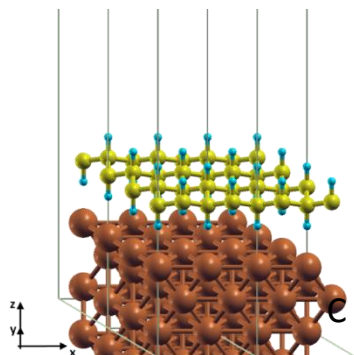
- The atomic structure of graphene is very simple: a one-atom-thick planar sheet of sp^2 -bonded carbon atoms that are densely packed in a honeycomb crystal lattice
- The bands of graphene have a linear dispersion near the Fermi energy, with symmetric effective mass of electrons and holes.
- Graphene exhibits **overstanding electrical** (RT electron mobility $\sim 200.000 \text{ cm}^2/(\text{V}\cdot\text{s})$; resistivity $\sim 10^{-6} \text{ }\Omega\cdot\text{cm}$), **thermal** (thermal conductivity $\sim 5000 \text{ W}/(\text{m}\cdot\text{K})$), **mechanical** (Young's modulus $\sim 1,100 \text{ Gpa}$; fracture strength 125 Gpa) and **optical properties** (97.7 % transmittance of white light).

Graphane (GH)

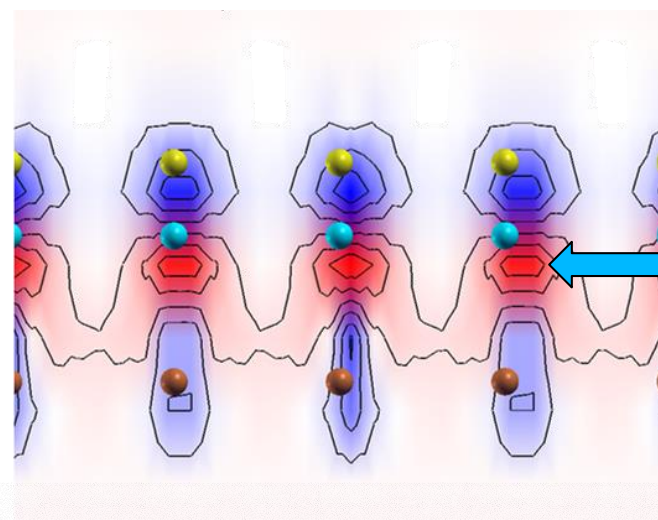


- Graphane is a two-dimensional hydrocarbon constituted by graphene fully-hydrogenated on both sides of the plane.
- The carbon atom hybridization is modified from sp^2 into sp^3 , giving it semiconductor properties rather than semi-metallic, as for graphene.
- DFT calculations estimated a direct band-gap of 3.5 eV at the Γ point. However high-level calculations based on the GW method predict band-gap values in the range 5.4 - 6.1 eV.

First Principles Atomistic Model of the Copper-Graphane Interface

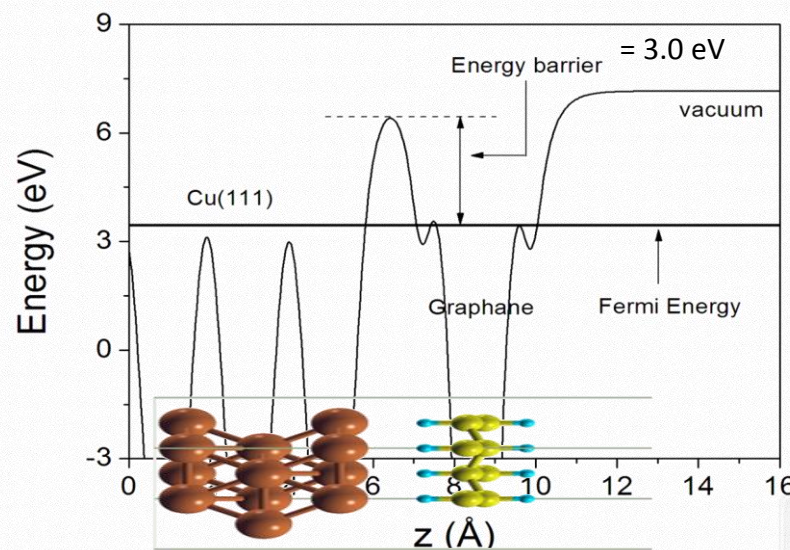


adhesion energy $0.219 \text{ eV } \text{\AA}^{-2}$
comparable to graphene



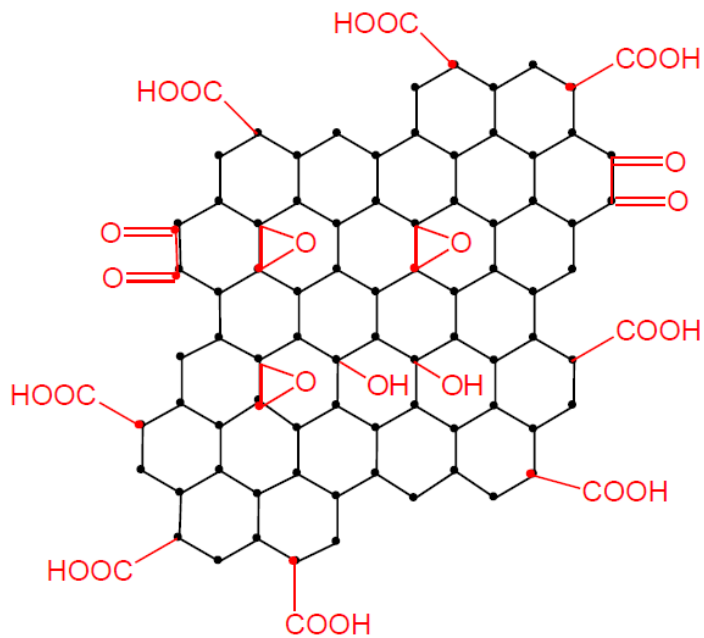
Charge accumulation at the interface

- The energy barrier of 3.0 eV at the interface, suggests that graphane could be used as an insulating thin coating or as charge transport layer in conjunction with metals and semiconductors for optoelectronic devices



Energy barrier calculation

Graphene Oxide (GO)



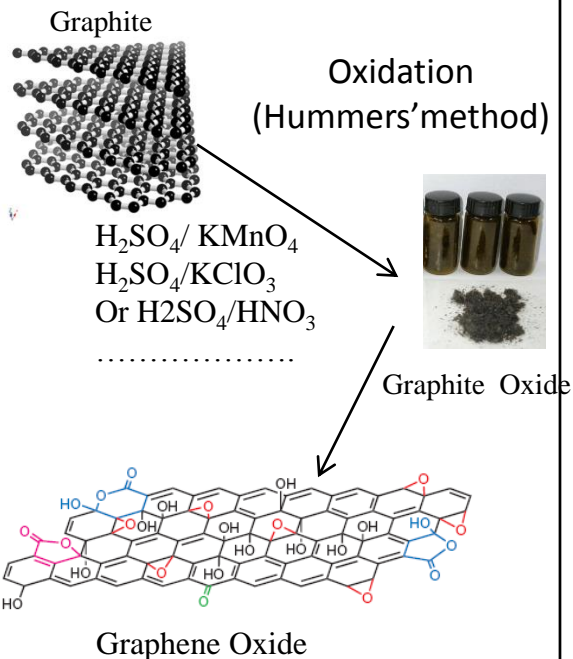
- The aromatic ring of graphene can be disrupted in the presence of strong oxidizing agents or gas-phase oxidation methods, in such a way to form graphene oxide (GO)
- Epoxide and hydroxyl groups are located in the basal planes
- Carbonyl and carboxyl groups are located at the edges
- GO composition strongly depends on many factors, such as the employed raw material, the type of oxidant, the reaction condition, etc.
- Recent models agree upon an amorphous structure without stoichiometric ratio
- Due to the top-down preparation procedure along the common chemical routes, no other species, neither covalently bonded hydrogen, can be present. Nevertheless, we can presume that via alternative bottom-up chemical-physical methods, such as by chemical vapor deposition (CVD), the formation of hydrogenated GO structures (HGO), cannot be precluded.

Synthetic routes towards O- and H-functionalized graphene

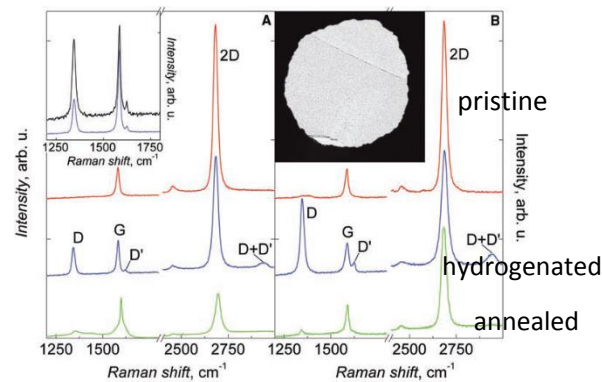
Top-Down Approach

Bottom-Up Approach

liquid-phase
(e.g., GH: Birch reduction
GO: Hummer's method)



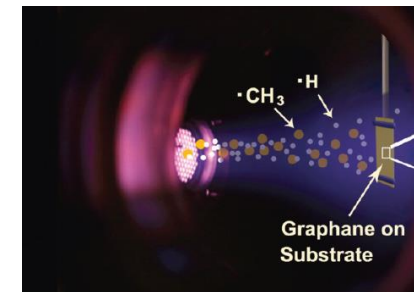
gas-phase
(e.g., GH: hydrogen plasma)



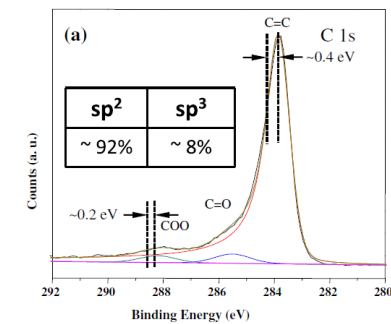
(A) Graphene on SiO₂
(B) Free-standing graphene.

Elias D C et al 2009 Science 323 610

Chemical Vapour Deposition
(CVD)

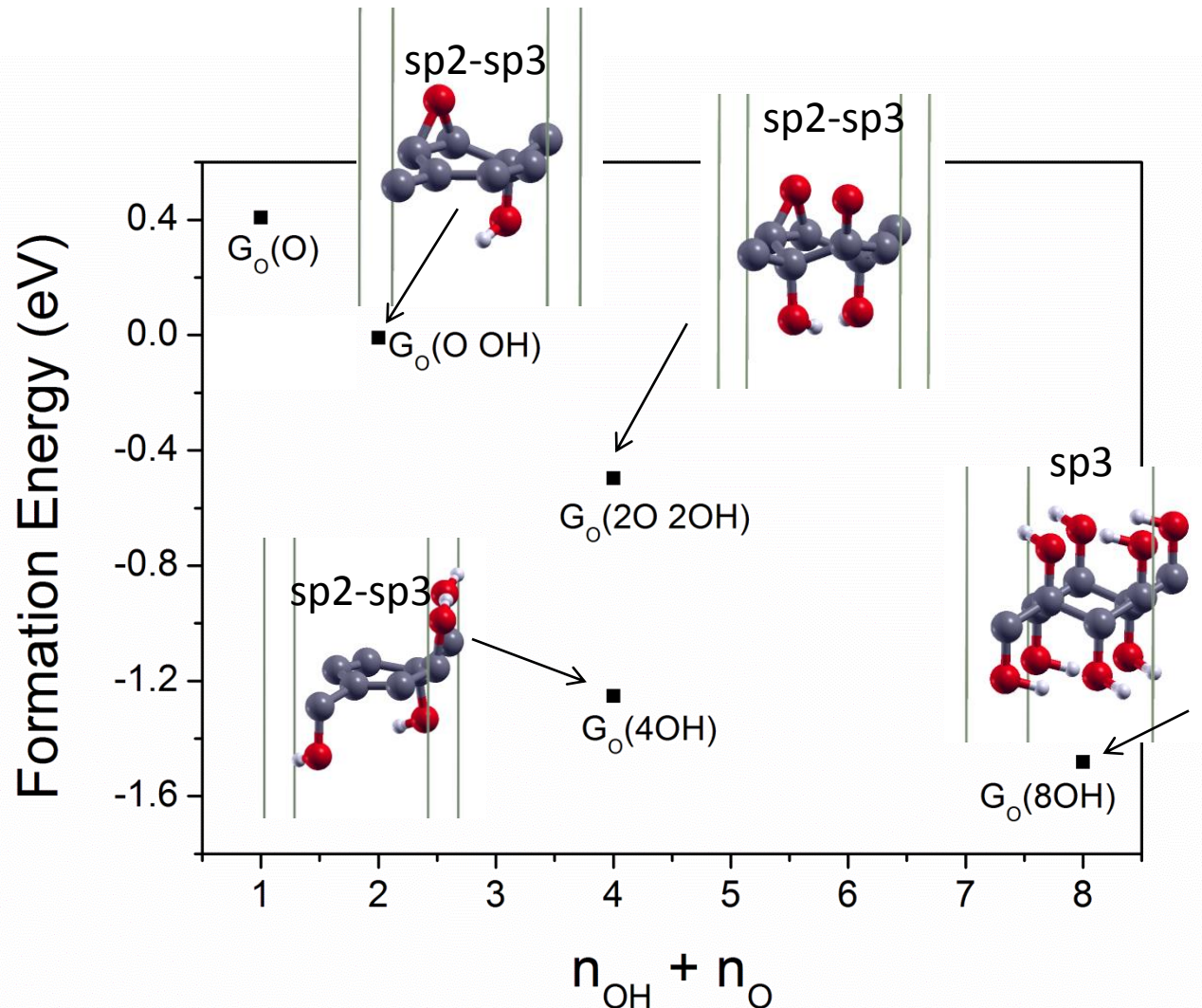


Wang et al 2010 ACS Nano 4 6146



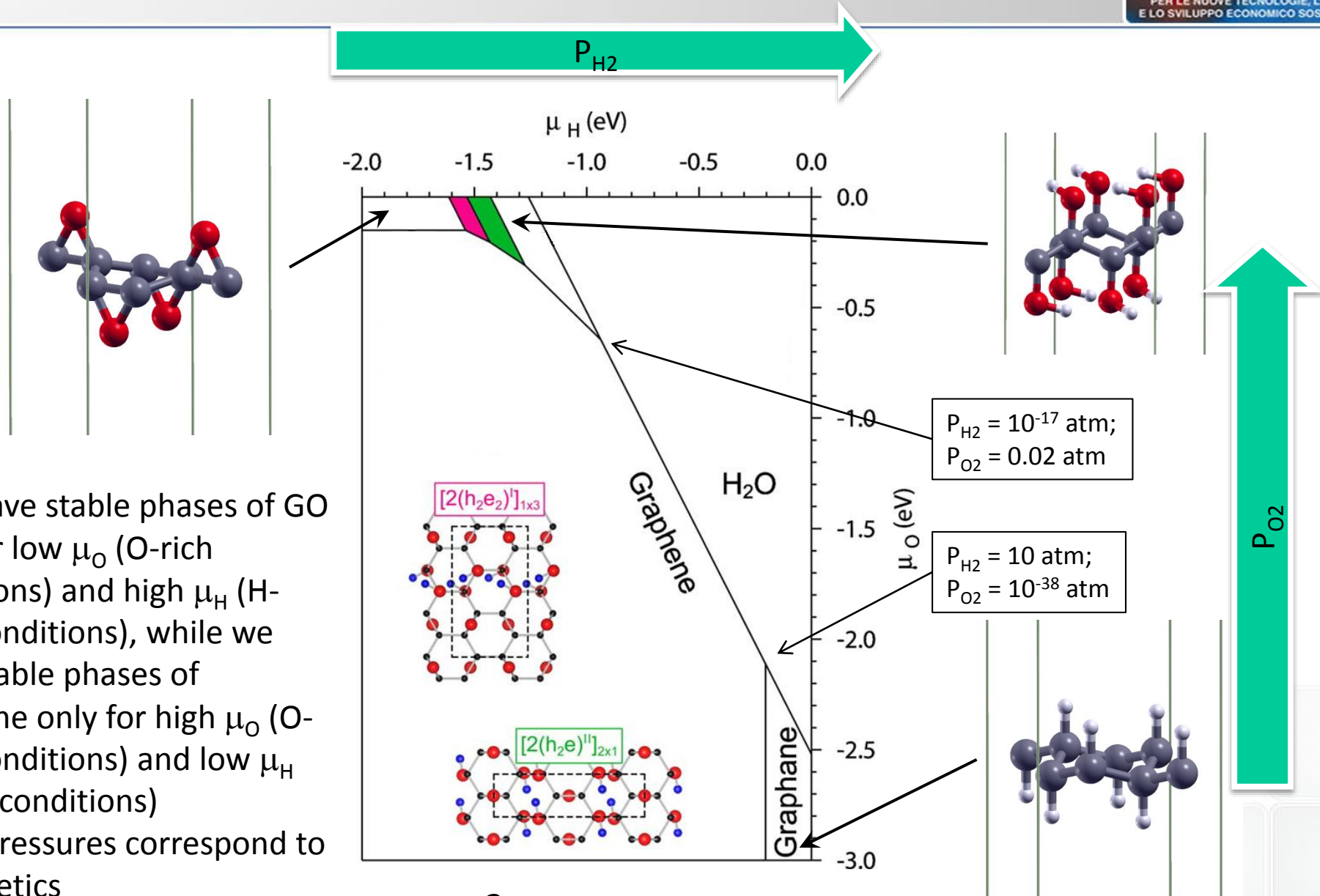
Paul et al. Carbon 49 (2011) pp 3789–3795

2 × 2 Supercell for GO: the stable structures (epoxide/hydroxide)



- The module of formation energy says how much stable or unstable is the system. Low formation energy (i.e. more negative values) corresponds to more stable systems.

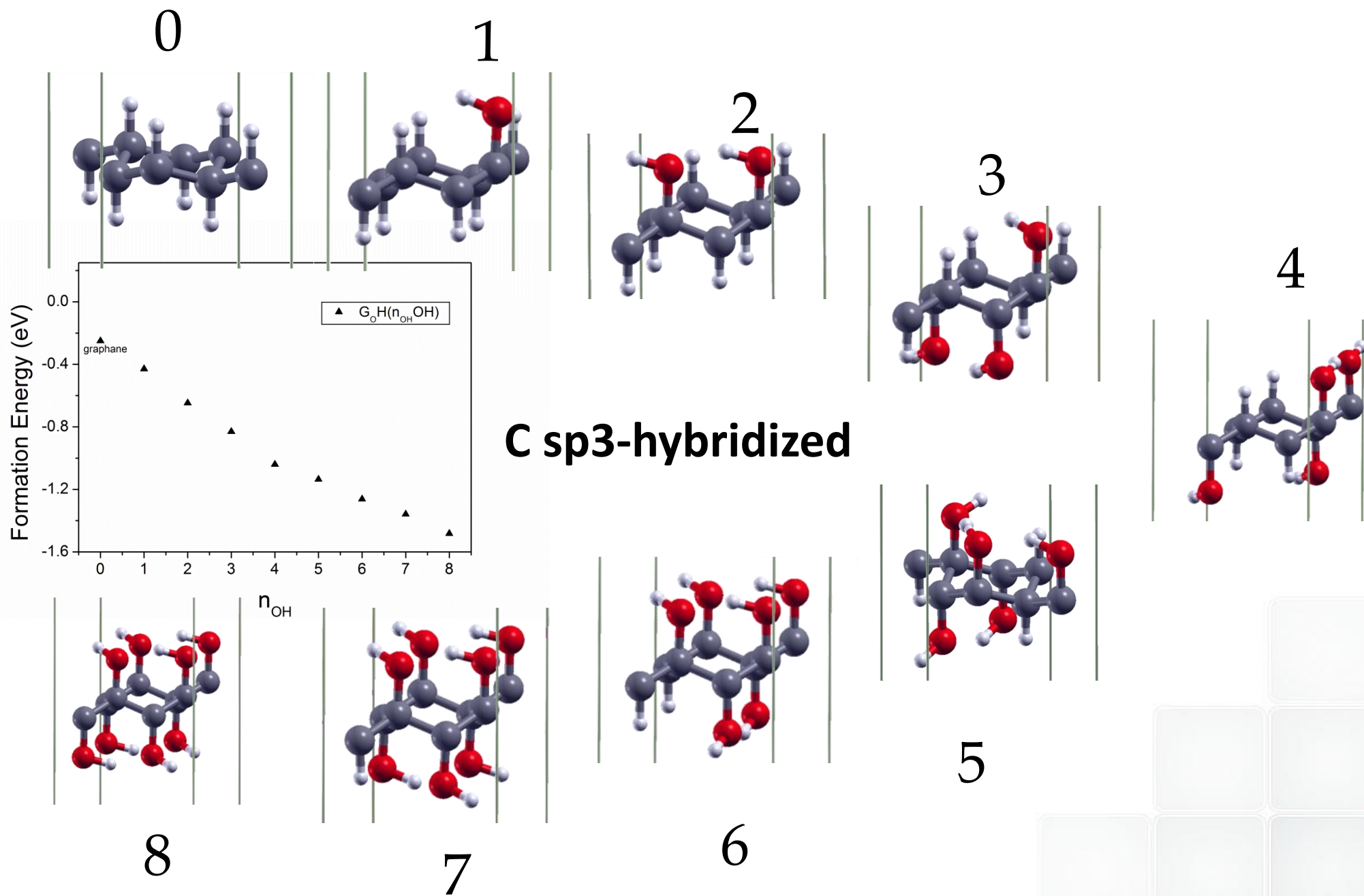
Phase Diagram of Graphene Oxide



- We have stable phases of GO only for low μ_O (O-rich conditions) and high μ_H (H-poor conditions), while we have stable phases of graphane only for high μ_O (O-poor conditions) and low μ_H (H-rich conditions)
- Low pressures correspond to low kinetics

C sp^3 -hybridized

HGO: H/hidroside functionalization



In conclusion...

- The formation of hydrogenated and non-hydrogenated graphene derivatives, functionalized with epoxide and hydroxyl groups, is possible only under extreme conditions.
- Moreover, the growth not only requires the stable phases to belong to the stability region of the phase diagram, but also needs to overcome the reaction barriers and have a favourable kinetic, which is difficult to envisage in presence of such low chemical potentials (and pressures)
- Besides, it is well known that in the presence of catalyst and molecular hydrogen the hydrogenation of alkenes takes place (that in non catalytic reaction can be achieved only at very high temperatures). In the CVD growth of carbonaceous films the presence of the catalyst reduces the barriers and can selectively promote the local exchange of H and O atoms from the gas phase and the growing carbon film.
- We also notice that by using plasmas it is possible to further modify the chemical potentials. Plasmas can dissociate H_2 and O_2 molecules into their atomic counterparts while also increasing the chemical potential of selected chemical species at selected surfaces by promoting the flux of charged ions and radicals, favouring their insertion in the growing lattice

- Stable phases of GO with low contents of hydrogen functionalization are found only for O-rich and H-poor conditions, while we have stable phases of GO with high contents of hydrogen functionalization only for O-poor and H-rich conditions. But, the partial pressures calculated are extreme
- However, in CVD growth in the presence of the catalyst and by using plasmas it is possible to further modify the chemical potentials and to achieve stable phase conditions. More investigations are required
- Moreover, some of the sp^2 - sp^3 graphene derivatives observed in experiments can be also metastables phases
- Functionalized graphene derivatives can be used as an insulating thin coating and/or as charge transport layer in conjunction with metals and semiconductors for optoelectronic devices (we have seen an application)

Acknowledgements



This theoretical work:

Nicola Lisi – *ENEA Casaccia*

Andrea Capasso – *IIT, Genoa*

Experiments:

TS.VII.D.4 (September 21th, 15:00): Nicola Lisi – *ENEA Casaccia* - *The growth of carbons on copper from ethanol vapours: a powerful and flexible technique*

Andrea Capasso – *IIT, Genoa*

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Luca Ortolani - *CNR, Bologna*

Thank you for your attention