Density Functional Theory Study of Graphene Oxide Obtained from Epitaxial Graphene: Computations Meet the Experiments

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Abstract

Graphene oxide is a complex material of both fundamental and applied interest [1-7]. Elucidating the structure of this material is crucial to achieve control over its properties and technological applications. Graphene oxide is a layered material, it is nonstoichiometric and hygroscopic, and its physical properties depend critically on synthesis procedures and post-synthesis treatments [3,4,7]. Nowadays, numerous efforts are in place to control the properties of this versatile layered carbon-based material to enable its applications in catalysis, optoelectronics, and filtration technologies.

This presentation reports on very recent density functional theory (DFT) studies of “epitaxial” graphene oxide (hereafter EGO), a particular type of graphene oxide obtained by chemical (Hummers) oxidation of multilayer graphene films grown epitaxially on silicon carbide [7]. This computational work encompasses the use of a variety of computational methods including Car-Parrinello DFT-based molecular dynamics simulations to generate model structures of EGO, the core-excited pseudo-potential technique to compute X-ray photoelectron spectroscopy (XPS) core-level energy shifts (Figure 1), the nudged-elastic band method to find reaction/diffusion transition states and energies (Figure 2), and statistical Monte Carlo simulations to mimic the aging of EGO [5]. The combination of these computational methods enabled us to interpret and achieve agreement with an extended set of experimental data on EGO, including XPS, Infrared spectroscopy (IR), X-ray diffraction (XRD), and Atomic Force Microscopy (AFM) measurements.

Thanks to the combination of computations and experiments, our studies have yielded a comprehensive atomistic understanding of EGO [1-7].

In summary, EGO exhibits a uniform layered structure, consisting of a stack of graphene planes hosting predominantly epoxide and hydroxyl groups, and water molecules intercalated between the oxidized carbon layers. As-synthesized EGO films present an O:C ratio of about 0.44; they incorporate a negligible quantity of water, and the graphene layer is richer in epoxide than hydroxyl groups. Chemical oxidation introduces also hydrogen species chemisorbed on the regular regions of the graphene planes [7]. These species react sequentially with epoxide and hydroxyl groups, leading to a decrease and increase of the epoxide and hydroxyl groups, respectively, as well as to the internal formation of water molecules [7]. The occurrence of these ageing processes and consequent production and partial loss of water molecules explain features in the XPS and IR spectra [3,4], and lead to devise a detailed picture of both the intra- and inter-layer structure of the EGO films. In particular, our calculations show that aged EGO encompasses layers presenting nanosized oxidized domains with high concentration of oxygen functionalities and local structural order, surrounded by regions of pristine graphene (Figure 3) [5]. The highly oxidized nanodomains are hydrophilic are attract water molecules, which are trapped in the vertical direction...
between oxidized domains belonging to layers stacked onto each other. The overall water content in the aged EGO films does not surpass 10% (of the total number of C atoms in the films). This quantity of water forms about one monolayer of molecules trapped between the hydrophilic domains of EGO, and it is thanks to the presence of these nanodomains and trapped water molecules that the interlayer spacing in EGO reaches a value of about 10 Å (Figure 3), in remarkable agreement with XRD measurements [4]. Interlayer distance and the amount of water intercalated in EGO are parameters directly linked to the elastic properties of these 2D films (Figure 3). The elastic properties of EGO have been measured by using AFM indentation measurements and the experimental data show a remarkable agreement with the results obtained from DFT calculations [1], providing further support for the validity of our combined computational and experimental analyses, and thus the atomistic picture of EGO (Figure 3). The insight gained so far about EGO, from chemical composition to the nanoscale characterization of the film structure, will be used to fine-tune synthesis procedures and properties of this important material.

References


