

First-principles study of the structure and mechanical properties of graphene oxide

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Abstract

Graphene oxide (GO) is a layered graphene with oxygen-contained functional groups, which plays an important role in synthesis of graphene from chemical reduction [1]. Also, due to abundant functional groups, GO shows promising applications in chemical engineering, energy storage, environmental science, and biotechnology. However, it's very difficult to determine atomistic structure of GO due to its nonstoichiometry since the oxygen-contained groups and their arrangements across the carbon network vary much more in different synthesis conditions. Using spectroscopic techniques, such as solid-state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge spectroscopy (XANES), and Raman spectroscopy, the types of oxygenated functional groups in GO can be determined [2]. Now it is commonly accepted that GO bears epoxy (C-O-C) and hydroxyl (C-OH) on its basal plane.

However, how are the epoxy and hydroxyl distributed spatially over the graphene plane? Numerous experimental measurements suggest that they are distributed amorphously; while theoretical simulations show that the epoxy and hydroxyl prefer to form ordered structure to lower the total energy. To address this controversial issue and gain a deeper insight into the structural characteristics of GO, we considered the possibility of amorphous structural models of GO and compared them with the ordered structures by using the plane-wave pseudopotential technique implemented in the CASTEP program [3]. Then, employing Vienna *ab initio* simulation package (VASP), we further studied the mechanical properties of GO for both the amorphous and ordered GO models [4].

According to some confinement rules, we randomly placed epoxy and hydroxyl groups on the basal graphene layer to construct GO models with tunable oxygen coverage (R) and ratio of hydroxyl to epoxy (OH : O) [3]. Then we compared the amorphous GO with the ordered structure proposed previously [5, 6]. It was found that formation of hydroxyl groups on graphene basal is easier than that of epoxy due to the effects of hydrogen bonds. At the same stoichiometry, ordered GO presents better thermodynamic stability than the amorphous one. But, when the coverage is less than 5%, amorphous GO can have comparable stability to the ordered GO. For the case of fixed OH : O ratio but different R s, optimized GO models with low energies always contain some local ordered structures. Similarly, for the case of constant R but different OH : O ratios, local ordered structures also exist in the energetically preferable GO models, as shown in Fig. 1. This can be attributed to formation of hydrogen bonds between the ordered functional groups, which can lower the energy and stabilize the GO structure. Therefore, the real GO sample fabricated in experiments may be in a local ordered but long-range amorphous pattern. On the other hand, for both the amorphous and ordered GO models, increasing the R will lead to a large band gap, as shown in Fig. 2, which provides an effective approach to tune the electronic properties of GO.

In addition, through comparing mechanical properties between the ordered and amorphous GO models, it was found that at the same stoichiometry, ordered GO has larger Young's modulus, intrinsic strength and critical failure strain than those of the amorphous GO, as shown in Table 1 [4]. Increase of the R will degrade the Young's modulus and intrinsic strength of GO. Generally, mechanical properties of GO depend mainly on the R and spatial distribution of functional groups (ordered or amorphous). Change of OH : O ratio only slightly fluctuate the Young's modulus. Particularly, GO shows significant strain-tuned electronic properties. Under uniaxial tensile strain, band gap of the GO gets shrinked with the strain due to weakening of C-O hybridization, as shown in Fig. 3. Therefore, in addition to change of R , external strain is another effective way to tune the electronic properties of GO.

References

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Table 1 For the case of OH : O = 2.00 but different R s, comparison of Young's modulus (E), intrinsic strength (τ_c) and critical failure strain (ϵ_c) between the ordered and amorphous GO models, along with that of the graphene ($R = 0\%$) for reference, where the van der Waals distance is taken to be 7 Å.

R	Ordered GO			Amorphous GO		
	E (GPa)	τ_c (GPa)	ϵ_c	E (GPa)	τ_c (GPa)	ϵ_c
0%	495	47.8	20%	495	47.8	20%
10%	469	46.3	18%	431	40.9	13%
20%	454	44.4	17%	395	37.5	13%
40%	421	40.0	16%	367	33.1	13%
50%	408	38.6	16%	325	27.9	10%

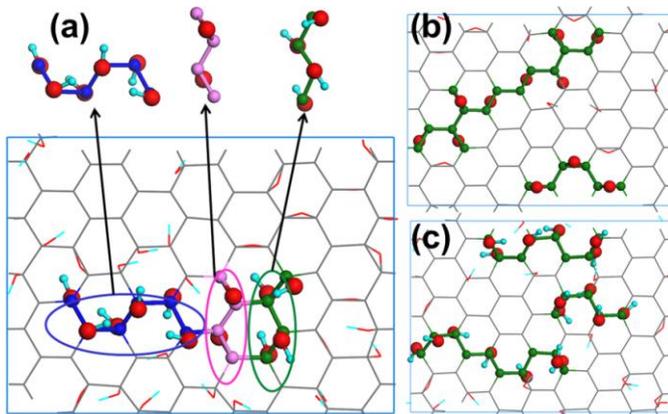


Figure 1. Local ordered structures in amorphous GO models. (a) has OH : O = 2.00 and $R = 70\%$; (b) has OH : O = 0.22 and $R = 50\%$; and (c) has OH : O = 8.00 and $R = 50\%$.

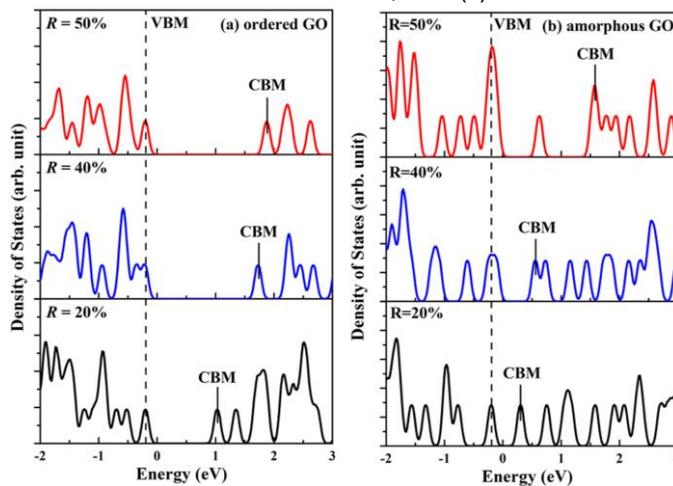


Figure 2. Increase of band gap with enlarging R for both ordered (a) and amorphous (b) GO.

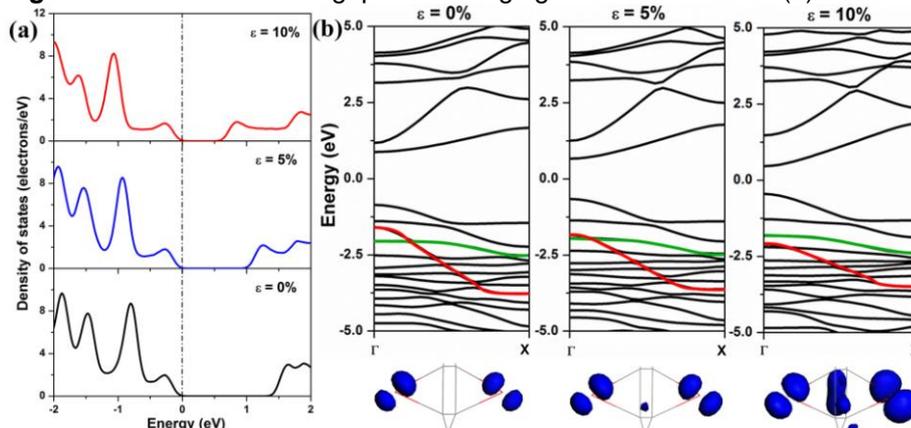


Figure 3. Shrinkage of band gap under uniaxial tensile strain for the ordered GO (a) and release of charge due to weakening of C-O hybridization under strain (b).