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Tailoring physical properties of graphene: Effects of hydrogenation, oxidation, and grain boundaries by atomistic simulations



Lizhao Liu^{a,b}, Junfeng Zhang^c, Haili Gao^d, Lu Wang^e, Xue Jiang^b, Jijun Zhao^{b,*}

^a School of Science, Dalian University of Technology, Panjin Campus, Panjin 124221, China

^b Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

^c School of Physics and Information Engineering, Shanxi Normal University, Linfen 041004, China

^d College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China

e Functional Nano & Soft Materials Laboratory (FUNSOM) and Collaborative Innovation Center of Suzhou Nano Science and Technology, Jiangsu Key Laboratory for

Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China

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ABSTRACT

Graphene, a two-dimensional monolayer of carbon atoms in honeycomb structure, is a research hotspot in multidisciplinary due to its excellent physical properties. To further extend the applications of graphene, various strategies have been proposed to tailor its physical properties. Recently, our group has carried out systematically computational studies on modifying graphene, including hydrogenation, oxidation, and introduction of grain boundaries. Both the hydrogenation and oxidation will convert sp² hybridized carbons into sp³ configurations, while formation of grain boundaries only makes the sp² carbon bonds distorted. Employing density functional theory calculations, structures, physical properties and applications of these modified graphene were explored, such as structural phase diagram, mechanical and electronic properties, and photocatalytic applications. It turns out that many physical properties of graphene are tunable, endowing graphene promising applications in various fields. In this review article, we will generally summarize our recent works on the hydrogenated graphene, graphene oxide, and graphene grain boundaries.

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1. Introduction

Graphene, a monolayer of graphite, was successfully obtained in 2004 through peeling highly oriented pyrolytic graphite by cellophane tape [1]. Since graphene is only one atom thickness, it is indeed a two-dimensional (2D) material. In particular, fabrication of the 2D graphene is a breakthrough work, which breaks previously theoretical prediction of inexistence of the 2D materials [2,3]. Afterwards, graphene triggers wide research interests in the 2D materials, where various 2D materials have been achieved [4,5], such as hexagonal boron nitride sheets [6,7], MX₂ (formed of transition metal atoms and chalcogens) monolayer [6,8], and silicene [9–13].

As a superstar nanomaterial, graphene holds great promise due to its excellent physical properties such as large mechanical strength, high thermal conductivity, and superior optical transmittance [14–16]. However, graphene is a semimetal with a zero gap where conduction bands and valance bands crossed at the Fermi

* Corresponding author. E-mail address: zhaojj@dlut.edu.cn (J. Zhao).

http://dx.doi.org/10.1016/j.commatsci.2015.06.032 0927-0256/© 2015 Elsevier B.V. All rights reserved. energy, forming Dirac cones. The zero gap of graphene limits its applications in semiconductor technology. Therefore, how to tune the physical properties (especially the electronic properties) of graphene, becomes a hotspot of graphene research.

Hydrogenation is a common way to convert sp^2 hybridization state of carbons into sp^3 configurations and then open a band gap in hydrogenated graphene (HG). Depending on hydrogen coverage and configurations, the band gap of HG with paired hydrogen vacancies can be tailored continuously from 0 to 4.66 eV. Particularly, the most stable graphane with fully hydrogenation on both sides is an insulator with a big energy gap of about 5.4 eV calculated with GW method [17], which has also been demonstrated in the reversible hydrogenation process of graphene by an electrical transport measurement [18]. Such tunable band gaps between mid-ultraviolet and near-infrared (NIR) regions (ca. 0.5–5 eV) may lead to potential applications of HG in future electronics and photonics [19–21].

Similarly, oxidation is another common approach to open a band gap in graphene oxide (GO) through converting sp² hybridized carbons into sp³ hybridizations. GO is a monolayer of graphite oxide, which can be obtained by exfoliating graphite oxide



into monolayers. Although numerous experimental characterizations demonstrated that epoxies (-O-) and hydroxyls (-OH) are the two dominant oxygen-containing groups on the graphene basal plane, the structure of GO is still ambiguous hitherto since the functional groups and their arrangements across the carbon network vary with different synthesis conditions [22]. The structure of GO has been intensively investigated via computer simulations. Generally, a structural model with epoxies and hydroxyls orderly arranged in a chained form is considered to be thermodynamic stable [23]. Moreover, by varying coverage, ratio and arrangement of the oxygen-containing groups, the physical properties of GO, such as thermodynamic stability, band gap, and mechanical strength, can be tailored. For example, depending on the coverage and ratio of the epoxies and hydroxyls [24], the band gap of GO is tunable from 0 to 4.0 eV from density functional theory (DFT) calculations. The tunable physical properties enable GO promising applications in numerous fields including transparent and flexible devices, photocatalyst, energy storage and biotechnology.

In addition, line defects in graphene like grain boundaries (GBs) can also modulate the mechanical and electronic properties of graphene. GBs are intrinsic structural elements in the polycrystalline graphene, which connect the single-crystal graphene domains. In the experimental fabrication of large-scale graphene, graphene domains have many possible growth orientations, which consequently result in different structures of GBs [25]. Depending on the structures of GBs, the physical properties of graphene varies a lot. The mechanical strength of a graphene GB shows a linear decrease as the inflection angle increases [26]. On the other hand, existence of GBs in graphene can open a moderate band gap up to 0.5 eV from first-principles predictions [27]. Thus, exploring the effects of GBs on the physical properties of graphene is significant for the device applications of graphene-based materials.

Recently, our group has carried out a series of computational studies to tailor the physical properties of graphene, which will be comprehensively reviewed in this article. Several strategies have been proposed to open the band gap of graphene, including hydrogenation, oxidation, and introduction of GBs. Among these three approaches, both the hydrogenation and oxidation can modify the band gap of graphene in a wide range, usually from 0 to 4.5 eV, depending on the coverage of hydrogen or oxygen groups. However, introduction of GBs can only open a small band gap, usually within 0.5 eV, since it only makes the sp² carbon bonds distorted. Other physical properties of the modified graphene, such as thermodynamic stability, mechanical strength, and electronic transport, have also been considered. Some related technological applications such as photocatalyst are also discussed.

2. Computational details

First-principles calculations were carried out to investigate the properties of the HG, GO, and graphene GBs.

First, structural modeling of the HG was started from the fully hydrogenated graphene (graphane) on two sides in the chairlike configuration due to its preferable stability and high symmetry [28]. Considering the nature of random distribution of H vacancies in graphane, a large orthogonal supercell ($C_{240}H_{240}$) was adopted with optimized lattice parameters of 26.417 and 25.420 Å, respectively. To avoid the interaction between periodic images, a vacuum thickness of ~15 Å was chosen. Employing density functional theory implemented in the DMol³ program [29,30], all the structures were fully relaxed without any symmetry constraint. The exchange-correlation functional was treated by the generalized gradient approximation (GGA) with the PW91 parameterization

[31]. Double numerical basis including d- and p-polarization function (DNP) was used for all-electron treatment. The Γ point and a 5 × 5 × 1 Monkhorst–Pack k-point mesh [32] were chosen for the geometry optimizations and calculations of electronic properties, respectively. The relaxation of atomic positions was considered to be converged when the change in total energy is less than 1.0×10^{-5} Ha/Å, and the force on each atom is less than 0.004 Ha/Å.

Then, both the ordered and amorphous GO models were investigated. The ordered GO models were constructed from motif-constructed models. Using a large 10×10 supercell, an epoxy group was first placed at the center of the supercell and then hydroxyl group(s) was put at the three nearby nonequivalent carbon sites around the epoxy group to find the low-energy zero-dimensional (0D) GO motifs. From the stable 0D motifs. 1D chains and further 2D GO models can be constructed. Employing the Vienna *ab initio* simulation package (VASP) [33] with the Perdew–Burke–Ernzerhof (PBE) approximation [34] for exchange-correlation interactions and the projector-augmented wave (PAW) method [35] for ion-electron interactions, structural phase of the motif-constructed GO models was predicted. The cut-off energy for the plane-wave-basis expansion is 544 eV. A vacuum thickness of 15 Å in the direction normal to the GO plane was adopted to separate the GO sheet from adjacent images. Both the atomic positions and the lattice vectors and angles were fully relaxed until the forces on all atoms are less than 0.01 eV/Å and the stresses on the cell less than 0.1 GPa. For different supercell sizes, the Brillouin-zone integrations are done with sufficient k-point sampling that ensures total energy convergence to 0.005 eV.

On the other hand, considering that the GO samples obtained in experiments are always disordered, presenting random configurations, we also studied the amorphous GO models. The amorphous GO models were started from a rectangular graphene supercell consisting of 80 carbon atoms. Afterwards, hydroxyl and epoxy groups were randomly placed on the graphene sheet using Monte Carlo method [36] according to some structural rules based on the 0D motifs, such as adding hydroxyl pairs. By varying the numbers of epoxy and hydroxyl groups within the simulation supercell, amorphous GO models with different coverages and hydroxyl to epoxy ratios can be formed. Using the plane-wave pseudopotential technique implemented in the CASTEP program [37], geometry optimizations and electronic property prediction were carried out. The exchange-correlation interactions were described by the GGA/PBE functional [34] and ion-electron interactions were described by the norm-conserving pseudopotentials [38]. A kinetic energy cut-off of 600 eV and the Γ point were used for geometry optimizations. The lattice parameter of 12 Å normal to the GO plane was chosen to avoid the interaction between the GO layer and its periodic images.

Besides, VASP with the PW91 functional [31] for the exchangecorrelation interaction and the PAW pseudopotential [35] for ionelectron interactions was adopted to calculate the mechanical properties of both the ordered and amorphous GO models under uniaxial tensile strains. A kinetic energy cutoff value of 800 eV was used to ensure good convergence of stress. During the geometry optimization, the k space for amorphous GO systems was sampled by the Γ point, and Monkhorst–Pack grids [32] with a separation of 0.03 Å⁻¹ were chosen for the ordered GO structures. The lattice parameter normal to the GO plane is chosen to be 15 Å to avoid the interaction between the GO layer and its periodic images. All the structures were fully relaxed using the conjugate gradient algorithm until the force on each atom was less than 0.01 eV/Å. After geometry optimizations, each structural model was stretched with a uniaxial strain step of 0.5% to obtain the mechanical parameters and 1% to get the failure behaviors.

Finally, structures, stabilities and mechanical and electronic properties of graphene GBs were also studied by the DFT calculations. The structures and electronic and mechanical properties of graphene GBs were investigated using the VASP code with PW91 functional [31] for exchange–correction interactions and PAW [35] for ion–electron interactions. The plane-wave basis was expanded to a cutoff energy of 400 eV. A vacuum space of 1.2 nm thickness was added to the direction perpendicular to the graphene sheet. For each GB configuration, the atomic coordinates and the in-plane supercell parameters were fully relaxed.

Starting from the equilibrium geometry, a series of uniaxial tensile strains were gradually applied with 1% increment perpendicular to the boundary line, while the atomic coordinates were fully relaxed at each strain step to obtain the stress corresponding to the stain. From the strain–stress curves, mechanical parameters and failure behaviors can be determined. Moreover, the failure behaviors of the graphene GBs were further simulated by molecular dynamics (MD) with a reactive empirical bond order potential [39]. All MD simulations were performed on a graphene monolayer of 600–1000 atoms within an NVT ensemble at 1500 K. The supercell size was about $6 \times 3 \times 2$ nm. Within the graphene plane, tensile strains perpendicular to the boundary line were gradually applied in 1% increment until complete failure of the graphene GBs. At each strain, the system was fully relaxed for 1 ns with a MD time step of 2 fs.

In addition to the electronic properties (electron density of states) calculated by the VASP, the transport properties of graphene GBs were investigated using the Nanodcal code, which combines first-principle technique with the Keldysh nonequilibrium Green's function (NEGF) [40–42]. Real space linear combination of atomic orbital (LCAO) basis set of DZP was used. The quantum conductance and quantum transmission were computed by including self-energies for the coupling of a 3-nm-wide scattering region to the semi-infinite graphene leads under the zero-bias voltage.

3. Band gap tuning of HG

Hydrogenation of graphene has attracted great interests owing to two issues: tuning band gap for graphene used in semiconductor-based electronic devices and possible devotions to hydrogen storage [18,43–45]. There are two kinds of typical free-standing HG structures with distinctive properties: H atoms adsorbed graphene (with only one or two H atoms), and graphane, a fully HG. The former can open a gap bigger than 1 eV accompanying with an inevitable mid-states, and the latter behaves as an insulator with a gap of 5.4 eV (from accurate GW calculations [17]). Considering that the zero band gap of pristine graphene and the large band gap of graphane suggest the enormous potential to tailor the band gap in a wide range by controlling the hydrogen coverage, we have systematically investigated the electronic structures of HG of different coverage and configurations using DFT calculations [19].

Starting from the chairlike configuration of graphane [28] represented by a large supercell containing 240 carbon atoms and 240 hydrogen atoms, three types of HG configurations were considered: (I) randomly removing H pairs from fully HG; (II) randomly removing individual H atoms from fully HG; (III) creating paired H vacancies according to some ordered pattern. For the configurations with randomly paired H vacancies, we studied a series of H coverages of 95.8%, 91.7%, 87.5%, 83.3%, 79.2%, 75%, 70.8%, and 66.7%, corresponding to C₂₄₀H₂₃₀, C₂₄₀H₂₂₀, C₂₄₀H₂₁₀, C₂₄₀H₂₀₀, $C_{240}H_{190}$, $C_{240}H_{180}$, $C_{240}H_{170}$, and $C_{240}H_{160}$ in our supercell model, respectively. Fig. 1 presents two examples of C₂₄₀H₂₁₀ and C240H160 supercells with random distribution of paired H vacancies. It was found that at the same H coverage, the partially HG configurations with paired H vacancies possess notably higher binding energies than those with unpaired H vacancies, indicating that the paired vacancies are more energetically favorable. The energetic preference of the paired H vacancies can be ascribed to paired dehydrogenation reducing the local strain around the unsaturated C atoms. In addition, the higher H binding energy for paired HG configurations at the H coverage of 70.8% than that for a H₂ molecule implies that formation of these partially hydrogenated graphene with sufficiently high H coverage from gaseous H₂ molecules and graphene is exothermic.

Afterwards, effects of removing radicals by C=C double bonds on the electronic structures of the HG were studied. HG with single H vacancies always presents some midstates in the gap region due to the unsaturated dangling bonds, which were also found by Lebegue et al. through introducing a single H vacancy in graphane [17]. Electronic density of the midstates mainly distribute around the unsaturated carbon atoms, whereas removal of nearest neighbor H atoms leads to the C=C double bonds, which in turn induce impurity states near the band edges. Thus we can observe a clean band gap of ~1.91 eV for C₂₄₀H₂₁₀ with paired vacancies (the inset figure of Fig. 2), implying that the insulating graphane becomes a semiconductor after partial dehydrogenation. Further reducing H coverage to 66.7% (C₂₄₀H₁₆₀) leads to the contact of edge states at



Fig. 1. (a) Top view (upper) and side view (lower) of partially hydrogenated graphane with 87.5% H coverage ($C_{240}H_{210}$), (b) top view (upper) and side view (lower) of partially hydrogenated graphane with 75% H coverage ($C_{240}H_{160}$). The gray balls stand for sp³ C atoms saturated with H atom, red balls highlight unsaturated sp² C atoms, and light-blue balls represent H atoms. Reprinted with permission from Ref. [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Energy gap of HG as a function of H coverage. The inset figure is density of states (DOS) of $C_{240}H_{210}$ with paired H vacancies. The gray balls stand for sp³ C atoms saturated with H atom, red balls highlight unsaturated sp² C atoms, and light-blue balls represent H atoms. Reprinted with permission from Ref. [19]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the valance band maximum (VBM) and the conduction band minimum (CBM) and then diminishes the band gap, as shown in Fig. 2. With low H coverage, there are enough H vacancies in graphene configurations, which may result in the contact of different H-vacancy clusters and make it impossible to confine the π electrons in pristine graphene into chairlike graphane lattice with sp³ hybridization. Therefore, it becomes necessary to avoid hydrogen atoms adsorption in patterns for tailoring the band gap of HG.

Generally, the band gap of HG can be continuously tuned from zero to about 5 eV via appropriate pairwise dehydrogenation of pure graphane, which may lead to potential applications in future electronics and photonics. Recently, successful synthesis of partially HG in various experiments also confirm the possibility to tailor the electronic properties of HG by controlling the H coverage and configurations. For example, Yang et al. [46] have observed both edge and interior HG with a large band gap of 4 eV detected by using UV–vis spectroscopy. Zhang et al. [47] reported a band gap of 1.8 eV in the partially HG sample was, which might correspond to the partially paired HG configuration with a H coverage of ~85% as suggested by Fig. 2.

4. Structure and mechanical properties of GO

4.1. Motif-constructed models

As identified by Cai et al.'s solid-state NMR experiment [48], epoxies and hydroxyls are the two dominant oxygen-containing groups on the graphene basal plane. Moreover, they are in proximity, possibly as nearest neighbors. Based on the experimental characterization, the stable GO structures with epoxies and hydroxyls from motif-constructed models were investigated [49]. The detailed scheme can be divided into three procedures: (1) setting up low-energy zero-dimensional (0D) GO motifs; (2) building low-energy 1D chains from the 0D motifs; (3) constructing 2D GO models from the 1D chains and searching for the stable structures.

First, to search for low-energy 0D motifs composed of various hydroxyl (**h**) and/or epoxy (**e**) functional groups, different kinds of $\mathbf{h}_m \mathbf{e}_n$ motifs in a systematic way were considered, including **h** or **e** monomer, **he**, **h**₂, or **e**₂ dimer, **h**₂**e** or **he**₂ trimer, **h**₂**e**₂ tetramer, and so on. Due to the **h**-induced dangling bond, the **h** monomer, **he**

dimer and \mathbf{he}_2 trimer are unstable. Fig. 3a shows the low-energy structure of stable motifs (up to $\mathbf{h}_2\mathbf{e}_2$). For each motif, two lowest-energy structures were labeled as I and II, and their energy differences referred to motif I. For motifs larger than $\mathbf{h}_2\mathbf{e}_2$, the stable motifs are combinations of the ones shown in Fig. 3a.

Then, it was found that the 0D motifs prefer to connect with each other to form 1D chains since formation of the chains considerably would stabilize the individual functional groups, as shown in Fig. 3b-d, where the three representative chains are formed by connecting the $(\mathbf{h}_2)^{I}$, $(\mathbf{e}_2)^{II}$ and $(\mathbf{h}_2\mathbf{e}_2)^{I}$ motifs in Fig. 3a. These results are also consistent with previous reports [23]. Interestingly, armchair chains are always more stable than the corresponding zigzag chains. For example, armchair **h** chain and **e** chain show lower energy than their corresponding zigzag chains by 0.30 eV/ \mathbf{h}_2 and 0.48 eV/ \mathbf{e} , respectively. The stability of armchair chains can be attributed to a band gap opening mechanism: the calculated local density of states reveals that the zigzag chains always have half-filled states (e.g., midstates) at the Fermi level, whereas the armchair chains always open a gap locally. The existence of midstates states can be attributed to the mismatch between zigzag chain and the underlying Kekulé structure, i.e., alternative single and double bonds, of graphene.

Similarly, 1D chains tend to bind with each other via strain compensation, lowering the total energy by \sim 0.03 to 0.05 eV/Å. This leads to various 2D GO structures with different C:O:H ratios. To confirm this result, we also carried out an extensive search of the GO structures that break the long-range order of the chains to ensure that we do not miss any obvious 2D GO structures. However, no structure as stable as the chain-like structures was found.

Finally, thermodynamic stabilities of these various 2D GO structures were studied by constructing the total-energy diagram in terms of the atomic chemical potentials of oxygen and hydrogen. Compared with the phase diagram in terms of composition variation [23], the advantage of this approach is its intimate connection with the growth conditions. In particular, we calculated the formation energy of the GO as a function of the chemical potentials of O (μ_0) and H (μ_H):

$$\Delta H_f = E_{tot}(C_l O_m H_n) - E_{tot}(C_l) - m\mu_0 - n\mu_H, \qquad (1)$$

where $E_{tot}(C_lO_mH_n)$ and $E_{tot}(C_l)$ are the total energies of the GO and pristine graphene unit cells that contains *l* carbon, *m* oxygen, and *n* hydrogen atoms. The reference energies for μ_0 and μ_H are those of the gaseous O_2 and H_2 molecules, respectively.

As shown in Fig. 4, thermodynamically stable GO can only exist at the extreme O-rich (high μ_0) and H-poor (low μ_H) conditions (upper left region of Fig. 4), with a competing factor of water. Four low-energy GO structures were found, which are the **h**-only $[4(\mathbf{h}_2)^I]_{1\times 2}$, the **h** and **e** co-existing $[2(\mathbf{h}_2\mathbf{e})^{II}]_{2\times 1}$ and $[2(\mathbf{h}_2\mathbf{e}_2)^I]_{1\times 3}$, and the **e**-only $[2(\mathbf{e}_2)^{II}]_{1\times 2}$ with decreasing μ_H , respectively, where the subscripts indicate number of unit cells. Among these four phases, only the $[2(\mathbf{h}_2\mathbf{e}_2)^I]_{1\times 3}$ phase has been previously proposed [23]. Moreover, the **e**-only phase, $[2(\mathbf{e}_2)^{II}]_{1\times 2}$, has been confirmed by Casabianca et al.'s ¹³C solid-state NMR measurements [50]. Besides, it can be noticed that formation of HG also requires stringent growth condition, i.e., extreme H-rich in this case. Despite that, HG has been achieved experimentally by using a hydrogen plasma source [18]. Therefore, we believe that under suitable conditions, all the four GO phases in Fig. 4 may be synthesized.

In addition, as indicated by Fig. 4, the fully covered GOs are stable. However, the observed GOs in experiment are usually the sp²-containing ones. Two reasons can accounts for this discrepancy: one is the attractive chain-chain interaction mentioned above and the other is the lattice relaxation of the fully covered GOs. Routinely, the fabricated GOs with relatively uniformly- (or homogenously-) distributed epoxides, hydroxides, and sp² carbon



Fig. 3. (a) Stable motifs of the functional groups on GO: the \mathbf{h}_2 dimer, the \mathbf{e}_2 dimer, the $\mathbf{h}_2\mathbf{e}$ trimer, and the $\mathbf{h}_2\mathbf{e}_2$ tetramer. Motif I are the lowest energy structures and motif II has the second lowest energy, along with their total-energy differences. Stable armchair chains of functional groups formed by polymerizing (b) $[(\mathbf{h}_2)^l]_n$, (c) $[(\mathbf{e}_2)^{ll}]_n$, and (d) $[(\mathbf{h}_2\mathbf{e}_2)^l]_n$. The red, black and blue balls represent O, C, and H atoms, respectively. Reprinted with permission from Ref. [49]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Total-energy stability diagram of the GO phases of various C:O:H ratios with respect to the chemical potentials of oxygen and hydrogen. Insets show the atomic structures of the corresponding GO phases. The $[2(\mathbf{h}_2 \mathbf{e})^{l}]_{2\times 1}$ and $[2(\mathbf{h}_2 \mathbf{e}_2)^{l}]_{1\times 3}$ phases are represented by pink and green colors, respectively. Reprinted with permission from Ref. [49]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is often accompanied by an incomplete oxidation [51–53]. Therefore, for such a GO to separate into an inhomogeneous phase composed of sp^2 carbon-only islands and other functional-group-containing islands, hydroxyl and epoxy groups have to be able to diffuse. Moreover, lattice relaxation is also needed to stabilize this inhomogeneous phase, which is a kinetic process. In real experimental fabrications, GOs are synthesized at certain temperature, which allows overcoming the kinetic barrier to obtain the inhomogeneous phase.

4.2. Random models

As predicted by our DFT simulations [49,54], the energetically preferable GO structure with both hydroxyls and epoxies is the one with functional groups closely arranged along the armchair direction of graphene basal plane in an ordered manner. However, the experimental fabrication usually obtained disordered GO samples, presenting random or amorphous GO configurations. Considering this discrepancy between experimental characterizations and theoretical predictions, we investigated the possibility of amorphous GO structural models to describe the disordered GO structures observed in experiments.

Starting from a rectangular graphene supercell consisting of 80 carbon atoms, hydroxyl and epoxy groups were randomly placed on the graphene sheet using the Monte Carlo method according to some structural rules based on the 0D motifs shown in Fig. 3. By varying the numbers of epoxy and hydroxyl groups within the simulation supercell, amorphous GO models with different oxygen coverages (R_s) and hydroxyl to epoxy (OH:O) ratios can be obtained, where the oxygen coverage is defined by the ratio of

the sp³ carbons (bonded with hydroxyl or epoxy groups) to the total number of carbons.

First, by fixing an OH:O ratio of 2.00 which falls in the range of 1.06–3.25 in experimental observations [55], a series of amorphous GO models with different oxygen coverages were constructed, including R of 10% (C8006H4), 20% (C80012H8), 30% (C80018H12), $40\%~(C_{80}O_{24}H_{16}),\ 50\%~(C_{80}O_{30}H_{20}),\ 60\%~(C_{80}O_{36}H_{24}),\ and\ 70\%$ (C₈₀O₄₂H₂₈), respectively. Then, DFT calculations were carried out to relax the amorphous models. For each coverage, ten amorphous GO models were initially generated by the Monte Carlo program for geometry optimization. During optimization, dissociation of epoxies, formation and release of H₂O molecules, breaking of carbon-rings on the basal plane, and other structural damages were observed in some random GO configurations, especially for those with relatively high coverage rates ($R \ge 30\%$). Therefore, to sieve ten optimized GO structures without above mentioned structural defects, tens or hundreds of GO models should be generated initially using the Monte Carlo program. Note that the selected ten configurations are all locally stable without structural damages. Finally, the lowest-energy structure among the ten sieved configurations was selected as the representative of each coverage for further investigations. On the other hand, in order to compare with their amorphous counterparts, ordered GO structural models with coverage of 10% (C₈₀O₆H₄), 20% (C₄₀O₆H₄), 33% (C₂₄O₆H₄), 40% $(C_{20}O_6H_4)$, 50% $(C_{16}O_6H_4)$, and 67% $(C_{12}O_6H_4)$ were also constructed from the $h_2 e_2^I$ chain (Fig. 3a) with an OH:O ratio of 2.00.

Fig. 5a displays the optimized amorphous GO structure with R = 70% and OH:O = 2.00. It can be noticed that the whole system is amorphous, but some ordered motifs appear in the short range, which are highlighted and shown individually on top of the graph. Especially, the epoxy and hydroxyl groups in the highlighted parts are arranged in an ordered manner, i.e., aggregating along either armchair or zigzag directions. The armchair chain is similar to the ordered **h**₂e¹/₂ motif in Fig. 3a. Moreover, these ordered fragments may aggregate. Such locally ordered motifs were also observed in the amorphous GOs with other coverage rates (R = 10%, 20%, 30%, 40%, 50%, and 60%), which seem to be a universal feature.

To be well considered, the amorphous GOs with the same coverage but different OH:O ratios were also built. Choosing a representative R of 50%, we constructed a series of models with OH:O ratios of 0.22 ($C_{80}O_{22}H_4$), 0.50 ($C_{80}O_{24}H_8$), 0.86 ($C_{80}O_{26}H_{12}$), 1.33 $(C_{80}O_{28}H_{16})$, 2.00 $(C_{80}O_{30}H_{20})$, 3.00 $(C_{80}O_{32}H_{24})$, 4.67 $(C_{80}O_{34}H_{28})$, 8.00 (C₈₀O₃₆H₃₂), respectively. Two of the optimized GO structures are presented as representatives: one with abundant epoxy groups (OH:O = 0.22, Fig. 5b), and the other with hydroxyl-rich groups (OH:O = 8.00, Fig. 5c). As highlighted in Fig. 5b, chained structures formed by epoxy and hydroxyl groups were observed in the epoxy-dominant structure (OH:O = 0.22)and hydroxyl-rich structure (OH:O = 8.00), respectively. In other words, amorphous GO structures with different OH:O ratios also contain the locally ordered structures to enhance the thermodynamic stability.

In brief, our computational results suggest that the stable amorphous GOs exhibit disordered features in the long range but contain ordered structural motifs in the short range. Particularly, in these locally ordered motifs, clusters completely formed by hydroxyl and/or epoxy groups were observed, in agreement with previous experimental [50,56] and theoretical [23,49] results.

Generally, observation of local ordered motifs can be explained by a compromise of the formation of hydrogen bonds, the existence of dangling bonds, and the retention of π bonds. When the functional groups aggregate, hydrogen bonds are formed to lower the energy and stabilize the structure. Fig. 6 shows the hydrogen bonds in the structural model of Fig. 5a. Obviously, hydrogen bonding network is amassed in the vicinities of those three ordered parts (highlighted in Fig. 5a). Besides, dangling bonds (or unsaturated electrons) also exist in the GO sheet, making it energetically unfavorable. Aggregation of epoxy and hydroxyl groups in an ordered way can efficiently eliminate these dangling bonds (or unsaturated electrons) by self termination, which further stabilizes the GO structure. Moreover, when the functional groups in the GO are assembled, large area of sp² carbon network will be separated from the sp³ domain, finally contributing to the sp²-containing GOs observed in experiments.



Fig. 5. Representatively thermodynamic stable models of amorphous GOs: (a) GO with *R* of 70% and OH:O of 2.00; (b) GO with *R* of 50% and OH:O of 0.22; (c) GO with *R* of 50% and OH:O of 8.00. The red atom is O, the gray atom is C, and the light blue atom is H, respectively. Reprinted with permission from Ref. [57]. Copyright (2012) Elsevier B.V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Hydrogen bonds in the amorphous GO with R of 70% and OH:O of 2.00. The hydrogen bonds are highlighted by green dish lines. Reprinted with permission from Ref. [57]. Copyright (2012) Elsevier B.V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The thermodynamic stabilities of these amorphous and ordered GOs can be discussed in terms of heat of formation (H_f) , as defined by the following equation:

$$H_f = E_{CxOyHz}(GO) - x E_C(graphene) - y/2 E_0(O_2)$$
$$-z/2 E_H(H_2)$$
(2)

where E_{CxOyHz} is the total energy of GO with the chemical formula of $C_xO_yH_z$, and E_C is the energy per carbon atom in graphene. E_O and E_H are the total energies of gaseous O_2 molecule and H_2 molecule, respectively.

The computed H_f as a function of coverage R for both amorphous and ordered GO structures is plotted in Fig. 7a. First, negative H_f values indicate that formation of GO through oxidation of graphene is an exothermic process. At the some coverage, the H_f of amorphous GOs is higher than that of the ordered counterparts by up to 0.19 eV per C atom, suggesting that amorphous GO is less stable than the ordered ones. Especially, the difference of H_f between amorphous and ordered GO structures reduces as the oxidation rate decreases. Extrapolation to low coverage limit shows that the amorphous GOs could be as stable as the ordered ones when R reaches below 5%. This result coincides with our finding that the homogenous GO phase is favored at low coverage.

whereas inhomogeneous GO phase or phase separation is more likely to occur at relatively higher coverage [49].

Meanwhile, heats of formation for the amorphous GO structures with a fixed *R* of 50% but different OH:O ratios are also calculated and presented in Fig. 7b. As OH:O ratio increases, the heat of formation decreases inversely, suggesting that the GO system becomes thermodynamically favorable. On the other hand, Fig. 7b also indicates functionalization of hydroxyl groups on the graphene sheet energetically prevails over epoxy groups, which is consistent with the previous theoretical results [23,24].

From the above discussions, we found that the ordered GO structures are preferable in energy, even the amorphous GO structures also contain some locally ordered motifs. But why it is hard to observe large-scale ordered GO structures in experiment? Several possible effects such as kinetic factors during growth process and configuration entropy must be taken into account. Since formation of GO through oxidation of graphene is an exothermic process, the functional groups can be easily added onto the graphene sheet. In the initial stage of growth, functional groups prefer to aggregate along the direction with lower growth barrier that is determined by the chemical environment of the existing groups on the GO layer. While considering the kinetic factors during growth, there are high diffusion energy barriers (up to 2.89 eV) between local minima to prevent growing large ordered structures [58]. In other words, the ordered structural models predicted by the theoretical simulations are only the consequence of thermodynamic factors but are prevented by the kinetic factors during realistic synthesis condition. Besides, the effect of configuration entropy [59], which prefers the disordered structures with high probability and becomes more significant at higher temperature, may also contribute to the experimentally observed amorphous GO structures. Recently, GO samples with ordered wrinkles have been synthesized, which confirmed the ordered arrangement of epoxide groups [50,56,60]. With improvement of experimental technology, we anticipate that the large-scale ordered GO with different functional groups will be fabricated in the future.

4.3. Mechanical properties

It is well-known that graphene presents excellent mechanical properties with a Young's modulus (*E*) of \sim 1.0 TPa and an intrinsic strength (τ) of 130 ± 10 GPa [61], which are promising for future nanoscale devices [62,63]. Since GO is the oxygen-functionalized graphene, one interesting fundamental question is how would



Fig. 7. (a) Heats of formation for the amorphous and ordered GO structures as function of coverage rate *R*; (b) Heats of formation of the amorphous GOs with *R* of 50% but different OH:O ratios. Reprinted with permission from Ref. [57]. Copyright (2012) Elsevier B.V.

the oxygen-containing groups affect the mechanical properties of the perfect graphene sheet. Experimental measurement demonstrates that mechanical properties of graphite oxide closely depend on the thickness. The reported *E* for graphite oxide show a wide distribution ranging from 6 to 42 GPa [64]. However, when the thickness of graphite oxide is reduced down to a few layers, its *E* increases dramatically to about 200 GPa [65,66]. Especially, GO monolayer has a much larger *E* with a mean value of 250 ± 150 GPa [67]. In addition to the thickness, what is the role of functional groups on the graphene basal plane? We have systematically investigated the mechanical properties of both ordered and amorphous GOs of different oxidation coverages with DFT calculations, focusing on the dependence of mechanical properties on the surface coverage, type, and arrangement (e.g., ordered versus amorphous) of functional groups [68].

First, we considered the effect of oxidation coverage R. As shown in Fig. 8a, taking the GOs with OH:O of 2.00 but different coverage as examples, the ordered GO has higher E than the amorphous one at the same R. As the R changes from 70% to 10%, E varies from 380 to 470 GPa for the ordered GOs, and from 290 to 430 GPa for the amorphous ones, respectively. The calculated values are in line with the measured E of 250 ± 150 GPa [66,67], as well as the theoretical *E* of \sim 325 GPa by assuming an interlayer van der Waals (vdW) distance of 7 Å [69]. Meanwhile, E decreases monotonically as R increases, owing to incremental breaking of perfect sp² carbon network. This trend is also consistent with the previous report that the Young's modulus decreases as the coverage of functional groups on graphene sheet increases [70]. For reference, the mechanical properties of the perfect graphene were also calculated. Taking a vdW distance of 3.34 Å [26,71], the *E* for the graphene was found to be 1037 GPa, in good agreement with the experimental value (*E* of \sim 1.0 TPa) [61]. To directly compare with the GO systems, by assuming an interlayer vdW distance of 7 Å, the *E* of the graphene was rescaled to be 495 GPa, which should represent the upper limits of GOs with coverage decreasing to zero.

On the other hand, to examine the effect of OH:O ratio, the mechanical properties of amorphous GOs with R of 50% but different OH:O ratios were investigated. As presented in Fig. 8b, the E fluctuates between 290 GPa and 338 GPa as the OH:O ratio varies. In other words, the effect of OH:O ratio on the mechanical properties of the amorphous GOs is less significant than that of the R. To further confirm this fluctuating effect, we also studied the case of

R = 20% but different OH:O ratios. Similarly, *E* shows a fluctuating behavior in the range of 390 ± 14 GPa. The main reason is that once *R* is fixed, the percentage of sp³ carbon atoms remains nearly constant; thus changing OH:O ratio only weakly affects the stability of the 2D graphene-based sheet. However, varying the OH:O ratio will lead to a change of GO thickness, which finally contributes this fluctuating behavior.

In addition, strain-stress curves of both ordered and amorphous GO structures are plotted to determine the fracture strain (ε_c), which is defined by the critical strain where the strain-stress curve starts to drop. The obtained intrinsic strength τ and the fracture strain are summarized in Table 1. It can be seen that both the τ and ε_c of the ordered GOs are higher than those of the amorphous GOs at the same R. As R increases, τ decreases for either ordered or amorphous GO structures because of breaking of sp² carbon network and lowing of stability. For comparison, the τ and ε_c of a pristine graphene sheet were also calculated, corresponding to R = 0%in Table 1. Taking a vdW distance of 3.34 Å, the τ of graphene is 100.1 GPa. Similarly, it was rescaled to 47.8 GPa by assuming an interlayer vdW distance of 7 Å to directly compare with the GO systems. Again, the calculated intrinsic strength of GO is comparable to that of previous empirical prediction [69], which gave the τ of \sim 31 GPa with an assumed vdW distance of 7 Å.

Finally, fracture behaviors of the GOs were further discussed. For the ordered GOs, the first fractured bond is always an sp³ hybridization C—C bond far away from the chained epoxide groups, as highlighted in blue in Fig. 9. Two factors may contribute to this

Table 1

The intrinsic strength τ and critical failure strain ε_c of the ordered and amorphous GOs with different *R* are listed, along with that of the pristine graphene (*R* = 0%) for comparison. Reprinted with the permission from Ref. [68]. Copyright (2012) Royal Society of Chemistry.

R (%)	τ (GPa)		ε_{c} (%)		
	Ordered GOs	Amorphous GOs	Ordered GOs	Amorphous GOs	
0	47.8		20		
10	46.3	40.9	18	13	
20	44.4	37.5	17	13	
40	40.0	33.1	16	13	
50	38.6	27.9	16	10	



Fig. 8. (a) *E* as a function of *R* for both ordered and amorphous GOs. The scaled values for perfect graphene sheet by assuming a vdW distance of 7 Å (filled square) are given for reference. (b) Relationship between *E* and OH:O ratio for the amorphous GO structures with *R* of 50%. The dashed lines bracket the range of *E* values. Reprinted with permission from Ref. [68].



Fig. 9. Fracture behavior of the ordered GO with *R* of 50% and OH:O of 2.00. The first fractured C—C bond is highlighted in blue and thick stick. Reprinted with permission from Ref. [68]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

phenomenon. First, the carbon atom bonded with a hydroxyl group has a larger bond angle ($\sim 105^{\circ}$) than that bonded with an epoxide group ($\sim 55^{\circ}$), which means a large prestress. Second, far away from the chained epoxide groups make the highlighted C=C bond unable to form hydrogen bonds with the epoxide groups, which also lower its stability. As for the amorphous GOs, due to the structural complexity, those with different *R* exhibit different failure behaviors. The first fractured bond depends on the structural details of the amorphous GOs.

5. Electronic properties of GO and photocatalytic applications

5.1. Electron DOS of GO

The experimentally fabricated GO is usually insulating with a large band gap [72,73]. Fortunately, the electronic property of the GO can be tuned by varying the coverage and relative ratio of the functional groups. We systematically explored the electronic properties of both the ordered and amorphous GOs, and their response to external tensile strain.

As shown in Fig. 10a, the ordered GO structures always present a clean band gap. As the coverage increases, the band gap is enlarged due to increasing portion of sp3 carbon and further destroying of the π -conjugated bonds. For the ordered GOs with R of 20%, 40%, and 50%, the computed band gaps are 1.22, 1.92 and 2.06 eV, respectively. However, as shown in Fig. 10b, DOS of the amorphous GOs usually exhibit some defective peaks around the Fermi level (i.e., mid-states), which indicates existence of certain amount of dangling bonds. If we ignore these mid-states since they barely affect the electrical conductivity in real materials applications [74] and only consider the band gap between the CBM and VBM, the band gaps of amorphous GOs with R of 20%, 40%, and 50% are about 0.53, 0.80 and 1.77 eV respectively. Thus, the band gaps of amorphous GOs show the same trend as the ordered GOs. Such reducing trend of band gap with increasing coverage in GOs also agrees with previous reports [24,75].

Furthermore, DOS of amorphous GOs with different OH:O ratios were also studied. Similarly, defective states exist around the Fermi level. Considering the band gap between the CBM and VBM, as the OH:O ratio increases, the band gap enlarges accordingly. For amorphous GOs with OH:O of 0.50, 2.00, and 8.00, their band gaps are about 1.46, 1.76 and 2.45 eV, respectively. Increase

of the band gap with OH:O ratio may be partially attributed to the hybridization of carbon atoms. Intuitionally, the carbon atom bonded with a hydroxyl group has a larger bond angle ($\sim 105^{\circ}$) than that bonded with an epoxide group ($\sim 55^{\circ}$); thus the former is very close to that of ideal sp³ hybridization state (109.47°). Therefore, carbon atoms in the GO structures with high OH:O ratio might be dominated by sp³ hybridization, which would lead to a large band gap [23,76].

5.2. Effect of tensile strain on the electronic properties

As mentioned above, the electronic properties of GO can be tuned by varying the oxidation coverage and the OH:O ratio. Is there any other approach to tune the electronic properties of GO? To answer this question, we studied the electronic properties of GO under uniaxial tensile strain. Taking an ordered GO structure with *R* of 50% and OH:O of 2.00, and an amorphous one with the same R and OH:O ratio as examples, their electron DOS under uniaxial tensile strain within the elastic region are plotted in Fig. 11, where the elastic strain limit is 11% for the ordered GO and 8% for the amorphous GO, respectively. As the GO sheets are uniaxially elongated from the equilibrium states, the gaps become narrower, implying a trend of metallization. For the ordered GO in Fig. 11a, the gap dramatically decreases by more than 50% as the GO sheet is elongated by 10%. By ignoring the defect-induced mid-states between the CBM and VBM, the gap variation is less pronounced in the case the amorphous GO, i.e., reduction by \sim 23% after 8% elongation, as shown in Fig. 11b. Therefore, applying external tensile strain is another way to tailor the electronic properties of GO.

To understand the strain-induced shrinkage of band gap, variation of band structures and the corresponding orbitals of the ordered GO are analyzed in Fig. 12. In the valence band region, it is noteworthy that one band (highlighted in red), which corresponds to a C—O hybridized molecular level, becomes lower and flatter under tensile strain compared with its initial state due to stretching bonds. As the lowering of this band, another band crossed with it (highlighted in green), which corresponds to a C—C hybridized molecular level, is lifted up due to breaking of lattice symmetry, causing a rise of the valence band. Similarly, the corresponding antibonding bands in the conduction band region are also split, resulting in a degradation of the conduction band. The lifting up of valence band and pushing down of conduction



Fig. 10. DOS of the ordered (a) and amorphous (b) GOs with R of 20%, 40%, 50%. Reprinted with permission from Ref. [57]. Copyright (2012) Elsevier B.V.



Fig. 11. Electron density of states as a function of tensile strain for the ordered (a) and amorphous (b) GOs both with *R* of 50% and OH:O of 2.00. Reprinted with permission from Ref. [68].

band together contribute to the decrease of band gap under tensile strain. Then, the orbital corresponding to the energy band highlighted in red is plotted to gain further insight of the band structures. As shown in the bottom of Fig. 12, this red energy band corresponds to a C—O hybridized molecular level. As the GO sheet is uniaxially elongated, the C—O hybridization becomes weaker and more electrons are released, resulting in an overall reduction of the band gap.

5.3. Photocatalytic applications

As reported, tunable band gaps of chemically derived GOs allow their promising performance in electronics and optoelectronics [77–79]. In particular, GO is promising for photocatalytic materials due to its superior electron mobility, high surface area, feasible assembly and tunable electronic band structures [80,81]. To gain deeper insight into the relationships between the



Fig. 12. Band structures and orbital variation of the ordered GO under tensile strain with *R* of 50% and OH:O of 2.00. Reprinted with permission from Ref. [68].

structure/composition of GO materials and their photocatalytic efficiency to guide future experiments, we have made a theoretical attempt to understand the main factors governing GO as a photocatalyst [82]. Based on our previous theoretical studies [49,57], two series of GO structural models with different OH:O ratios and coverages were considered, i.e., *R* of 25% ($C_{48}O_8H_4$), 33% ($C_{36}O_8H_4$), 50% ($C_{24}O_8H_4$), 67% ($C_{24}O_12H_6$) for OH:O of 1:1, and *R* of 20% ($C_{40}O_6H_4$), 33% ($C_{24}O_6H_4$), 40% ($C_{20}O_6H_4$), 50% ($C_{16}O_6H_4$), 67% ($C_{12}O_6H_4$) for OH:O of 2:1. The epoxy and hydroxyl groups aggregate along arm-chair direction and form stable one-dimensional chain configurations on the basal plane.

First, the electronic structures of those stable GO were investigated using DFT calculations. As presented in Table 2, the band gap of GO calculated by HSE06 is widened from 0 to 4.13 eV with increasing coverage of hydroxyl, epoxy, or both the groups. Meanwhile, with the same coverage, the band gap of a GO sheet can be further tailored by the relative OH:O ratio, which can be associated with the environment of chemical potentials of H and

Table 2

Work function (WF), band gap (E_g), and band positions ($\triangle E_1$ and $\triangle E_2$) for GO systems with different OH:O ratios and coverage. The values for graphene, —OH or —O— fully-covered GO are also presented for comparison. Reprinted with permission from Ref. [82]. Copyright (2013) Elsevier B.V.

Compounds	0H:0	R (%)	WF (eV)	$E_{g} (eV)$	$\triangle E_1$ (eV)	$\triangle E_2$ (eV)
Graphene	-	0	4.40	0	-	-
C_8O_4	-0-	100	8.034	6.2	2.364	2.606
$C_8O_8H_8$	—ОН	100	5.505	4.32	3.205	-0.115
$\begin{array}{c} C_{40}O_{6}H_{4}\\ C_{24}O_{6}H_{4}\\ C_{20}O_{6}H_{4}\\ C_{16}O_{6}H_{4}\\ C_{12}O_{6}H_{4} \end{array}$	2:1 2:1 2:1 2:1 2:1	20 33 40 50 67	5.123 5.295 5.76 5.785 5.465	1.135 1.518 2.398 2.698 4.13	0.512 0.411 0.46 0.754 3.065	-0.307 -0.123 0.708 0.714 -0.205
$\begin{array}{c} C_{48}O_8H_4\\ C_{36}O_8H_4\\ C_{24}O_8H_4\\ C_{24}O_{12}H_6 \end{array}$	1:1 1:1 1:1 1:1	25 33 50 67	5.511 5.765 6.489 6.781	1.568 1.865 2.545 2.609	0.497 0.54 0.495 0.268	-0.159 0.095 0.819 0.841

O [83]. Similar to the band gap, the work function (WF) of a GO sheet is also sensitive to its coverage. It was found that the WF of GO systems with OH:O of 1:1 increases drastically from 5.51 eV to 6.78 eV as the coverage rises from 25% to 67%. At the same coverage, the WF of epoxy-rich GO is higher than that of the GO functionalized by hydroxyl-rich groups. For example, the WF of GO with *R* of 50% and OH:O of 1:1 is 6.49 eV and it drops to 5.79 eV for OH:O of 2:1. Fully covered GOs with only hydroxyl or epoxy groups also show the same trend. The modification of work function can be attributed to the following two factors: (1) charge distribution induced by the chemical bonds formed between the carbon atoms and the -O- or -OH species; (2) formation of hydrogen bonds between the hydroxyl and the epoxy functional groups.

To make a better comparison of their reducing and oxidizing power for different GO structures, Table 2 also lists their energy differences as $\triangle E_1$ and $\triangle E_2$, which are defined by the following formulae:

$$\Delta E_1 = E_{\mathrm{H}^+/\mathrm{H}_2} - E_{\mathrm{CBM}},\tag{3}$$

and

$$\Delta E_2 = E_{\rm VBM} - E_{\rm H_2O/O_2},\tag{4}$$

where $E_{\text{H}^+/\text{H}_2}$ is the reduction potential, $E_{\text{H}_2\text{O}/\text{O}_2}$ is the oxidation potential. If both $\triangle E_1$ and $\triangle E_2$ are positive, simultaneous production of H₂ and O₂ is thermodynamically favorable.

To evaluate their photocatalytic potential further, the redox energy levels of the GOs with respect to the water oxidation/reduction potential levels were aligned, as displayed in Fig. 13a. The computed band gaps (1.87 eV for $C_{36}O_8H_4$, 2.55 eV for $C_{24}O_8H_4$, 2.61 eV for $C_{24}O_8H_4$, 2.40 eV for $C_{20}O_6H_4$, and 2.70 eV for $C_{16}O_6H_4$) suggest that all these five GO systems have suitable band gap for visible light photocatalytic activity and favorable band positions for water splitting. Among these GOs, $C_{24}O_{12}H_6$ with 67% coverage has the largest $\triangle E_2$, while $C_{16}O_6H_4$ with 50% coverage has the largest $\triangle E_1$ (Table 2). This indicates that the oxidizing and reducing capability is strongest for the $C_{24}O_{12}H_6$ and $C_{16}O_6H_4$, respectively. Meanwhile, the calculated $\triangle E_1$ and $\triangle E_2$ values of



Fig. 13. (a) Site levels of VBM and CBM for GO with OH:O of 1 and OH:O of 2 but different coverage, respectively. The dot lines are standard water redox potentials. The reference potential is the vacuum level. (b) Calculated optical absorption curves for GO with OH:O of 1:1 and OH:O of 2:1 under different coverage, respectively. Reprinted with permission from Ref. [82]. Copyright (2012) Elsevier B.V.

 $C_{16}O_6H_4$ are 0.75 eV and 0.71 eV, respectively; thus $C_{16}O_6H_4$ is predicted as a highly efficient visible-light driven photocatalyst.

The optical absorption spectra of these GO systems were also simulated to examine whether they meet the criteria of band gap and band edge position for a visible light photocatalysis. Fig. 13b shows that some selected GO systems ($C_{24}O_8H_4$, $C_{24}O_{12}H_6$, $C_{20}O_6H_4$, and $C_{16}O_6H_4$) are able to harvest the major portion of solar light (590–730 nm). On the other hand, the optical absorption curves for all the GO systems show multi-peak feature, which are beneficial to extent the light absorption area and perhaps improve the absorption efficiency of visible light.

Very recently, we extent our research to covalent organic framework (COF) [84], which possesses unique advantages of low cost, easy fabrication and mechanical flexibility. Using first-principles calculations, we identified the covalent triazine framework (CTF) as a new class of 2D visible-light-driven organocatalyst for water splitting. The band alignment and light harvesting capability of these 2D-CTFs can be tailored by the number of layers and pore size as well as nitrogen content, which provide effective strategies in designing and assembling CTF subunits for optimal performance. Note that many conventional inorganic materials and devices have now found their organic counterparts, such as organic superconductors [85], organic light-emitting diodes (OLED) [86], organic solar cells [87], organic field effect transistors [88], organic topological insulators [89,90]. Our theoretical prediction not only answers the question whether an organocatalysts for water splitting exist among the broad range of possible organic materials but also would motivate scientists to further explore other unknown areas of 2D functional organic materials.

6. Structures and mechanical properties of graphene GBs

In addition to hydrogenation and oxidization, incorporation of GBs is also an important approach to tune the physical properties of graphene. Particularly, as typically intrinsic defects, graphene GBs are inevitable in fabricating the large-scale graphene materials by using exfoliation or chemical vapor deposition (CVD) method [91–93]. Many intrinsic properties of the pristine graphene sheet would be significantly affected by the existence of GBs in realistic graphene materials. Then, elucidating the effect of GBs is crucial for the future technological applications of polycrystalline graphene

materials, which has become a focus of graphene research recently [94–96]. Employing DFT calculations, we have systematically investigated the structures, stabilities, and mechanical and electronic properties of graphene GBs [26,27,97–99].

6.1. Structural models of graphene GBs

A graphene GB can be characterized by its misorientation angle $\theta = \theta_L + \theta_R$, where θ_L or θ_R is the angle of the crystallographic direction between in pristine graphene and in the left or right domain. For a polycrystalline graphene with periodically arranged defects on the boundary, a more appropriate definition is to use the translation vectors (n_L , m_L) and (n_R , m_R) of left and right domains along the defect line, respectively [100,25]. These two types of definitions can be bridged through the following formula:

$$\theta = \tan^{-1}[\sqrt{3} \ m_L/(m_L + 2n_L)] + \tan^{-1}[\sqrt{3} \ m_R/(m_R + 2n_R)]$$
(5)

For a periodic GB, the periodic length L can be defined by the (n, m) index of either left part or right part:

$$L_L = |n_L a_1 + m_L a_2| = a_0 \sqrt{n_L^2 + n_L m_L + m_L^2}$$
(6)

or,

$$L_{R} = |n_{R}a_{1} + m_{R}a_{2}| = a_{0}\sqrt{n_{R}^{2} + n_{R}m_{R} + m_{R}^{2}},$$
(7)

where $a_0 = a_1 = a_2 = 2.46$ Å is the length of unit vectors of graphene lattice. For the GBs with different periodic lengths between the left and right domains, the mismatch can be defined as:

$$\delta = |L_L - L_R| / \min(L_L, L_R). \tag{8}$$

Clearly, to form a stable GB, the periodic lengths of the left and right domains must equal ($L_L = L_R$) or be very close (relatively small δ). Because of high formation energy and seldom observation in experiments [92,101], defects like quadrangles, octagons, or nonagons were ruled out. Moreover, some complex and large-scale distortions like wrapping and scrolling were also ignored even if they may exist in realistic polycrystalline graphene samples [102].

According to the detailed distribution of pentagons and heptagons on the boundary, the GBs we constructed can be cataloged into four classes as follows: (I) pentagon–heptagon pairs periodically separated by one or more hexagons; (II) individual pentagons



Fig. 14. Structural models for graphene GBs of classes I and II. Reprinted with permission from Ref. [26].

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Fig. 15. Structural models for graphene GBs of classes III and IV. Reprinted with permission from Ref. [26].

Table 3

Summary of \sum , θ and *L* of symmetric GBs. The *E*_{form} is the minimum value of all GB isomers along with previous theoretical values for references. Reprinted with permission from Ref. [26]. Copyright (2012) American Chemical Society.

Σ	GB	θ (°)	L(nm)	E _{form} (eV/nm)			$E_{\text{form}} (\text{eV/nm})$	
				This work	Previous results			
7	(2, 1) (2, 1)	21.8	0.654	3.44	3.38 [25], 4 [107], 4.3 [108]			
13	(3, 1) (3, 1)	32.2	0.889	2.91	3 [100], 4.34 [107], 3.8 [108]			
19	(3, 2) (3, 2)	13.2	1.065	3.51	3.13 [107], 4.79 [108]			
21	(4, 1) (4, 1)	38.2	1.127	3.99				
31	(5, 1) (5, 1)	42.1	1.355	4.26				
37	(4, 3) (4, 3)	9.4	1.483	2.83				
39	(5, 2) (5, 2)	27.8	1.529	4.60				
43	(6, 1) (6, 1)	44.8	1.578	3.69				
49	(5, 3) (5, 3)	16.4	1.683	4.71				
52	(6, 2) (6, 2)	32.2	1.780	3.23				

(heptagons) with or without other defects periodically distributed along the boundary line; (III) two or more adjacent pentagon–heptagon pairs separated by hexagons; (IV) periodically repeated pentagon–heptagon pairs constituting an entire boundary, as shown in Figs. 14 and 15, where the GB isomers with the same translation vector are labeled with $(n_L, m_L)|(n_R, m_R)-iq (q = 1, 2, 3, ..., N)$.

To evaluate the thermodynamic stabilities of a graphene GB, the formation energy (E_{form}) was adopted, as defined by:

$$E_{form} = (E_{GB} - N \times E_{gr})/2L, \tag{9}$$

where E_{gr} is the energy per carbon atom of the pristine graphene, N is the number of carbon atoms in the graphene GB supercell, L stands for the periodic length of the boundary, and factor 2 accounts for two boundaries in one supercell, respectively. Besides, another parameter, coincident site lattice (CSL) value (\sum), can also roughly characterize the stability, which is usually related to the growth process of the polycrystalline graphene materials [103]. For a symmetric $(n_L, m_L)|(n_R, m_R)$ GB, it can be determined by:

$$\Sigma = \sqrt{n_L^2 + n_L m_L + m_L^2} = \sqrt{n_R^2 + n_R m_R + m_R^2}$$
(10)

Table 3 lists the CSL value \sum , misorientation angles θ and periodic length *L* resulted from the DFT calculations. It can be noticed that GBs with a misorientation angle lower than 7° are absent since low misorientation angle will result in very long periodic length along the boundary, making DFT calculations impossible. Except for some GBs with very low misorientation angle, the formation energies from our calculations are consistent with previous experimental observations [104] and theoretical explorations [103,105,106].

Previously, Kim et al. [101] reported GBs with misorientation angles of 10.9° and 25.6°. According to our results, asymmetric GB with the a misorientation angle of 25.6° (10.9°) can be formed with the periodic length up to 7 nm (2.5 nm). Instead, several asymmetric GBs with different combinations of translation vectors match the misorientation angle of 25.6°, i.e., (5, 1)](4, 3) GB with θ = 25.8°, (6,0)](4,3) GB with θ = 25.7°, and (4, 1)](3, 2) GB with θ = 25.3°. Small difference in their formation energies (4.55– 6.34 eV/nm) suggests their possible co-existence in experiments. Similarly, GBs with a misorientation angle of 10.9° are also asymmetric, such as (5, 0)](4, 1) GB and (4, 2)](3, 3) GB. Therefore, in addition to symmetric twin GBs considered in previous theoretical studies, the present asymmetric ones are also helpful to understand the graphene GBs observed in experiments.

6.2. Mechanical properties of graphene GBs

As reported before, isolated defects, such as mono-vacancies and Stone-Wales rotations [109], slits [110,111], and holes [110],

would weaken the mechanical properties of graphene. Since GB can be regarded as a line defect in graphene, how will it affect the mechanics properties of graphene? Taking the 20 graphene GBs in Fig. 16 as representatives, the intrinsic strengths and failure behaviors under tensile strains were explored [26]. Each structure was uniaxially stretched from the equilibrium geometry to obtain the stress, which was further rescaled by a factor of Z/d_0 to obtain the equivalent stress on the graphene sheet, where Z = 1.2 nm is the thickness of vacuum space and vdW distance d_0 is 0.334 nm for graphene [71]. Afterwards, the intrinsic tensile strengths and critical failure strains can be obtained from the strain–stress curves. Table 4 summarizes the critical failure strain and intrinsic strength of the 20 graphene GBs, as well as their structural parameters and stabilities.

As mentioned above, a GB can be characterized by the misorientation angle θ between the two domains. However, the intrinsic strength of GB shows no clear correlation with the misorientation angle θ , as shown in Table 4. Instead, it exhibits an interesting dependence on the inflection angle α for those inflected GBs, which can be fitted into a linear function empirically:

$$\tau (\text{in GPa}) = \tau_0 - 0.75\alpha \text{ (in degree)}, \tag{11}$$

where $\tau_0 = 102$ GPa is the calculated intrinsic strength of graphene in zigzag direction, as plotted in Fig. 17a. Generally, the buckled GBs possess lower strength (46–78 GPa) with regard to the flat ones (71–93 GPa). Especially, for the flat GBs, an intrinsic strength as high as 93 GPa can be achieved, which nearly approaches that of the perfect graphene (102 or 113 GPa). Meanwhile, intrinsic strengths of the flat (2, 1)|(2, 1) and (3, 1)|(3, 1) GBs agree well with Grantab et al.'s recent DFT predictions [112], i.e., ~93 GPa for the (2, 1)|(2, 1) GB and ~95 GPa for the (3, 1)|(3, 1) GBs, respectively.

In addition to the inflection angle, intrinsic strengths of flat GBs also rely on the formation energy, as shown in the inset graph of Fig. 17a. For example, both (3, 1)|(3, 1) and (5, 0)|(3, 3) GBs are flat with zero inflection angle, but their intrinsic strengths differ significantly due to the difference in formation energy, i.e., 93 GPa and 3.3 eV/nm for (3, 1)|(3, 1) GB vs. 76 GPa and 5.1 eV/nm for (5, 0)(3, 3) GB, respectively. In other words, the intrinsic strength of a graphene GB sensitively rely on the detailed arrangement of the pentagon/heptagon defects, which was identified by Wei et al.'s simulation [113]. For the inflected GBs, especially for those with large α , pentagons and heptagons are usually distributed separately from each other along the boundary line, which would induce large off-plane local distortions similar to nanocones or nanopringles [107] and thus significantly reduce the strength of a graphene sheet. Our theoretical prediction was also confirmed by the TEM observation of polycrystalline graphene samples in Wu's experiment [114], where the GBs sometimes failed after continuous exposure to the electron beam due to reduced strength.

We further explored the fracture behaviors of graphene GBs. It was found that the first broken bond is a 7-6 bond, the one shared by a heptagon and another hexagon, consistent with Grantab et al.'s MD results [112]. Fracture of the 7-6 bond can be ascribed to the moderate reduction of bond population by ${\sim}5\%$ with regard to a standard C-C bond in pristine graphene. After that, a complete failure would occur rapidly along the boundary, leading to a sharp drop of the stress. Moreover, the dependence of intrinsic strength on inflection angle can be also related to the effective projected length of the critical 7-6 bond along the direction perpendicular to the boundary. However, further MD analysis at high temperature indicated that fracture starts with the Stone-Wales (S-W) transformation of a 7-6 bond on the boundary [97]. This fracture behavior resembles the "hot" mechanism for formation of S-W defects (i.e. dislocation dipoles) in carbon nanotubes at high temperature [115]. In particular, as shown Fig. 17b, intrinsic strengths of inflected GBs at various temperatures (1 K and 1500 K) follow



Fig. 16. Structures for the 20 GB representatives belong to classes I-IV. Reprinted with permission from Ref. [26].

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Table 4

Structural, energetic, and mechanical properties of the 20 GBs where α is the inflection angle. Reprinted with permission from Ref. [26]. Copyright (2012) American Chemical Society.

GB	α	θ (°)	L (nm)	E _{form} (eV/nm)	ε_{c} (%)	Class	τ (GPa)
Graphene (ZZ)	0	0	0.246	0	19	-	102
Graphene (AC)	0	0	0.246	0	23	-	113
(3, 1) (3, 1)	0	32.2	0.889	3.3	11	IV	93
							~95 [112]
(2, 1) (2, 1)	0	21.8	0.654	3.4	14	Ι	89
			0.65 [100],	3.4 [100], 4.0 [107], 4.3 [108]			~93 [112]
(6, 0) (4, 3)	0	34.7	1.481	4.9	12	II	84
(5, 0) (3, 3)	0	30.0	1.239	5.1	10	IV	76
			1.250 [100]	5.0 [100]			
(6, 1) (6, 1)-i1	0	44.8	1.622	5.0	12	Ι	71
(4, 1) (3, 2)-i1	31.80	31.8	1.095	5.6	14	II	78
(4, 1) (4, 1)-i2	37.00	38.2	1.127	4.1	15	II	72
							~57 [112]
(7, 0) (5, 3)	40.00	38.2	1.709	4.8	13	II	74
(3, 1) (2, 2)	42.00	16.1	0.868	5.1	16	Ι	74
(3, 2) (3, 2)	45.85	13.2	1.065	3.6	19	Ι	72
(5, 3) (4, 4)	46.70	8.2	1.690	2.8	13	Ι	68
(4, 2) (3, 3)	50.80	10.9	1.279	3.4	16	Ι	71
(4, 3) (4, 3)	51.30	9.4	1.483	3.0	18	Ι	72
(5, 2) (6, 1)-i2	52.70	36.3	1.540	4.8	17	II	66
(4, 1) (3, 2)-i2	53.80	25.7	1.111	4.7	21	Ι	63
(5, 2) (5, 2)	57.50	27.8	1.529	4.7	19	III	51
(6, 1) (6, 1)-i2	61.40	44.8	1.578	3.8	20	III	50
(5, 2) (6, 1)-i1	64.04	36.3	1.506	5.1	17	III	49
(4, 1) (4, 1)-i1	71.67	38.2	1.117	4.7	24	III	47
(5, 1) (5, 1)	72.22	42.1	1.355	4.4	23	III	46
(-,)((-, -)					-		~49 [112]

the same basic relationship described by Eq. (11), where $\tau_0 = 130$ GPa at 1 K and $\tau_0 = 70$ GPa at 1500 K, respectively. Therefore, the relationship between the intrinsic strength and the inflection angle seems to be universal and irrelevant with system temperature.

6.3. Electronic and transport properties of graphene GBs

Furthermore, effects of the GBs on the electronic properties of graphene were also investigated. For most GBs, the incorporation of heptagonal and pentagonal rings does not significantly modify the electronic properties of graphene, as shown in Fig. 18a. Generally, semimetal behavior of the pristine graphene is still retained with only enhanced electron DOS near the Fermi level as predicted by the previous theoretical calculations [25,116]. However, some GBs can open a small band gap, such as the two isomers of (4, 1)|(4, 1) GBs labeled as (4, 1)|(4, 1)-i1 and (4, 1)|(4, 1)-i11)-i2 (Fig. 16). The theoretical band gaps from PW91 calculations are $\sim 0.2 \text{ eV}$ for the (4, 1)|(4, 1)-*i*1 GB and $\sim 0.15 \text{ eV}$ for the (4, 1)|(4, 1)-i2 GB, respectively. More accurate HSE06 calculation yields a band gap of 0.5 eV for the (4, 1)|(4, 1)-i1 GB, as shown in Fig. 18b. Intuitionally, these two GB isomers have the same misorientation angle of 21.8° as the experimentally observed (2, 1)|(2, 1)|GB [117], but with different periodic lengths and arrangements of defect rings on the boundary. Meanwhile, the E_{form} of (4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4, 1)|(4,1)-i1 GB (4.7 eV/nm) and (4, 1)|(4, 1)-i2 (4.1 eV/nm) are close to that of (2, 1)|(2, 1) GB (3.4 eV/nm). Therefore, these two GB isomers have large probability to be found in experiments.

This band gap opening can be attributed to local sp^2 -to- sp^3 rehybridization mechanism [76,118,119]. First, for the two inflected GB isomers, both the average bond length in the heptagon (1.464 Å) and average bond angle of pentagon (109.7°) deviate from those in the perfect hexagonal lattice (1.42 Å and 120°), leading to a distorted sp^2 hybridization. Moreover, the well separated heptagons and pentagons result in local curvature around the defects with a large inflection angle of 72°. Since the GB is a local defect, the induced band gap would only affect the local electronic

states of the polycrystalline graphene flake and its amplitude is not as large as that due to chemical functionalization [19,57]. Although only two GBs isomers were found to open the band gap of graphene, we anticipate that some other GBs may also have the possibility to induce a band gap. Therefore, introducing GBs is potential way for band engineering of graphene-based materials.

In addition to the electronic structures, transport properties of the graphene GBs were also studied since they are of key importance for future microelectronics. In the non-equilibrium state, a boundary in polycrystalline graphene may either transmit charge carriers with enhanced conductivity [120] or reflect them with a transport gap [100,25], depending on the relationship of translation vectors between the left and right domains. To examine the effects of GB on the transport properties of graphene materials, DFT-based non-equilibrium Green's function calculations were carried out on the selected GBs. According to Yazyev et al.'s studies [100,25], although most GBs can transmit electrons perfectly, a $(n_L, m_L)|(n_R, m_R)$ GB with $n_L - m_L \neq 3N$ and $n_R - m_R \neq 3N$ (or $n_L - m_L \neq 3N$ and $n_R - m_R = 3N$, where N = 0, 1, 2, ...) would exhibit a transport gap described by:

$$E_t \approx \frac{1.38}{L(\mathrm{nm})} (\mathrm{eV}), \tag{12}$$

where *L* is the periodic length of GB. This theory was further confirmed by our DFT calculations [27]. For most GBs explored, conduction electrons can transmit across the boundary perfectly. As shown in Fig. 19a, both the pristine graphene and the (2, 1)|(2, 1) GB present zero transport gap. On the other hand, some particular GBs with translation vectors relation $n_L - m_L = 3N$ and $n_R - m_R \neq 3N$ (or $n_L - m_L \neq 3$ N and $n_R - m_R = 3N$), e.g., (3, 1)|(2, 2) GB (Fig. 19bd) and (5, 0)|(3, 3) GB, show transport gaps of about 1–1.5 eV.

Table 5 summarizes the transport gaps of these GBs in Fig. 19 and compared with the values obtained from Yazyev's formula described in Eq. (12). Generally, good agreement is obtained. Besides, the calculated transport gap of (5, 0)|(3, 3) GB of 1.03 eV also coincides well with the value (1.04 eV) from previous calculations using nonequilibrium Green's function [100,25]. The



Fig. 17. (a) Intrinsic strength for graphene GBs as a function of the inflection angle α with open triangles for flat GBs, open circles for inflected GBs, and filled triangle for pristine graphene. The dashed line is a linear fit for those inflected GBs and inset graph is the intrinsic strength versus formation energy for the flat GBs. Reprinted with permission from Ref. [26]. Copyright (2012) American Chemical Society; (b) temperature and inflection angle dependent intrinsic strength of inflected GBs. The dashed line and dash-dotted line are linear fits for the inflected GBs at 1 K and 1500 K, respectively. Reprinted with permission from Ref. [97]. Copyright (2013) Royal Society of Chemistry.



Fig. 18. (a) DOS of the pristine graphene (dashed line) and (2, 1)|(2, 1) GB (solid line). (b) DOS of (4, 1)|(4, 1)-i1GB from HSE06 calculation. The Fermi level is set to be zero. Reprinted with permission from Ref. [27].



Fig. 19. Transmission coefficients of (a) (2, 1)|(2, 1) GB (in blue) and pristine graphene (in red), (b) (3, 1)|(2, 2)-*i*1, (c) (3, 1)|(2, 2)-*i*2 and (d) (3, 1)|(2, 2)-*i*3 GBs. Dotted line in (a) stands for the Fermi level. Reprinted with permission from Ref. [27]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5

Periodic lengths *L* and transport gaps (E_t [25]) of the selected GBs, where the E_t^a is obtained by Yazyev's formula in Eq. (12). Reprinted with permission from Ref. [27]. Copyright (2012) American Institute of Physics.

GB	(5, 0) (3, 3)	(3, 1) (2, 2)- <i>i</i> 1	(3, 1) (2, 2)- <i>i</i> 2	(3, 1) (2, 2)- <i>i</i> 3
L (nm)	1.239	0.868	0.868	0.868
$E_t (eV)$	1.03	1.45	1.54	1.29
$E_t^a (eV)$	1.11	1.59	1.59	1.59

presence of transport gap indicates that the low energy carriers can be totally blocked within a defined energy range.

As suggested by Yazyev et al. [100,25], the transport gap only relies on the periodic length along the boundary. However, other factors, such as the topology of defect rings, may affect the transport behavior. We compared the transport behaviors of three isomers of (3, 1)|(2, 2) GB, i.e., (3, 1)|(2, 2)-i1, (3, 1)|(2, 2)-i2 and (3, 1)(2, 2)-i3, as shown in Fig. 19b-d. They have different topologies of defect rings, but the same misorientation angle as well as nearly identifical period length. As presented in Table 5, Yazyev's formula gives the same transport gap of 1.59 eV for all the three (3, 1)|(2, 2)|GB isomers. However, the computed transport gaps of the three (3, 1) (2, 2) GB isomers by non-equilibrium Green's function calculations are silightly different, which are 1.45 eV, 1.54 eV and 1.29 eV for the (3, 1)|(2, 2)-i1, (3, 1)|(2, 2)-i2 and (3, 1)|(2, 2)-i3 GB respectively. Therefore, detailed atomic structures in the GB region also play some roles on the transport gaps as well as the transmission coefficients. For example, the (3, 1)|(2, 2)-i1 GB presents largest coefficients compared with the others. In short, the transport gap not only depends on the translation vector's relationship and the periodic length along the grain boundary, but also is affected by the detailed defect topology.

7. Conclusions

To summarize, we have proposed various strategies to tailor the physical properties of graphene. Hydrogenation of the graphene can engineer its band gap continuously from 0 to 4.66 eV through controlling hydrogen coverage and configurations. The tunable gap lies between the midultraviolet and NIR regimes, leading to potential applications of (partially) hydrogenated graphene in electronics and photonics. Oxidization of graphene leads to another interesting material, GO, which can be regarded as graphene functionalized by oxygen-containing groups. By changing the coverage, relative ratio, and arrangement of the functional groups, physical properties of GO can be controlled, including the thermodynamic stabilities, electronic properties and mechanical properties. In addition to the functional groups, applying external tensile strain is another effective approach to modify the electronic properties of GO. These tunable properties of GO make it promising in various fields, such as electronic and photonic devices, energy storage, and biotechnological sciences. Especially, tunable electronic properties of GO enable its promising applications in photocatalysis. An ordered GO phase of C₁₆O₆H₄ with hydroxyl and epoxy groups orderly arranged along the armchair direction is predicted as a highly efficient visible-light driven photocatalyst. Furthermore, introducing GBs can also tailor the properties of graphene. For the inflected graphene GB, its mechanical strength is almost linearly decreased with the increasing inflection angle, which seems to be a universal rule independent of temperature. Meanwhile, the mechanical properties and fracture behavior of the graphene GBs also rely on the detailed arrangement of the pentagon/heptagon defects. In some case, introducing GB may also open a band or transport gap in graphene, which provides a potential approach for the engineering of graphene-based materials and devices.

Nowadays, graphene and graphene-based materials have been widely applied in various fields. To improve the device performance, new strategies should be proposed to efficiently modify the physical properties of graphene-based materials. We anticipate that our theoretical studies may stimulate further efforts in this field and eventually lead to novel graphene-based materials and devices in the future.

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