LETTER

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LETTER

Nacre-inspired design of graphene oxide–polydopamine nanocomposites for enhanced mechanical properties and multifunctionalities

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Abstract

Inspired by the hierarchical structure of nacre and the robust adhesive ability of mussel threads, graphene oxide–polydopamine (GO–PDA) nanocomposites are designed and synthesized to achieve enhanced mechanical properties and to provide additional functionalities. Here we report a joint experimental/computational investigation of GO–PDA nanocomposites, proposing a probable chemical reduction mechanism of PDA to convert GO to reduced GO (rGO), which helps increase the electrical conductivity. The most stable chemical connection between PDA and GO is also proposed. Our artificial nacre-like GO–PDA nanocomposites are shown to have higher tensile strength and toughness compared to natural nacre. The pulling tests conducted by molecular dynamics simulations, which are supported by our experiments, reveal that the enhanced mechanical strength of GO–PDA nanocomposites mainly originates from the additional non-covalent interactions provided by PDA. The humidity-driven shrinking mechanism of GO–PDA nanocomposites due to non-uniform stresses on the GO–PDA sheets is also discovered in our simulations and supported by our experiments. The findings in this work can help improve and tune the properties of GO–PDA nanocomposites and might also apply to other 2D materials.

Introduction

Developing new materials with superior mechanical properties and multi-functionalities is an ultimate goal towards advanced engineering applications. Composites are widely used in the design of tunable materials for specific properties such as light weight and high flexibility, as well as high strength and toughness [1, 2]. However, most engineering materials sacrifice strength for toughness. Biological materials, on the other hand, do not face this tradeoff due to their hierarchical structures and multi-functional abilities optimized by nature during millions of years of evolution [3, 4]. The most studied model is the nacreous part in some mollusk shells [5]. Nacre is made up 95 vol% of calcite minerals and with 5 vol% of biopolymer proteins [6]. The toughness of nacre is around 3000 times higher than its base material (i.e., the brittle calcite minerals) alone [7]. Thus, nacre provides excellent guidelines for creating high-performance composites.

Following the principle of composite design, the base material carries most of the external loads, and thus it must be stiff and strong enough to take the normal stresses; the intermediate material occupies most of the volume, and thus it must be light enough and able to carry the shear stresses necessary to hold the base material together [8, 9]. In this regard, polydopamine (PDA), a mussel-inspired material, is an excellent agent for being an intermediate material due to its extraordinarily robust adhesive ability. PDA is synthesized by the oxidative polymerization of dopamine under alkaline conditions [10]. It shares the main components with mussel adhesive proteins such as Mytilus edulis foot protein-5 (Mefp-5), which is composed of a repetitive catechol-
amine structure of 3,4-dihydroxy-L-phenylalanine (DOPA) [11, 12]. As in the case of mussel threads, PDA can spontaneously attach to almost any solid material with high bonding strength even under wet conditions [10, 13, 14].

To create nacre-inspired nanocomposites with high strength and toughness, choosing a strong base material is essential. Graphene is a promising candidate due to its remarkable properties that arise from the two-dimensional sp² carbon honeycomb structure. Pristine graphene has been shown to be the strongest material ever measured. It has a tensile strength of 130 GPa [15], which is at least 200 times stronger than A36 steel. Despite this potential, graphene still has a long way to go before it reaches large-scale commercial utilization because it is considerably expensive and challenging to produce in mass quantity, as well as to create 3D materials for bulk applications. An alternative material with similar mechanical properties is graphene oxide (GO), for which a homogeneous colloidal suspension can be readily prepared in aqueous media for versatile mass production and further treatment. The chemical structure of GO is characterized by the presence of oxygen-containing functional groups (i.e., epoxy and hydroxyl groups) on its graphene basal plane, and carboxylic groups along the edges. Consequently, GO sheets are hydrophilic and can be quickly dispersed in water under mild ultrasonic treatment. The properties of GO depend on its condition (e.g., the density of functional groups and defects), and its tensile strength has been reported as around 63 GPa [17]. Although GO is weaker than graphene (63 GPa versus 130 GPa), it is still much stronger than most engineering materials. For practical applications, 2D micrometer-scale GO sheets can be assembled into 3D centimeter-scale GO films (also called ‘GO papers’) through solution-casting or vacuum-filtration techniques [18–20]. The resultant GO papers are stabilized by interlayer hydrogen-bonding between oxygen-containing functional groups and present a nacre-like cross-sectional structure resulting from the stacking of several hundred GO sheets.

In GO papers, the hydrogen-bonding network formed between oxygen-containing functional groups on adjacent GO sheets, as well as with water molecules in the environment, is significantly weaker than covalent carbon–carbon bonds in the GO basal plane. The breakage of the hydrogen-bonding network due to external loads leads to the sliding of adjacent GO sheets, which is corresponding to delamination damage [21], and eventually to the failure of the GO paper. Consequently, the strength of GO papers mainly depends on the strength of the interlayer interactions (the limiting factor) instead of the much stronger carbon–carbon bonds. As a result, the actual strength of GO papers (i.e., around 76–293 MPa) [19, 22–27] reported in the literature is much inferior to that of individual GO sheet. To overcome this apparent limitation of GO papers, a variety of polymers have been applied to reinforce GO papers by enhancing the interlayer interactions. Some examples are poly(vinyl alcohol) (PVA) [28–30], poly(methyl methacrylate) (PMMA) [28] poly(acrylic acid) (PAA) [31] and poly(etherimide) (PEI) [32]. Despite many reinforcement polymers having been applied, only one kind of mechanical properties, such as strength or toughness, has been improved by embedding one of these polymers. On the other hand, PDA is a unique reinforcing agent that has been confirmed to simultaneously improve the strength and toughness of GO papers due to its special chemical composition and excellent adhesive properties [23–27].

In alkaline aqueous solutions of GO/dopamine, dopamine can self-polymerize into PDA via the formation of covalent linkages between 5,6-dihydroxyindole (DHI) basic units as well as react with GO. The resultant GO/PDA dispersion is the precursor of GO–PDA papers. Despite the successful experimental synthesis of GO–PDA papers, which have enhanced mechanical properties and electrical conductivity compared to pristine GO papers [26], the mechanisms regarding how PDA reacts with GO and where the enhanced mechanical properties come from, are not yet understood. Additionally, integrating GO and PDA creates unexpected functionalities such as humidity-driven self-folding ability. This self-folding ability of GO–PDA papers has been applied to create humidity sensors [33], wormlike walking devices [33, 34], self-folding boxes [34], robotic hands [34], and microrobots [34]. Swelling/shrinking is a common behavior, especially for porous materials (e.g., wood, clay) since the volume expands while water molecules fill the porous space and shrinks when water molecules are gone. However, this dynamic response is more difficult to achieve for non-porous materials, for which the underlying mechanism is more complicated. In the case of GO–PDA papers, the shrinking/swelling mechanism of their 2D layered structure is still unclear. Here we report a joint experimental/computational investigation of GO–PDA papers, which provides the in-depth answers of these fundamental questions, promotes the disclosing of their important structural information, and paves the way for new strategies in the fabrication process. This work reveals the strengthening and self-folding mechanisms of GO–PDA papers at the molecular level through a multiscale modeling approach that integrates density functional theory (DFT) calculations, molecular dynamics (MD) simulations, and experimental characterizations. In particular, we show clear evidence of the role of noncovalent interactions in the mechanical properties of GO–PDA papers and show the mechanism of water hydration/dehydration in the material. These results highlight the possibility to further improve the molecular design of GO–PDA papers.

Beyond the specific case of GO–PDA papers, this work also highlights the approach of using atomistic simulations to help design new materials. We show how by applying this ‘materials by design’ paradigm, one can
quickly predict the influences of material's components such as the molecular structure, water content, and other molecular features on its macroscopic properties. For some material properties which cannot be easily measured by using current experimental techniques, one can unlock the structure–property relationships by applying this 'materials by design' paradigm. Consequently, this bottom-up design approach can guide experimental synthesis in a more rational way, since the structure–property relationships discovered in simulations define the links between the molecular features, macroscopic properties, and the experimental conditions to reach the desired properties. The experimental procedures and material characterizations provide important feedback which can be implemented in the simulations to further optimize the design through an iterative process. This advanced design approach makes the production of materials more efficient and reduces the number of experiments required by incorporating atomistic design into the fabrication process.

Results and discussion

Chemical reactions between PDA and GO sheet
Due to the high reactivity of PDA and enhanced mechanical properties of PDA-reinforced GO papers, GO and PDA should be connected via strong covalent bonding in GO–PDA papers [27]. Thus, our investigation starts with DFT calculations (see methods section) to find the most probable chemical connections between PDA and GO. Note that there is currently no experimental method able to accurately identify this connectivity due to the difficulties of assessing the detailed chemical structures and molecular weight distribution of PDA, especially when PDA polymerizes in the presence of other materials such as GO in this case. To simplify this problem, DHI, the main fundamental building block of PDA [35], is adopted in our DFT calculations and MD simulations. Based on this building block, various molecular models are created to exemplify possible chemical connections between PDA and GO. As mentioned before, GO contains three main oxygen-containing functional groups, namely epoxy, hydroxyl, and carboxylic groups. Epoxy groups are known to be especially reactive, and thus they are considered as the most probable reaction sites in GO. In the first step, we assume that the chemical reaction leads to the formation of covalent bonds between epoxy groups on GO and DHI. Accordingly, a new covalent bond is added in our molecular model to connect the epoxy group on a GO flake and a DHI molecule. Figure 1(a) shows one of the possible initial structures (Structure I). After the structure is relaxed in DFT geometry optimization, it converges to a non-bonded structure (Structure II). Additionally, all other possible initial structures with connections between the epoxy group and a DHI molecule converge to non-bonded structures. These non-bonded structures suggest the extraction of an oxygen atom from the GO flake that leads to a possible reduction process from GO to reduced GO (rGO), which is in accordance with the experimental observations of PDA-driven GO reduction [26].

In the first step, we show that the chemical reaction with oxygen atoms leads to the reduction of GO. Thus, in the second step, the covalent bonding in GO–PDA papers is assumed to occur between a carbon atom in GO and a carbon atom in DHI. Four possible connections between GO and DHI are explored. Unlike the previous case, in which the connection is made to an oxygen atom, these four molecular models all converge to bonded structures. The optimized geometries of these four molecular models are shown in figure 1(b). The relative energies with respect to the most stable structure (Structure IV), are +16.52 kcal mol$^{-1}$ for Structure I, +19.51 kcal mol$^{-1}$ for Structure II, and +5.94 kcal mol$^{-1}$ for Structure III. The most stable structure (Structure IV) is adopted to build our MD models of GO–PDA papers. To show that the formation of carbon–carbon bonds between GO and DHI is possible, we compare the reactivity of pristine graphene and that of GO by using the Fukui function. The plots in figure 1(c) indicate that, apart from the expected high reactivity along the edges, the presence of oxygen-containing functional groups activates some carbon atoms on the graphene basal plane. Structures II and III in figure 1(c) show that the reactivity of some carbon atoms upon electrophilic or nucleophilic attack is enhanced by the presence of oxygen atoms in the GO flake, compared to the pristine graphene flake (Structure I) where only the edges are shown to be reactive. As a result, these reactivity-enhanced carbon atoms in GO can react with DHI radicals, leading to the structures discussed in figure 1(b).

Water effects on interlayer spacing
As shown in figure 1(b), DHI radicals can react with GO and embed into GO sheets by intercalating into the interlayer space. Since GO is hydrophilic in nature, water is usually occupied the interlayer spacing of GO and GO–PDA papers. However, the effects of water on the interlayer spacing of GO and GO–PDA papers remain unclear because current experimental approaches have difficulty accurately measuring the water content and the interlayer spacing at the same time. In this work, we use MD simulations to get insight into the effects of water on the interlayer spacing. Due to the computational limitations, the length-scale of GO and GO–PDA models in our simulations cannot match the real size of these materials, which is usually on a scale of several micrometers in thickness and a few centimeters in the in-plane directions. Our nanoscale GO and GO–PDA models consist of
four GO or GO–PDA sheets with dimensions of 50 Å by 100 Å (see methods section). We are aware that these models are much smaller than experimental GO and GO–PDA sheets, but similar models have already been proved useful to study GO and GO–PVA papers in the literature [30].

We conducted experiments to measure the interlayer spacing of GO and GO–PDA papers to compare with our simulation results. Our x-ray diffraction (XRD) patterns (figure S1 is available online at stacks.iop.org/NANOF/1/011003/mmedia) present the typical patterns of GO and GO–PDA papers. The layer-to-layer distance (d-spacing) of GO papers is about 8.6 Å ($2\theta = 10.3^\circ$). The result of GO–PDA papers shows no peaks at 10.3°, which indicates that most of the oxygen-containing functional groups of GO have been efficiently removed [36]. However, a peak at 7.6° with a d-spacing of 11.6 Å is found in the result of GO–PDA papers. Due to the intercalation of PDA, the interlayer spacing of GO–PDA papers is larger than that of GO papers [37, 38].

Figure 2(a) shows snapshots of the GO and GO–PDA models with different water content after MD equilibrations (see methods section). Figure 2(b) shows the interlayer spacing of the GO and GO–PDA models with different water content. Our scanning electron microscope (SEM) images of GO and GO–PDA papers are shown in figure 2(c). In the GO models, the interlayer spacing is 5.35 Å, 5.83 Å, 6.28 Å, 7.19 Å, and 8.10 Å, corresponding to a water content of 0 wt%, 8 wt%, 15 wt%, 27 wt%, and 35 wt%, respectively. The interlayer spacing of the GO models increases as the water content increases. This result is consistent with the previous computational studies [30, 39], but smaller than our experimental measurement (8.6 Å) and other experimental results from the literature (7.6–9.7 Å) [19, 25–27, 40, 41]. The reason for this mismatching comes from the difficulty of achieving relatively dry GO papers in experiments. GO papers are synthesized in water solution; thus they contain a large amount of water in between GO sheets when they are produced. Even after dehydration,
there is still an approximately one-molecule-thick layer of water tightly bonded to GO sheets via hydrogen bonding. This water monolayer is extremely difficult to remove without damaging GO papers [42]. Consequently, the GO models in the dry (0 wt%) and near-dry (8 wt%) conditions, which have much small interlayer spacing, are unlikely to be observed in experiments. On the other hand, the interlayer spacing of the GO models in the wet (15, 27, and 35 wt%) conditions are closer to that of GO papers in experiments.

In the GO–PDA models, the interlayer spacing is 10.14 Å, 9.45 Å, 9.34 Å, 9.74 Å, and 10.55 Å, corresponding to the water content of 0 wt%, 8 wt%, 15 wt%, 27 wt%, and 35 wt%, respectively. This result is close to our experimental measurement (11.6 Å) and other experimental results from the literature (9.5–10.3 Å) [25–27]. Compared to the GO models, the interlayer spacing of the GO–PDA models is less sensitive to water content (figures 2(a) and (b)). Unlike the GO models, in which the interlayer spacing increases monotonically as the water content increases, the interlayer spacing of the GO–PDA models decreases when a small amount of water (8 and 15 wt%) is added. In the dry condition, the oxygen-containing functional groups on adjacent GO–PDA sheets cannot interact with each other due to the large interlayer spacing, which is presumably caused by the existence of PDA (figure 2(a)). When a small amount of water is added, there is sufficient space between GO–PDA sheets for hosting water molecules without increasing the interlayer spacing. Furthermore, these water molecules act as bridges that form hydrogen bonds with the oxygen-containing functional groups of adjacent GO–PDA sheets; thus, these water molecules pull adjacent GO–PDA sheets closer and reduce the interlayer spacing. However, once a large amount of water (27 and 35 wt%) is added, there is no space available between GO–PDA sheets for hosting additional water molecules. As a result, the interlayer spacing has to increase to enable additional water storage.

Mechanical properties of GO and GO–PDA papers
To understand the strengthening mechanism of PDA in GO–PDA papers as well as to reveal water effects on mechanical properties of GO–PDA papers, the small-scale GO and GO–PDA models used to study the interlayer spacing are adopted to estimate their mechanical strengths. As mentioned before, the failure mechanism of GO-based papers is mainly the sliding of adjacent sheets. Thus, the adhesive strengths between adjacent sheets govern the mechanical strengths of GO-based papers. To estimate the adhesive strengths, tensile strains are applied in the simulations to pull the first and third sheets to the right and the second and fourth sheets to the left (figure 3(a)). Only the stresses in the center regions (the red-boxed region in figure 3(a)) of the models are measured during the pulling tests to eliminate boundary effects. This kind of mechanical behavior can also be
described with analytical models, such as tension-shear (TS) or deformable TS models if all required parameters are known \[43\].

Based on the pulling test results in figures S2 and S3, the adhesive forces of the GO and GO–PDA models with different water content are shown in the left chart in figure 3(b). In the chart, the adhesive forces increase as the water content increases due to the existence of more hydrogen bonds provided by water molecules. Furthermore, the adhesive forces of the GO–PDA models are higher than those of the GO models with the same water content. This result is due to the additional adhesive forces provided by PDA (DHI units) in the GO–PDA models. The right chart in figure 3(b) shows the adhesive strengths of the GO and GO–PDA models with different water content based on the pulling test results in figures S2 and S3. In the chart, the GO model is stronger than the GO–PDA model in the dry (0 wt%) condition. Interestingly, when a small amount of water (8 and 15 wt%) is added, the GO–PDA models have similar adhesive strengths compared to the GO models. When more water (27 and 35 wt%) is added, the GO–PDA models become stronger than the GO models. Unlike the adhesive forces discussed above, the adhesive strengths of the GO–PDA models are not always higher than those of the GO models with the same water content. The reason is that the GO–PDA models have larger interlayer spacing compared to the GO models (figures 2(a) and (b)); the adhesive strength is defined as the adhesive force divided by the cross-sectional area, and larger interlayer spacing means a larger cross-sectional area. However, as mentioned before, GO papers in the dry (0 wt%) and near-dry (8 wt%) conditions are unlikely to be observed in

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**Figure 3.** Mechanical properties of GO and GO–PDA papers. (a) Snapshot of the GO–PDA model with 15 wt% water content during pulling test. The stress is derived from the center region (red-boxed region) with a length of 50 Å to eliminate the boundary effects. PDA (DHI units) is shown in orange color and water molecules are shown in blue color for clarity. (b) Adhesive forces and strengths of the GO and GO–PDA models with different water content. The simulation results are the averaged results obtained from three sets of the GO and GO–PDA models, which are created with different random distributions of hydroxyl groups, epoxide groups, and DHI units. (c) Stress–strain curves (left two charts) of GO and GO–PDA papers measured in the experiments at 33% and 75% RH, respectively. The comparisons of the GO and GO–PDA papers at 33% and 75% RH in strength and toughness are shown in the right two charts, respectively.
experiments. Consequently, based on the simulation results, we conclude that GO–PDA papers are stronger than GO papers in normal conditions.

We also conducted experiments to measure the mechanical properties of GO and GO–PDA papers to compare with our simulation results. The left two charts in figure 3(c) show the stress–strain curves of GO and GO–PDA papers at 33% and 75% relative humidity (RH), respectively. It can be seen that PDA simultaneously enhances the strength and toughness of the GO paper, consistent with the previous report [26]. The right two charts in figure 3(c) show the comparison of the GO and GO–PDA papers at 33% and 75% RH. Compared to the pristine GO paper, the strength and toughness of the GO–PDA paper at 33% RH are increased by 32% and 123%, respectively. When the RH increases to 75%, the GO–PDA paper is still stronger than the GO paper, with enhancement of 24% in strength and 36% in toughness. This result indicates that water content has a significant influence on the mechanical properties of GO and GO–PDA papers. Note that the maximum strength of the GO–PDA papers reaches up to 170 MPa in our experiments, which is higher than that of natural nacre, with 105 MPa for abalone nacre and 140 MPa for pearl oyster nacre [44]. Additionally, the maximum toughness of the GO–PDA papers is also higher than that of natural nacre (i.e., 5.6 MJ m\(^{-3}\) versus ~1.0 MJ m\(^{-3}\)) [44].

Since the size of GO and GO–PDA models in the simulations is much smaller than the real size of these materials in experiments, there are some intrinsic differences between the simulations and experiments. Unlike the small GO and GO–PDA sheets in the simulations, large GO and GO–PDA sheets are difficult to stack perfectly to form GO or GO–PDA papers in experiments. Therefore, wrinkled and ripped structures are often observed in GO-based papers in experiments but are absent in the simulations. Additionally, to simplify the problem, defects are not considered in this work; while defect-free GO and GO–PDA papers do not exist in the real world, one should be aware of the fact that defects can significantly reduce the mechanical properties of materials. Consequently, the adhesive strengths predicted in the simulations are much higher than the experimental measurements. In this regard, this work does not aim to reproduce the exact mechanical strengths of GO and GO–PDA papers at the macro-scale but rather to describe the interactions between GO and PDA at the nanoscale for understanding the source of the enhanced mechanical strength. Moreover, some experimental studies on GO–PDA papers suggested that the enhanced mechanical strength of GO–PDA papers comes from covalent cross-links between adjacent GO–PDA sheets when embedding PDA [27]. Although this seems like a rational explanation, since covalent cross-links are much stronger than hydrogen bonds, there is no clear evidence showing that covalent cross-links are formed in GO–PDA papers. In fact, even though we do not include any covalent crosslinks in the GO–PDA models, higher adhesive strengths compared to the GO models are still observed in the simulations. It was found in the literature that the mechanical strength of GO–PDA papers is about 35% greater than that of GO papers [26], which is in good agreement with our experimental and simulation results (figure 3). Therefore, even though there are covalent cross-links formed between adjacent GO–PDA sheets, the contribution from these cross-links compared to non-covalent interactions might be negligible. A possible explanation for this behavior is that as DHI units form covalent bonds with GO sheets, they get fixed to the GO sheets, limiting their mobility and ability for further reaction. As a result, as two GO–PDA sheets stack together, the probability for the DHI units on the adjacent GO–PDA sheets to reach each other and form cross-links should be low.

Shrinking mechanism of GO–PDA paper

The shrinkages of the GO and GO–PDA models during dehydration in the simulations are less than 1%. To show that these values are not from numerical errors associated with the size of the models, the large-scale GO and GO–PDA models are used for this work (see methods section). The large-scale GO and GO–PDA models are first equilibrated in a wet condition with the water content of 35 wt% and then equilibrated in the dry (0 wt%) condition, where the water molecules are removed. Two different boundary conditions (BCs) are applied to simulate the free and fixed BCs to measure the shrinkage and associated stress, respectively. In the free BC, the GO and GO–PDA models can freely shrink or swell to relax their internal stresses. Accordingly, the amount of shrinkage or swelling can be observed and measured in the simulations. In the fixed BC, the lengths of the GO and GO–PDA models are fixed after the water molecules are removed, and the stresses associated with shrinkage or swelling can be calculated. The changes in the lengths and stresses of the GO and GO–PDA models during dehydration in the free and fixed BCs are shown in figures 4(a) and (b). In the GO model, a shrinkage of 0.1% in the in-plain longitudinal direction and corresponding shrinking stress of around 200 MPa are measured. In the GO–PDA model, the shrinking stress is similar to that of the GO model, which is around 200 MPa. However, the shrinkage in the GO–PDA model (0.6%) is much larger than that of the GO model (0.1%). The result is in good agreement with our experiment observations. In order to in situ assess the shrinking stress of GO and GO–PDA papers, the wet samples are fixed by Instron grips with a very weak tensile force, which makes the samples in the tensile state. After the tensile force is stable, a heater with the temperature of 200 °C is placed near one side of the samples to make rapid water evaporation, and the force caused by the shrinkage of samples is recorded. As
shown in figure S4, a significant contraction stress (∼17 MPa) are monitored in both GO and GO–PDA papers when the water is evaporated by heating.

The snapshots of the GO–PDA model in the wet and dry conditions are shown in figures S5 and 4(c), respectively. In the wet condition (figure S5), the DHI units in the GO–PDA model are surrounded by interlayer water molecules. As a result, the DHI units have low probability to interact with each other, and thus they stay in their positions while interacting with the water molecules. On the contrary, in the dry condition (figure 4(c)), the DHI units interact with each other since the water molecules are removed. These DHI units have a low mobility compared to water molecules because they are fixed on the GO–PDA sheets; thus they generate non-uniform stresses on the GO–PDA sheets while interacting with each other. These non-uniform stresses provided by DHI units ripple the 2D structure of the GO–PDA model and reduce the length.

Conclusions

In this work, we use multiscale modeling methods including DFT calculations and MD simulations to design a series of nacre-like GO–PDA papers, which are further produced by experimental synthesis. Consistent with the simulation design, these GO–PDA papers have remarkable properties with (1) the strength up to 170 MPa, (2) the toughness up to 5.6 MJ m⁻³, and (3) the shrinking strain up to 0.6%. Based on our DFT calculations, the most probable chemical reaction mechanisms between PDA and GO are proposed. The result explains the chemical reduction mechanism of PDA to convert GO to rGO and shows the most stable chemical connection between PDA and GO. The water effects on the interlayer spacing and mechanical properties of GO and GO–PDA papers are also discussed. Our simulated pulling tests, which are supported by our experiments, reveal that the enhanced mechanical strength of GO–PDA papers mainly comes from the additional non-covalent interactions provided by PDA (DHI units), instead of from covalent cross-links between adjacent GO–PDA sheets suggested in other studies. This finding implies an opportunity to further increase the mechanical properties of GO–PDA papers, if a large number of covalent cross-links can form to connect GO–PDA sheets.
together. Additionally, the humidity-driven shrinking mechanism of GO–PDA due to non-uniform stresses on the GO–PDA sheets is discovered in our simulations and supported by our experiments. The high mechanical properties and shrinking ability of GO–PDA papers make the material a good candidate for creating humidity-driven self-folding devices.

Methods

DFT methodology
The ORCA quantum chemistry package [45] is implemented for the DFT calculations in this work. All molecular structures under consideration are fully optimized by using the B3LYP [46, 47] functional together with the 6–31 G(d) basis set [48]. Within this methodology, the dual descriptor of the Fukui function has been calculated for characterizing the local reactivity. This function can be interpreted as the change of the electron density $\rho(\tau)$ at each point $\tau$ when the total number of electrons (N) is changed. In practice, the Fukui function describes how the electron density changes in response to an increase or a decrease in the number of electrons. Therefore, it can be employed to predict the preferred site for either a nucleophilic or electrophilic attacks [35].

GO and GO–PDA models
GO is oxygenated with hydroxyl and epoxide groups distributed throughout the graphene basal plane. In this work, we create GO models with a stoichiometry of two epoxy groups and one hydroxyl group per twelve carbon atoms, while the empirical formula is C$_{12}$O$_2$(OH). This 4:1 carbon–oxygen ratio is commonly found in experiments [49, 50]. Two different sizes of GO and GO–PDA models are created: small-scale and large-scale. The small-scale GO and GO–PDA models consist of four GO or GO–PDA sheets with a dimension of 50 Å by 100 Å; the large-scale GO and GO–PDA models also consist of four GO or GO–PDA sheets but with a dimension of 25 Å by 1000 Å. The initial interlayer spacing in the models is set to 45 Å to prevent interlayer interactions between adjacent GO or GO–PDA sheets in the initial configuration. Hydroxyl and epoxide groups are added randomly on either side of the graphene basal plane. Five different amounts of water (e.g., 0, 8, 15, 27, and 35 wt%) are added to the small-scale GO and GO–PDA models for the investigation of water effects on the structural and mechanical properties. The water content in the models is defined by the mass of the water molecules divided by the total mass of the GO sheets and water molecules. Note that the molecular structures of PDA are still controversial even after significant experimental and theoretical efforts over past years. The consensus is that the fundamental building blocks of PDA are DHI and its redox forms [35, 51–54]. Based on our DFT calculations (see results and discussion section), the most stable structure (Structure IV in figure 1(b)) is adopted to create the GO–PDA models. The GO in the GO–PDA models has the same empirical formula as the GO model, namely C$_{12}$O$_2$(OH). The only difference between GO and GO–PDA models is the presence of DHI units in the GO–PDA models. These DHI units are randomly added on either side of the graphene basal plane. The mass ratio of DHI units in the GO–PDA models is about 23 wt%.

Atomistic modeling and equilibration
MD simulations are implemented using large-scale atomic/molecular massively parallel simulator (LAMMPS) [55] with ReaxFF, a first-principle-based general bond-order dependent force field that provides a description of bond breaking and bond forming [56]. The existing version of ReaxFF for hydrocarbons described first by van Duin et al [56] and extended to hydrocarbon oxidation by Chenoweth et al [57] is adopted in this work. This version of ReaxFF has been widely used for studying graphene oxidation and GO-based materials [39, 58, 59]. However, to simulate GO–PDA papers, force field parameters for nitrogen—carbon—hydrogen are also required. Thus, the force field parameters for nitrogen—carbon—hydrogen proposed by Kamat et al [60] are also adopted in this work. These parameters were optimized against quantum and experimental data and can reproduce the physical and chemical reactions between nitrogen—carbon and nitrogen—nitrogen [60], as well as the complex chemistry involved in char combustion [61]. In the MD simulations, the time step is set to 0.25 fs to ensure stability and to reflect the high vibration frequency of hydrogen. After energy minimization with the conjugate gradient (CG) algorithm, the GO and GO–PDA models are first equilibrated with the isothermal–isobaric (NPT) ensemble at a constant temperature of 10 K and pressure of 1.013 bar in the x- and y-directions, and 1013 bar in the z-direction for 100 ps. The low temperature in the simulations prevents the water molecules from forming water clusters, and the high pressure in the z-direction allows the GO and GO–PDA sheets to assemble into layered nanocomposites much faster than at low pressures. Since we are interested in the properties of GO and GO–PDA nanocomposites at room temperature and the atmospheric pressure, the GO and GO–PDA models are then equilibrated in the NPT ensemble at a constant temperature of 300 K and pressure of 1.013 bar in all directions for another 100 ps. Periodic boundary conditions (PBCs) are applied in all
directions during these two steps of simulations. The interlayer spacing of the GO and GO–PDA models is calculated after the second step of simulations is finished.

The small-scale GO and GO–PDA models are adopted to study the mechanical properties of GO and GO–PDA papers. The equilibrium structures obtained from the simulations described above are adopted in the pulling tests for evaluating their mechanical strengths. To simulate the TS behavior in the pulling tests, the PBC directions during these two steps of simulations. These edges are only fixed in the y-direction and are free to move in the other two directions. Here we use a displacement control method to perform the pulling tests. During the pulling tests, the simulation boxes are stretched in the y-direction with a strain incensement of 1.25% every 25 ps. The stress in the pulling direction is derived from the center region with a length of 50 Å to eliminate the boundary effects and is averaged over a time interval of the last 5.0 ps in each pulling step to reduce stress fluctuations. The large-scale GO and GO–PDA models are adopted to study the shrinking ability of GO and GO–PDA papers. The large-scale models in the wet condition (35 wt%) are equilibrated with the same two steps of simulations described above for the small-scale models. The water molecules are then removed to simulate the dehydration process in experiments. The large-scale models are then equilibrated in the NPT ensemble at a constant temperature of 400 K and pressure of 1.013 bar for 1.0 ns. The high temperature accelerates the equilibration speed in the simulation, thus reducing the simulation time for the equilibration. In the final step, the large-scale models are then equilibrated in the NPT ensemble at a constant temperature of 300 K and pressure of 1.013 bar (in all directions in the case of free BC and in the x- and z-directions in the case of fixed BC) for another 100 ps.

### Preparation of GO and GO–PDA papers and mechanical measurements

GO aqueous suspension and other reagents are purchased from Sigma-Aldrich, USA. All reagents are used as obtained without further purification. To synthesize GO–PDA papers, Tris buffer solution (pH 8.5) and dopamine are added into a GO aqueous dispersion with the final GO/DA weight ratio of 90/10 and GO concentration of 1 mg ml⁻¹. The resultant solution is continuously stirred for 24 h at room temperature to synthesize GO–PDA suspension. Finally, 15 ml GO and GO–PDA suspension is used to make GO and GO–PDA papers by the vacuum filtration method, which is performed using a standard setup with a PC membrane (pore size, 0.2 mm; diameter, 47 mm; Sigma-Aldrich).

The mechanical properties of GO and GO–PDA papers are tested by using an Instron 3366 machine (Instron, Norwood, US) in the tensile mode at 25 °C with a tensile speed of 0.1 mm min⁻¹. The environmental RH is 33%. To record the mechanical properties of GO and GO–PDA papers at 75% RH, the samples are incubated in saturated NaCl salt solutions (75% RH) for 24 h. To measure the shrinking stresses the wet samples are fixed by Instron grips with a very weak tensile force to keep samples at the tensile state. After the force is stable (around 1 min), a heater (200 °C) is placed near one side of the samples to make rapid water evaporation. The distance of grips is fixed during the measurements. The morphology of rabbit synovial fibroblasts is characterized by SEM (Zeiss Ultra 55 field emission SEM, Harvard University Center for Nanoscale Systems) at an acceleration voltage of 5 kV. To prevent electrical charging, all specimens are coated with a 5 nm thick Pd/Pt layer before observation. XRD patterns were recorded on a Bruker-AXS x-ray diffractometer (Bruker AXS, Inc., Madison, WI, USA) with Cu Kα radiation (λ = 1.542 Å).

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### References


[18] Ling S et al 2014 Directed growth of silk nanofibres on graphene and their hybrid nanocomposites ACS Macro Lett. 3 146–52
[26] Lee W et al 2013 Simultaneous enhancement of mechanical, electrical and thermal properties of graphene oxide paper by embedding Carbon 65 296–304
[27] Cui W et al 2014 A strong integrated strength and toughness artificial nacre based on dopamine cross-linked graphene oxide ACS Nano 8 9511–7
[49] Cao C, Daly M, Singh C V, Sun Y and Filleter T 2015 High strength measurement of monolayer graphene oxide Carbon 81 497–504
[51] Chen C et al 2013 Self–assembly of tetramers of 5,6-dihydroxyindole explains the primary physical properties of eumelanin: experiment, simulation, and design ACS Nano 7 1524–32
[53] Chen C-T, Chuang C, Cao J, Ball V, Ruch D and Buehler M J 2014 Excitonic effects from geometric order and disorder explain broadband optical absorption in eumelanin Nat. Commun. 5 3859