Mechanical properties and thermal conductivity of graphitic carbon nitride: A molecular dynamics study

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Abstract

Graphitic carbon nitride (g-C3N4) nanosheets are among 2D attractive materials due to presenting unusual physicochemical properties. Nevertheless, no adequate information exists about their mechanical and thermal properties. Therefore, we used classical molecular dynamics simulations to explore the thermal conductivity and mechanical response of two main structures of single-layer triazine-based g-C3N4 films. By performing uniaxial tensile modeling, we found remarkable elastic modulus of 320 and 210 GPa for two different structures of g-C3N4 sheets. Using equilibrium molecular dynamics simulations, the thermal conductivity of free-standing g-C3N4 structures were also predicted to be around 7.6 W/mK and 3.5 W/mK. Our study suggests the g-C3N4 films as exciting candidate for reinforcement of polymeric materials mechanical properties.

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1. Introduction

Two-dimensional (2D) materials that are consisting of few atomic layers have attracted tremendous attention due to presenting unique properties with promising prospects for extremely broad applications from nanoelectronics to aerospace structures. The significance of 2D materials was primarily raised by the great success of graphene [1–3], with a unique combination of exceptionally high thermal [4], mechanical [5] and electrical properties [6]. The application of graphene in nanoelectronics is however limited because it does not present a bandgap and being categorized as a semi-metallic material. To surpass this limitation and open a bandgap in graphene, the common strategies involve complex physical or chemical modifications such as chemical doping [7–9]. Nevertheless, an alternative simpler route is to use an inherent semiconducting materials like hexagonal boron-nitride (with bandgap of ~5.8 eV [10]) or MoS2 sheets (1.8 eV bandgap [11]). However, due to chemical limitation, the desirable approach is yet to complement the electronic properties of the carbon-only graphite/graphene system that combines 2D atomic crystallinity and inherent semiconductivity [12]. To this aim, one possible candidate is graphitic carbon nitride (g-C3N4) which consists exclusively of covalently-linked, sp2-hybridized carbon and nitrogen atoms [12,13]. Recently and for the first time, macroscopically large crystalline thin films of s-triazine-based, g-C3N4 (SgCN) films have been fabricated using an ionothermal, interfacial reaction [12]. Interestingly, experimental measurements and first principles density functional theory calculations suggest that SgCN has a bandgap of between 1.6 and 2.0 eV [12]. This short bandgap places the SgCN within the family of small bandgap semiconductors such as Si and GaAs, which proposes SgCN as an excellent candidate for nanoelectronic devices. We note that tri-triazine-based, g-C3N4 (TgCN) is also another form of graphitic carbon-nitride that has been experimentally fabricated and widely used for various applications [14]. We remind that in addition for application as 2D semiconducting materials in nanoelectronics, SgCN and TgCN films have great potential for energy conversion and storage, environmental applications including direct methanol fuel cells, catalysis, photocatalysis and CO2 capture [14–17]. Graphitic carbon nitride are obviously “sustainable”, as they are composed of carbon and nitrogen only, and can be prepared from simple precursors at a low cost [14].

As promising materials to be used in a wide variety of applications, the comprehensive understanding of thermal and mechanical properties of SgCN and TgCN films is also of a crucial importance. We note that while the recent experimental study [12] proposes a route to fabricate large crystalline thin films of SgCN, to the best of our knowledge TgCN structure is currently available only at nanoscale and stacked forms [14]. However, likely to SgCN films, fabrication of macroscopic forms of TgCN nano-
sheets is also potentially expectable. Due to difficulties of experimental characterization of material properties at nanoscale, numerical and theoretical methods could be considered as an alternative approach [18]. To this purpose, we used classical molecular dynamics simulations to provide an overall image concerning the thermal conductivity and mechanical response of SgCN and TgCN nanosheets.

2. Atomistic modeling

From theoretical point of view, there are several hypothetical phases of carbon nitride that naturally exist such as \( x, \beta, \) cubic, pseudocubic, and graphitic structures \([13,14]\). Among all these allotropes, g-C\(_3\)N\(_4\) is understood to be the most stable structure under ambient conditions \([13,14]\). Nevertheless, among different g-C\(_3\)N\(_4\) structures, up to date, only s-triazine-based g-C\(_3\)N\(_4\) (SgCN) has been synthesized in a form as that of graphite, consisting of macroscopic crystalline thin films \([12]\). On the other hand, tri-triazine-based, g-C\(_3\)N\(_4\) (TgCN) is another form of graphitic carbon-nitride that is widely used in chemical applications \([14]\). Accordingly, we construct molecular models to evaluate the thermal and mechanical properties of SgCN and TgCN sheets. In Fig. 1, atomic structures of SgCN and TgCN films are illustrated that are consisting of triazine units (ring of C\(_3\)N\(_3\)). In a SgCN film, a periodic array of single carbon vacancies exists while in a TgCN membrane three carbon atoms are removed in every repeating vacancy. We studied the tensile response and thermal conductivity of SgCN and TgCN films along armchair and zigzag directions (as shown in Fig. 1) in order to assess the intensity of anisotropic effects.

Molecular dynamics (MD) simulations in the present investigation were performed using LAMMPS \( \text{(Large-scale Atomic/Molecular Massively Parallel Simulator)} \) \([19]\) package. The accuracy of molecular dynamics predictions for a particular structure is strongly dependent on the accuracy of utilized force fields for describing the interatomic forces. In this work, we used the Tersoff potential \([20,21]\) for introducing bonding interactions between carbon and nitrogen atoms. We used the set of parameters proposed by Lindsay and Broido \([22]\) and Matsunaga et al. \([23]\) for carbon and nitrogen atoms, respectively. Accordingly, the Tersoff potential parameters for carbon–nitrogen interactions were obtained using Eq. (1e) in Ref. \([20]\). It is worthy to note that the optimized Tersoff potential by Lindsay and Broido \([22]\) could predict the phonon dispersion curves of graphite in closer agreement with experimental results than the original Tersoff potential. We also found that optimized Tersoff potential could predict the mechanical properties \([24]\) and thermal conductivity \([25]\) of pristine graphene in closer agreement with experiments than other common potential functions for the modeling of carbon atoms. In our previous work, we studied the mechanical response of nitrogen doped graphene. Interestingly, recent density functional theory study \([26]\) confirms the accuracy of our predictions for mechanical properties of nitrogen doped graphene. We note that the time increment of all simulations was fixed at 0.5 fs. Based on the recent experimental findings \([12]\), we assumed the thickness of 0.328 nm for SgCN and TgCN membranes. Moreover, in all MD simulations periodic boundary conditions were applied in planar directions to minimize the finite length effects.

In this study, thermal conductivity of SgCN and TgCN films was evaluated using equilibrium molecular dynamics (EMD) method. To this aim, the structures were first relaxed to zero stress along the planar direction at room temperature using the Nosé–Hoover barostat and thermostat (NPT) method. The structures were then further equilibrated at constant volume and 300 K using Berendsen thermostat method. At this point, the system is at accurate equilibrium conditions and the energy of the system is conserved by performing the constant energy (NVE) calculations. The EMD method relies on relating the ensemble average of the heat current auto-correlation function (HCACF) to the thermal conductivity \( k \), via the Green–Kubo expression:

\[
k_s = \frac{1}{\mathcal{V} k_B T} \int_0^\infty \langle J_s(t) J_s(0) \rangle \, dt
\]

where \( x \) denotes the three Cartesian coordinates, \( K_B \) is the Boltzmann’s constant, \( V \) and \( T \) are the volume and temperature of the system, respectively. The auto-correlation functions of the heat current \( \langle J_s(t) J_s(0) \rangle \) can be calculated using the heat current \( J(t) \) as expressed by \([19]\):

\[
J(t) = \sum_i \left( e_i \vec{v}_i + \frac{1}{2} \sum_{i<j} \left( \vec{f}_{ij} \cdot \left( \vec{v}_i - \vec{v}_j \right) \right) \right)
\]

here, \( e_i \) and \( v_i \) are respectively the total energy and velocities of atom \( i \), \( f_{ij} \) and \( r_{ij} \) are respectively the interatomic force and position vector between atoms \( i \) and \( j \), respectively. By performing the constant energy simulations, the heat current values along armchair and zigzag directions were recorded to calculate the HCACFs. Several independent simulations were performed and the obtained HCACFs were averaged to calculate the effective thermal conductivity using Eq. (1).

The mechanical response of SgCN and TgCN sheets was analyzed by performing uniaxial tensile simulations. Before applying the loading conditions, structure was relaxed to zero stress at room

Fig. 1. Atomic structure of (a) s-triazine-based g-C\(_3\)N\(_4\) (SgCN) and (b) tri-triazine-based g-C\(_3\)N\(_4\) (TgCN).
temperature using the NPT method. For the loading conditions, the periodic simulation box size along the loading direction was increased by a constant engineering strain rate of $1 \times 10^3$ s$^{-1}$ at every simulation time step. To ensure perfect uniaxial stress conditions, periodic simulation box along the sample width was altered using the NPT method. Virial stresses were calculated at each strain level to obtain engineering stress–strain response.

### 3. Results and discussions

In this study, the thermal conductivity of SgCN and TgCN is obtained using EMD method. In this method there is no imposed driving force and periodic boundary conditions are applied in planar direction, hence the system is always at equilibrium condition. The main disadvantage of EMD method is that it converges very slowly and several independent simulations are necessary to obtain converged thermal conductivity [27]. However, because a heat source and sink are not used in the EMD method, the size effect is much less severe than that for the direct (non-equilibrium) method [27]. In this regard, EMD studies on bulk silicon [27] and graphene [28] have confirmed that the thermal conductivity converges for system’s sizes by almost two orders of magnitude smaller than the structure’s mean-free path. In Fig. 2, the calculated thermal conductivity of SgCN and TgCN as a function of correlation time is shown. To ensure the size independency of calculated thermal conductivities, we performed the simulations for three samples with different number of atoms and system sizes from 16 nm to 50 nm. For each sample, the calculations were performed for ten different simulations with uncorrelated initial conditions and obtained results were averaged. The results depicted in Fig. 2 are then the average of those along the armchair and zigzag directions. The EMD results for both structures reveal that at the correlation time of 5 ps, the thermal conductivity is well-converged. The obtained results shown in Fig. 2, clearly confirm the size independency of estimated thermal conductivities for SgCN and TgCN films. Accordingly, based on the EMD approach, the thermal conductivity of free-standing SgCN is predicted to be $7.7 \pm 0.6$ W/mK. In addition, our EMD results reveal that SgCN present around 12% higher thermal conductivity along the armchair direction in comparison with zigzag. On the other hand, we found a thermal conductivity of around $3.5 \pm 0.3$ W/mK for suspended TgCN sheets. Our results for TgCN films suggest the independency of thermal conductivity to the chirality direction. The lower thermal conductivity of TgCN in comparison with SgCN is intrinsically because of increasing of phonon scattering rate due to the larger vacant area in TgCN films. Phonon scattering could also explain the isotropic thermal conductivity response in TgCN films. The predicted thermal conductivities for graphitic carbon-nitride structures are by two orders of magnitude lower than that of graphene sheets. We note that thermoelectric application of graphene is limited due its high thermal conduction properties. However, because of remarkably close atomic structures of graphene and g-C$_3$N$_4$ films, they could be considered as unique candidates for chemical integration. In this regard, fabrication of graphene/g-C$_3$N$_4$ hetero-structures could be considered as a promising approach for tuning the graphene thermal conductivity. This could enhance the thermoelectric figure of merit in favor to reach a high efficiency carbon-based thermoelectric material.

The loading strain rates applied in the molecular dynamics simulations are commonly in several orders of magnitude higher than the conventional experimental tests. Thus, we performed the simulations at different strain rates to investigate the strain rate dependency of the acquired mechanical properties. In Fig. 3, we plot the acquired uniaxial stress–strain responses of single-layer SgCN and TgCN films for different strain rates. Our results confirm that for both, SgCN and TgCN films, the strain–strain curves for different strain rates coincide up to the tensile strength. This issue confirms that the obtained elastic properties are independent of loading strain rates. In addition, to examine the intensity of loading direction effect on the mechanical properties, we also studied the tensile response along armchair and zigzag loading directions. In this case we found that elastic properties of SgCN and TgCN films are convincingly independent of loading direction. To summarize, our atomistic modeling yield elastic modulus of $320 \pm 5$ GPa and $210 \pm 5$ for SgCN and TgCN films, respectively. On the other hand, as an overall trend we found that the tensile strength and corresponding failure strain decreases by decreasing the strain rate. However, our results show that after the strain rates of $10^2$ s$^{-1}$ and $3 \times 10^3$ s$^{-1}$, the loading rate effect decreases considerably for SgCN and TgCN films, respectively. Therefore, our MD modeling predict tensile strength of around 40 GPa and 25 GPa for SgCN and TgCN films, respectively. This way, the ratio of elastic modulus with respect to the tensile strength for the both studied structures would be around 8 which is similar to the experimental observation regarding the defect-free graphene sheet [5]. The predicted mechanical properties by our MD study suggest the triazine-based, g-C$_3$N$_4$ films as remarkably strong materials. In comparison with defect-free graphene sheets, the elastic modulus of SgCN film is almost one third of those of graphene [5]. Presenting remarkably high mechanical properties, also recommend the SgCN and TgCN films as an excellent candidate to reinforce mechanical properties of polymeric materials [29]. Porous structure of SgCN and TgCN films leads to their lower stiffness and higher flexibility in comparison with graphene sheets. The high flexibility of additives could cause to reduce the stress concentration and postpone crack initiation in response. Therefore, in comparison with graphene flakes, it
could be expected that nanocomposites made from graphitic carbon nitride films could present higher tensile strength responses. We note that due to presence of saturation limits in enhancement of nanocomposites materials elastic response \cite{30}, the elastic stiffness of polymer nanocomposites made from SgCN or TgCN are expected to be close to that fabricated from same sized graphene flakes.

In Fig. 4, we illustrate the deformation process of a TgCN film along the armchair direction at different stages of loading. Our atomistic modeling suggests that during the loading condition the TgCN sheets extend uniformly and remain defect-free up to the tensile strength. We found that the tensile strength is a point that the first debonding occurs (Fig. 4a), which rapidly propagates (Fig. 4b and c) and leads to the specimen rupture (Fig. 4d). In this case, the initial debonding and subsequent rupture are found to occur at very close strain levels which accordingly suggest the brittle failure mechanism for TgCN nanosheets. As shown in Fig. 4d, during the crack growth in the sample, carbon–nitrogen chains form cross the sample that tend to keep the two sides of cracks connected. As it can be observed from Fig. 4d, the crack edges are mainly along the zigzag direction which reveals that debonding and crack growth happen by breaking of carbon–nitrogen bonds mostly along the armchair direction. For different strain rates and also in the case of SgCN films, we found similar failure mechanism.

4. Summary

Triazine-based graphitic carbon nitride structures are among attractive 2D-semiconducting material due to their unusual physicochemical properties. Experimental studies have illustrated considerable prospects for their applications in nanoelectronics, energy conversion and storage, environmental applications, catalysis and photocatalysis. Accordingly, no adequate information exists about thermal conductivity and mechanical properties of these structures. Accordingly, we conducted atomistic simulations to study the mechanical properties and thermal conductivity of two main structures of graphitic carbon nitride structures at room temperature. The Tersoff potential was used to introduce bonding interactions between carbon and nitrogen atoms in our molecular dynamics modeling.

Using equilibrium molecular dynamics simulations, the thermal conductivity of free-standing SgCN and TgCN were predicted to be 7.7 ± 0.6 W/mK and 3.5 ± 0.3 W/mK, respectively. Our results suggest that SgCN present around 12% higher thermal conductivity along the armchair direction in comparison with zigzag. On the other hand, by performing uniaxial tensile simulations, we found that pristine SgCN films can present elastic modulus of 320 ± 5 GPa and tensile strength of around 40 GPa. In addition, our MD results suggest that TgCN films can yield elastic modulus 210 ± 5 GPa and tensile strength of around 25 GPa. Our results suggest the triazine-based graphitic carbon nitride structures as remarkably strong and flexible 2D materials well suited for reinforcement of mechanical properties of polymeric materials.

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