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The formation of Cr₂O₃ nanoclusters over graphene sheet and carbon nanotubes

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ABSTRACT

Carbon supported metal oxide nanoparticles hold promise for various future applications in diverse areas including spintronics, catalysis and biomedicine. These applications, however, typically depend on the structure and morphology of the nanoparticles. In this contribution, we employ classical molecular dynamic simulations based on a recently developed force field to study the structural properties of Cr_2O_3 nanoclusters over graphene and carbon nanotubes. We observe that Cr_2O_3 nanoclusters tend to aggregate over both freestanding graphene and carbon nanotubes and form larger nanoclusters. These large nanoclusters are characterized by their worm-like shape with a lattice constant similar to that of bulk Cr_2O_3 . We also investigate the structural deformation induced in graphene due to the presence of Cr_2O_3 nanoclusters.

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1. Introduction

 Cr_2O_3 oxide is an inorganic compound which has been extensively studied in recent years. It has unique properties for application as pigment, in spintronic devices, and for its piezomagnetism [1,2]. In addition to its bulk, various sizes of Cr_2O_3 nanoclusters were also experimentally realized [3–5] which could be deposited on different substrates. Since the fabrication of two dimensional graphene and one dimensional carbon nanotubes (CNTs), decorating these allotropes of carbon with Cr_2O_3 nanoclusters (NCs) has been the subject of intensive experimental research with potential applications in Li-ion batteries and spintronic devices [6–9,1].

Graphene and CNTs decorated with nanoclusters as a new class of hybrid nanomaterials could potentially display not only the unique properties of nanoclusters [10], graphene, and CNTs [9,8,11–13], but also additional novel physical and chemical properties due to the interaction between graphene and CNTs with the attached nanoclusters. Recently, Cr_2O_3 nanostructures were deposited on a single layer of graphene using a hydrothermal approach [8]. In this experiment the authors observed the aggregation of Cr_2O_3 nanostructures on graphene. It was found that graphene can effectively enhance the electrochemical properties of Cr_2O_3 making graphene-based Cr_2O_3 composites promising systems for Li-ion batteries applications.

Filling CNTs with Cr₂O₃ has applications in spintronic devices [1,2]. Bajpai et al. [1] reported the encapsulation of Cr₂O₃ nanoclusters in CNTs. They showed the feasibility of filling CNTs with Cr₂O₃, thereby fabricating an intrinsically landscaped functional material which is shielded by a protecting carbon shell and may exhibit tunability of magnetism with applied magnetic fields as well as electric fields. It is thus of interest to study the structural and morphological properties of Cr₂O₃ nano-particles (NPs) on graphene and carbon nanotubes. While several molecular dynamics simulations on Cr_2O_3 were previously performed [14–16], there are to the best of our knowledge no simulation studies yet on Cr₂O₃ NPs on graphene and carbon nanotubes. We here study the structural properties of small clusters of Cr₂O₃ on graphene and CNTs using a recently developed ReaxFF force field [17]. We employ the semi-classical ReaxFF force field [18], as it allows to combine an accurate representation of the system with the ability to perform large scale simulations. This reactive bond-order-dependent force field can be helpful for studying the cluster formation and their ambient condition properties. In particular we consider the behavior of the Cr₂O₃ clusters and how they influence graphene and CNTs. We consider the temperature dependence of the different nanoclusters concentrations and show that any initially ordereddistribution of Cr₂O₃ nanoclusters over graphene deforms to the



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random disordered morphology. The small clusters aggregate quickly and tend to form worm-like structures.

The paper is organized as follows. In Section 2 we briefly present our molecular dynamic approach and the model that we used through the calculations. Section 3 contains the main results for the structural deformation of Cr_2O_3 nanoclusters over graphene. In Section 4 we present the main result of formation of Cr_2O_3 nanoclusters over carbon nanotubes. Finally, a conclusion is presented in Section 5.

2. The model and computational methods for $\mbox{Cr}_2\mbox{O}_3$ nanoclusters over graphene sheet

Cr₂O₃ has the corundum type crystal structure with space group $R\overline{3}c$. It can be regarded as a hexagonal (with 6 formula units) and rhombohedral (with 2 formula units) cell. Using the rhombohedral unit cell we have first created nanoclusters with two different sizes, i.e. NC_{40} with 40 atoms and NC_{90} with 90 atoms. In order to study the dynamics of these clusters over graphene we distribute different concentrations of these clusters over graphene. In Fig. 1(a), (c), (e), (g) we show the top view of the initial distribution of different concentrations of Cr₂O₃ which cover 2%, 7%, 12%, and 17% (the ratio of cluster area to the graphene surface) of the graphene surface, respectively. The numbers and sizes of the clusters we have used for each concentration is: $(5 \times NC_{40})$ for 2%, $(10\times NC_{40}+4\times NC_{90})$ for 7%, $(15\times NC_{40}+8\times NC_{90})$ for 12%, and $(20 \times NC_{40} + 12 \times NC_{90})$ for 17% coverage. A graphene sheet with dimension $16.7 \times 18.1 \text{ nm}^2$ containing 12.000 carbon atoms is used as the substrate. In the case of the CNT we distributed $15 \times NC_{40}$ Cr₂O₃ clusters containing 600 atoms over the CNT. The number of carbon atoms in the CNT is about 3200 atoms.

In order to describe the interatomic interactions in our molecular dynamic simulations, we have used the ReaxFF potential for Cr₂O₃ [17]. The ReaxFF force field is a general bond-order dependent potential that provides an accurate description of chemical reactions. The connectivity in the entire system is recalculated in every iteration and non-bonded interactions (van der Waals and Coulomb interactions) are calculated between all atom pairs, irrespective of the connectivity [18–20]. The Cr/O ReaxFF potential that is used in the current MD simulations has been developed by training the ReaxFF force field parameters against extensive density functional theory calculations. The ReaxFF parameters are fitted against energy-volume relationship (equation of state), cohesive energies, valence angle energies, and surface energies of different Cr bulk phases as well as Cr-oxides, CrO₂, Cr₂O₃, and

Cr₃O₄. In Ref. [17], the authors further validate their developed ReaxFF potential within a series of MD simulations for bulk Cr₂O₃. They found that the crystal structure of bulk Cr₂O₃ remains stable up to 2600 K in agreement with experiments.

The AIREBO interatomic potential is used to describe carboncarbon interactions in graphene [21], and a Lennard Jones (LJ) potential for the interactions between Cr_2O_3 clusters and graphene. In order to check if the LJ potential can correctly describe the interactions between clusters and carbon atoms, we have performed DFT calculations for a small cluster of Cr_2O_3 on top of 17.3×19.7 Å² graphene sheet. Using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [22] we optimized the total system of Cr_2O_3 clusters on top of graphene. We found the shortest distance of 3.02 Å between the cluster and graphene in the relaxed structure which indicates that there is no binding between the cluster and carbon atoms (any strong C—O bond should be of about 1.16 Å). This confirms that the LJ potential in our MD simulations can correctly describe the interactions between clusters and carbon atoms in both graphene and CNT.

The Lennard-Jones parameters, σ and ϵ , for the C—O, and C—Cr are calculated from the customary Lorentz-Berthelot mixing rules [23]

$$\sigma_{\text{C-A}} = [\sigma_{\text{C-C}} + \sigma_{\text{A-A}}]/2, \quad \epsilon_{\text{C-A}} = [\epsilon_{\text{C-C}} \times \epsilon_{\text{A-A}}]^{1/2}, \tag{1}$$

where σ_{A-A} is the collision diameter and ϵ_{A-A} is the depth of the energy well between two atoms with A \in [Cr, O]. The parameters we used in our simulations are $\sigma_{C-C} = 3.369$ Å [24], $\sigma_{Cr-Cr} = 2.335$ Å [25], $\sigma_{0-0} = 2.951$ Å [26], and $\epsilon_{C-C} = 2.63$ meV [24], $\epsilon_{Cr-Cr} = 498.6$ meV [25], $\epsilon_{0-0} = 5.1$ meV [26].

All molecular dynamics simulations were carried out with the LAMMPS code [27]. First we relax the system during 100 ps at room temperature in the (NPT) ensemble with a time step of 0.1 fs. Temperature and pressure are controlled using a Nosé-Hoover thermostat and barostat. After reaching equilibrium we investigate the structural deformation of Cr_2O_3 clusters for 900 ps. For the case of Cr_2O_3 clusters over CNTs, we followed the same approach as for graphene but we performed the simulations for 2 ns to ensure that the system is fully relaxed.

3. Cr₂O₃ nanoclusters on graphene

Here we study the self-assembly of Cr_2O_3 nanoclusters on graphene. The upper panels in Fig. 1 show the initial structures and the lower panels show the final structures of Cr_2O_3 clusters, after 1 ns simulation, for 2% (a,b), 7% (c,d), 12% (e,f), and 17% (g,h)



Fig. 1. The upper panels show the initial (t = 0) and the lower panels show the final (t = 1 ns) configurations at T = 298 K for 2% (a,b), 7% (c,d), 12% (e,f), and 17% (g,h) concentrations of Cr₂O₃ clusters on graphene.



Fig. 2. (a) Side view of the final configuration (t = 1 ns) of Cr_2O_3 nanoclusters with 17% concentration over graphene at room temperature. (b)–(d) Radial distribution function (RDF) of Cr–O, Cr–Cr, and O–O.



Fig. 3. Configuration of Cr_2O_3 clusters on top of graphene (in the case of highest cluster concentration), (a) before and (b) after joining the two large clusters. The arrows in (a) and (b) point out the positions where two large clusters connecting together. (c) Potential energy of the system as a function of time. The red circle indicates a sharp drop corresponding to the moment where the two large clusters in (a) and (b) join. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

concentrations (the percentage indicates the amount of graphene surface area covered by Cr_2O_3 clusters). It is seen that larger nanoclusters of Cr_2O_3 are formed. Depending on the initial size of Cr_2O_3 clusters and their density, large elongated structures are formed over the graphene surface. The formation of such large size of clusters is due to the strong interactions between the Cr_2O_3 clusters and the weak Van der Waals interactions between the clusters and the graphene surface.

The calculated radial distribution function (RDF) of Cr—O, Cr—Cr and O—O, in the case of highest concentration of Cr_2O_3 nanoclusters are shown in Fig. 2. It is seen that there is a signature of crystalline structure due to the presence of considerable second peaks. Note that we have calculated the RDF for all the atoms in clusters as the Cr_2O_3 nanoclusters in our simulations have a thickness of only a few atoms, forming a surface-like structure on graphene (see the side view in Fig. 2(a)). The first peak in the RDF of Cr—O (1.85 Å), see Fig. 2(b), is close to the Cr—O bond length obtained by ReaxFF in the case of bulk Cr_2O_3 (1.95 Å). The first peak in the RDF of Cr—Cr and O—O (see Fig. 2(c), (d)) occur at 3.3 Å and 2.45 Å which are longer than the corresponding Cr—Cr bond lengths in Cr bulk (2.4 Å) and Cr_2O_3 bulk (2.6 Å), and O—O bond lengths in O_2 molecule (1.21 Å) and Cr_2O_3 bulk (2.2 Å). This indicates that there is no strong Cr—Cr and O—O bonding in the clusters. In comparison the aggregation of transition metal (TM) NPs on graphene shows quite different results [24]. In this case the formed nanoclusters are locally "trapped" by the graphene out-of plane ripples and they do not aggregate. This is the direct consequence of the strong interactions between the clusters and graphene in contrast to our case in which we have weakly van der Waals interactions between Cr_2O_3 clusters and freestanding graphene.

Aggregation of Cr_2O_3 nanoclusters lowers the potential energy. In Fig. 3(a) and (b) we show two long nanoclusters before and after connecting together. Fig. 3(c) shows the corresponding energy variation in the potential energy with time. The sudden drop in the potential energy is an indication of the energy reduction during the aggregation. Therefore, the formation of larger clusters is energetically favorable.

Fig. 4(a) and (b) shows the density plots of the out-of plane component of the carbon atoms of graphene (at time 0.9 ns and at room temperature) for the lowest (2%) and highest concentrations (17%) of Cr_2O_3 coverage, respectively. The initial height of carbon atoms is set to zero. It is seen that for a fixed temperature (room temperature) the height variation of carbon atoms is larger in the case of highest concentration (Fig. 4(b)) compared to the lowest one (Fig. 4(a)). In fact, the aggregation of small Cr_2O_3 nanoclusters and formation of large clusters not only pulls the under-



Fig. 4. The height of carbon atoms in graphene for the final snapshot (t = 1 ns) with (a) 2% and (c) 17% concentrations of Cr₂O₃ clusters at T = 298 K. The initial position of graphene is set to zero and the units are Å.



Fig. 5. Standard deviation of the height $\langle h^2 \rangle$ of graphene as a function of temperature for pristine graphene (blue circles), 2% (green triangles) and 17% (red squares) concentrations of Cr₂O₃ clusters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

neath graphene downward but also induces large fluctuations into the graphene sheet around the clusters.

We also calculated the height variation of the graphene membrane due to the presence of Cr_2O_3 nanoclusters for the different temperatures. In Fig. 5 we depict the average value of the height fluctuations $\langle h^2 \rangle$, where *h* denotes the height of carbon atoms in the graphene membrane with respect to the center of mass of the carbon atoms. We show the evolution of $\langle h^2 \rangle$ with temperature



Fig. 7. Potential energy as a function of the simulation time for the system shown in Fig. 6. Insets show snapshots of the system corresponding to the indicated time.

for two systems with lowest and highest cluster concentrations, respectively. In order to investigate the effect of clusters on graphene we also compared the results with pristine graphene with the same size. At a fixed temperature we observe that $\langle h^2 \rangle$ increases by increasing the cluster concentration. Note that as a function of temperature, $\langle h^2 \rangle$ increases in pristine graphene and low cluster concentration while it decreases at high cluster concentration. This different behavior is due to the formation of large clusters in the case of high concentrations, which strongly deforms the graphene sheet but flattens out with increasing temperature. In



Fig. 6. The initial (t = 0) (a), (b) and final (t = 2 ns) (c), (d) configurations of Cr_2O_3 clusters over the CNT at room temperature.



Fig. 8. Radial distribution function (RDF) of Cr–O, Cr–Cr, and O–O in Cr₂O₃ nanoclusters over CNT at room temperature.

the case of low concentration of Cr_2O_3 nano-clusters, several small clusters are formed, leading to only a small deformation of the graphene sheet which only very weakly depends on temperature.

4. Cr₂O₃ nanoclusters on carbon nanotubes

In this section, we study the self assembly and the dynamics of the Cr₂O₃ clusters around and inside the CNT. We applied periodic boundary conditions on both sides of the CNT with diameter R = 13.85 Å and put Cr_2O_3 clusters over and inside it. Note that due to the used periodic boundary condition the type of CNT edges is not important. In Fig. 6 we present the results for the initial and final (at 2 ns) configurations of the Cr₂O₃ clusters distributed over the CNT at room temperature. Similar to the Cr₂O₃ clusters over graphene, we observe aggregation of clusters both inside and around the CNT. Interestingly, the clusters inside the tubes are attracted by the outside clusters with the CNT wall in between them. It has been experimentally observed that both the antiferromagnetic and ferromagnetic Cr₂O₃ nanoclusters aggregate inside a CNT [1]. In this experiment the authors demonstrate that the structure of the CNT remains stable within the filling process. In Fig. 7 we plot the potential energy of the system as a function of time up to 2 ns simulation time. Similar to the case of clusters on top of graphene the potential energy of the system decreases with time as the clusters join. There are several jumps that happen at times when two large Cr₂O₃ clusters join together yielding a more stable structure. The figure shows representative snapshots taken at $t \approx 0.3$ ns and $t \approx 0.4$ ns corresponding to the moments before and after joining two big clusters.

Fig. 8 shows the radial distribution function Cr—O, Cr—Cr, and O—O for Cr_2O_3 clusters over the CNT at room temperature. As for the case of clusters on top of graphene, the first peak in the RDF for the Cr—O bond occurs at 1.85 Å which is close to the Cr—O bond length obtained by ReaxFF for the bulk of Cr_2O_3 .

5. Summary

In summary, we have performed MD simulations to study the self-assembly of Cr_2O_3 clusters on top of two well-known carbon allotropes: graphene and CNT, employing a recently developed ReaxFF parametrization. We observe that the Cr_2O_3 nanoclusters self-assemble very quickly and form large clusters over the graphene sheet and CNT within a molecular time scale. This indicates that Cr_2O_3 NPs are highly mobile and deformable on these substrates. In fact, the weak Van der Waals interactions between the clusters and graphene (or CNT) together with the strong interatomic interactions in Cr_2O_3 nanoclusters lead to the formation of worm-like large nanoclusters instead of dome-shaped nanoclusters.

ters. We found the cluster aggregation to occur on both the inner and outer surfaces of CNT. The corresponding Cr—O bond of the formed nanoclusters over both graphene and CNT is close to that of bulk Cr₂O₃. For the case of Cr₂O₃ nanoclusters on graphene we have demonstrated that the formation of large clusters highly deform graphene at room temperature while the graphene sheet flattens out as a function of temperature.

Decorating graphene and CNTs with magnetic Cr_2O_3 clusters could be very useful for tuning/controlling the graphene and CNTs electrochemical properties. Graphene based Cr_2O_3 composites can enhance electrochemical performance in Li-ion batteries [8]. Our study may guide future experiments towards new applications in spintronics and biomedicine using decorated graphene and CNTs with metal oxides.

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