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Coalescence of gold nanoparticles around the end of a carbon nanotube: A molecular-dynamics study

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ABSTRACT

Coalescence of gold nanoparticles (Au NPs) around the end of a multi-walled carbon nanotube (MWCNT) and their interaction with the CNT at elevated temperatures may often be important processes during the fabrication of CNT-metal composite (e.g., through laser sintering). However, an atomic-scale fundamental study of such processes through molecular dynamics (MD) simulations has been rarely reported to the authors' best knowledge. Such a study has been reported in this paper. First, MD-predicted NP melting points are compared with experiment-deduced results from the literature to at least partially test the modeling approach. Then the coalescence of 3-nm Au NPs around the end of a MWCNT and their interactions with the CNT are studied through MD simulations. The simulated period includes a 100-ps heating period (at the end of which the system is raised to a certain heating temperature) followed by another 500-ps period. Studies have been performed under different CNT diameters, and for different heating temperatures. Several interesting phenomena have been found under the studied conditions, such as: (i) a CNT with a sufficiently large diameter can draw some Au atoms into the tube, even though the heating temperature (600 K) is well below the melting point of the Au NPs. Such an interesting capillary effect of CNT below the metal NPs' melting point has been rarely reported before to the authors' best knowledge; (ii) Under a heating temperature of 800 K, at the end of the simulated period, lattice structures can still be observed in the merged Au nanocluster if no CNT is nearby; however, the Au atoms become mostly disordered if the NP coalescence takes place near the end of a CNT; and (iii) if significant entrance of Au atoms into the CNT occurs, the arrangement of most Au atoms inside the CNT also follows a multi-layer tube pattern.

1. Introduction

Metallic nanoparticles, e.g., gold nanoparticles (Au NPs), have attracted lots of research attentions because of their current or potential applications in several areas, such as additive manufacturing, flexible electronics, catalysis, drug delivery and sensing, etc. [1–4]. During processes related to some applications, coalescence of metal nanoparticles under certain conditions may often be involved. Therefore, it is important (and may be very valuable to related applications) to understand the interaction mechanisms and coalescence processes of metal nanoparticles, which has drawn lots of research attentions (e.g., [3–10]).

Carbon nanotubes (CNTs) have outstanding electrical and mechanical properties [11–13], and hence are often applied in composites to enhance material properties. The fabrication of CNT-metal composites may often involve sintering of CNTs and metal NPs at elevated temperatures induced by laser or furnace heating. For example, Kang et al. [14] and Zhao et al. [15] studied the fabrication of CNT-silver composites onto a flexible substrate through sintering of mixtures of CNTs and metal NPs with a laser beam and in a furnace, respectively. During laser or furnace-based sintering of CNTs and metal NPs, the coalescence of metal NPs in the presence of CNTs and the interactions among CNTs and different NPs at elevated temperatures are expected to occur, and are very critical processes that may strongly affect the properties and performance of the sintered composites. Hence, a good understanding of the coalescence and interaction processes is very important.

Molecular dynamics (MD) simulation provides a tool that is very powerful in the exploring and understanding of process mechanisms at the atomic scale; and it has been applied by researchers to investigate the coalescence of metal NPs (e.g., [16–18]), the interaction of metal nanoclusters with *the sidewalls* of CNTs (e.g., [19,20]), or the interaction of a single NP with the ends of CNTs (e.g., [21]). Ref.19 reported MD simulations on the heating and cooling processes of silver nanoclusters supported by a single-walled CNT near its sidewall, while in Ref. [20] the processes of CNT-supported Ag-Au alloy nanoclusters (near the CNT

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sidewall) were studied through MD simulations. Ref.21 reported MD simulations of nanoscale soldering processes, where an Ag nanoparticle was positioned between the ends of two CNTs. However, to the authors' best knowledge, previous research work has been rarely reported on the coalescence of multiple metal NPs and their interactions with a CNT, *near the end* (instead of the sidewall) of the CNT, which is a common and hence important situation. It is expected that the coalescence and interactions that occur near the end of a CNT may have significant differences from those that occur near the sidewall of a CNT, and hence deserve further research attentions.

In this work, MD simulations have been conducted to study and help understand the coalescence of gold nanoparticles (Au NPs) initially placed around the end of a multi-walled carbon nanotube (MWCNT), and the interactions among the NPs and the CNT, under elevated temperatures that can be potentially induced by pulsed-laser heating. First, the MD modeling approach is tested (at least partially) by comparing model-predicted melting points of NPs with experiment-deduced results from the literature. Then the model is expanded and adjusted to study and help understand the interactions among multiple Au NPs and a multi-walled carbon nanotube (MWCNT); and model calculations have been performed under different elevated temperatures and for different nanotube diameters. Adaptive common neighbour analysis (CNA), radial distribution function (RDF) and mean squared displacement (MSD) have been employed to help obtain a good understanding of the coalescence and interaction processes.

2. Model setup

Fig. 1 shows the overall initial configuration and geometrical setup of the MD model to investigate the coalescence and interactions of five Au NPs initially positioned around one end of a MWCNT (which is a double-walled nanotube in this work). Such a setup has been used in the simulated cases (when a CNT exists) shown later in Figs. 3–9. Initially, the center-to-center distance between adjacent Au NPs is 3.4 nm, while the distance between the center of the central Au NP and the end of the MWCNT is 1.9 nm. In this study, the initial diameter of each Au NP is set as 3 nm, while the MWCNT has an armchair structure and could have different diameters in different simulated cases (see Table 1 for some of the CNT parameters). The initial length of the MWCNT is set as 8 nm for all the simulated cases with a CNT. The non-periodic shrink-wrapped boundary condition [22] is applied in all directions, which sets the faces of the MD simulation domain box in a way to include all the atoms inside the box.

First, the whole system (including the CNT and the NPs) is equilibrated for 500 ps at the temperature of 300 K. The moment at the end of the equilibration stage is set as time t = 0 ps. Then the whole system is heated to around a certain targeted heating temperature in 100 ps, and is maintained in the constant-energy ensemble (NVE) for another 500 ps. The heating stage period is set at 100 ps to mimic the heating effect that can be potentially induced by a laser pulse with a duration on the order of ~100-picosecond (ps). Different targeted temperatures will be studied, which can be potentially achieved with laser pulses at different fluences in practice. It is assumed that the whole system is in vacuum and the gravity force has been neglected. The possible heat dissipation into the ambient vacuum environment is not considered in the MD simulations. During the equilibration and heating stages, the system is kept in the NVT ensemble where the Nose-Hoover thermostat [23] has been applied to control the temperature. Then the NVE ensemble is used during the subsequent 500-ps period. Throughout each simulation, the motion of each carbon atom in the CNT has been constrained in a region near its initial location to avoid the possible CNT drifting or rotation; and under such conditions the interactions among the Au NPs and the MWCNT will be studied in this paper through MD simulations.

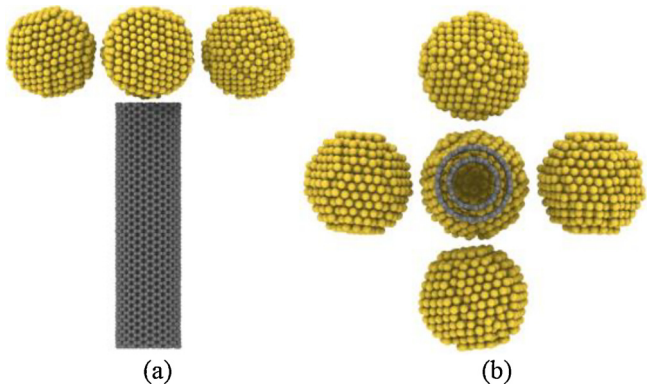

Fig. 1. Initial configuration and geometrical setup of the MD model: (a) side view, and (b) view from the bottom end of the MWCNT (Yellow atoms represent Au atoms, while black atoms represent carbon atoms. Four Au NPs surround the central Au particle with a center-to-center distance of 3.4 nm; and the center of the latter is 1.9 nm away from the end of the CNT whose diameter in different cases is listed in Table 1) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

In this work, the well-known embedded-atom-method (EAM) potential [24,25] has been employed for the Au-Au interaction, while the C—C interaction is described using the adaptive intermolecular reactive empirical bond-order (AIREBO) potential [26], and the Au-C interaction is described using the Lennard-Jones (LJ) potential with parameters taken from [27], where the primary energy well depth $\varepsilon = 0.0341$ eV and the collision diameter $\sigma = 3.003$ Å. The Molecular Dynamics (MD) simulations are carried out based on the open source code called "Large-scale Atomic/Molecular Massively Parallel Simulator" (LAMMPS) [22]. The equation of motion for the involved atoms is numerically integrated with the Verlet algorithm [22,28] using a time step of 2 fs. In each simulation, the CNT is generated in VMD [29]. Visualization of the simulation results has been processed with OVITO [30].

3. Results and discussions

3.1. MD model comparison with experiment-deduced results

First, the MD-predicted melting points of Au NPs at different sizes will be compared with experiment-deduced results shown in [31] to test (at least partially) the modeling approach employed in this study. A separate MD model is set up, which only involves one or more Au NPs of certain sizes without a CNT. The center of mass of each NP is assumed to be fixed during the MD calculations. It should be noted that for very small Au NPs, e.g., diameters of 3 nm or 4 nm, the MD model setup consists of multiple non-interacting NPs (which are positioned relatively far away from each other) to reduce the fluctuation of results. For larger NPs, in each simulation the MD model setup only consists of one NP. During each MD simulation, after a 1-ns equilibration stage at 300 K, the Au NPs are then heated from the temperature of 300 K to 1400 K with a step of 100 K. At each step, after the heating is finished, the system is maintained at the targeted temperature in the NVT ensemble for a period of 500 ps; and the average potential energy per atom (PE/atom) time-averaged for the last 300 ps of the period is calculated and recorded. Similar steps have been employed for a cooling process following a reverse temperature order. During each simulation, the temperature step is changed to a smaller value of 20 K when the temperature is around the melting or freezing point of the gold nanoparticles. Similar to Section 2, the shrink-wrapped boundary condition and the Nose-Hoover thermostat have been used in the simulations.

Fig. 2(a) shows the melting points of gold nanoparticles versus the particle diameters. It can be seen that the model-predicted melting points agree with the experiment-deduced results taken from [31] reasonably well, although some differences do exist. The results in the figure show that the melting point drops as the particle size decreases,