Theoretical Investigation on the Thermal Stability of Hollow Gold Nanoparticles

Luyun Jiang,† Xing Yin,† Jianwei Zhao,*† Hongmei Liu,† Yunhong Liu,† Fenying Wang,† Junjie Zhu,† Freddy Boey,‡ and Hua Zhang‡

Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210008, P. R. China, and School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Received: June 4, 2009; Revised Manuscript Received: August 27, 2009

The thermal stability of hollow gold nanoparticles has been studied by molecular dynamics (MD) simulations. On the basis of the MD simulation results, the hollow nanoparticles have been classified into three categories, namely, stable, half-stable, and unstable systems. The stability of hollow nanoparticles strongly depends on the wall thickness and the aspect ratio, defined as the outer radius over the wall thickness. These features can be further presented in a two-dimensional phase space according to a large number of simulations. By using this stability diagram, the collapsing mechanism has been proposed.

1. Introduction

Hollow nanoparticles have attracted increasing interest due to their unique properties, such as the increased surface area and low density. These special nanoparticles play critical roles in many research areas, including catalysis, chemical or biological sensors, drug delivery, and container. Among the various geometric features of hollow materials, two important features are highlighted, i.e., shell thickness and cavity size. It is believed that these two parameters have the inherent relationship with the nanoparticle stability, thereby dominating the performance and the lifetime of the future devices. Modulating and controlling these two geometric parameters of hollow nanoparticles are, therefore, desired in experiments. For instance, Bao et al. have synthesized hollow nanocrystals with a diameter of ∼6 nm and wall thicknesses of ∼2 nm. Yin et al. have synthesized hollow nanocrystals with an average outer diameter of ∼15 nm through a mechanism analogous to the Kirkendall effect. Chah et al. obtained gold nanoparticles with the pore diameter of 7.8 nm.

In order to correlate the geometrical parameters with the material stability, molecular dynamics (MD) simulation, a powerful tool instead of the direct synthesis, is widely used. In this study, the effect of aspect ratio (the ratio of outer radius over wall thickness) and wall thickness on the thermal stability of hollow gold nanoparticles have been investigated. The interaction between gold atoms is described by the embedded-atom method. On the basis of the MD simulation results, the stability can be presented in a two-dimensional phase space. A theoretical method to predict the boundary in the phase diagram has been developed as well. By using this technique, the collapsing mechanism of the hollow nanoparticles is proposed. The method proposed herein may also guide the further experiments.

2. Methodology

Gold hollow nanoparticles were chosen as a hot research topic because of their special surface property. Figure 1 shows a typical starting structure of a hollow gold nanoparticle obtained by cutting a sphere from the face-centered cubic (fcc) gold crystal followed by cutting a sphere cavity. The simulated system is referred to as inner diameter−outer diameter using the gold crystal lattice parameter, 0.408 nm, as the length unit. For instance, the model 20−22 means the inner diameter is as large as 20 crystal cells, corresponding to 8.160 nm, while the outer diameter 22 crystal cells corresponds to 8.976 nm. Before relaxation of the atomic configuration, the hollow gold sphere displays a perfect crystalline form, as evidenced by the radius distribution function analysis. A time step of 1.6 fs is used for all MD simulations. The temperature of the system is kept constant at 300 K during the whole process with a velocity rescaling method. The interaction between gold atoms is described by the embedded-atom method (EAM) potential. After Daw et al. developed the EAM potential based on the density

Figure 1. The hollow gold nanoparticle is constructed with an fcc gold crystal. To observe the hollow structure, one-fourth was cut from the model.
functional theory (DFT) in 1983, it has been proven that this potential can provide a relevant description of the surface effect, impurity and defect properties of the bulk crystals of transition metals, particularly for the fcc metals.\(^{33-37}\) The calculation of the interatomic potential in metals is shown as

\[
E = \frac{1}{2} \sum_{i} V(r_i) + \sum_{i} F(\rho_i) \quad \rho_i = \sum_{j \neq i} q(r_{ij})
\]

where \(E\) is the total energy of the system, \(V(r_i)\) represents the pair interaction energy between an atom \(i\) and its neighboring atom \(j\), \(q(r_{ij})\) is the electronic density function, and \(F(\rho_i)\) represents an embedding function accounting for the effects of the free electrons in the metal.\(^{35,38}\) All used parameters are obtained from the literature.\(^{38}\) MD simulation is performed with a self-developed code, NanoMD.\(^{22,39}\) The reliability of the program has been verified carefully by not only a large number of simulations, such as nanostretching,\(^{22}\) nanobreaking,\(^{40}\) and the formation of monoatomic chain,\(^{41}\) but also comparison with experiments.\(^{42}\)

3. Results and Discussion

3.1. Three Kinds of Thermal Stabilities of Hollow Gold Nanoparticles. 3.1.1. Three Kinds of Potential Variations during the Relaxation. Finding an indicator correlating with the system stability is of primary importance in this study. Besides the direct observation of the atomic structure, we have found that the potential curve may well-present the nature of the material stability. Depending on the wall thickness and the aspect ratio, various potential curves could emerge during the long-term relaxation. The initial state of the hollow nanoparticle model possesses high potential energy, which can be reduced by the following relaxation. After carefully analyzing the simulation results, we summarized three kinds of potential changes, corresponding to three kinds of thermal stabilities. Figure 2 shows the typical potential curves of three representative samples. The inserted figure was drawn on the logarithmic scale. Model 4.5–5.5 shows a sharp potential drop and requires only \(1 \times 10^5\) steps to reach the potential plateau. The potential decrease from the initial state to the final state is over 0.05 eV. However, for model 19.5–22.5, the potential drops more slowly, and it requires more than \(1 \times 10^5\) steps to reach the potential plateau. Meanwhile, the decrease in potential is reduced to about 0.003 eV. In contrast, Figure 2c shows a totally different feature for model 28–36. The potential experiences a relatively large fluctuation at the beginning and then becomes stable after enough relaxation. There is no obvious change in the mean potential, though the initial fluctuation is as large as 0.0005 eV. We have also carefully checked all other samples and found all of them can be classified into these three categories, namely unstable system (such as model 4.5–5.5), half-stable system (such as model 19.5–22.5), and stable system (such as model 28–36), respectively.

3.1.2. Three Kinds of Structural Revolutions. Knowing the structural revolutions associated with the potential change is helpful for clarifying the three categories of material stabilities. Here we chose the examples with a similar outer diameter for comparison. Figure 3 shows some representative snapshots of the three kinds of stability during the relaxation processes. Model 15–21 shows a stable feature, keeping a perfect hollow structure from the beginning to the stage with enough relaxation time. We have also used the radius distribution function analysis (see Supporting Information) to further confirm this feature. Model 18–22 gives the half-stable feature, showing partial collapse with a reduced radius. However, model 18–22 still has a hollow structure while unstable model 18–20 becomes a solid sphere. From the atomic structure (see Supporting Information), more details of this process are obtained. It starts from the \(\{111\}\) crystal surface and then gradually spreads to other parts of the sphere. This kind of anisotropic collapse can be observed only for the half-stable system. For the unstable system, the collapse is too fast to identify which facet the collapse follows. Therefore, model 18–20 exhibits an isotropic shrinking.

Figure 2. The potential as a function of the relaxation time: (a) the unstable model 4.5–5.5, (b) the half-stable model 19.5–22.5, and (c) the stable model 28–36.
Thermal Stability of Hollow Gold Nanoparticles

<table>
<thead>
<tr>
<th>Stable system 15–21</th>
<th>Half-stable system 18–22</th>
<th>Unstable system 18–20</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 fs</td>
<td>0 fs</td>
<td>0 fs</td>
</tr>
<tr>
<td>12000 fs</td>
<td>8000 fs</td>
<td>3200 fs</td>
</tr>
<tr>
<td>24000 fs</td>
<td>15200 fs</td>
<td>6400 fs</td>
</tr>
<tr>
<td>36000 fs</td>
<td>24000 fs</td>
<td>16000 fs</td>
</tr>
<tr>
<td>480000 fs</td>
<td>480000 fs</td>
<td>480000 fs</td>
</tr>
</tbody>
</table>

Table 1. The cross-sectional views of stable model 15–21, unstable model 18–20, and half-stable model 18–22 in the initial state and final state.

The whole thermal stability diagram is separated into three distinct regions, i.e. stable, half-stable, and unstable regions, respectively.

To study the relationship between the wall thickness and the stability, the systems with equal aspect ratio but different wall thicknesses have been analyzed in Figure 5. Along the increase of the wall thickness, the stability increases progressively. This tendency exists in all other systems with the same aspect ratio, as seen directly from the thermal stability diagram. For example, in the systems of aspect ratio 5.5 (line a in Figure 5), model 4.5–5.5 is unstable, while models 9–11, 13.5–16.5, 18–22, and 22.5–27.5 are half-stable, and sequentially, models 27–33 and 40.5–49.5 are stable. This phenomenon is consistent with common sense. The thicker the wall is, the more stable the system will be. From the microscopic viewpoint, the crystal slip is the first step for the collapse, which needs the strong kinetic energy of atoms to confront the slip potential barrier, the minimum energy required for the crystalline system transferring from one configuration to another along a particular crystal plane. When the slipping direction is perpendicular to the hollow ball surface, according to the potential superposition, the slip potential barrier is nearly proportional to the atomic layers. When a slippage tends to occur along a slope, more atomic layers may impede this process, leading to the anisotropic collapse. As observed from the cross-sectional views in Figure 4, unstable system 18–20, half-stable system 18–22, and stable system 15–21 have two, four, and six atomic layers, respectively. Therefore, the increase of wall thickness enhances the slip potential barrier, baffling the collapse. As a result, the stability of the system is improved.

To give more physical insights into the material thermal stability, we further analyzed the stability diagram for those systems with the same wall thickness as indicated by the vertical lines in Figure 5. When the wall is thinner than 2.0, as indicated by line b, the line starts from the unstable region and then comes to the half-stable region. In contrast, when the wall is thicker than 2.5, the line starts from the stable region and then comes to the half-stable region. This is an interesting result. When the wall thickness is fixed, the larger hollow nanoparticle may have more unstable structure.

3.3. The Collapsing Mechanism. Many parameters might affect the collapsing process, such as the crystal vibration, thermodynamic movement, and kinetic motion. Here we propose...
a possible interpretation for the collapsing mechanism. In the relaxing stage, there are two kinds of transformations for the hollow gold nanoparticle. One is that the stable system shows a placid adjusting that varies slightly in a small scale. The reason is that the kinetic energy fails to counteract the slip barrier. Another transformation undergoes a severe collapse for the half-stable system and unstable system. It is believable that the collapse depends on both the slip barrier and the kinetic energy of atoms. The collapse would happen as long as the kinetic energy is strong enough to confront the barrier to slip. It might be also stopped while the kinetic energy cannot overcome the increased barrier, because the wall thickness grows gradually with the collapse propagation.

In all our system, the total number of atoms stays constant during the whole relaxation. It can be named as the isometric dot in the thermal stability diagram. The line made by the isometric dot is the so-called isometric line. In the perfect sphere system, the line is described by the isometric equation as

$$d^3(3p^2 - 3p + 1) = C$$

where $d$ stands for the wall thickness, $p$ is the aspect ratio, and $C$ is a constant. Different isometric lines have different $C$ values. The thermal stability diagram is related with the temperature as well. We simulated the models at 300 K to investigate the thermal stability diagram. Figure 6 shows various isometric lines with $C = 10^0, 10^1, 10^2, 10^3, 10^4, 10^5, 10^6$, respectively. Even if the system collapses, the atom number keeps constant. The system jumps from one isometric dot to another one following the isometric line. Note that this equation is only suitable for the system with a sphere structure.

3.4. Boundary between Three Regions in the Thermal Stability Diagram. Usually, scientists focus on how to prepare the perfect hollow nanoparticles in experiments. It is expected that this desire can be satisfied by the thermal stability diagram, especially the isometric line that separates the half-stable space and unstable space. In practice, when a synthesized sample is half-stable at the beginning, it may experience the structural revolution to reach a stable status. This process accelerates along the isometric line until reaching the stable region, where the slip barrier impedes the collapse propagation. The collapse then slows down, and finally, the system stops in the stable region. In contrast, the unstable system crashes totally and becomes a solid nanoparticle in which the aspect ratio is equal to 1.

There is a specific isometric line indicating the boundary between the half-stable region and unstable region. The boundary is well-fitted with the isometric equation (line e in Figure 5). Another boundary is between the stable region and half-stable region, as indicated by the line d. It consists of the systems in which the atomic kinetic energy just matches the slip barrier. It is noteworthy that there is no unstable system when the wall thickness is larger than 2.0, suggesting that the stable hollow gold nanoparticles with wall thickness smaller than 2.0 cannot be experimentally synthesized at 300 K. On the basis of the previous report, the surface tension can also be considered to explain the decrease with decreasing the system size. The equation is described as

$$\frac{\sigma}{\sigma_o} = 1/(1 + 2\delta/r)$$

where, $\sigma$ is the surface tension when the curvature radius is $r$, and $\sigma_o$ is the surface tension in the planar surface. $\delta$ is a constant in the nanometer scale depending on the materials. This theory has been developed by Koga et al., which indicates that on the nanometer scale, especially below 10 nm, the decrease of surface tension is more dramatic. That is to say, with the increase of aspect ratio, the surface tension will increase. As a result, the slip potential barrier might be overcome.

4. Conclusion

We have studied the stability of hollow gold nanoparticles using molecular dynamics simulations. The thermal stability diagram is obtained, which could be used to guide experimental researchers to synthesize hollow gold nanoparticles. From the simulation results and the theoretical analyses, several important conclusions are obtained.

(i) During the relaxation process, the hollow gold nanoparticles exhibit three kinds of potential change and structural variations, based on which the concerned hollow gold nanoparticles can be classified into three categories, i.e., stable, half-stable, and unstable systems.

(ii) The thermal stability of hollow gold nanoparticles depends on the wall thickness and the aspect ratio to a great extent. When the aspect ratio keeps constant, the thermal stability increases with the wall thickness. When the wall thickness stays constant, the hollow gold nanoparticle is half-stable with an increased aspect ratio.

(iii) The collapsing mechanism has been investigated. If the kinetic energy is strong enough to confront the slip barrier, the collapse happens. With the growth of wall thickness, the collapsing speed is reduced until the collapse stops.

(iv) The thermal stability diagram is concluded on the basis of the numerous MD simulations, which could be useful to the experimental synthesis. At a temperature of 300 K, there is no way to get a hollow nanoparticle with a vacancy smaller than 2.0 crystal lattice. In addition, as reported in the literature, all previously synthesized hollow gold nanoparticles are in the theoretically predicted stable region of the phase diagram.

Acknowledgment. We thank the support from the National Natural Science Foundation of China (20821063 and 20873063) and the National Basic Research Program of China (973 Program, 2007CB936302).

Supporting Information Available: Additional information as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

Thermal Stability of Hollow Gold Nanoparticles


(10) Fujikawa, M.; Shiokawa, K.; Sakakura, I.; Nakahara, Y. Nano Lett. 2006, 6, 2925.
JP905280G