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金纳米球热力学稳定性的理论研究

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Theoretical Investigation on the Thermal Stability of Au Hollow Nano-Particle

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Abstract: Due to the significant importance in many applications, the thermal stability of hollow gold nano-particles has been studied theoretically by using ultra-large molecular dynamics simulation. By changing the nano-particle size while keeping the aspect ratio constant, it was found that the large gold nano-particle has better thermal stability than the small ones.

Key words: molecular dynamics simulation; hollow gold nano-particles; collapsed

0 Introduction

Hollow metal nano-particles have captured the great attention recently. The increased surface area, low density, saving of material and concomitant reduction in cost coupled with the interesting optical properties of such structures make these materials promising in many fields such as catalysis[1], chemo-sensing[2], encapsulation[3], drug delivery[4] and cancer hyperthermia[5]. Hollow metallic nano-particles may be prepared by coating the surface of latex particles[6], silica beans[7,8], gold and silver nano-particles by the desired materials and then etching away the core while retention of the core leads to the formation of thin metallic shells [9]. Among these systems, the gold hollow nano-particles are very promising, and being studied intensively recently [10]. Due to predict indeed the occurrence, moleculat dynamics was used[11]. Such as Chui et al. has focused on theoretical study of nanoparticles using molecular dynamics[12]. One vital factor predominating the utility of these materials in practice is the thermal stability. In order to tune the electronic properties, the shell was synthesized as thin as possible. Under this circumstance, the thermal stability is especially concerned. In order to investigate this issue and give an instruction in the materials synthesis, in the present work, we will study theoretically the effect of aspect ratio, an important factor governing the nano-particle thermal stability, by using an ultra-large molecular dynamics (MD) simulations[13].

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1 Caculation method

The gold hollow nano-particles was constructed with FCC (Face-Centered Cubic) gold crystal with cutting the concentric sphares, as shown in Fig.1. The ratio of out radius over inter radius is defined as the aspect ratio and denote as R_{out}–R_{int}, where R is in crystal cell corresponding to 0.408 nm per cell. 9 samples whose out radius, R_{out}, ranges from 2.04 to 20.4 nm but with the same aspect ratio R_{out}/R_{int}=1.25 were studied in this paper. MD calculations were performed with the self-developed software NanoMD[13]. A time step of 1.6 fs is used for all simulations. The temperature of the system is kept constant at 300 K during the whole process using a velocity rescaling method [13,14]. The interactions between gold atoms were described by Morse potnetial[15] and EAM potential[16]. It has been proven that these potentials can provide a relevant description of the surface effect and defect properties of the transition metals with FCC structure[10].

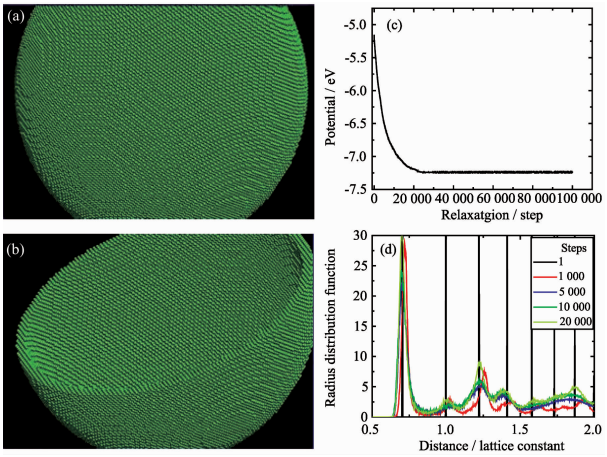

Fig.1 (a) Atomic configuration of the hollow gold nano-particles of model 40~50; (b) Cross section of the model system 40~50; (c) Potential as a function of the relaxation time; (d) Radius distribution function before and after adequate relaxation as marked in the potential curve

2 Results and discussion

Before the relaxation of atomic configuration, the gold hollow ball display a perfect crystalline form, as shown in Fig.1a and the cross sectional view in Fig.1b. The crystallographic features can also be identified from the radius distribution function (RDF) analysis (the vertical solid lines in Fig.1d), from which we may find very shape peaks at 0.7 and 1.0 of lattice constant corresponding to the first and second nearest neighbors of gold atoms. The relaxation may optimize the relative position of the nearest atoms lowering the interatomic interaction. This may reflected from the potential drop curve as shown in Fig.1c. Unlike the most dynamic processes, the reconstruction of the hollow ball follows a different mechanism as evidenced by the inserted semi-logarithmic plot. Three unique steps can be identified, in terms of the slow variation at beginning, followed by a sudden drop of potential, and the reaching of an energy plateau finally. At the first thousand steps, the hollow ball remains in a stage of accumulating power; in particular, the transformation from a perfect crystalline form needs some initiators. Therefore, at this stage, defects and dislocations increase gradually. When the hollow ball has adequate amount of defects and dislocations, an avalanche-like decrease of potential takes place. This indicates that the atomic structure of the hollow gold nano-particle is quickly collapsed. This character is of particular importance for the MD simulation. Without this avalanche-like collapse, the MD simulation needs too long time to reach the stable energy plateau. When the high-energy hollow structure reaches a relative stable configuration, it may impede the further collapse. In the exponential decay range, a half-life of 8.6 ps indicates that the relaxation to a stable crystallographic structure is very fast. This result also inferred that the normal characterization technique, such as TEM and spectroscopy couldn't track this process.

A sequential four representative RDF analyses were compared in Fig.1d. At first stage (1 000 steps) the first peak position is located at 0.718 far from the ideal crystalline form, indicating that all atoms are located in an active position. With increasing the relaxation time, this peak position shows an obvious left shift. When the relaxation time is longer than 20 000 steps, the peak position becomes stable, locating at 0.70 that is close to the ideal value. This result means that after adequate relaxation, the hollow ball may reach a relatively good crystalline form.

The final atomic configuration reached is dependent on the systems as demonstrated by the series of simulations in present work. Interestingly, the large system looks more stable as compared with those small ones, when they have the same aspect ratio. Fig.2 presents the cross-sectional view of the systems concerned with various radii. From the figure we may find the small systems, such as 8~10 and 12~15, have completely collapsed, forming a solid ball. Due to such significant transformation, the final atomic structure looks more amorphous. The systems with moderate size, such as 16~20 and 20~25, have experienced partial collapse. Although the hollow remains in these moderate systems, we can observe the shrink of the radii of both out sphere and inter sphere. Unlike the small systems, they display some crystal domains, but many defects and dislocations are visualized from the sectional view. For the large size of the hollow ball, 24~30 and 28~35 for example, their structure remains almost unchangeable. Very few dislocations can be observed. This is probably due to the thick shell of the system, in which the dislocation is hardly generated.

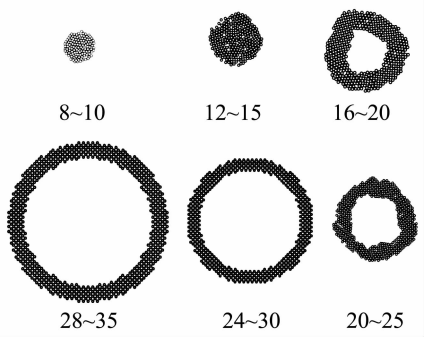

Fig.2 Cross sectional view of the systems after adequate relaxation

A detailed comparison of the thermal stability of the series of hollow gold nano-particles has been given in Table 1. Even all systems have the same aspect ratio; the final atomic configuration is dependent on the thickness of the shell. There are two critical thickness values. One is between 0.612 and 0.816 nm and the other between 1.020 and 1.224 nm. Below the first critical thickness, the metal atoms may have adequate thermal energy to overcome the motion barrier to generate dislocation. Then the sliding along (111) facet takes place till the complete collapse. The samples between the first and second critical thickness show only partial reconstruction around the weak connections due to the discrete feature of the crystal. However, this feature is vanished as the hollow ball size increases. Specifically, when the size is larger than the 24~30 system, the hollow ball tends to be symmetric, and the shell is thick enough to impede the generation of defects and propagation of dislocation. In this work, the thinnest thickness of the stable gold hollow nano-particles is estimated to be around 1.8 nm, which is reasonable as compared with those reported in literatures. Theoretical prediction is a little smaller, because the gold hollow ball consists of perfect single crystal in simulation. On the contrary, a mean thickness is reported experimentally, which may have a fluctuation in thickness. The stability of the real system is dependent on the thinnest part of the shell.

Table 1 Summary of the stability of the hollow gold nano-particles with different radius (nm)

System*	Thickness of shell	Final hollow radius	Property
4~5	0.204	0.0	Collapsed
8~10	0.408	0.0	
12~15	0.612	0.0	
16~20	0.816	1.80	Semi-collapsed
20~25	1.020	2.75	
24~30	1.224	4.90	Stable
28~35	1.428	5.71	
32~40	1.632	6.53	
40~50	2.040	8.16	

*System denote as R_{out}–R_{int}.

3 Conclusions

In su mmary, the theoretical molecular dynamics simulations were performed for the series of hollow gold nano-particles with the same aspect ratio. The results confirmed that the shell thickness is an important factor governing the thermal stability of the hollow ball. When the shell thickness is comparable to the crystal cell lattice, the discrete crystallography results in a dynamic evolution of the sample. Defects and dislocations were generated and propagated quickly till a complete collapse. When a thick shell is applied, the sample

shows a continuous feature. The perfect crystalline structure remained even after long time relaxation.

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