Nanoscale Res Lett (2009) 4:269–273
DOI 10.1007/s11671-008-9236-z

NANO EXPRESS

Structure of Unsupported Small Palladium Nanoparticles

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Received: 9 October 2008 / Accepted: 17 December 2008 / Published online: 7 January 2009
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Abstract A tight binding molecular dynamics calculation has been conducted to study the size and coordination dependence of bond length and bond energy of Pd atomic clusters of 1.2–5.4 nm in diameter. It has been found that the bond contraction associated with bond energy increases in the outermost layer about 0.24 nm in a radial way, yet in the core interior the bond length and the bond energy remain their corresponding bulk values. This surface bond contraction is independent of the particle size.

Keywords Lattice parameters · Atomic simulation · Bond energy · Nanoparticles

Introduction

It is reported that the lattice parameter (LP) of nanoparticles depends on particle size [1–12], and several theoretical models have also been established to find the relation between LP and the particle size [13–16]. For non-spherical particles, the shape effect on LP can be approximately predicted by the shape factor [16], where the shape factor is a modified parameter to describe the shape effect. However, the previous work in theories or experiments only gave the mean values of LP, and the difference between the interior core and the exterior surface is not considered. It is known that the surface atoms of nanoparticles have large dangling bonds, but low coordination number (CN) than the bulk, which may cause the surface to be different from the bulk. Also, the LP in the surface may be different from the bulk. To understand the structure of nanoparticles, it is needed to study the structure rigorously.

Back to 1995, Lamber et al. [8] reported that the LPs of small Pd particles of 1.4–5 nm decrease with decreasing particle size due to the surface effect, which clarify the contradictions of LP of Pd particle reported in literatures [5–7]. Silva et al. simulated the LP of Pd particles by molecular dynamics simulation method, where the simulated results are consistent with the experiments of Lamber et al. [9]. Also, the experiments are well consistent with results of Continuous Media (CM) model [16], where the CM model regarded the nanoparticles as ideal spherical crystals generated from bulk, and then approaching to thermodynamic equilibrium to form a nanoparticle. However, in the experiments, the simulation or the theory, only the mean values of LP are obtained, and we do not know the different lattice variation between the surface and the interior core.

In this paper, we will reconsider the LP of Pd nanoparticles in detail, and discover the different structure of surface and core. Also, the bond energy and the CN will be discussed.

Simulation Details

The molecular dynamics simulation package, MATE RIALS EXPLORER [17], was used in the present work.

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The simulation was performed in NVT ensemble with tight binding potential (Φ) developed by Cleri and Rosato [18], which has the following form

$$\Phi = \sum_i \left(E_b^i + E_r^i\right) \quad (1)$$

where

$$E_r^i = \sum_j A_{\alpha\beta} \cdot \exp\left[-p_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1\right)\right]$$

is the two-body term, and

$$E_b^i = -\sqrt{\rho_i}$$

$$\rho_i = \sum_{j\neq i} \zeta_{\alpha\beta}^2 \cdot \exp\left[-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1\right)\right]$$

is the many-body term. The α and β represent the atomic species of atoms i and j, respectively. $A_{\alpha\beta}$, $\zeta_{\alpha\beta}$, $p_{\alpha\beta}$, and $q_{\alpha\beta}$ are the potential parameters, $r_0^{\alpha\beta}$ denotes the nearest neighborhood distance, and r_{ij} is the distance between the atom i and j. Values of the parameters for Pd are listed in Table 1 [18]. This potential function can be used to simulate the properties of elements (Al, Ti, Zr, Co, Cd, Zn, Mg, Ni, Cu, Au, Rh, Pd, Ag, Ir, Pt, and Pb) and binary alloys (NiAl and CuAu).

The spherical Pd nanoparticles were generated from the ideal Pd crystal. The number of atoms was 38, 68, 92, 164, 298, 370, 490, 682, 1,048, 1,830, 2,598, 3,396, and 4,874, where the particle size ranges from 1.2 to 5.4 nm. The free boundary condition was applied, and the time step was chosen as 2 fs. To obtain the most stable structure, the annealing method was used presently. Since the melting temperature of nanoparticles depends on particle size, different annealing temperature was chosen to avoid the phase transition. For 38, 68, 92, 164, 298, 370, and 490, respectively, the simulation started from 300 K, and the initial 30,000 steps was to relax the structure at 300 K. The following 70,000 step decreases the temperature from 300 K to 0 K. For 682, 1,048, 1,830, 2,598, 3,396 and 4,874, respectively, the simulation started from 500 K, and the initial 30,000 steps was to relax the structure at 500 K. The following 120,000 step decreases the temperature from 500 K to 0 K.

Table 1 Cleri and Rosato Potential parameters for Pd [18]

$A_{\alpha\beta}$ (eV)	$\zeta_{\alpha\beta}$(eV)	$p_{\alpha\beta}$	$q_{\alpha\beta}$	$r_0^{\alpha\beta}$ (nm)
0.1746	1.718	10.867	3.742	0.2749

Results and Discussion

To prove the efficiency of present simulation, the simulated LP of Pd nanoparticles are shown in Fig. 1. The LP is the mean value of LP for every particle, while the experimental values given by Lamber et al. are also the mean values. In Lamber's experiments, small particles of Pd were prepared in a plasma polymer matrix. This technique used for the production of particles embedded in a plasma matrix provides particles which are uniform in size and free from impurities. Since the plasma polymer matrix is an amorphous structure, the Pd particles prepared are close to the situation of free-standing particles. Therefore, the experimental Pd particles are similar to our simulated ones. It is obvious that the LP decreases with decreasing particle size, which is confirmed by Lamber's experiments and the present simulation. Furthermore, the present results are well consistent with experiments in the whole size studied (1.2–5.4 nm). Silva [9] simulated the LP of Pd particles previously, however, they only studied the size about 1.4–3.0 nm, and the difference between their simulation and experiments becomes larger when the particle size increases. It should be pointed out that all the present simulated LPs lie in a smooth curve except the second small size $n = 68$, where its lattice is amorphous rather than crystal-like. According to Fig. 1, we may say that the present simulation is reliable, and the following analysis is also reasonable.

Figure 2 shows the atomic cohesive energy of small Pd particles. Apparently, for small Pd particles, the atomic cohesive energy decreases with decreasing particle size. It should be mentioned that the energy of all size lies in a smooth curve including the size $n = 68$ (amorphous structure). These results suggest that the cohesive energy may be insensitive to the lattice structure. For the crystalline Pd particle, the first nearest interactions are close to

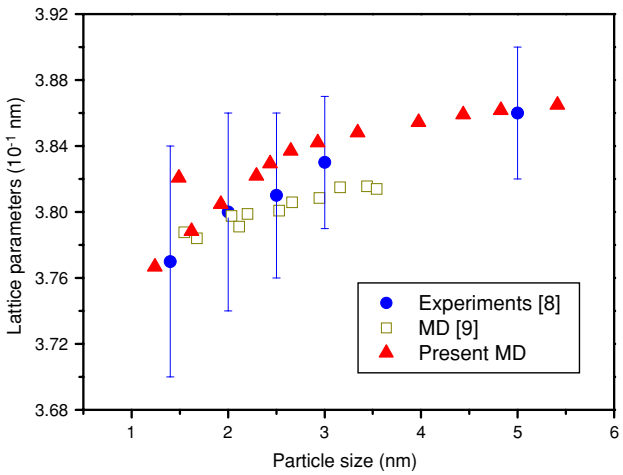

Fig. 1 Lattice parameter of Pd nanoparticles versus particle size

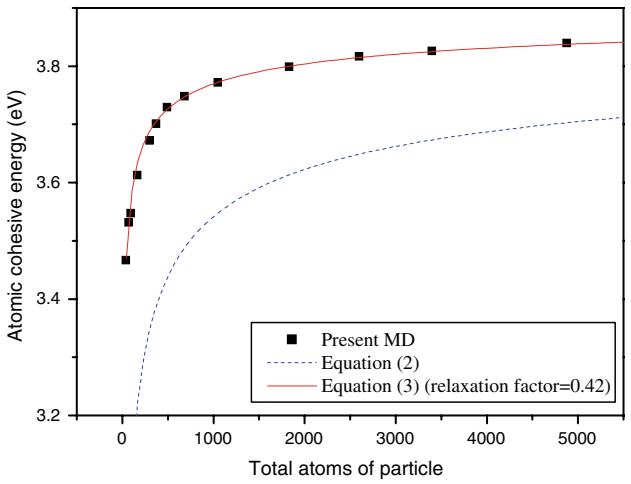

Fig. 2 Atomic cohesive energy of Pd nanoparticles versus total atoms of each particle

these of amorphous ones. The cohesive energy is mainly determined by the first nearest interaction, thus both amorphous and crystalline particles lies in the same smooth curve. One may conclude that the LP may be regarded as a criterion to determine whether the structure is crystal-like, but the cohesive energy cannot. In our previous work, we developed a model to account for the size dependence of cohesive energy of a particle with n atoms, which is [19]

$$E_{\text{part}} = E_{\text{bulk}}(1 - n^{-1/3}) \tag{2}$$

where, E_{part} and E_{bulk} are the cohesive energy of particle and the corresponding bulk materials. This model can only be used to the un-relaxed structure. Generally, the relaxation may decrease the free energy and increase the cohesive energy according to the thermodynamic laws. To describe the relaxation effect, here we introduce a new parameter δ, namely the "relaxation factor". After inserting this factor into Eq. 1, we have

$$E_{\text{part}} = E_{\text{bulk}}(1 - \delta \cdot n^{-1/3}) \tag{3}$$

Comparing Eq. 2 and Eq. 3, one can find that a term $(1 - \delta) \cdot n^{-1/3} E_{\text{bulk}}$ was added in Eq. 3, where this term is just the increased energy due to the surface relaxation. According to thermodynamics, every system approaches to the configuration with low energy, thus the free energy decreases after relaxation, and the cohesive energy increases. For unsupported particles, the relaxation factor δ is smaller than 1, where the value can be obtained by fitting simulation or experimental values. The present fitted value is $\delta = 0.42$. Apparently, the results considered the relaxation effect are more close to the simulation values.

As shown above, both the LP and the cohesive energy of Pd particles decrease with decreasing particle size. However, these are the mean values of all atoms for a particle, where the surface atoms and the interior ones are not distinguished. Recently, the difference between surface and the core of gold particles has been reported experimentally by Huang et al. [20]. They used nanoarea coherent electron diffraction to probe the surface structures of Au nanocrystals with several nanometers, and found that the surface bonds contract but the bonds of interior atoms are almost unchanged comparing with the bonds of bulk gold. Therefore, it is important to discuss the bond difference between the surface and the interior atoms in detail. We have calculated the nearest distance of atoms to the center of each particle, and the results of $n = 682$, 1,830, 3,396, and 4,874, respectively, are shown in Fig. 3. It is shown that the nearest distance (or bond length) keep almost constant in the core, but decreases quickly in the out shell. Here we take the size $n = 1{,}830$ for example to explain the structure of the unsupported particles.

Figure 4 gives the nearest distance and the atomic cohesive energy of $n = 1{,}830$ vary with the distance to center (DTC). Both keep constants when the DTC is smaller than 1.44 nm, where the corresponding values are 0.274 nm and 3.93 eV. For bulk Pd, the nearest distance is 0.2749 nm and the atomic cohesive energy is 3.89 eV. The difference between the core value and the bulk is 0.3% for nearest distance, and 1.0% for atomic cohesive energy. When the DTC is larger than 1.44 nm, the nearest distance and the atomic cohesive energy decrease with the increasing DTC. It should be pointed out that both parameters decrease from DTC = 1.44 nm.

As mentioned by experiments and BOLS theory, the surface atoms have lower CN. Here we counted the CN of each atom, the results of $n = 1{,}830$ are shown in Fig. 5. Since the bulk Pd is FCC structure, then CN = 12. For the core of $n = 1{,}830$, the CN also equals to 12. The CN of surface atoms is smaller than 12, which is 11, 10, 9, 8, 7, and 5, respectively. The CN depends on the shape of the

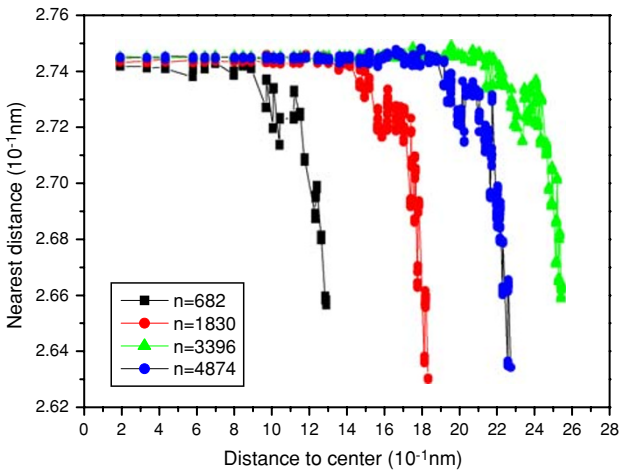

Fig. 3 Average bond length of Pd particles versus DTC in different particle size

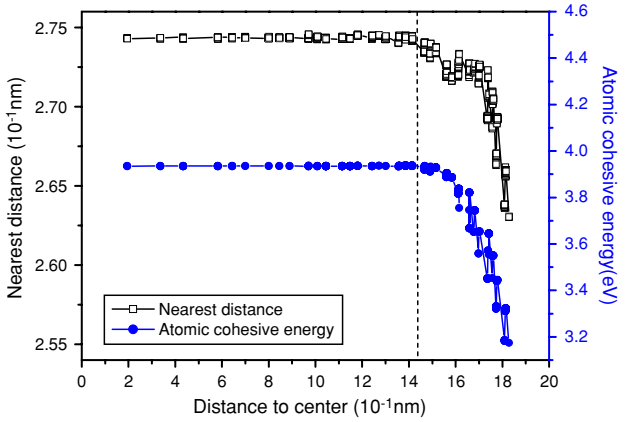

Fig. 4 Nearest distance and atomic cohesive energy of Pd particles with 1,830 atoms versus DTC

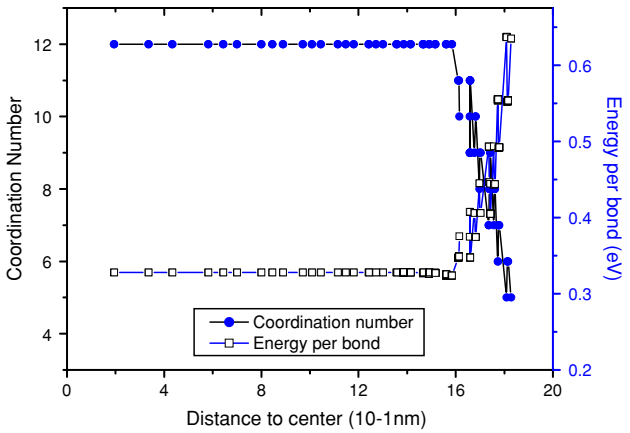

Fig. 6 Coordination number and energy per bond of Pd particles with 1,830 atoms versus DTC

nanoparticles. Comparing with the CN and the nearest distance, we find that the nanoparticle may be classified as surface, subsurface, and core, which is denoted as *A*, *B*, and *C* in Fig. 5. In *A* region (1.84 nm > DTC > 1.60 nm), the CN smaller than 12 and the nearest distance decreases; in *B* region (1.60 nm > DTC > 1.44 nm), the CN is equal to 12 and the nearest distance decreases; and in *C* region (DTC < 1.44 nm), the CN is 12 and the nearest distance remains constant. The *B* region may be regarded as a transitional region from the core to the surface.

Figure 6 shows that the bond energy and the CN vary with DTC. The bond energy of each atom is equal to the result of the atomic cohesive energy divided by its CN. When the DTC < 1.6 nm, the CN = 12 and the bond energy remains 0.324 eV. When DTC > 1.6 nm, the CN decreases from 12 to 5, and the bond energy increases from 0.324 eV to 0.635 eV. Apparently, the CN imperfection increases the bond strength, which is qualitatively consistent with the predictions of BOLS model [21]. In BOLS model, every spontaneous process obeys the minimum energy principles, and the bond contraction along with the bond energy increases. The CN decreases or the dangling bonds strengthen the nearest bonds, which is just proved by the present results.

Based on the discussion above, the structure of a small Pd particle can be classified into three regions from center, i.e., the core, the subsurface, and the surface. The thickness of the surface is about 0.24 nm, and the subsurface is about 0.16 nm, where the values are independent of the particle size. In the core, the bond length and the bond energy are almost the same as the corresponding bulk values; in surface, the bond length contracts but the bond energy increases; and in the subsurface, the bond energy keeps the bulk value but the bond length contracts. The subsurface can be regarded as a transitional region from the core to the surface. The three shell model has also been found in copper particles by Meyer and Entel [22]. It should be mentioned that in our previous BE model [23], we assumed that the atoms in a nanoparticle can be classified as the exterior and the interior atoms, where the exterior atoms is only the first layer of nanoparticles. According to the present simulation results, this assumption is reasonable and applicable.

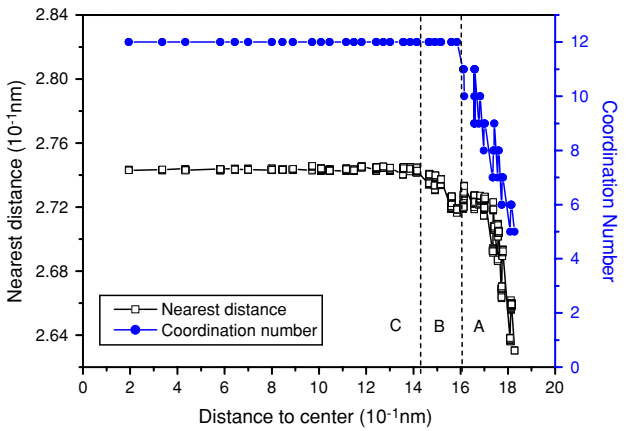

Fig. 5 Nearest distance and CN of Pd particles with 1,830 atoms versus DTC

Conclusions

The tight binding molecular dynamics simulation method has been used to study the structure of small Pd particles. The simulated mean LP decreases with decreasing particle size, which is well consistent with the experimental values. It is found that the structure of an unsupported Pd particle can be divided into three regions, i.e., the core, the subsurface, and the surface. The thickness of the surface is about 0.24 nm, and the subsurface is about 0.16 nm, where both the values are independent of the particle size. Furthermore, the bond energy increases and the bond length decreases with the decrease in CN.

Acknowledgment This work was supported by China Postdoctoral Science Foundation (No. 20070420185) and Postdoctoral Science Foundation of Central South University.

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