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Effect of Atomic Under-coordination on the Properties of Ag and Cu nanoclusters

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ABSTRACT

Density functional theory calculations have been carried out to investigate the effect of the atomic under-coordination on the bond contraction, lattice strain, and electron configuration of Cuboctahedral and Marks decahedral structures of silver and copper nanoclusters. Our calculated results are consistent in trend with experimental measurements including extended X-ray-absorption fine structure (EXAFS), scanning tunneling microscope/spectroscopy (STM/S), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectra (UPS). This agreement approved the prognostications made on the bond-order-length-strength (BOLS) correlation and nonbonding electron polarization (NEP), suggesting that atomic under-coordination at the surface of nanoclusters cause bond contraction, which then leads to lattice strain, charge densification, core electron entrapment, as well as polarization of valence charge. The results of this work will contribute to the understanding of the intriguing properties of Ag and Cu nanoclusters.

Keywords: Metallic nanostructures, under-coordinated atoms, DFT calculations, electronic structures, bond contraction

1. INTRODUCTION

Noble metallic nanoparticles (NPs) have been studied extensively because of their new and attractive chemical and physical characteristics compared to their bulk counterparts [1]. For instance, silver and copper NPs are magnetic whereas their bulk counterparts are diamagnetic [2]; bulk Ag is good conductor but becomes an insulator as the cluster size is reduced to a few nanometers [3]; and as the size is reduced to nanometer scale, Ag and Cu clusters show enhanced catalytic ability for H₂O oxidation and CO reductions [4] and surface plasmon resonance [5].

A main difference between nanostructures and the corresponding bulk materials is the dramatically increased surface-to-volume ratio γ . It has been realized the interaction between the atoms in the outermost few atomic layers, referred to as under-coordinated atoms, play a significant role on determining the properties of metal NPs. Enormous efforts have been dedicated to study the fundamental mechanism of silver and copper nanoclusters [6, 7]. Recent studies including X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscope/spectroscopy (STM/S) have been used to study the properties of silver and copper NPs, which are observed positive shifts of the core level binding energies and “red” shift of valence local density of states [8-11]. However, a complete understanding of the underlying mechanisms including size dependence of lattice strain, binding energy shifts, as well as hybridization of Ag [10] and Cu [12] are still lacking.

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In this work, we focus on silver and copper nanoclusters and studied the effect of atomic under-coordination on the bond contraction, lattice strain, charge densification, core level shift (CLS), as well as polarization of valence charge at different sizes based on the bond-order-length-strength (BOLS) correlation and nonbonding electron polarization (NEP) theory [3, 7]. Density functional theory (DFT) calculations using DMOL³ code for non-periodical system has been carried out, and the obtained results are compared with the experimental observations. Agreement between theoretical and experimental results approved our prognostications made on BOLS-NEP theory. It is found the atomic under-coordination induces the bond contraction, lattice strain, charge transfer, deepening of quantum trap, and polarization, which then give rise to the intriguing properties of silver and copper NPs.

2. THEORETICAL MODEL AND CALCULATION METHOD

2.1 BOLS correlation

According to the BOLS-NEP theory [7], shortening and strengthening of the bonds between under-coordinated atoms at the surface promote local densification and quantum entrapment of electron binding energy, and the size dependence of the effective atomic coordination number (CN) z_i , bond contraction coefficient C_i , depth of the potential trap (bond energy) E_i , induced binding energy shift ΔE_v , as well as lattice strain ε can be expressed by:

$$\begin{cases} z_1 = 4(1 - 0.75/K); z_2 = z_1 + 2; z_3 = 12 \\ C_i = d_i / d_b = 2[1 + \exp((12 - z_i)/(8z_i))]^{-1} \\ E_i = C_i^{-m} E_b \\ \Delta E_v(K) = E_v(K) - E_v(0) = (E_v(\infty) - E_v(0))(1 + \Delta_H) \\ \varepsilon(K) = 1 + C_i \end{cases} \quad (1)$$

where K is a dimensionless parameter and equals to the ratio of the nanoparticles radius (R) to the bond length (d); subscripts i and b represent the i th atomic layer from the surface and bulk, respectively; m is the bond nature index, which correlates the bond length and energy; $E_v(0)$ is the core-level position of an isolated atom, $E_v(K)$ and $E_v(\infty)$ are the XPS peaks of the v th band and the bulk counterpart, respectively; and Δ_H is the atomic under-coordination induced perturbation to the Hamiltonian.

2.2 Core-shell configuration

For a nanocluster consisting of N atoms, the dependence of a given quantity Q on the size can be expressed by [1]

$$\begin{cases} Q(K) = Q(\infty) + \sum_{i \leq 3} N_i(q_i - q_b) \\ Q(\infty) = Nq_b \end{cases} \quad (2)$$

where $Q(K)$ and $Q(\infty)$ correspond to with and without the effect of CN imperfection, respectively; q_i and q_b are the local density of Q at the i th atomic layer from the surface and in the core, respectively. The difference between bulk and nanoclusters is,

$$\frac{Q(K) - Q(\infty)}{Q(\infty)} = \sum_{i \leq 3} \frac{N_i(q_i - q_b)}{Nq_b} = \sum_{i \leq 3} \gamma_i \left(\frac{\Delta q_i}{q_b} \right) = \Delta_q \quad (3)$$

By combining Eqns (1), (2), and (3), we can obtain the following expressions:

$$\Delta_q = \begin{cases} \Delta_{\Delta E_v} \\ \Delta_\varepsilon \end{cases} = \sum_{i \leq 3} \gamma_i \begin{cases} (C_i^{-m} - 1) \\ (C_i - 1) \end{cases} \quad \begin{matrix} \text{(CLS)} \\ \text{(Strain)} \end{matrix}$$

$$\gamma_i = \frac{V_i}{V} = \frac{N_i}{N} = \frac{\tau C_i}{K} \leq 1 \quad (4)$$

where τ is the shape factor and equals to 1, 2, and 3 for a thin film, a cylindrical rod, and a nanosphere, respectively and V_i is the volume of the i th atomic layer. Thus, the lattice strain and CLS consist of the extrinsic and intrinsic variables of $(\tau, K, K^{-1}; m, z_i, d_i, E_i)$.

Generally, the measured size dependence of $\varepsilon(K)$ and $\Delta E_v(K)$ of nanostructures is inversely proportional to K . By equating the experimental scaling correlation with the theoretical illustration, we obtain the following equation:

$$Q(K) = Q(\infty) \begin{cases} (1 + bK^{-1}) & \text{(Measurement)} \\ (1 + \Delta'_q \tau K^{-1}) & \text{(BOLS theory)} \end{cases} \quad (5)$$

where $Q(\infty)$ is the bulk value and obtained by the intercept of measured $Q(K)$ versus K^{-1} plot and $b = \tau \Delta'_q$ with $\Delta'_q = \Delta_q K / \tau$.

2.3 Computational details

We carried out DFT calculations on silver and copper NPs and compared our results with experimental observations. Since the Cuboctahedral (CO) and Marks decahedral (MD) structures have been shown to be stable for Ag and Cu NPs [13, 14], during our calculations 13-, 55-, and 147-atom CO structures and 13-, 49-, and 75-atom MD structures are considered (see Figure 1). The DFT calculations were carried out using DMol³ code with the local-density approximation-Perdew-Wang-92 (LDA-PWC) and semi-core pseudopotential [15, 16]. In geometry optimization, the tolerance limit of energy, displacement, and forces are 10^{-5} Hartree, 0.005 Å, and 0.002 Hartree/Å, respectively.

Figure 1. (Color online) Schematic drawing of Ag_N and Cu_N nanoclusters with Cuboctahedral structures consisting of (a) 13, (b) 55, and 147 atoms, as well as Marks decahedral structures consisting of (d) 13, (e) 49, and (f) 75 atoms. White color represents atoms at different shells while red and blue colors indicate atoms in the core.

3. RESULTS AND DISCUSSION

Table 1 listed the results determined by DFT calculations, indicating spontaneous bond contraction. The bond contraction coefficient of Ag atoms in the skin is -3.86%, -6.45%, and -6.08% for CO structures (with 13, 55, and 147 atoms) and -4.81%, -4.03%, -4.55% for MD structures (with 13, 49, and 75 atoms), respectively. Similar trend is observed for the under-coordinated atoms of Cu nanoclusters. The negative sign reveals the shrinkage of the bond length for silver and copper nanoclusters. Moreover, the extent of bond length contraction depends on effective coordination number CN (see Table 1). For example, the bond contraction coefficient of Ag_{147} cluster decreases from -6.08% for the outermost shell to -2.01% for the core as CN changes from 3.14 to 12.00. Similarity, the bond contraction coefficient of Cu_{75} decreases from -33.27% for the outermost shell with CN = 3.10 to -31.27% for the core with CN = 5.10. The results calculated here via combining BOLS correlation with DFT calculations are consistent with the previously published results. For example, Hansen et al. [17] reported the bond contraction of copper NPs composed of 100-1000 atoms by molecular-dynamics simulations. Moreover, DFT calculations have shown that the bond contraction is about 12.5%, 13.2%, 13.6%, and 18.6% for Ag, Cu, Ni, and Fe atomic chains [18], and 9.6%, 11.5%, 10.1%, 13.3%, 10.6%, 14.8% for Ag, Au, Cu, Ni, Pd, and Pt monoatomic chains, respectively [19]. The bond contraction is also observed by extended X-ray-absorption fine structure (EXAFS) for silver and copper nanoclusters [20, 21], as well as copper and nickel nanoclusters deposited on carbon substrate [22].

The lattice strain estimated based on BOLS correlation using Eqns (4) and (5) (solid line), and the measured values of the mean lattice strain (scattered data) are plotted in Figure 2(a). To evaluate the intercepts and slopes in scaling law, the experimental data was linearized with the least-root-mean-square optimization method. Our calculations include experimental results of Ag(111) and Ag(220) surfaces [23] and Cu(111) and Cu(220) surfaces [24]. It is found the mean lattice strain is function of the nanocluster size and decreases drastically with decreasing K , indicating the effect of atomic under-coordination on the lattice strain.

From the energy point of view, any process tends to continue in the direction of minimizing the system energy. Hence, the potential well depth in the vicinity of the under-coordinated atoms or the single bond energy will be increased following the bond contraction, and electrons have a higher density at the surface than in the core, referred to as charge transfer. Energetically, the core level energy will go deeper, and extent is determined by the overlap and exchange integrals, or the coupling of the inter-atomic potential and the specific Bloch wave functions. Therefore, the charges will be localized at the surface due to the surface potential depression and the energy levels of core electrons deepening, which in turn polarize the loosely bond valence electrons. The calculated charge transfer of silver and copper nanoclusters using Mulliken charge population analysis [25] are listed in Table 1, where “-” and “+” signs correspond to gain and loss in charge, respectively. It is found that the outermost shells gain excess charge whereas the interior shells loss due to the decreased CN. For instance, the calculated charge transfer of Ag₁₄₇ decreases from -0.554 to 0.036 e as CN is increased from 3.14 to 12.00, and decreases from -1.541 to 1.469 e as CN is increased from 3.10 to 5.10 for Cu₇₅. Thus, the electrons transfer from the interior to outermost shells of nanoclusters, which confirm the BOLS-NEP expectations and is consistent with the reported results on metallic NPs such as Ag and Cu nanoclusters [26].

Table 1. Atomic CN z_i , bond contraction coefficient $C_i = d_i/d_b$, and Mulliken charge transfer (e) of Ag_N and Cu_N nanoclusters at different positions of atoms with CO and MD structures.

Structure	Position	Atomic CN z_i	Contraction Coefficient (C_i-1 (%))		Mulliken Charge Transfer (e)	
			Ag	Cu	Ag	Cu
CO ₁₃	1~2	2.00	-3.86	-5.52	-0.216	-0.228
CO ₅₅	1~2	2.80	-6.45	-8.42	-1.034	-1.240
	2~3	4.80	-2.26	-3.38	0.960	1.140
CO ₁₄₇	1~2	3.14	-6.08	-8.23	-0.554	-0.300
	2~3	5.14	-2.78	-3.82	0.650	0.380
	3~4	12.00	-2.01	-3.40	0.036	0.037
MD ₁₃	1~2	2.43	-28.97	-30.37	-0.184	-0.128
MD ₄₉	1~2	2.86	-31.17	-32.02	-0.482	-0.768
MD ₇₅	1~2	3.10	-32.02	-33.27	-1.105	-1.541
	2~3	5.10	-30.42	-31.27	1.043	1.469

Figure 2(b) plotted the BOLS reproduction of CLS of the Ag-3*d* and Cu-2*p*, which is extracted using Eqns (4) and (5) and X-ray photoelectron spectroscopy (XPS) measurements, are achieved via linearizing the measured data of silver and copper binding energy versus $1/K$. The details of calculations can give in Ref. [27, 28]. The value of bond nature index m varied with the interaction between the metallic NPs and substrates. For instance, $m = 1.0000$ for Ag NPs deposited on CeO₂ and HOPG substrates due to the lack interaction between silver NPs and both substrates [9, 29], whereas $m = 3.8200$ is used for Ag NPs on Al₂O₃ substrate because of the interaction between Ag NPs and the substrate [30]. m equals to 1.8175, 4.8800, and 1.2675 for Cu NPs deposited on Dow Cyclotene 3022 (CYCL)/Ar⁺ substrate [8], Si surface [31], and Al₂O₃ (80K) substrate [32], respectively because of the interaction between Cu NPs and substrates. The calculated binding energy of Ag-3*d*_{5/2} and Cu-2*p*_{3/2} for an isolated Ag and Cu atoms and the shifts with respect to the bulk values is about 363.03 and 4.63 eV, and 931.0 and 1.70 eV, respectively. A positive CLS is observed in our calculation when the nanocluster size decreases. Consistency between BOLS correlation and experimental results of

silver and copper nanoclusters [8, 9] confirmed the proper selection of the m values and the role of CNs imperfection on the skin for the mean lattice strain and the CLS.

Figure 2. (Color online) (a) Consistency in trend between theoretical prediction (solid line) and various experimental observations (scattered data) of the mean lattice contraction of Ag and Cu NPs reprinted from Refs. [23, 24] and (b) BOLS reproduction (solid line) and the XPS measurement-extracted (scatter data) of Ag-3d and Cu-2p CLS reprinted from Refs. [8, 9, 29-32].

Based on BOLS-NEP theory, the dense and tight core electrons will then polarize the conductive s -electrons of silver and copper nanoclusters and the extent of polarization increases when electron flows from the core to the skin with lower atomic CN. Figure 3 showed the calculated density of states (DOS) of silver and copper nanoclusters with CO₁₃, CO₅₅, CO₁₄₇, MD₁₃, MD₄₉, and MD₇₅ structures. It is found that the size of NPs plays an important role in polarization. For instance, the peaks of DOS shift from -3.62 eV to -2.95 eV for Ag₁₄₇ to Ag₁₃ nanoclusters with CO structures, and from -1.99 eV to -1.47 eV for Cu₇₅ to Cu₁₃ nanoclusters with MD structures, respectively. The calculated results based on BOLS-NEP theory is consistent with the experimental observations including STM/S for silver clusters and silver chains on Ag(111) substrate [10] and copper clusters and copper chains on Cu(111) substrate [11]. Moreover, the dependence of the valence charge polarization on CN has been suggested by the previous calculations of the unoccupied DOS peaks for Ag monomer and dimer [33]. In addition, ultraviolet photoelectron spectra (UPS) revealed the expansion and shift of Ag-4d and Cu-3d band because of the charge polarization in small cluster [34, 35]. Therefore, the bond contraction at the surface due to atomic under-coordination gives rise to the lattice strain, densification and entrapment of charge, as well as polarization of silver and copper nanoclusters.

Figure 3. (Color online) Calculated valence density of states of Ag_N and Cu_N nanoclusters (a) CO structures composed of 147, 55, and 13 atoms and (b) MD structures composed of 75, 49, and 13 atoms.

4. CONCLUSIONS

DFT calculations have been carried out to explore the origin intriguing properties of silver and copper nanoclusters, and the consistency between the calculated results and the experimental observations confirmed our prognostications made on the BOLS-NEP correlation. The atomic under-coordination induces local bond relaxation, lattice strain, charge densification, quantum entrapment, as well as valence charge polarization, giving rise to the intriguing properties of silver and copper nanoclusters such as enhanced catalytic ability and transition from conductor to insulator.

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