Coordination-resolved local bond strain and 3p energy entrapment of K atomic clusters and K(110) skin

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Abstract

We have examined the atomic coordination effect on the local bond strain and the 3p core-level shift of K(110) skin and nanoclusters using a combination of the bond order-length-strength correlation notion, tight-binding approach, density functional theory calculations, and photoelectron spectroscopy measurements. It turns out that: (i) the 3p core-level shifts from 15.595 ± 0.003 eV for an isolated K atom by 2.758 eV to the bulk value of 18.353 eV; (ii) the effective atomic coordination number reduces from the bulk value of 12 to 3.93 for the first layer and to 5.81 for the second layer of K(110) skin associated with the local lattice strain of 12.76%, a binding energy density 72.67%, and atomic cohesive energy -62.46% for the skin; and, (iii) K cluster size reduction lowers the effective atomic coordination number and enhances further the skin electronic attribution. Results have revealed that the 3p core-level shifts of K(110) and nanoclusters originate from perturbation of the Hamiltonian by under-coordination induced charge densification and quantum entrapment.

Keywords: K nanoclusters and solid skin, XPS, DFT, BOLS, energy entrapment

1. Introduction

With the miniaturization of a substance down to nanometer scale, it poses some novel physical properties[1,2] such as insulator- or semi-conductor-like properties[3], lower melting point[4], contrary trend of elastic modulus[5] and bulk modulus[6], etc. All these properties are closely related to the relaxation of bonds among under-coordinated atoms[7] at a solid skin and in an atomic cluster, which the associated energies and the localization and polarization of electrons at these atomic sites are of great importance to the behaviour of the nanoscaled materials, like crystal growth[8,9], adsorption[10], doping[11], decomposition[12], catalytic reactivity [13], work function[14], etc. For example, Pt[15] has good catalytic effect to many reactive system, low-coordinated atoms are increased with the decreasing of Pt nanoparticle size, where more than 70% of the surface is made up of low-coordination sites for the smallest Pt nanoparticles. Because of the change of local electronic properties caused by under-coordination, many properties of nanoclusters and solid skin are different from the corresponding bulk and single atom, such as cohesive energies[16], segregation energies[17,18], heats of mixing[19], and charge transfer[20].

Potassium (K) has been widely used in medical[21], biological[22], biochemical[23], agricultural applications[24,25]. However, the electron nature, structure and properties of K nanoclusters and solid skin are still less understood. Core-level photoelectron spectroscopy has been used to probe the metallic nature of K clusters. Simultaneously, the emergence of the core-level shifts has been monitored by the core-level photoelectron(PE) spectroscopy[26]. For example, Mikkela *et al.* measured the 3p core-level PE spectra of K clusters for several different sizes and found the 3p core-level binding energy of cluster change significantly compared to the bulk value[26]. Although the core-level binding energy of K nanoclusters has been measured[27,28], the energy is indeed a mixture of the bulk component and the skin sublayers. The law governing the energetic behavior of electrons and the electronic

properties change of the surfaces skin and nanoclusters remains unclear.

In recent years, bond order-length-strength (BOLS) correlation[29] mechanism successfully predict atomic cohesive energy application of CdS, CdSe, Bi₂Se₃, and Sb₂Te₃ nanostructures[30], and the tensile strain-induced Raman shift of C-C bond in graphene[31]. In this work, based on the combination of the BOLS correlation, tight-binding (TB) theory, photoelectron spectroscopy (XPS), and the density functional theory (DFT):

- (i) We have explored the bond and electron characteristic of K surfaces and nanoclusters.
- (ii) We calculated the 3p core level shift (CLS) of K upon bulk, surface, and nanocrystal formation, leading to a comprehensive knowledge about the variation of energy shifts, lattice strain, binding energy density, and atomic cohesive energy.
- (iii) Comparing the experiment data and DFT calculation with BOLS prediction, confirm our prediction that atomic undercoordination of K cluster and solid surface induces bond relaxation and leads these changes sequentially.

2. Principles

2.1 BOLS–TB notation

The core idea of the bond order-length-strength (BOLS) correlation mechanism is that if one bond breaks, the neighboring ones become shorter and stiffer. Consequently, local strain and quantum trapping are formed immediately nearby the potential barrier at sites surrounding the broken bonds, as shown in **Fig. 1**. According to the BOLS correlation[2], the shorter and stronger bonds between under-coordinated atoms result in local densification and quantum entrapment of the core electrons. The effective atomic coordination number (CN) has a serious impact on the bond length and strength between under-coordinated atoms, which can be expressed as:

$$\begin{cases} c_z = d_i/d_b = 2/\{1 + \exp[(12 - z_i)/(8z_i)]\} & \text{(bond strain)} \\ c_z^{-m} = E_z/E_b & \text{(bond strength)} \\ E_D(z) = c_z^{-(m+3)} E_D(12) & \text{(binding energy density)} \\ E_C(z) = z_{ib} c_z^{-m} E_C(12) & \text{(atomic cohesive energy)} \end{cases} \quad (1)$$

where C_i is the coefficient of bond contraction, z_i is the effective CN of an atom in the i th atomic layer of surface, i counts from the outermost atomic layer inward up to the third layer ($i \leq 3$), d_i and E_i are the bond length and bond energy in the i th atomic layer, respectively, E_b is the bulk bond energy and d_b is the bulk bond length of the corresponding material, E_C is the atomic cohesive energy (E_i , single bond energy multiplies the atomic CN). Where m is the bond nature indicator, $z_{ib} = z_i/z_b$, is the reduced CN with $z_b=12$ being the bulk standard. The bond nature indicator m represents how the bond energy changes with bond length, and $m = 1$, for most metal.

On the basis of tight-binding (TB) theory, the Hamiltonian and the wave function describing an electron moving in the ν th orbit of an atom in the bulk solid is [32]:

$$H(\Delta_H) = \left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r) \right] + V_{\text{cry}}(r)(1 + \Delta_H) \quad (2)$$

The single-body Hamiltonian is perturbed by the shorter and stronger bonds, denoted with Δ_H , the intra-atomic potential $V_{\text{atom}}(r)$, determines the ν th core level energy. Regarding the core level energy of a material, we have mainly focused on two characteristic energies: the ν th energy level of an isolated atom $E_\nu(0)$ and the bulk shift $\Delta E_\nu(12) = E_\nu(12) - E_\nu(0)$, where $z = 12$ means the bulk counter part. The former is the integral of the eigenwave function and the intra-atomic potential, and the latter is its energy shift upon bulk solid formation. Both $E_\nu(0)$ and $E_\nu(12)$ for the particular ν th band are intrinsically constant, disregarding the coordination and chemical environment of a given material, which follow the expressions[33]:

$$\begin{cases} E_v(0) = \langle \phi_v(r) | V_{\text{atom}}(r) | \phi_v(r) \rangle & \text{(Core level energy)} \\ \Delta E_v(12) = \beta + z\gamma \propto \langle E_b \rangle & \text{(Core level shift)} \\ \beta = \langle \phi_v(r) | V_{\text{crys}}(r) | \phi_v(r) \rangle \propto \langle E_b \rangle & \text{(Exchange integral)} \\ \gamma = \langle \phi_v(r) | V_{\text{crys}}(r) | \phi_v(r') \rangle \propto \langle E_b \rangle & \text{(Overlap integral)} \end{cases}$$

$$\begin{aligned} \Delta E_v(z) &= \langle v, i | V_{\text{cry}}(r)(1 + \Delta_H) | v, i \rangle \left[1 + \frac{z \langle v, i | V_{\text{cry}}(r)(1 + \Delta_H) | v, j \rangle}{\langle v, i | V_{\text{cry}}(r)(1 + \Delta_H) | v, i \rangle} \right] \\ &\cong E_b(1 + \Delta_H) \left(1 + \left(\frac{z\gamma}{\beta} < 3\% \right) \right) = E_z \end{aligned} \tag{3}$$

where, $\phi_v(r)$ ($r \neq r'$) is the Bloch wave function at specific sites r . $z = 0$ and 12 represent an isolated atom and an atom in the ideal bulk, respectively. $|v, i\rangle$ is the eigenwave function at the i th atomic site with z neighbours, Because $\langle v, i | v, j \rangle = \delta_{ij}$, with the Kronig function δ_{ij} (if $i = j$, $\delta_{ij} = 1$; otherwise, $\delta_{ij} = 0$), E_b represents the single bond energy in the ideal bulk, and any perturbation to the bond energy E_b will shift the core level accordingly. The exchange integrals β and overlap integrals γ are relative to the cohesive energy per bond $\langle E_b \rangle$. Any perturbation to the exchange integrals and overlap integrals causes shifts in the energy level, so the core level energy shifts depend on the bond energy. Incorporating the BOLS into the TB approximation yields, an extension of the atomic coordination-radius premise of Pauling[34] and Goldschmidt[35] has resulted in the BOLS-TB notion, dominates the shift of binding energy, can be reorganized as:

$$\Delta E_v(z) = E_v(z) - E_v(0) = \Delta E_v(12)(1 + \Delta_H) = (E_v(12) - E_v(0))(1 + \Delta_H)$$

so,

$$\begin{cases} \Delta_H = \sum_{i \leq 3} \gamma_i \Delta_i = \tau K^{-1} \sum_{i \leq 3} C_{z_i} \Delta_i = \tau K^{-1} \Delta'_H = \tau K^{-1} \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) & (\text{Nanocluster}) \\ \Delta_i = \frac{E_z}{E_b} - 1 = C_{z_i}^{-m} - 1 & (\text{Solid skins}) \end{cases} \quad (4)$$

The v th energy level of an isolated atom $E_v(0)$ and the bulk shift $\Delta E_v(12) = E_v(12) - E_v(0)$, where $z = 12$ means the bulk counterpart. $\sum_{i \leq 3} C_{z_i} \Delta_i = \Delta'_H$ and $\gamma_i = \tau C_{z_i} K^{-1}$ is the surface-to-volume ratio, proportional to τ ($\tau = 1, 2$, and 3 corresponds to the dimensionality of a thin plate, a cylindrical rod and a spherical dot, respectively), and inversely proportional to the dimensionless size K . $K = R/d_b$ is the number of atoms lined along the radius of a spherical nanoclusters. The Δ_H sums over only the outermost three atomic layers; the Δ_i represents the perturbation to the individual i th surface layer. For $i > 3$, the atomic bonds are assumed to be set sufficiently deep into the bulk of the solid such that they do not experience significant deficiencies in atomic coordination number (CN) unlike those at and near the surface. The under-coordinated atoms in the surface skin of nanoclusters and bulk solid contribute to the additional perturbation Δ_H to the overall Hamiltonian. The $\Delta_H(\tau, K^{-1}, m, z, d, E)$ covers all the possible extrinsic contributions from the shape (τ), size (K^{-1}) and the intrinsic contributions from bond nature (m), coordination number (z), bond length (d) and bond energy (E) to the Hamiltonian. The m , d , and E values will be modulated by chemical reaction, externally thermal and mechanical stimulations, and in hence the Hamiltonian is **changed**.

2.2 Skin and Size effects

We have the following relations for the surface binding energy (BE) shift according to BOLS-TB notation:

$$\frac{\Delta E_v(z)}{\Delta E_v(12)} = \frac{E_v(z) - E_v(0)}{E_v(12) - E_v(0)} = \frac{E_z}{E_b} = C_z^{-m} = 1 + \Delta_i$$

or $E_v(0) = \frac{C_{z'}^m E_v(z') - C_z^m E_v(z)}{C_{z'}^m - C_z^m} \quad (z' \neq z)$

$$E_v(z) - E_v(0) = [E_v(12) - E_v(0)] \times C_z^{-m} \quad (5)$$

With the derived $E_v(12)$, $E_v(0)$, the bond-nature indicator m , and the given z values for the outermost three atomic layers, we are able to decompose the measured XPS spectra into the corresponding surface and bulk components with different-coordination number with the relations derived from Eq. (5):

$$\Delta E_v(12) = E_v(12) - E_v(0), E_v(0) = \frac{C_{z'} E_v(z') - C_z E_v(z)}{C_{z'} - C_z} \quad (z' \neq z) \quad (6)$$

In order to explore the relations between a core level shifts and coordination number, we can combine the Eq. (1) and Eq. (5)[36-41]:

$$E_v(z) = \Delta E'_v(z) + E_v(12) \text{ or } \Delta E_v(z) = \Delta E'_v(z) + \Delta E_v(12)$$

$$z_i = 12 / \left\{ 8 \ln \left(\frac{2}{\left(\frac{\Delta E_v(12)}{\Delta E_v(z)} \right)} - 1 \right) + 1 \right\} \quad (7)$$

From the relationship of Eq. (7), we set up a bridge of XPS measurement and DFT calculation. $\Delta E_v(z) = E_v(z) - E_v(0)$ and $\Delta E'_v(z) = E_v(z) - E_v(12)$ represent CLSs of an isolated atom and an atom in the ideal bulk, respectively. Incorporating the BOLS-TB and DFT, when we get the $\Delta E_v(12)$ from XPS decompose, we can derive atomic effective CN(z) through putting the value of CLS into Eq. (7) [42].

With the obtained CLS, and the derived z value, bond nature, and bond length, we are able to predict the z -resolved local lattice strain (ε_z), energy level shift (ΔE_z), atomic cohesive energy ($\delta E_C(z)$) and binding energy density ($\delta E_D(z)$), follows the relation:

$$\begin{cases} \varepsilon(z) = C_z - 1 & \text{(local lattice strain)} \\ \Delta E_v(z) = \Delta E_v(12)C_z^{-m} & \text{(core level shift)} \\ \delta E_c(z) = E_c(z) / E_c(12) - 1 = z_{ib}C_z^{-m} - 1 & \text{(atomic cohesive energy)} \\ \delta E_d(z) = E_d(z) / E_d(12) - 1 = C_z^{-(m+3)} - 1 & \text{(binding energy density)} \end{cases} \quad (8)$$

Where $z_{ib} = z / 12$ is the relatively reduced CN, $z = 12$ is the bulk value and $m = 1$ for most metal.

Similarly, based on the tight-binding theory and BOLS correlation, using the sum rule of the core-shell structure while taking the surface-to-volume ratio into effect, we can deduce the size dependence of v th energy level of solid clusters, $E_v(0)$, and its bulk shift, $\Delta E_v(12)$, as follows:

$$E_v(K) = E_v(12) + [E_v(12) - E_v(0)]\Delta_H = E_v(12) + [E_v(12) - E_v(0)]\tau K^{-1} \sum_{i \leq 3} C_z (C_z^{-m} - 1) \quad (9)$$

Here, the size-induced BE shifts for nanoclusters depends inversely on the size in the form of, $E_v(K) = A + BK^{-1}$, where A and B are constants that can be determined by finding the intercept and the slope of the $E_v(K)$ line, respectively. According to the relationship of K and N , $K^{-1} = (3N/4\pi)^{-1/3} = 1.61N^{-1/3}$, we can deduce the form of N versus BE shift into $E_v(N) = A + 1.61BN^{-1/3} = A + B'N^{-1/3}$, and incorporating the follows:

$$\begin{cases} K^{-1} = (3N/4\pi)^{-1/3} = 1.61N^{-1/3} \\ N = 4\pi K^3 / 3 \end{cases} \quad (10)$$

We can obtain the N -dependence of the core level BE:

$$E_v(N) = E_v(12) + 1.61\tau N^{-1/3} \Delta E_v(12) \sum_{i \leq 3} C_{z_i} (C_{z_i}^{-m} - 1) \quad (11)$$

2.3 DFT calculation methods

In addition, we conducted first-principles DFT calculations on the optimal K_N clusters[43,44] to verify our BOLS-TB predictions. The relativistic DFT calculations were conducted using the Vienna Abinitio simulation package (VASP) and the basis set is plane wave. In our recent papers, we used Dmol3 to caculate the size of Pb and Mo nanoclusters. And the calculated method and basis set of different software are different, but their results are similar. VASP calculation should test the exchange-correlation function and choose core band potential function. Calculations were focused on the change of optimal the bond relaxation, charge transfer[45], geometric structures and size dependence, and the energetic distribution of the core band of K nanoclusters, as shown in **Fig. 2**. Further more, we also compared the computational results with the photoelectron spectroscopy measurements. The DFT exchange-correlation potential utilized the local-density approximation (LDA)[46] for geometry and electronic structures[47]. The initial cutoff energy 350 eV was used for optimizing the structure of K clusters. Precise calculation for refined structures, final and accurate energy values were computed by the same code using a cutoff energy of 400 eV in all the cases. K cluster was included in a supercell of $28 \times 28 \times 28 \text{ \AA}^3$ to avoid spurious interactions among periodic images. In calculations, all atoms were fully relaxed by using the conjugate gradient method until residual forces on constituent atoms were less than $5 \times 10^{-2} \text{ eV/\AA}$, and in determining mechanical properties, the value of convergent force increases to $1 \times 10^{-3} \text{ eV/\AA}$. In addition, A k-point sampling of $1 \times 1 \times 1$ Monkhorst–Pack grids in the first Brillouin zone of the cell was used in the calculation.

3.Results and discussion

3.1. Core level quantum entrapment of surface

XPS[48] provides a powerful means for studying the electronic binding energy of

both solid skins and bulk of K, the energy shift of the core level fingerprints the interaction between the atoms that drive the unusual behavior of the skin and atomic clusters. In order to calibrate and quantify the electron binding energy shift of K surface, we decomposed the XPS spectra from clean K(110) surface[27,28] with three components, corresponding to the bulk (B) and surface skins S_2 , S_1 , as shown in **Fig. 3a** and **Fig. 3b**, from higher (smaller absolute value) to lower BE after the subtraction of the Shirley background[49]. And the Zone-selective photoelectron spectroscopy (ZPS)[50] was also invented to purify local and quantitative information on the bonding and electronic dynamic associated with the undercoordination system. Procedures employed in the ZPS include: (i) collects the referential XPS spectrum from a clean surface at an angle approaching the surface normal and a plural of spectra from the surface at larger emission angles or from the same surface being conditioned or alloyed; (ii) subtracts the referential spectra from the ones to be examined upon proper background correction and peak area normalization under the guideline of spectral area conservation. The rule of peak area conservation guarantees that the integration of each spectrum is proportional across to eliminate the scattering effect. Here, the ZPS was collected from the same defect-free surface at two different emission angles: 0° and 55° , as shown in **Fig. 3c**. We can also obtain the optimal component energies, the corresponding z_i , which were all summarized in **Table 1**, the information about component energies obtained by XPS and ZPS are consistent.

Including the common B component ($z = 12$) gives a total of $l = 3$ components for the Na(110) surface. A total, $N = C_l^2 = l! / [(l-2)!2!] = 3$, of values is possible for $E_v(0)$. Then we can find the average $\langle E_v(0) \rangle = \sum_N \langle E_{vi}(0) \rangle / N$ with standard deviation σ of $E_{3p}(0)$ calculated using a least root-mean-square method. A fine tuning of the CN values of the components will minimize σ and improve the accuracy of the effective CN for each sublayers. Then the core level $E_v(0)$ of an isolated K atom was derived and confirmed. It has been derived that the 3p BE of bulk and surface skin shift deeper from 2.758 to 3.162 eV with respect to that of the isolated K (15.595 ± 0.003

eV) atoms. Based on the Eq. (5) and the obtained value of $E_{3p}(0)$ and $\Delta E_{3p}(12)$, the z -resolved 3p BE shift for K skin can be expressed as:

$$E_{3p}(C_z) = \langle E_{3p}(0) \rangle \pm \sigma + \Delta E_{3p}(12)C_z^{-m} = 15.595 \pm 0.003 + 2.758C_z^{-1}$$

The effective atomic CNs of the top and second K(110) atomic layers are 3.93 and 5.81 [51]. With the derived z value and the 3p BE for each XPS component, we could predict the z -resolved ε_z , $\Delta E(z)$, δE_C and δE_D of the K(110) skin, as shown in **Fig. 3d** and **Table 1**. It shows the ε_z contracting up to 13%, δE_D enhancing up to 73%, and δE_C weakening up to 62% of K surface skins up to three atomic layers in depth. This derived fundamental information is of great importance in determining the surface properties and surface processes, because the defects, surfaces, and nanostructures of various shapes are correlated by atomic under-coordination. The interaction between the under-coordinated atoms and the electronic distribution is the origin of the unusual performance of such under-coordinated systems.

3.2 Coordination-resolved local bond strain and nanoclusters

Clusters have a considerable number of the under-coordinated atoms which are located in the surface sites. **Fig. 4** shows the 3p-orbit local DOS of K_{44} , K_{46} , K_{55} clusters. From which, we obtained the binding energy and energy density evolution of atoms at different nanoclusters sites, as seen in **Table 2**. Then, We calculated atomic CN(z) using **Eq. (7)**. The conclusion in **Table 2** reveals that with the decrease of effective CNs(z), the BE shifts become larger, the result shows that under-coordination induced BE shifts, for example, when the CN value of atoms reduce from 12(bulk) to 5.12 and 2.67, the BE shift are 0.25 and 0.75, respectively. **Fig. 5** compares the derived CN and BE shifts at different atom sites between different structures of K: O_h44 , $C_{3v}46$, O_h55 . We found an atom has same CN and BE shifts when it has same number of neighbor atoms. For example, we can find the BE shifts of the third atom in K_{44} and K_{46} , and the seventh and eighth atoms in K_{55} are equal ($\Delta E(z) = 0.25$), and they also have the same derived CN(5.12), because these

atoms have the same number of the nearest neighbours, and they also have the consistent surrounding structures. Therefore, combining the calculations of BOLS-TB and DFT, atomic coordination can resolve cluster core level shifts.

When the number(N) of K nanoclusters reduce from 55 to 13, the average effective CN value are 3.53 and 2.73, respectively. Our calculations confirm the spontaneous bond contraction in the K clusters disregarding the sizes and structures, as shown in **Table 3**. Atomic under-coordination leads spontaneous bond contraction of first and second atom layer in nanocluster, according to BOLS notation, we can predict atomic undercoordination shortens and strengthens the remaining bonds between undercoordinated atoms. In fact, the highly coordinated atoms prefer larger first-neighbor distances than the under-coordinated ones. Therefore, atoms in the interior of cluster exhibit ideal distance of the bulk, while skin atoms show bond contraction.

The spontaneous process of bond contraction and strengthening will cause local densification and quantum entrapment of binding energy. **Fig. 6a** shows DFT calculations of the 3p-orbit DOS for K of I_h13 , C_{524} , C_{125} , C_{147} , I_h54 , I_h55 clusters. DFT calculations derived that the peaks of shift toward deeper binding energies as the cluster size is reduced. Therefore, because of local bond strain and quantum entrapment, core level shift happens while the K cluster sizes are reduced.

3.3 N -dependence of nanoclusters

In the BOLS convention[15,52-55], we choose the first and third atoms of K_{44} cluster for the standard reference $CN(z)$ for the atoms at sites of first and second atomic layers and combining the BOLS convention, we can estimated $z_1 = 2.67$ and $z_2 = 5.12$. From the relation of $C(z_i)$ in **Eq. (1)**, we obtained C_1 and C_2 being 0.7850 and 0.9162, respectively. With the value of $\Delta E_{3p}(12)$ derived from surface analysis, we can calculate the BE change without any assumptions:

$$\begin{cases} E_{3p}(N) = E_{3p}^{\text{Fermi}}(12) + 1.601\tau N^{-1/3}(\text{eV}) & (\text{Experiment}) \\ E_{3p}(N)' = E_{3p}(12)' + 1.601\tau N^{-1/3}(\text{eV}) & (\text{Calculation}) \end{cases}$$

and,

$$\begin{cases} \Phi = E_{3p}^{\text{Fermi}}(12) - E_{3p}'(12) \text{ (eV)} \\ \Phi_1 = E_{3p}^{\text{vacuum}}(12) - E_{3p}^{\text{Fermi}}(12) \text{ (eV)} \end{cases} \quad (12)$$

We have checked the value derived from the DFT calculation data, $\Delta E_{3p}(N)$ is mainly attributed to size contribution, $\Phi_1 = 2.30$ eV is the work function[26]. **Fig. 6b** shows that the 3p core band core level shift of size-selected free K_N nanoclusters increases linearly with $N^{-1/3}$ and shape factor τ adjustable because the shape of clusters are not ideal spherical, here $\tau = 2.01$. If we can get the information about 3p core band, we can determine the $\Phi = 2.21$ eV and the bulk value difference between DFT calculation and experiment according to the slope and intercept derived from size-induced BE shifts and **Eq. (12)**:

$$\begin{cases} E_{3p}(N) = 20.620 + 1.853N^{-1/3} \text{ (eV)} & \text{(Experiment)} \\ E_{3p}'(N) = 15.595 + 1.853N^{-1/3} \text{ (eV)} & \text{(Calculation)} \end{cases} \quad (13)$$

As shown in **Fig. 6b**, the BOLS prediction is generally consistent with the core-level BE in both the experiment and the DFT calculation.

Finally, we can obtain the relationship of effective CN and atomic number N based on **Eq. (7)** and **Eq. (11)**:

$$z_i = 12 / \left\{ 8 \ln \left(\frac{2 \left(\Delta E_{3p}(12) + 1.601N^{-1/3} \right)}{\Delta E_{3p}(12)} - 1 \right) + 1 \right\} \quad (14)$$

As shown in **Fig. 7**, the value of effective CN is reduced with the decrease of atomic number, and we can predict the effective CN of K nanocluster easily when we get the atomic number.

Such a consistency of DFT calculations, XPS measurements and BOLS

predictions evidences that the local bond contraction and quantum entrapment surrounding under-coordinated atoms will lead to positive BE shifts for K surfaces and atom clusters. In consequence, both the size- and the skin-induced energy shifts of K surfaces and atomic clusters are dominated by the shorter and stronger bonds between under-coordinated atoms.

4. Conclusion

Incorporating the DFT calculations and XPS measurements has led to consistent insight into the physical origin of the localized edge states of K solid skin and clusters which confirmed the BOLS-TB predictions of the atomic CN effects on the local bond relaxation, electron binding-energy shift, atomic cohesive energy, and their coordination- resolved shifts of K skins and nanoclusters. Analyzing the XPS spectra for the K(110) surface was clarified that K(110) 3p shifts positively by 2.758 eV from a value of 15.596 eV for an isolated atom to 18.354 eV for the bulk. The interaction between under-coordinated atoms caused local strain, local densification and entrapment of the core electrons, which perturbed the Hamiltonian and hence dominated the unusual behavior of K surfaces and nanoclusters. We also have demonstrated the DFT calculation on N -dependence of the core level BE shifts, and quantitative information about under-coordinated atoms. The findings should be helpful for applying K skins and nanoclusters in practical application, such as catalytic enhancement, applications in electronics and optics, and designing nanocrystals with desired structures and properties.

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Table and Figure captions:

(a)

(b)

Fig. 1 (a) The BOLS correlation mechanism (solid line) formulates the atomic “CN-radius” convention of Pauling[34] and Goldschmidt[35] with further evidence (scattered symbols) measured from nanomaterials and surfaces, and (b) Schematic illustration of the broken-bond induced local strain and quantum entrapment at the terminating edges up to three atomic layers.

(a)

(b)

Fig. 2 Geometrically optimised (a) O_h44 , $C_{3v}46$, O_h55 ; (b) I_h13 , C_{s24} , C_{125} , C_{147} , I_h54 and I_h55 structures of K clusters.

Fig. 3 (a), (b) Decomposed XPS spectrum and (c) ZPS of the K(110) surface with the three Gaussian components representing the bulk B and surface skins S_2 and S_1 from higher(smaller absolute value) to lower BE. (d) Atomic cohesive energy δE_C and BE density δE_D . **Table 1** and **Table 2** show the derived information completely.

Fig. 4 DFT-derived LDOS for (a) O_h44 , (b) $C_{3v}46$, (c) O_h55 structures of K clusters.

Fig. 5 Coordination number (z)-resolved CLS ($\Delta E'_{3p}(z) = E_{3p}(z) - \Delta E_{3p}(12)$) of K clusters.

Comparisons of CLS among the results of DFT calculations for K_{44} , K_{46} , K_{55} .

Fig. 6 (a) Size-induced quantum entrapment of K_N clusters. (b) BE shift of size-selected free K_N clusters versus $N^{-1/3}$. Comparisons of CLS among DFT calculated data and experimental data of different K nanoclusters size.

Fig. 7 (a) Atomic CN versus $N^{-1/3}$ for K nanoclusters, the value of effective coordination is reduced with the decrease of atomic number.

Table 1 The effective CN(z), local lattice strain ($\varepsilon_z = (C_z - 1)(\%)$), relative core-level shifts ($\Delta E_{3p}(z) = E_{3p}(z) - E_{3p}(0)$ and $\Delta E'_{3p}(z) = E_{3p}(z) - \Delta E_{3p}(12)$), relative atomic cohesive energy ($\delta E_C = (z_{ib} C_z^{-1} - 1)(\%)$) and the relative BE density ($\delta E_D = C_z^{-4} - 1(\%)$) in various registries of K(110) surface.

	i	$E_{3p}(i)$	z	$\Delta E(z)$	$-\varepsilon_z$	$-\delta E_C$	δE_D
	Atom	15.595	0	---	---	---	---
	B	18.354	12	2.758	0	0	0
K(110)	S ₂	18.551	5.81	2.955	6.671	48.123	31.806
	S ₁	18.757	3.93	3.162	12.764	62.458	72.670

Table 2 The average effective CN (z), relative core-level shifts ($\Delta E'_{3p}(z) = E_{3p}(z) - E_{3p}(12)$), relative atomic cohesive energy (δE_C) and the relative BE density (δE_D) in various registries of K clusters.

	Atom position	$E_{3p}(i)$	z	$\Delta E'_z$	$-\delta E_C$	δE_D	$\Delta E_{3p}(i)$
K ₄₄	1	15.936	2.67	0.753	71.656	163.331	3.511
	2	15.717	3.33	0.534	66.913	102.107	3.292
	3	15.434	5.12	0.251	53.431	41.911	3.009
	4	15.183	12	0	0	0	2.758
K ₄₆	1	15.865	4.08	0.381	61.332	67.307	3.139
	2	15.841	4.29	0.357	59.748	60.718	3.114
	3	15.736	5.12	0.252	53.432	41.911	3.010
K ₅₅	1	16.109	2.73	0.727	71.570	143.889	3.485
	2	16.068	2.83	0.686	70.182	155.566	3.444
	3	16.073	2.83	0.692	71.236	155.566	3.449
	4	15.856	3.57	0.474	65.143	88.465	3.232
	5	15.830	3.73	0.448	63.953	80.863	3.206
	6	15.700	4.52	0.318	58.005	54.508	3.076
	7	15.635	5.12	0.253	53.432	41.911	3.011
	8	15.635	5.12	0.253	53.432	41.911	3.011
	9	15.412	10.33	0.030	13.038	4.1457	2.788
	10	15.382	12	0	0	0	2.758

Table 3 The cluster strain ($C_d = (d_i/d_b - 1)(\%)$) and relative core-level shifts

($\Delta E'_{3p}(z) = E_{3p}(N)' - E_{3p}(12)'$) from various registries of K nanoclusters.

$$(\Phi_2 = E_{3p}^{vacuum}(12) - E_{3p}(12)').$$

	N	$E_{3p}(i)$	$\Delta E'_z$	z	d_i	C_d
K Cluster (DFT)	13	15.850	0.730	2.728	4.230	-8.183
	24	15.800	0.680	2.852	4.221	-8.379
	25	15.763	0.643	2.955	4.278	-7.141
	47	15.718	0.598	3.092	4.313	-6.382
	54	15.620	0.500	3.451	4.221	-8.379
	55	15.603	0.483	3.529	4.196	-8.921
K Cluster	90	15.570	0.450	3.682	---	---
	650	15.400	0.280	4.841	---	---
$(\Phi_2 = 5.501 \text{ eV})$	1900	15.310	0.190	5.904	---	---
	3800	15.260	0.140	6.766	---	---
Experiment	Bulk	15.120	0	12	4.607	0