COMMENTS

Comment on "Stability of Scanning Tunneling Microscopy Tip-Induced Bimetallic Nanoclusters: Influence of Hardness and Composition on the Cohesive Energies"

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Received: June 13, 2005; In Final Form: July 12, 2005

In 2002, we developed a model to account for the cohesive energy of nanoparticles (or nanoclusters),[1,2] which was named the surface area difference (SAD) model in our further work.[3] Recently, Harinipriya and Sangaranarayanan have made a comment on the SAD model, in which they thought that the SAD model was "inadequate to investigate the energetic when different compositions of nanoclusters can be fabricated by suitable experimental protocols".[4] In this Comment, we demonstrate that the SAD model can be improvised in order to estimate the cohesive energies of nanoclusters of different compositions, and the resulting values are in agreement with those of Harinipriya and Sangaranarayanan.[4] Because the SAD model is based on the original concept of cohesive energy, it can be used to predict the cohesive energy of nanoclusters with different compositions, which will be discussed in more detail below.

Since the cohesive energy of a material is the energy needed to divide the material into isolated atoms, in other point, the direct result of cohesive energy is to generate a new surface. The increased surface energy should equal the cohesive energy of the material, which results from the surface area difference between the total atoms and the material. This is the basic concept of the SAD model.[1−3] In the SAD model, the surface of the material approximately denotes the first layer of the material.

For a nanocluster A_xB_{1-x}(A and B denote two elements, and x is the atom percent of element A, and then, $1 - x$ is the atom percent of element B), the total number of atoms is n. Then, the number of atoms of A is nx, and the number of atoms of B is $(1 - x)n$. The atomic diameters of A and B are d_A and d_B, and the surface energies per unit area of A and B are γ_A and γ_B, respectively. The surface energy of A with nx atoms is $nx\pi d_A^2\gamma_A$, and the surface energy of B with $(1 - x)n$ atoms is $n(1 - x)\pi d_B^2\gamma_B$; then, the total surface energy of n atoms is $nx\pi d_A^2\gamma_A + n(1 - x)\pi d_B^2\gamma_B$.

If the surface of a nanocluster is spherical, its surface energy is $\pi D^2\gamma_{AB}$, where D is the diameter of the nanocluster and γ_{AB} is the surface energy per unit area. Without considering the surface segregation, the surface energy per unit area can be estimated by γ_A and γ_B, i.e.,

$$\gamma_{AB} = x\gamma_A + (1 - x)\gamma_B \tag{1}$$

For a nonspherical nanocluster, the surface energy can be written as $\pi\alpha D^2\gamma_{AB}$, where α is the shape factor. The shape factor is defined as the surface area ratio of a nonspherical nanocluster and the corresponding spherical nanocluster in identical volumes. For spherical nanoclusters, we have $\alpha = 1$, and for nonspherical nanoclusters, $\alpha > 1$ (for instance, the shape factor of cubic nanoclusters equals 1.24). The details of the shape factor have been presented in ref 5.

Since the nanocluster consists of n atoms, its volume is related to the volume of n atoms, i.e., $f{\cdot}\pi D^3/6 = nx\pi d_A^3/6 + n(1 - x)\pi d_B^3/6$, where f is the packing factor (e.g., $f = 0.74$ for face-centered cubic structure). Then, we have

$$n = \frac{f{\cdot}D^3}{xd_A{}^3 + (1 - x)d_B{}^3} \tag{2}$$

According to the SAD model, the surface energy difference between the nanocluster and its total atoms is the cohesive energy of the nanocluster. Therefore, the cohesive energy (E_n) can be written as

$$E_n = nx\pi d_A{}^2\gamma_A + n(1 - x)\pi d_B{}^2\gamma_B - \pi\alpha D^2\gamma_{AB} \tag{3}$$

Since $E_A = N_0\pi d_A^2\gamma_A$ and $E_B = N_0\pi d_B^2\gamma_B$[1−3] ($N_0$ is the Avogadro's number), we can rewrite eq 3 as the following form by considering eq 1

$$E_c = xE_A\left(1 - \frac{\alpha D^2}{nd_A{}^2}\right) + (1 - x)E_B\left(1 - \frac{\alpha D^2}{nd_B{}^2}\right) \tag{4}$$

Equation 4 is a more general relation for cohesive energy per mole (or per atom, which depends on the unit of E_A or E_B) of nanoclusters. The case mentioned in refs 1−3 can be regarded as a special case of eq 4. For instance, for pure spherical nanoclusters of composition A, we have $x = 1$, $\alpha = 1$, and $n = D^3/d_A^3$, and then, eq 4 is simplified as $E_c = E_A(1 - d_A/D)$, which is just the expression obtained in our previous work.[1,2]

Furthermore, eq 4 can be used to account for the cohesive energy of nanoclusters with different compositions. Here, we take a Au−Cu nanocluster of 26 Cu atoms and 11 Au atoms as an example, where the system has also been discussed in ref 4. Apparently, we have $x = 0.703$ and $n = 37$. The cohesive energies of pure Au and pure Cu are 3.81 and 3.49 eV,[6] and the corresponding diameters are 0.2884 and 0.2556 nm,[7] respectively. We regard Au−Cu nanoclusters as the close-packed structure, and then, the packing factor is 0.74.[6] The values of the shape factor are chosen as 1 (spherical shape) and 1.49 (tetrahedral shape), which are the up and down limits of regular polyhedral shapes.[5] The calculated cohesive energy of spherical Au−Cu clusters is 2.25 eV, and that of regular tetrahedral Au−Cu clusters is 1.60 eV. In general, with regular polyhedral shape-like Au−Cu nanoclusters of the same size, the cohesive energy should be in the middle of ∼1.60−2.25 eV, which agrees with the value of 1.83 eV given by Harinipriya and Sangaranarayanan.[4]

In summary, the SAD model is based on the basic concept of cohesive energy, which can be used to predict the cohesive energy of nanoclusters with different compositions. Furthermore, the shape effect on cohesive energy has also been considered in the SAD model.

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10.1021/jp053163o CCC: $30.25
Published on Web 10/27/2005

Acknowledgment. This work was supported by National Natural Science Foundation of China (no. 50401010).

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