Shape factor of nonspherical nanoparticles

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The properties of nanoparticles depend on the particle size [1–7], which is different from those of the corresponding bulk materials. Different models [2, 3, 5, 6, 8] have been used to explain the size-dependent properties, where the nanoparticles are regarded as ideal spheres. In the past few years, polyhedral, disk-like nanoparticles have also been observed [9, 10], however, the reported models cannot predict the particle-shape effect on the properties of nonspherical nanoparticles.

In our previous work, we have developed a model to account for the size effect on the lattice parameters of spherical nanoparticles [2], which have been generalized for nonspherical nanoparticles by introducing a shape factor [11]. The concept of shape factor has been mentioned in reference [11], and will be discussed in detail presently. Furthermore, we will derive some useful relations between the particle size, the number of surface atoms, the shape factor, and the number of total atoms of nonspherical nanoparticles.

The shape factor (α) is defined as the ratio of the surface area of a nonspherical nanoparticle (S') to that of a spherical nanoparticle (S), where both of the nanoparticle have identical volume, i.e.

$$\alpha = \frac{S'}{S} \tag{1}$$

On the basis of this definition, the geometry of nonspherical nanoparticle can be described by the particle size and the shape factor. The particle size is defined as the diameter of the corresponding spherical nanoparticle, and the difference between spherical nanoparticles and nonspherical nanoparticles is well described by the shape factor.

The shape factor of spherical nanoparticles equals 1, which means that the spherical shape has been included in the definition of shape factor. The shape factor of nonspherical nanoparticles is larger than 1, which means that the shape factor can approximately describe the shape difference between spherical and nonspherical nanoparticles. The shape factor is defined as the ratio of surface areas, which is a dimensionless parameter. Furthermore, it is convenient to calculate the shape factors of different shapes.

For smooth surface, the surface area can be calculated by area integral. However, only the surface of nanoparticles in large particle size can be regarded as smooth surface. Generally, the nanoparticles are in polyhedral shapes, and their surface is composed of different planes. Then the surface area of a nanoparticle is the sum of all area of the planes, i.e.

$$S' = \sum_k S_k \tag{2}$$

where S_k is the area of the plane k.

On the basis of Equations 1 and 2, we can calculate the shape factor of some special shapes. The volume and the surface area of the corresponding spherical nanoparticle are $(4/3)\pi R^3$ and $4\pi R^2$, where R is its radius.

1) Regular tetrahedral nanoparticle:
If the edge is a, we have $(\sqrt{2}/12)a^3 = (4/3)\pi R^3$ based on the volume relation, i.e.,

$$a = \sqrt[3]{\frac{16\pi}{\sqrt{2}}} R.$$

Simple calculation shows that the surface area of regular tetrahedral nanoparitcles is $18.725R^2$, and then its shape factor is 1.49.

2) Regular hexahedral nanoparticle:
If the edge is a, we have the relation

$$a = \sqrt[3]{\frac{4}{3}\pi} R$$

based on the volume relation, and the surface area is $15.591R^2$, and then the shape factor is 1.24.

3) Regular octahedral nanoparticle:
If the edge is a, we have the relation

$$a = 2.071R$$

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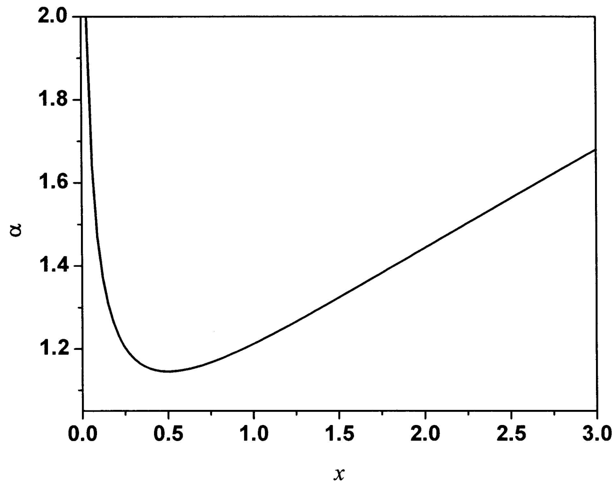

Figure 1 The shape factor of disk-like nanoparticles as a function of x based on Equation 3.

based on the volume relation, and its surface area is $14.857R^2$, and then the shape factor is 1.18.

4) Disk-like nanoparticle:

We assume its radius is l and its height is h. The volume relation results in

$$R^2 = \left(\frac{3}{4}\right)^{2/3} l^{4/3} h^{2/3}.$$

The surface area of a disk-like nanoparticle is $2\pi l^2 + 2\pi l h$, and then its shape factor can be expressed as $\alpha = (2\pi l^2 + 2\pi l h)/4\pi R^2$. Let $l = xh$ $(x > 0)$, then we can rewrite the shape factor as

$$\alpha = \frac{1+x}{1.65x^{1/3}} \tag{3}$$

The relation between α and x is plotted in Fig. 1. It is shown that the shape factor of disk-like nanoparticles is larger than 1.15, which is the minimum value corresponding to $x = 0.5$. It should be mentioned that the shape factor approaches to infinity in the condition of $x \to \infty$ or $x \to 0$, which means that the concept of the shape factor can only deal with the particles in nanometer and cannot be generalized to macroscopic size. As a summation, the shape factors of special shapes have been listed in Table I.

It should be mentioned that the shape factor in the present work can only approximately describe the shape difference between the spherical nanoparticles and the polyhedral nanoparticles. The "approximately" is stressed here due to the fact that some different polyhedral shapes may have the identical shape factor, because the shape factor is defined by the surface area. However, our further work shows that the present definition of shape factor is enough to predict the shape-dependent properties of nanoparticles.

TABLE I The calculated shape factors for special shapes

Particle shape	Shape factor (α)
Spherical	1
Regular tetrahedral	1.49
Regular hexahedral	1.24
Regular octahedral	1.18
Disk-like	>1.15

In our previous work, we have obtained some useful relations between the particle size, the number of surface atoms, and the number of total atoms of spherical nanoparticles [12]. For nonspherical nanoparticles, these relations should be generalized by considering the shape factor.

For a nonspherical nanoparticles, the volume is $(1/6)\pi D^3$ (D is the diameter of the corresponding spherical nanoparticle). If an atom is regarded as ideal sphere, its volume is $(1/6)\pi d^3$ (d is the diameter). The total number of the atoms of the nanoparticle (n) equals the ratio of the volume of the nanoparticle to that of per atom, i.e.

$$n = \frac{D^3}{d^3} \tag{4}$$

The surface area of a spherical nanoparticle is πD^2, and then the surface area of nonspherical nanoparticle is $\alpha\ \pi D^2$ based on the definition of shape factor. A surface atom contributes $(1/4)\pi d^2$ (the area of its great circle) to the surface area of the nanoparticle, and then the number of the surface atoms (N) equals the ratio of $\alpha\ \pi D^2$ to $(1/4)\pi d^2$, i.e.

$$N = \frac{4\alpha D^2}{d^2} \tag{5}$$

Equation 5 shows that the number of the surface atoms is related to the particle size and shape factor, although the total number of the atoms only depends on the particle size according to our definition (Equation 4).

In most cases, the ratio of the number of surface atoms to that of the total atoms is more useful, which can be obtained easily by Equations 4 and 5, i.e.

$$\frac{N}{n} = \frac{4\alpha d}{D} \tag{6}$$

Apparently, N/n is also a function of the particle size and the shape factor.

Equations 4, 5, and 6 are the basic relations for nonspherical nanoparticles. If $\alpha = 1$, the relations reduce to these of spherical nanoparticles, which means that the present relations are more general than those in reference [12]. It is shown that the input parameter of these relations is the diameter of atoms, which can be computed by the lattice parameters for three basic structures BCC, FCC, and HCP [2]. The more general method to obtain the diameter of atoms is by the atomic volume per mole, i.e., the atomic volume per mole of materials divided by Avogadro constant is the volume per atom. Furthermore, the volume per atom equals $\pi d^3/6$, and then the diameter can be obtained. For instance, the atomic volume per mole of Cu is 7.11 cm^3 [8], and the calculated volume per atom of Cu is 0.282 nm.

The calculated results on Cu nanoparticles and the values from literature [13] are plotted in Figs 2 and 3.

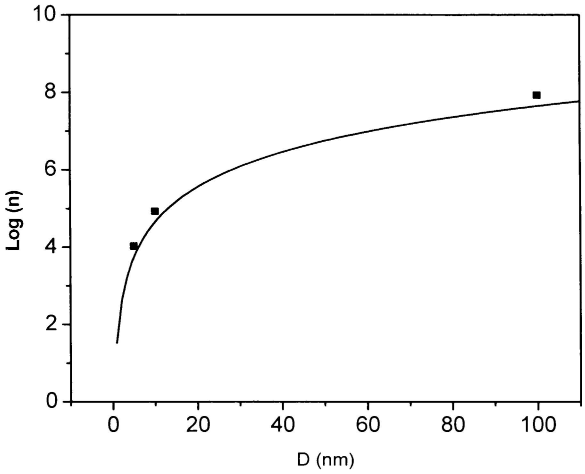

Figure 2 The total number of Cu nanoparticles as a function of particle size. The symbols "■" denote the values in literature [13].

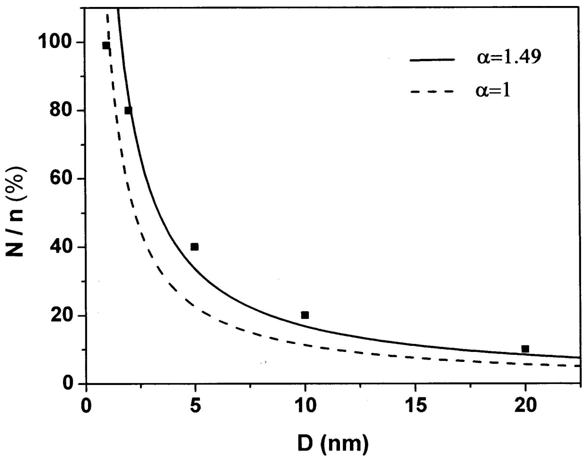

Figure 3 The percentage of surface atom of Cu nanoparticles as a function of particle size in different shape factor. The symbols "■" denote the values in literature [13].

In Fig. 3, the values in literature are close to the calculated ones of $\alpha = 1.49$ (regular tetrahedral shape); it suggests that the particle shape should be taken into consideration when we calculate the number of the surface atoms of nanoparticles. As mentioned above, the lattice parameter of nanoparticles depends on the particle size [2]; however, the variation of the lattice parameter is less than 1% for most of nanoparticles [2], which is ignored in the present method.

In conclusion, we have proposed a new parameter, i.e., shape factor, to account for the particle shape difference between the spherical nanoparticles and nonspherical nanoparticles. The shape factors of special shapes have been calculated. By considering the shape factor, some useful relations of nonspherical nanoparticles have been derived. Considering the fact that most of the special properties of nanoparticles depend on the size and the shape of nanoparticles, we are confident that the shape factor and the relations obtained may have potential application in the research of nanoparticles.

Acknowledgments

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

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Received 9 February
and accepted 23 October 2004