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Surface energetic and bonding characteristics of tetrahexahedral platinum nanocrystals enclosed by high-index facets*

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This paper uses a molecular static approach with a many-body potential to investigate the surface energetic and bonding characteristics of tetrahexahedral platinum nanocrystals enclosed by high-index facets such as {210}, {310}, {410}, {520} and {730}. It mainly focuses on the effect of crystal size and surface Miller index on these characteristics. The results show that the surface energy and dangling bond density increase with decreasing diameter of tetrahexahedral nanocrystals and generally show an order of {210} > {730} > {520} > {310} > {410}. However, this order is not valid at crystal sizes below 7 nm or so. The results of corresponding surfaces are also presented for comparison.

Keywords: nanocrystal, surface energy, dangling bond, molecular static calculation
PACC: 6146, 6810C, 7115Q

1. Introduction

Nanocrystals, whose typical sizes range from 1 to 100 nm, have attracted a great deal of interest because of a number of exciting potential applications in catalysis as well as electronic and optical nanodevices.[1−3] With the decrease of crystal size to nanoscale level, the crystals are formed by a reduced number of atoms and a large fraction of them occupies the surfaces. The strong size effects resulting from this reduction process may lead to novel and different behaviours. However, the physical and chemical properties of crystals are determined not merely by their size but also by their shape.[4] Nanometre-size crystals produced experimentally in several ways, such as atomic deposition, mechanical milling, chemical methods, and gas-aggregation techniques, may be of spherical, octahedronal, tetrahedronal, decahedronal, dodecahedronal or even cubic shape, depending on their detailed production process.[5−9] Different shapes mean that these crystals are surrounded by different surfaces, resulting in various properties. For example, some experiments show that high Miller index planes, such as {210} and {410}, generally exhibit much higher catalytic activity than the most common stable planes, such as {111} and {100}, because high Miller index planes have a higher density of atomic steps, ledges, and kinks, which usually serve as active sites for breaking chemical bonds.[10]

Recently, Sun *et al* reported that unusual tetrahexahedral platinum nanocrystals with a large density of atomic steps and dangling bonds have been prepared through an electrochemical treatment of platinum nanospheres, which exhibited remarkable thermal stability and greatly enhanced catalytic activity in comparison with the spherical Pt and the commercial Pt/C catalyst.[11,12]. As part of a series of this research, in this paper we present further characterization of surface energetic and bonding characteristics of the relaxed tetrahexahedral Pt nanocrystals through theoretical calculations. Our study will consider the influence of high-index facet and crystal size on these characteristics. This paper is organized as follows. In Section 2, we give a brief description of the computational method and in Section 3, we present and discuss the results. Comparisons with the results of Pt bulk are also presented in this section. We summarize and conclude in Section 4.

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2. Computational methods

In molecular static calculations, we use quantum corrected Sutton–Chen (Q–SC) type potentials[13] to describe metallic interatomic interactions. These potentials represent many-body interactions, and their parameters are optimized to describe the lattice parameter, cohesive energy, bulk modulus, elastic constants, phonon dispersion, vacancy formation energy, and surface energy, leading to an accurate description of many properties of metals and their alloys.[13−16] For the SC type force field, the total potential energy for a system of atoms can be written as

$$U = \sum_i U_i = \sum_i \varepsilon \left[\frac{1}{2} \sum_{j \neq i} V(R_{ij}) - c_0 \sqrt{\rho_i} \right], \quad (1)$$

where $V(R_{ij})$ is a pair interaction function defined by the following equation

$$V(R_{ij}) = \left(\frac{a_0}{R_{ij}} \right)^n, \quad (2)$$

which accounts for the repulsion between the i and j atomic cores, ρ_i is a local electron density accounting for cohesion associated with atom i defined by

$$\rho_i = \sum_{j \neq i} \phi(R_{ij}) = \sum_{j \neq i} \left(\frac{a_0}{R_{ij}} \right)^m. \quad (3)$$

In Eqs.(1)–(3), N and R_{ij} are the total atomic number of the nanocrystal and the distance between atoms i and j, respectively, a is a length parameter scaling all spacings (leading to dimensionless V and ρ), c is a dimensionless parameter scaling the attractive terms, ε sets the overall energy scale, n and m are integer parameters such that $n > m$. Given the exponents (n, m), c_0 is determined by the equilibrium lattice parameter, and ε is determined by the total cohesive energy. For the Q–SC type potential of Pt, the parameters are given as follows: $n = 11$, $m = 7$, $\varepsilon = 9.7894$ meV, $c_0 = 71.336$, and $a_0 = 3.9163$ Å.

Tetrahexahedral nanocrystals are constructed from cutting a bulk fcc single crystal by certain surfaces with definite crystallographic orientations. As a result, we obtain five nanocrystals with tetrahexahedron shape enclosed by high-index facets, i.e. {210}, {310}, {410}, {520} and {730}, respectively. These tetrahexahedral nanocrystals and their surface illustrations are presented in Fig.1.

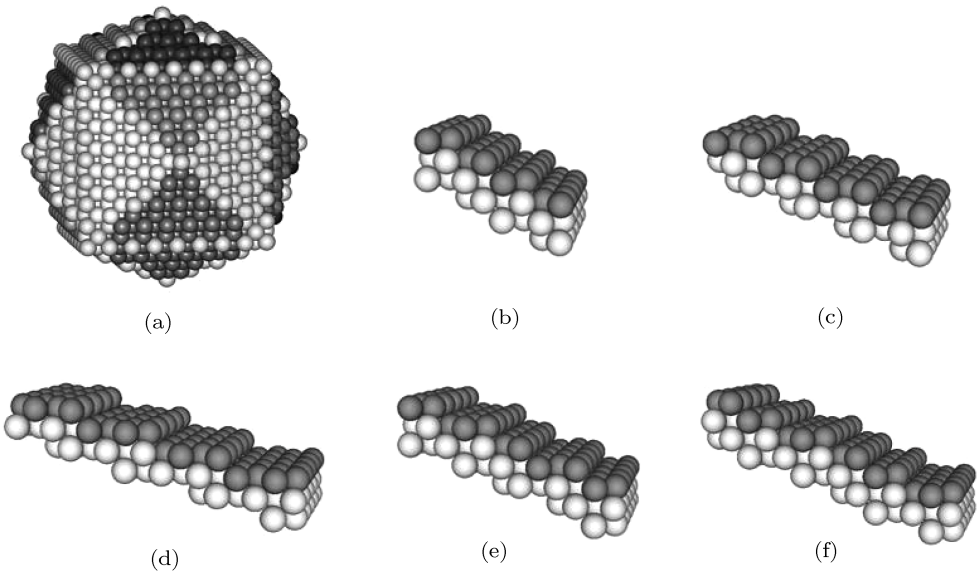


Fig.1. Illustration of atomic configuration of a tetrahexahedral platinum nanocrystal (a), and atomic arrangements of (b) {210}, (c) {310}, (d) {410}, (e) {520}, and (f) {730} surfaces.

We have performed molecular static simulations to relax these nanocrystals to a local minimum energy state using the conjugate gradient method. After full relaxation, they are in an equilibrium state without any external force. It is difficult to define the size of a tetrahexahedral nanocrystal due to its polyhedral shape. Conventionally, we introduce a sphere whose volume is equal to the initial volume of the crystal by the following formulation

$$V = \frac{Na_0^3}{4} = \frac{1}{6}\pi d^3, \tag{4}$$

where N and d are the total atomic number and the diameter of the crystal, $a = 3.9163$ Å is the lattice parameter of Pt bulk. Nanocrystal diameter considered in this paper ranges from 2.77 to 38.6 nm.

3. Results and discussion

Surface energy is an important determinant in crystal growth, heating mechanism and surface reconstruction etc..[17−19] It quantifies the disruption of intermolecular (interatomic) bonds that occurs when a surface is created. In the physics of solids, surfaces must be intrinsically less energetically favourable than the bulk of a material; otherwise there would be a driving force for surfaces to be created, and surface is all there would be. Therefore, the surface energy may be defined as the excess energy at the surface of a material in comparison with the bulk. For a nanocrystal, at ground state it can be calculated from the energy difference between the nanocrystal and its bulk counterpart when the entropic factors are zero through the following equation:

$$\gamma_{\text{surf}} = \frac{\left(\sum_{i=1}^{N} U_i\right) - NU_{\text{coh}}}{S}, \tag{5}$$

where U_i is the binding energy of the ith atom, U_{coh} the cohesive energy per atom in the bulk solid, and S the surface area of the nanocrystal.

Figure 2 shows the dependence of the surface energy on nanocrystal diameter. It is clear that the surface energy of a nanocrystal strongly depends on the crystal size. For nanocrystals enclosed by the same surface, the surface energy increases with the decrease of diameter and is substantially higher than that of the bulk surface. It is well known that a high surface energy often acts as an additional thermal source for melting, evaporation, sintering and crystallization processes.[13,17−20] For example, the size dependence of the crystal melting point for a given material usually shows monotonic decrease with decreasing size.[21,22] This aforementioned phenomenon could be partly associated with the higher surface energy at smaller size.

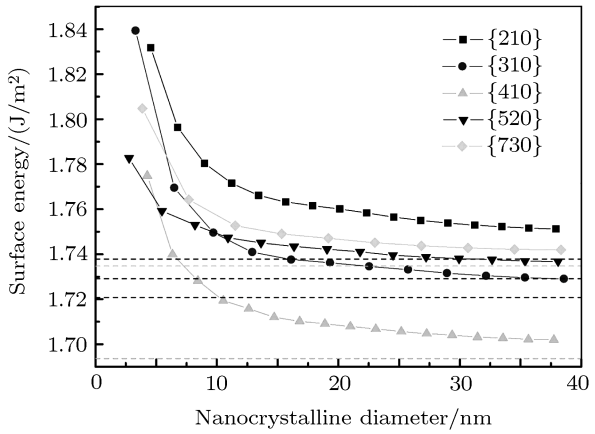


Fig.2. The diameter dependence of the surface energy of tetrahexahedral platinum nanocrystals after full relaxation. The order of horizontal dash lines from up to down denotes the calculated results of {210}, {730}, {520}, {310} and {410} bulk surfaces.

Surface atoms can be composed of edge atoms and facet atoms. The higher Miller index facets enclose, the more edge atoms in the surface, so that an open surface should be followed in order by {210}, {730}, {520}, {310} and {410} as shown in Figs.1(b)–1(f). Considering the fact that the {520} surface is periodically composed of one {210} subfacet followed by one {310} subfacet, and the {730} surface is periodically composed of two {210} subfacets followed by one {310} subfacet, we may expect that the surface energy of {520} and {730} facets is between that of {210} and that of {310}. Our calculated results show that the surface energy of a tetrahexahedral nanocrystal generally presents the following order: {210} > {730} > {520} > {310} > {410}. As expected, the more open surfaces possess a higher energy than the closely packed surfaces for fcc metal. However, this order is broken for crystal sizes below 9 nm, as illustrated in Fig.2. This can be attributed to small size effects. Nanocrystals of very small size are composed of hundreds or thousands of atoms, which are almost located in the surface region. It is known that nanoparticles of fcc metals at small sizes tend to adopt non-crystalline structures, such as icosahedra and truncated decahedra, as they trade internal strain for energetically favourable close-packed surface facets.[2] Our study shows that the facets of the fully-relaxed nanocrystals at small crystal sizes are deviated

from the initial facets as constructed from fcc structure. As a result, the facets of the small-sized crystal are not well defined. Furthermore, their area might not be precisely calculated. Therefore, there are some irregular variations on the small scale, as presented in Fig.2.

In catalytic chemistry, the catalytic reactions preferentially take place on the surface. Surface structural characteristics play an important role at some stage of the chemical processing. Therefore, it is crucial to investigate the atomic bonding characteristics of a nanocrystal related to the crystal size and enclosed surface. Here, we use the concept of coordinate number to analyse the atomic bonding state of the surface region. The coordination number, defined originally by Werner, is the total number of neighbours of a central atom in a chemical compound.[23] In material science, the bulk coordination number is the number of atoms touching any other atom in a crystal lattice. In a face-centred cubic (fcc) crystal, the bulk coordination number is 12. It differs from the surface coordination number which is always less than the bulk one. The surface coordination number depends on the Miller index of the surface. For example, it is 8 and 9 for the {100} and {111} surface, respectively. A dangling bond is used to denote the lost atomic coordination, and characterizes the atomic bonding states of the surface. For nanocrystals, the periodic structure is broken on the surface, resulting in the small coordinate number and high dangling bond of surface atoms.

Figure 3 illustrates the dependence of the dangling bond density (the number of dangling bonds per surface area) on crystal diameter. The results clearly demonstrate that this density increases with decreasing nanocrystalline diameter, showing a remarkable size effect. Especially, when the diameter is smaller than 10nm, this effect is strong. Figure 3 also shows that the dangling bond density calculated from the bulk surface is evidently lower than that of the nanocrystal. The former should be the limit value of the latter when the crystal diameter tends to infinity. The dangling bond density relies strongly on the Miller index of the surface. The highest is the {210} facet, the lowest is the {410} facet. All calculated high-index facets display a higher surface dangling bond density than low-index facets such as {100}.[24,25] This should be beneficial to the catalytic reactions on these high-index surfaces.

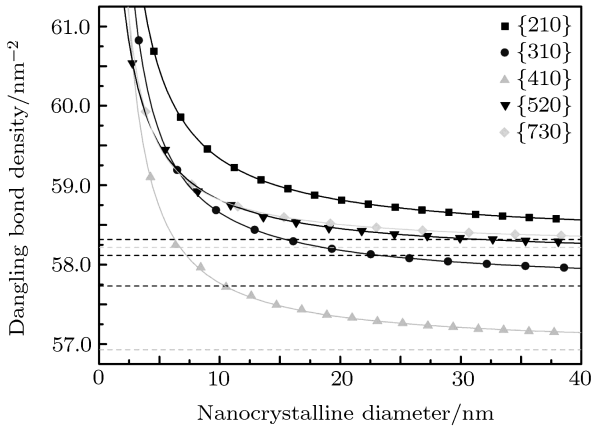


Fig.3. Surface dangling bond density as a function of diameter for tetrahexahedral platinum nanocrystals. The solid lines denote the fitted curves using equation (6). The order of horizontal dash lines from up to down denotes the calculated results of {210}, {730}, {520}, {310} and {410} bulk surfaces.

Further, we analyse the dangling bond states of surfaces by consideration of surface composition. Here, interior atoms whose coordination number is 12 are not contributive for the dangling bond density. Therefore, the surface dangling bond density of a nanocrystal of diameter d with a given structure can be written in the form

$$\rho = \frac{ad^2 + bd + c}{d^2} = a + bd^{-1} + cd^{-2}, \qquad (6)$$

where three terms represent surface contributions from facets, edges, and vertices, respectively. Here, the parameter a is the dangling bond density of the bulk surface and describes the dangling bond state of the surface when the diameter is infinitely large. We use Eq.(6) to fit the density–diameter relationship depicted in Fig.3 by using least squares method, and present the fitted results in Table 1.

It may be seen from this table that the parameter a is ordered according to {210} > {730} > {520} > {310} > {410}. The same order is presented for the parameter b, which reflects the contribution from the edge atoms of a nanocrystal. This indicates that the edge of the {210} surface possesses the highest dangling bond density in all high index surfaces considered in this paper. The parameter c reflects the contribution from the vertice atoms of nanocrystal. In fact, the number of these atoms and the total number of their dangling bonds are independent of nanocrystal size, resulting in remarkable effects on the fitted parameter c at small sizes. We eliminate this effect on

the fitting process by ignoring the data points of small diameter nanocrystals and obtain the fitted results of parameter c, as shown in Table 1. This parameter is between 4.7 and 4.8, and is closely associated with the Miller index of facets.

Table 1. The fitted values of three parameters in Eq.(6).

surface	a/nm^{-2}	b/nm^{-1}	c
{210} facet	58.31672	9.71665	4.74341
{310} facet	57.73061	8.80793	4.35524
{410} facet	56.92803	7.64456	3.75731
{520} facet	58.07528	9.27796	3.90858
{730} facet	58.21609	9.62042	3.78185

4. Conclusions

Platinum nanocrystals of unusual tetrahexahedral shape, which may improve the efficiency of chemical processes such as those used to catalyze fuel oxidation and produce hydrogen for fuel cells, have prompted strong interest in their characterization and properties. Surface characteristics are crucial to understand the thermodynamic and chemical process of these nanocrystals. In this paper, we have used a molecular static approach with a Q-SC many-body potential to study the surface energetic and bonding characteristics of tetrahexahedral platinum nanocrystals enclosed by high-index facets such as {210}, {310}, {410}, {520} and {730}. We have investigated the dependence of the surface energy and dangling bond density on crystal size and surface Miller index. The results show that the surface energy and dangling bond density increase with decreasing Pt nanocrystal diameter and present generally an order of {210} > {730} > {520} > {310} > {410}. However, this order is invalid at crystal sizes below 7 nm or so because surface characteristics are significantly affected by the structural relaxation of the nanocrystal. It would be interesting to further investigate the surface characteristics of fully-relaxed nanocrystals such as surface structures and atomic bonding at small crystal sizes, which needs our study in the future.

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