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STUDY ON THE STRUCTURES OF SUPPORTED NANOCLUSTERS ON PT(111) SURFACE UNDER A MICROSCOPE TIP

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The manipulation of a single atom by a tip is a well-studied and effective means to fabricate supported nanostructures. However, in practice, atom-by-atom manipulation adds complexities and difficulties. We propose a method for obtaining different structures of supported nanocluster by placing the tip at a certain height above the cluster. Pt-supported nanoclusters can be changed to a three-dimensional structure. Analysis of nearest neighbor bonds is used to explain the change.

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Keywords: Supported cluster, Structure, Tip, Metal surface

1. Introduction

Supported nanoclusters are the foundation of many nanodevices, such as the quantum dot laser [1] and the nanogratings [2], which prompted a plethora of theoretical and experimental studies in the strucures of supported clusters. Among the methods in practice, the single-atom manipulation by tip is used and studied as its advantage in the atomic precision. This method, first introduced by Eigler et al, moved an atom by vertical and lateral manipulations and first realized with scanning tunneling microscope (STM) tip in the experiment in 1990 [3-10]. For nonconductive surfaces, the atomic force microscope (AFM) can also achieve the manipulation with atomic precision [11-12]. A shortcoming of the method is that in the construction of a cluster with certain structure, every atom is in a different environment, which causes the different path and manipulation parameters for each atom [13]. To overcome these difficulties in practical experiments, we studied the structure of supported nanocluster under a fixed tip.

2. Methods

As illustrated in Fig. 1, the system studied is a tip and a nanocluster supported on a slab. The substrate is a 15-layer (111) slab, and each layer contains 20 × 20 atoms. Periodic boundary conditions are imposed in the XY plane, with the periodic vectors $\vec{a}_1, \vec{a}_2$ (see Figure1). The size n of the supported nanocluster ranges from 2 to 39 atoms. The tip is composed of four (111) layers, with a single-atom apex. In the study, the tip and the bottom four layers of the slab are fixed, to mimic a rigid tip and a semi-infinite slab. The Z component deduced from the distance between

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the tip apex atom and the surface is defined as the tip height H.

We investigate the metal system of Pt. The method used to obtain the optimal structure employs the genetic algorithm [14-15] method and the conjugate gradient method, with semi-empirical potentials to describe the interaction between atoms. This semi-empirical method enables more atoms to be calculated, which is quite expensive for the first principle method. To obatin better accuracy,we choose potentials that can describe well the atomic interactions in the surface environment. The semi-empirical method used for Pt system is the surface-embedded atom method (SEAM) potential given by Haftel and Rosen [16-17].

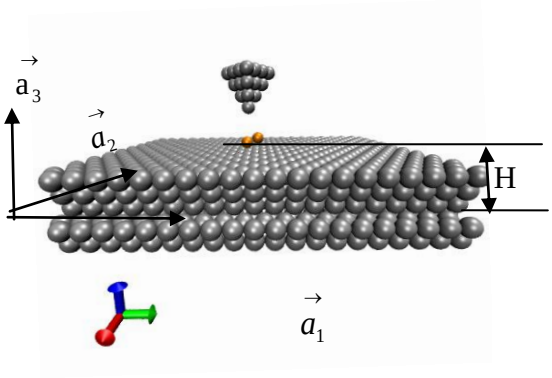


Fig. 1 Simulation model composed of tip, nanocluster, and substrate. The periodicity is determined by vectors $\vec{a}_1$ *and* $\vec{a}_2$ *parallel to the surface. The tip is placed above the supported nanocluster.*

3. Results and discussions

If the tip is sufficiently high above the surface, the tip-adatom interaction is almost negligible and the optimal structure of the supported nanocluster is a two-dimensional structure with close-packed arrangement and maximum nearest neighbor (NN) bonds. If the tip is lower in height, this nanocluster is of a different structure.

Consider a supported nanocluster with six adatoms (Fig. 2). For a tip height larger than 6.4 Å, the supported nanocluster forms a regular triangular shape, with adatoms adsorbed at fcc sites. the supported nanocluster is in the regular triangular shape, with adatoms adsorbed at the fcc site.For tip heights smaller than 6.4 Å, the supported nanocluster is a three-dimensional structure. As the change derives from the interaction between the tip and other atoms and the tip-surface distance is beyond the cutoff distance of the potential, we focus on the tip-adatom interaction in the study. In the three-dimensional structure, he tip-adatom interaction is sufficiently strong to displace one adatom from the surface and the other five adatoms from their fcc sites.

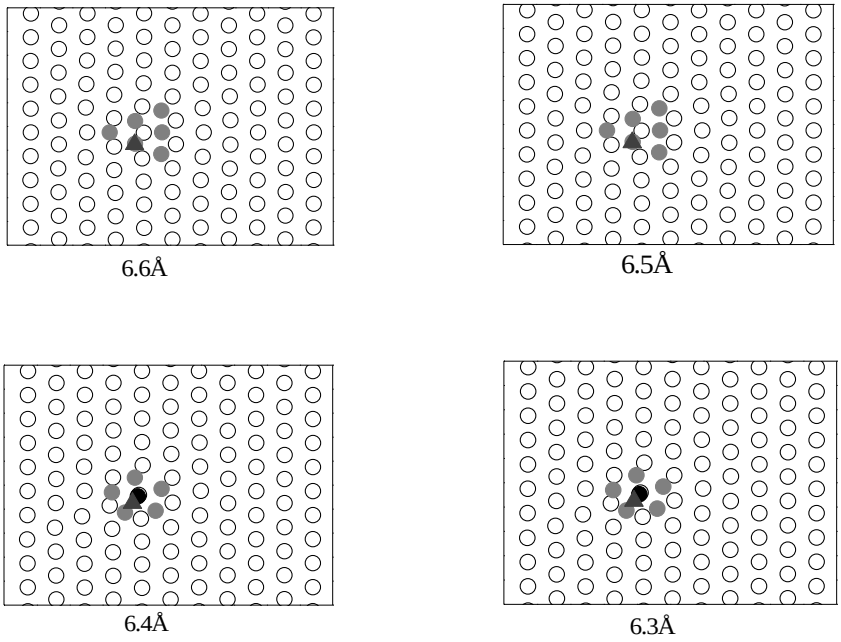


Fig. 2 Supported nanocluster structures with tip apex above the fcc site: (a) XY plane images for different tip heights; (b) three-dimensional images of two structures. The circles represent the surface atoms, the dark dots represent adatoms, the black dots represent the adatom displaced from the surface and the triangle represents the tip apex atom.

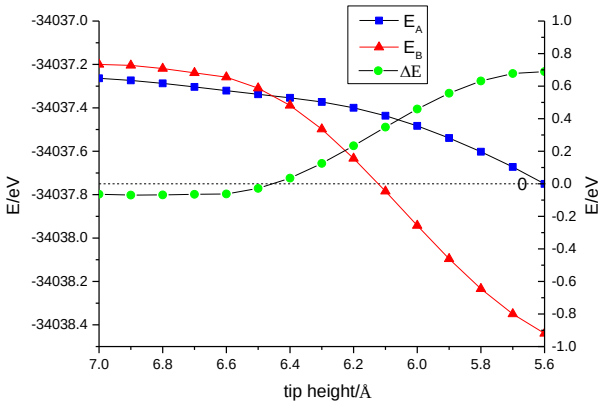
The number of NN and next-NN (NNN) bonds can provide a rough estimate of the energy of the system. From Table 1(a), at tip height smaller than 6.4Å, structure B (the three-dimensional structure) has one extra NN bond than structure A (the regular triangle structure) for tip heights smaller than 6.4 Å. The height 6.4Å is the threshold height for the system. Table 1(b) lists the number of NN bonds between the tip and the adatoms for structure A and B. For the three-dimensional and two-dimensional structures, the number is one and zero, respectively. The adatom-tip interaction is enhanced and forms a NN bond, which forces a change in the number of NN bonds of the system. As shown in Table 1(c), the energy of the two structures decreases as the tip height decreases. The increase of the slope of structure B at 6.5Å can be explained by the small distance between the adatom displaced from the surface and the tip apex atom at about less than 2.0Å. The slope of structure B with smaller atomic distance is larger than the slope of structure A for tip heights smaller than 6.5 Å. The energy difference between the two structures becomes larger as tip height decreases, with structure B having the lowest energy at tip heights smaller than 6.4 Å.The value of the energy difference, such as 0.7eV at 5.6Å, indicates the structure is robust against disturbances such as thermal diffusion of atoms.

tip heihgt structure	6.6(Å)	6.5(Å)	6.4(Å)	6.3(Å)
A	1208	1208	1208	1208
B	1208	1208	1209	1209
ΔE	-0.062	-0.028	0.035	0.13

(a)

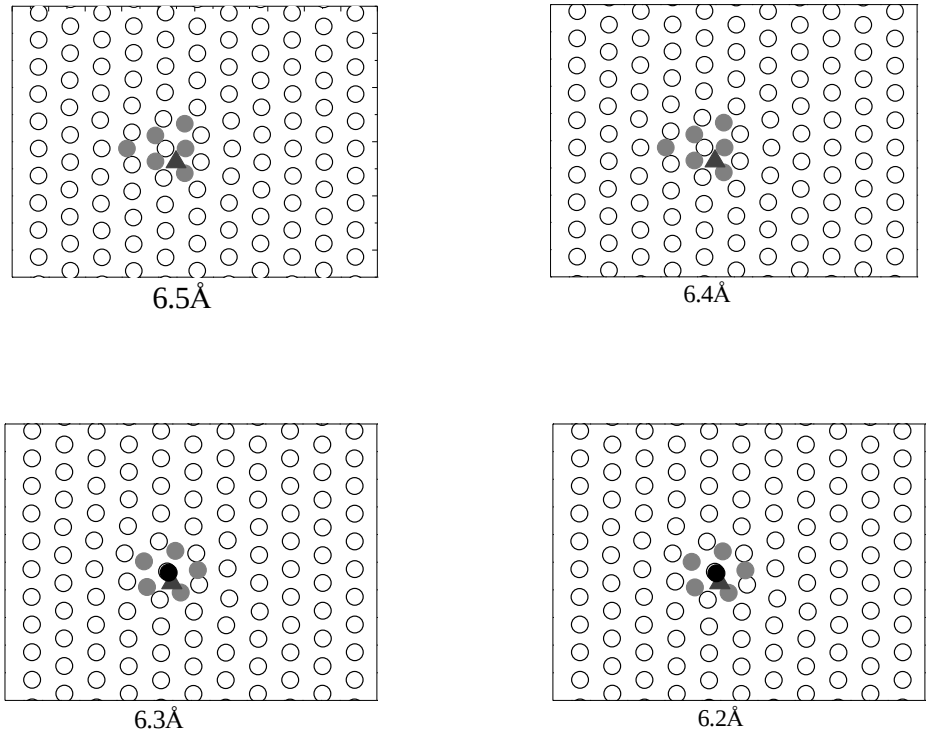
tip heihgt structure	6.6(Å)	6.5(Å)	6.4(Å)	6.3(Å)
A	0	0	0	0
B	0	0	1	1

(b)

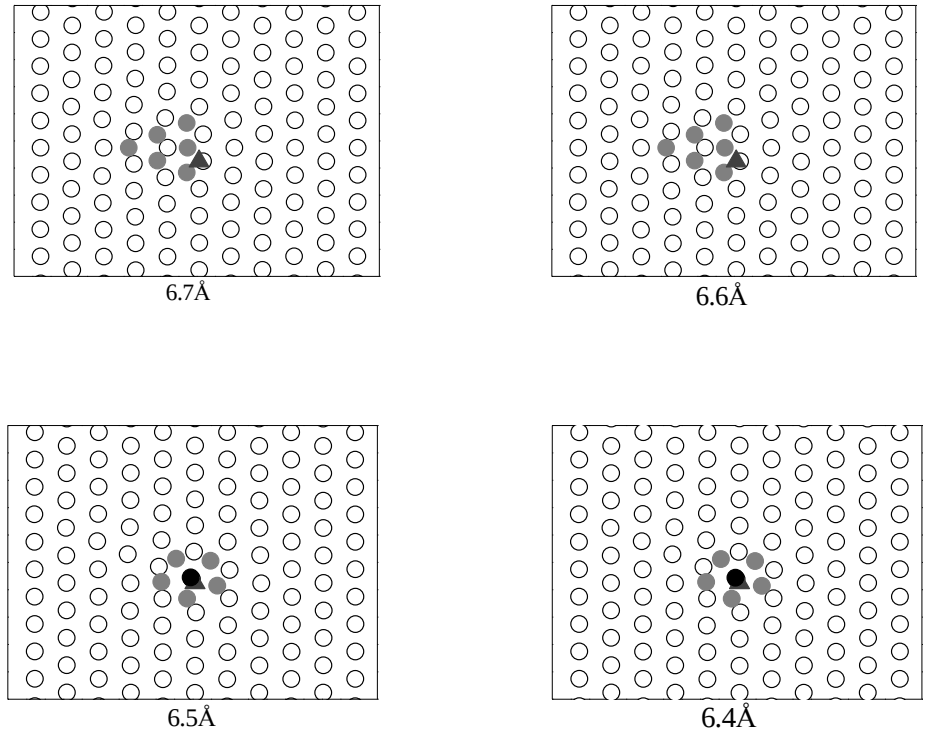


(c)

Table 1. Number of NN bonds for the regular triangular shape structure (A) and the three-dimensional structure (B). (a) gives the number of the NN bonds of the system and (b) the number of the NN bonds between cluster and tip, (c) tip-height dependence of energy for the two structures and energy difference $\Delta E = E_A - E_B$.



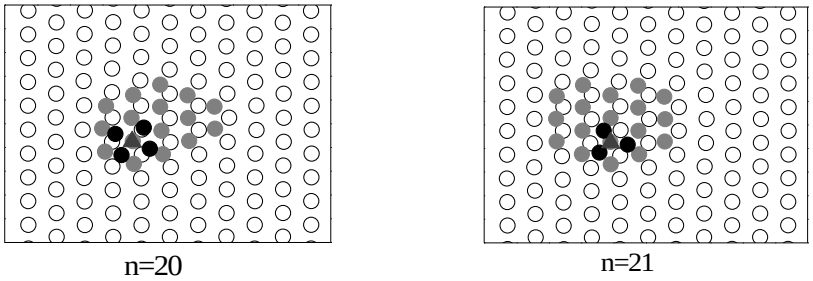
(a)

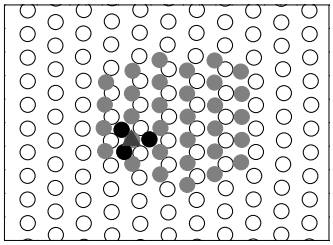


(b)

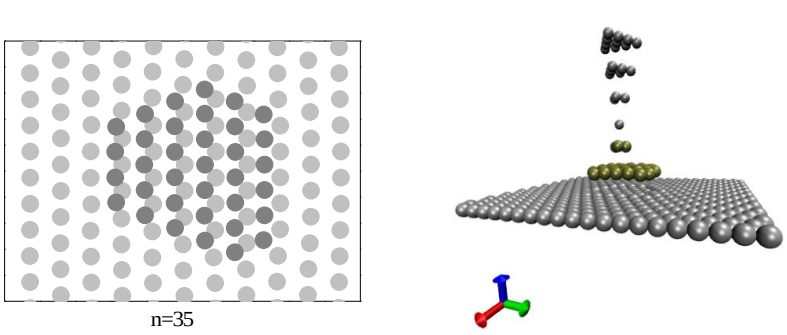
Fig. 3 .The XY plane images for different tip heights. The tip apex atom of (a) is above the hcp site and the tip apex atom of (b) is above the atop site.

As shown in Fig. 3, While the tip-height dependence of the energy is the same, the threshold height differs being 6.4 Å for the tip above a fcc absorption site, 6.3 Å for the tip above a hcp absorption site, and 6.5 Å for the tip above an absorption site. This behavior also applies to supported nanoclusters with more adatoms ($n \leq 35$), as indicated in Fig. 4, with different three-dimensional structures and different tip-height thresholds. As the structure is insensitive to the X and Y components of the tip apex, we obtain for medium-sized clusters ($n \leq 35$) a three-dimensional cluster by simply placing a tip at a lower height.





(a)



(b)

Fig. 4 Supported nanocluster with more adatoms. For tip heights smaller than the threshold value, the structure of the supported nanocluster is three-dimensional. (a) gives XY plane images of three-dimensional supported nanoclusters, the number of adatoms is given beneath each image; (b) is the XY plane image of a two-dimensional nanocluster in the absence of a tip and the three-dimensional image of a three-dimensional supported nanocluster. The nanocluster contains 35 atoms.

In simulations, the change in shape only depends on the mechanical interaction between tip and adatoms. With this means, both STM and AFM are capable of assembling the specific nanocluster structures. There is no essential electric field for the STM tip. The value of the threshold height and its independence of the XY plane parameters also simplify the fabrication of any nanocluster irrespective of structure in actual experiments.

4. Conclusion

Using the genetic algorithm method based on the SEAM potential, we investigated the optimal structure of the supported nanocluster on a Pt(111) surface under the presence of the tip. For tip heights smaller than a certain threshold value, the structure of the supported nanocluster, the three-dimensional structure, is different from that in the absence of a tip. Analysis of NN and NNN bonds explains the change of the lowest-energy structure. As this change is insensitive to the X and Y components of the apex atom of the tip and only depends on tip height and the number of adatoms, compared to single-atom manipulation, this method helps reduce the difficulties in fabricating supported nanostructues.

Acknowledgments

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