Peculiar distribution of Pd on Au nanoclusters: First-principles studies

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Through systematic density-functional calculations, we found that Pd atoms in Au nanoclusters may only take (111) facets while leaving (001) facets with pure Au. This is promoted by the tendency that Pd prefers to form bonds with Au rather than Pd. The segregation from the (001) facet to the (111) facet appears to occur easily. The local activity of Pd is somewhat dependent on the size of cluster and on the site of substitution. The peculiar distribution pattern of the active constituent should strongly alter the chemical properties of bimetallic nanoclusters toward catalyzing reactions.

I. INTRODUCTION

Au-Pd bimetallic nanoparticles are very important catalysts for many chemical reactions such as CO oxidation,[1,2] H_2 oxidation to H_2O_2,[3] alcohol oxidation,[4] and vinyl acetate (VA) synthesis.[5] Most atoms in nanoparticles are exposed to vacuum and their electronic properties are substantially different from those in bulk or surface forms. However, it is still unclear how the two compositions mix in nanoentities and how they perform synergistically in catalytic processes for different reactions. Pd atoms were found to form second neighborhoods on Au(001) and Au(111) surfaces, and appropriate distances between adjacent Pd atoms were assigned as a prime factor for the extremely high reactivity and selectivity of PdAu(001) toward VA synthesis.[5–8] Nevertheless, Pd distribution on small Au facets may not adopt the same mode because of the size reduction. To control the chemical properties of innovative nanocatalysts, it is important to determine the preferential distribution pattern of Pd on PdAu bimetallic nanoparticles.

It is known that in the gas phase Au clusters adopt various extraordinary arrangements such as cuboctahedra, icosahedra, or truncated icosahedra (*Ih*), marks decahedra and truncated decahedra (*Dh*), as well as single or multiple twin face-centered-cubic (fcc) or hexagonal-close-packed (hcp) structures. Typically, small Au clusters adopt icosahedral structures, whereas medium and large Au clusters form decahedral and truncated octahedral structures, respectively.[9] In a recent molecular dynamic simulation, Liu *et al.*[10] found that Pd-Au bimetallic clusters may take icosahedral nanorod, fcc nanorod, and fcc cluster structures, depending on their initial temperature and composition. They also predicted that $Au_{core}Pd_{shell}$ clusters underwent a transition to $Pd_{core}Au_{shell}$ structure above 500 K because of the difference in surface energies of Pd and Au (Ref. 10). Using the aberration corrected electron microscopy, Mejia-Rosales and co-workers[11,12] observed that the final structure of Pd-Au alloyed particles is neither cuboctahedral nor icosahedral but has very rough surfaces with isolated Pd sites surrounded by Au atoms. Very few structural analyses have been reported for supported PdAu nanoparticles. For pure Pd on MgO(001), Rossi and co-workers,[13] and Barcaro[14] found that the transition from the best gas phase structures toward the fcc epitaxial form takes place between sizes 11 to 13. It is perceived that most supported nanoparticles larger than 20–30 atoms adopt their bulklike structure in the core region.

In this paper, we explore the preferential patterns of Pd distribution on Au nanoparticles through systematic density-functional calculations. Significantly, we found that Pd strongly prefers the (111) facets compared to the (001) facets. Furthermore, Pd substituents tend to form second neighborhoods in the central region of the (111) facets, as opposed to separating toward the edge sites on (001) facets. As a result, one may expect essentially no Pd atoms on the (001) facets of Au clusters. This is an important finding for the studies of catalytic properties of nanoparticles, especially for those reactions that rely on the ensemble effects.[5,15–18]

II. COMPUTATIONAL DETAILS

Our modeling clusters were cleaved from fcc bulk Au. We focused on the distribution pattern of Pd in Au facets with different orientations and sizes. To construct the (001) and (111) facets with either (3×3) or (4×4) Au rows, we used Au_{55}, Au_{79}, Au_{92}, and Au_{98} clusters, as sketched in Figs. 1 and 2. The calculations were performed in the framework of density-functional theory (DFT), using the generalized gradient approximation (GGA) for the description of exchange-correlation interaction.[19] The effects of ionic cores were represented by ultrasoft pseudopotentials,[20] as implemented in the Vienna *ab initio* Simulation Package (VASP).[21] To simulate isolated clusters, we used a cubic supercell of 25 Å in each dimension; therefore, the interaction between clusters in the adjacent cells was sufficiently reduced. The energy cutoff for the wave-function expansion was 350 eV; and we used the single $\bar{\Gamma}$ point to sample the small Brillouin zone. Positions of all atoms were fully relaxed under the guidance of the calculated atomic forces with a criterion $F < 10^{-3}$ eV/Å.

The stability of different Pd distribution patterns is characterized by the Pd formation energy defined as

$$E_{Pd} = -[E_{PdAu\text{-}cluster} - E_{Au\text{-}cluster} + N_{Pd}(E_{Au\text{-}atom} - E_{Pd\text{-}atom})]/N_{Pd}. \quad (1)$$

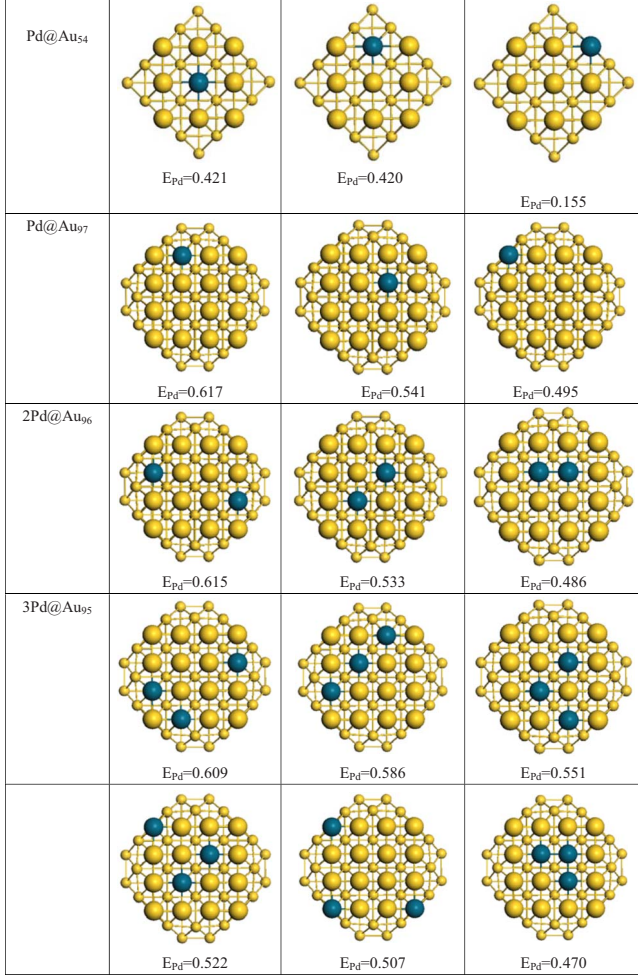Here $E_{PdAu\text{-}cluster}$ and $E_{Au\text{-}cluster}$ are the total energies of PdAu

FIG. 1. (Color online) The selected optimized structures and their formation energies of Pd distribution on (001) facets of Au_{55} and Au_{98}. The yellow (light gray) and blue (dark gray) balls are Au and Pd atoms, respectively.

FIG. 2. (Color online) The selected optimized structures and their formation energies of Pd distribution on (111) facets of Au_{79} and Au_{92}. The yellow (light gray) and blue (dark gray) balls are Au and Pd atoms, respectively.

and pure Au clusters, respectively. We assumed that the reservoirs of Pd and Au are free atoms. Thus the total energies of single Au ($E_{Au\text{-}atom}$) and Pd ($E_{Pd\text{-}atom}$) atoms were used as references in Eq. (1). This equation is different from that defined in our previous surface calculations in Ref. 7, where we assumed that the reservoir for Au is its bulk for the preparation of bimetallic surfaces on metals. Since nanoclusters are mostly fabricated on oxides and the Pd and Au atoms are more likely detached as individual atoms, the definition in Eq. (1) should be more appropriate for studies of nanoclusters. Nonetheless, the values of E_{Pd} from these two definitions differ only by a constant, 2.99 eV. The sequence of energy preference is independent from this artificial choice.

III. RESULTS AND DISCUSSIONS

We first discuss the preferential site of a single Pd atom on the (001) facets, using the Au_{55} and Au_{98} clusters as templates. From the results of E_{Pd} shown in Fig. 1 for the three nonequivalent positions, a single Pd substituent prefers the face center on the Au_{55} cluster but the edge site of the Au_{98}
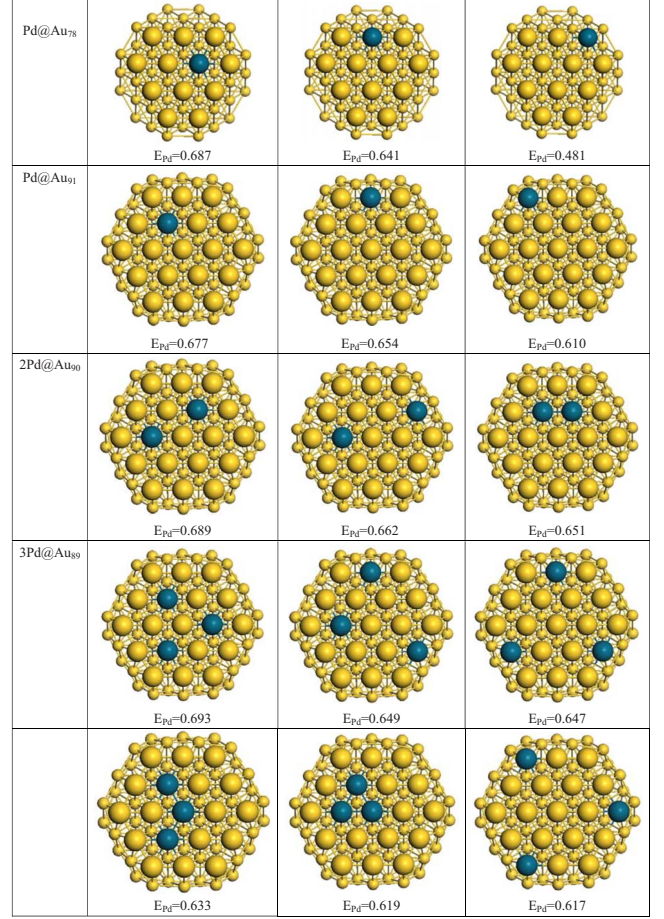
cluster. The corner site is the least preferred site for Pd and the energy difference is as large as 0.266 or 0.122 eV for the two clusters, respectively. This stems from the fact that Pd-Au bonds are substantially stronger than the Au-Au bonds, as discussed in Ref. 7.

For isomers with two and three Pd atoms on the (001) facet of the Au_{98} cluster, we investigated 19 nonequivalent configurations. From the formation energies of representative configurations in Fig. 1, it is clear that Pd atoms tend to separate apart on (001) facets with each Pd taking an edge site. The effective repulsion among Pd substituents on the Au(001) facets is more obvious in the results for isomers with three Pd atoms in Fig. 1. It is interesting that the energies follow the rule,

$$E_{Pd}(N_{Pd}) = [\Sigma E_{Pd}(1) - N_{SN}E_{SN} - N_{FN}E_{FN}]/N_{Pd}. \quad (2)$$

Here the summation is for the contribution of each Pd atom (i.e., E_{Pd} for Pd at Au_{97}). The best fit gives $E_{SN}=0.008$ eV and $E_{FN}=0.110$ eV for each Pd atom, indicating that the formation of Pd second or first neighbor dimer on the (001) facet is unfavorable. This is somewhat different from the results for the PdAu(001) bimetallic surface, where the formation of Pd second neighborhoods is slightly favorable.
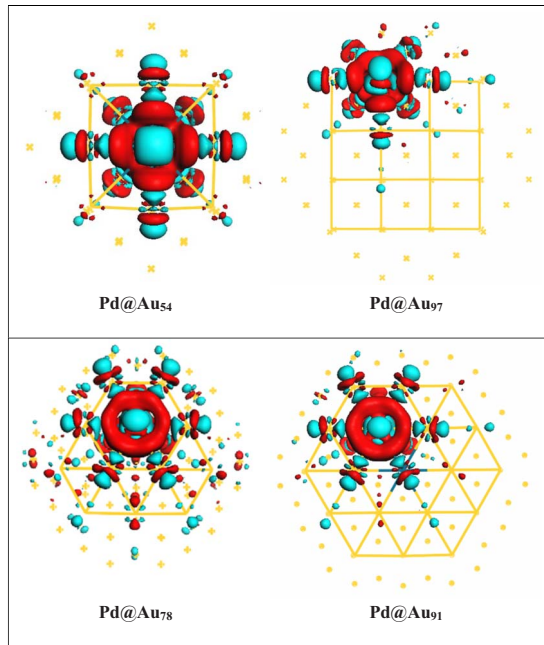
FIG. 3. (Color online) The charge difference $\Delta\rho = \rho_{PdAu} - \rho_{Au} - \rho_{Pd\_atom}$ for the most stable configurations of PdAu$_{54}$, PdAu$_{97}$, PdAu$_{78}$, and PdAu$_{91}$. The red (dark gray) and cyan (light gray) regions represent charge accumulation and depletion, respectively.

The difference obviously results from the size effect.

In contrast to what occurs on the Au(001) facets, the second neighborhood Pd ensembles are preferred on the (111) facet of Au nanoclusters, as was found on the PdAu(111) surface. If we fit the formation energies in Fig. 2 according to Eq. (2), the values of E_{SN} and E_{FN} are about -0.021 and 0.052 eV, respectively. A single Pd atom prefers to be adjacent to the edge of the (111) facets on both Au$_{79}$ and Au$_{92}$ clusters. The corners are still the least favorable sites. The absence of the Pd first neighborhood on PdAu clusters was also observed experimentally.[6] Using CO as the probing molecule, Luo *et al.*[6] identified the isolated Pd sites as a unique surface ensemble on PdAu clusters supported on SiO$_2$. Through TEM observations and molecular dynamics (MD) simulations, Mejia-Rosales *et al.*[12] also found that the most common site on the surface of PdAu cluster comprises a hexagonal array of gold atoms with a Pd atom in the center.

Strikingly, E_{Pd} enhances drastically on Au(111) facets compared to those on Au(001) facets. One may thus envision that the surface Pd atoms gather on the (111) facets whereas the (001) facets are left empty with pure Au on three-dimensional clusters. This process should be easy to occur under ambient condition since Pd prefers the edge sites on (001) facets and is ready to segregate to the central region on the (111) facets with other Pd atoms. The absence of Pd from the (001) facets should have an important impact in the catalytic properties of Pd-Au nanoparticles and thus deserves more careful examinations. One direct approach is to get high-resolution images of bimetallic clusters, a few nanometers in diameter through the scanning tunnel microscope (STM). Indirect explorations using small molecules such as CO may also disclose information about the surface mor-
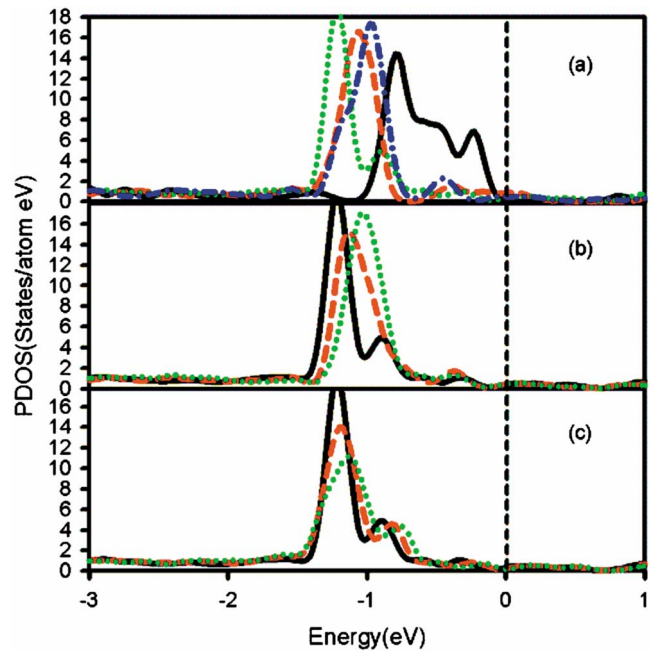

FIG. 4. (Color online) The projected density of states of the Pd d band of (a) a monomer on Au$_{55}$ (black/solid line), Au$_{79}$ [red (gray)/dash line], Au$_{92}$ [green (light gray)/dotted line], and Au$_{98}$ [blue (dark gray)/dash-dot line]; (b) a monomer at the center (black/solid line), edge [red (gray)/dash line], and corner [green (light gray)/dotted line] sites of Au$_{92}$; and (c) a monomer (black/solid line), dimer [red (gray)/dash line], and trimer [green (light gray)/dotted line] on Au$_{92}$.

phology. Experimentally, Chen *et al.* found that the CO stretching frequencies on the annealed PdAu(001) and PdAu(111) surfaces are 2104 and 2088 cm^{-1}, respectively. This provides a signature of surface orientation for experimental exploration for Pd distribution. For more quantitative comparisons, we are working on calculations for CO adsorption energies and for stretch frequencies on different facets, sites, and ensembles on PdAu nanoclusters. Results will be reported elsewhere.

As was discussed in Ref. 7, Pd-Au bonds are somewhat stronger than Pd-Pd and Au-Au bonds because of their ionic feature. Similarly, we plot the charge differences for Pd monomer on Au$_{55}$, Au$_{98}$, Au$_{79}$, and Au$_{92}$ in Fig. 3. The strong ionic bonding is found between Au and Pd sites, and the Pd atoms transfer electrons to the region between Au-Pd in all cases investigated here. Therefore, the argument that the peculiar ionic feature of the heterometallic bond stabilizes the Pd-Au neighborhoods also applies here. In the light of this picture, it is not surprising that surface Pd atoms prefer the Au(111) facets since it has large numbers of Pd-Au bonds [nine Pd-Au bonds on the (111) facets versus eight Pd-Au-bonds on the (001) facets]. On the other hand, the binding energies are also substantially affected by large relaxations near the corner and edge sites. For the PdAu$_{54}$, PdAu$_{97}$, PdAu$_{78}$, and PdAu$_{91}$ clusters, the energy gains through the relaxation from their ideally cleaved geometries are as large as 0.92, 1.96, 2.18, and 3.01 eV, respectively. Typically, the bond lengths are shortened by 2%–3% at the edge and corner sites and such a large relaxation is the prime

factor for the preference of Pd at edge sites on the Au(001) facets, where one Pd-Au bond is missing. Nonetheless, the relaxation effect is not adequate to compensate the loss of two Pd-Au bonds for Pd at the edge sites on the Au(111) facets. Therefore, the relaxation effect is very significant for the determination of surface morphology of nanostructures, especially when the energy difference is small.

On the PdAu bimetallic surfaces, it was found that Pd monomers show atomiclike character with a narrow and fully occupied d band.[7] On PdAu clusters, the electronic properties of Pd atoms should depend on the cluster size and also the location they substitute. To discuss their chemical properties, we present the projected density of states (PDOS) of Pds d states in Fig. 4. Among the parameters, the most striking dependence is on the cluster size. In particular, the DOS curves for Pd on Au_{55} are very broad and also close to the Fermi level. The second robust parameter to tune the DOS feature is the site. The positions of the d-band center for Pd on the (111) facet of Au_{92} are ranged from the lowest as center→edge→corner. The involvement of second neighbors also slightly modifies the DOS curves. It should be noted that the character of Pd d band on Au_{92} or Au_{98} is very close to these on PdAu(111) and PdAu(001) surfaces.[7]

Using CO as the probing molecule, we found that the adsorption energy increases to 1.38–1.55 eV on $PdAu_{54}$ with the edge site Pd being the most active. The CO adsorption energies on $PdAu_{78}$ are 1.26, 1.35, and 1.39 eV for Pd at the center, edge, and corner sites, respectively. Clearly, the ligand effects[22] on bimetallic nanoclusters are strongly enhanced in small clusters. In contrast, individual Pd on large clusters behaves quite similarly to those on flat PdAu surface toward adsorption of CO and the ensemble effects should be the key factor for their catalytic properties for some complicate reactions, e.g., VA synthesis.

IV. CONCLUSIONS

In conclusion, from the density-functional total-energy calculations, we found that Pd may only take the (111) facets of Au nanoclusters while leaving the (001) facet with pure Au. This is supported by the fact that Pd-Au bond is more favorable compared to either Au-Au or Pd-Pd bonds. Since the ensemble effects are crucial for many chemical reactions, such a peculiar distribution pattern of active constituent should have a strong impact on nanocatalysis. For the rational development of bimetallic nanocatalysts, further theoretical studies are needed to address the effects of substrates, temperature, and adsorbates.

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