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## First-principles-based optimization of electronic structures for bimetallic nanoparticles



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### ABSTRACT

Based on the first-principle calculation combined with cluster expansion technique and Monte Carlo statistical simulation, we propose an optimization of local electronic structure in bimetallic nanoparticles. We apply the proposed optimization to Pt-Rh nanoparticles, and find that Pt *d*-band center can be quantitatively described by finite set of basis functions in terms of atomic arrangements. Consequently, electronic structures of Pt *d*-band at specific site can be reasonably controlled by changing surrounding atomic arrangements, which enables systematic changes in molecular adsorption energy.

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### 1. Introduction

Metal nanoparticles have been actively investigated so far for wide range of physical and chemical applications, since they can exhibit significantly different characteristics from corresponding bulk due to high surface-to-volume ratio and finite-size effects [1–5]. In recent years, bimetallic nanoparticles are extensively investigated both theoretically and experimentally, where alloying other elements into metal nanoparticles can significantly enhance the catalytic properties. Recently, theoretical prediction of phase diagrams for alloy nanoparticles has extensively investigated such as phase diagram for Ag-Cu nanoparticles [6] considering their particle size and shape factor, that for Ag-Au nanoparticles [7] where generalized equations for thermodynamic variables are proposed, and that for Cu-Ni nanoparticles [8] further considering chemical composition and melting temperature. For catalytic properties such as molecular adsorption, since they are significantly affected by electronic structures where the corresponding chemical reactions occur, correlations between molecular adsorption and the electronic structures especially at alloy surfaces including transition elements have been actively investigated by density functional theory (DFT) calculations [9–15]. Important information from these calculations is that stability of adsorbates on surfaces is reasonably characterized by the *d*-state

electronic contribution at the surface. Particularly, the *d*-band center of  $\epsilon_d$ , which is defined by the band center of *d*-state contribution measured from the Fermi energy, can be a simple and well-related parameter to describe adsorption energetics. Although such electronic structures at alloy surfaces can be significantly affected by surrounding atomic arrangements, theoretical investigations on how atomic arrangements change the electronic structures at specific sites of bimetallic nanoparticles have been confined to artificially constructed or experimentally reported structures. Very recently, temperature and composition dependence of *d*-band center for bimetallic nanoparticles has been studied by first-principles calculations [16] including configurational effects in bimetallic nanoparticles, while the study does not explicitly address the characteristic relationship between atomic arrangements and electronic structure for the nanoparticles.

In the present study, we propose systematic optimization of electronic structures for bimetallic nanoparticles based on combination of DFT calculation and cluster expansion (CE) technique [17,18], which clarifies the relationship between atomic arrangements and electronic structure at given site: Application of the CE technique to prediction of stable alloy nanoparticles has been successfully performed by our previous studies [19–21]. This enables to effectively find suitable atomic arrangements on the nanoparticle having desirable value of *d*-band center. Applicability of the present optimization is demonstrated for one of the well-investigated system of Pt-Rh nanoparticle for enhanced catalytic property including NO<sub>x</sub> reduction, CO chemisorption,

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and hydrogenation [22,23]: The Pt-Rh nanoparticles are synthesized by variety of experiments such as polyol synthesis, NaY-supported clusters using ion-exchange method, colloid synthesis in polymer solutions using borohydride-reduction, and pulsed laser ablation [1,24–29,22]. We show that  $d$ -band center of Pt atom at vertex site is controllable at any value within the range between  $-2.2$  and  $-1.9$  eV by changing surrounding atomic arrangements, which leads to controlling CO molecular adsorption energy at corresponding site.

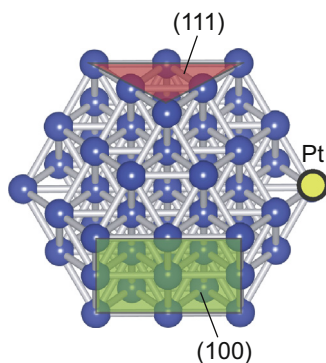
## 2. Methodology

In the present study, we choose Pt-Rh nanoparticles consisting of 55 atoms with cuboctahedron shape, where the 55-atom nanoparticle is considered interesting due to its intermediate size between finite molecules and fully metallic systems [30], and the cuboctahedron shape has been studied based on a semi-empirical model for segregation in  $\text{Pt}_{28}\text{Rh}_{27}$  nanoparticles and is synthesized for 55 Pt atoms [31–33]. Very recently, we have comprehensively investigated energetic stability of the Pt-Rh nanoparticles in cuboctahedron shape, where strong dependence of segregation on composition of the nanoparticle is found [19–21]. Here we focus on the electronic structure for single Pt atom at vertex site in  $\text{Pt}_{28}\text{Rh}_{27}$  nanoparticles, and consider the changes in atomic arrangements for the rest 54 sites. Fig. 1 shows the cuboctahedron nanoparticle having (111) and (100) surfaces of underlying fcc lattice, and the vertex site where a Pt atom occupies is represented by a yellow circle.

The CE technique is applied to express the  $d$ -band center of the single Pt atom at vertex site in terms of the surrounding atomic arrangements  $\vec{\sigma}$ , which is given by

$$e_d^{\text{Pt}}(\vec{\sigma}) = \sum_{\alpha} V_{\alpha} \left\langle \prod_{i \in \alpha} \sigma_i \right\rangle, \quad (1)$$

where  $\alpha$  means cluster consisting of a set of sites  $i$  on the cuboctahedron nanoparticle other than a vertex site of interest,  $V_{\alpha}$  represents expansion coefficient called “effective cluster interaction” (ECI) for cluster  $\alpha$ ,  $\sigma_i$  is a pseudospin variable that takes  $+1$  ( $-1$ ) when site  $i$  is occupied by Pt (Rh) atom, and  $\langle \rangle$  means average over all clusters that are symmetry-equivalent to cluster  $\alpha$  on the nanoparticle. The summation is taken over all symmetry-nonequivalent clusters in the nanoparticle other than a vertex site. Great advantage to use CE is that since a set of  $\langle \prod_{i \in \alpha} \sigma_i \rangle$ , called “cluster function”, is a complete and orthonormal basis function to express any scalar property in terms of atomic arrangement,  $e_d^{\text{Pt}}$  can be reasonably described by a function of surrounding atomic arrangements when we can successfully obtain accurate ECIs. In order to determine the



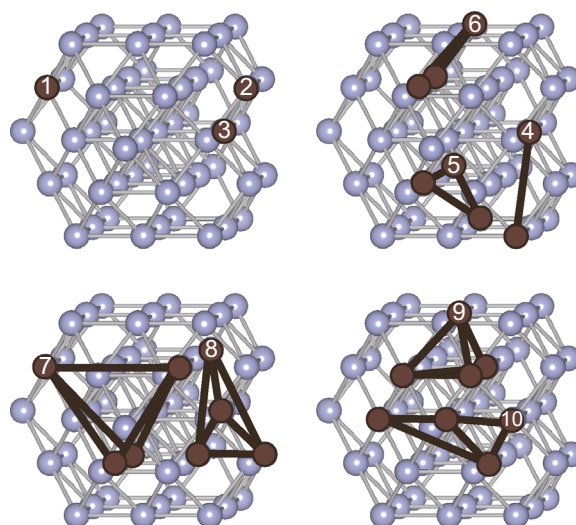
**Fig. 1.** 55-atom cuboctahedron nanoparticle used in the present study, which have (111) and (100) surfaces of underlying fcc lattice.  $d$ -band center of single Pt atom at a vertex site is focused on, which is represented by a yellow circle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ECIs,  $e_d^{\text{Pt}}$  is calculated for ordered structures through first-principles calculation, which are least-square fitted to the CE expression of Eq. (1). The first-principles calculations are employed using a DFT code, the Vienna *Ab-initio* Simulation Package (VASP) [34,35]. We estimate  $e_d^{\text{Pt}}$  for 140 ordered structures in 55-atom cuboctahedron nanoparticle. The 55-atom nanoparticle is put in cubic cell with each side of 2 nm, which is confirmed to be sufficient in terms of cell-size dependence of total energy. All-electron Kohn-Sham equations are solved by employing the projector augmented-wave (PAW) method [36,37], within the generalized gradient approximation (GGA) of Perdew-Wang 91 form to exchange-correlation functional [38]. A plane-wave cutoff energy is set at 360 eV throughout the present calculations. Brillouin zone integration is performed on the basis of the Monkhorst-Pack scheme [39] with an  $1 \times 1 \times 1$   $k$ -point mesh. Geometry optimization is performed until the residual forces become less than 1 meV/Å. For the practical application of the cluster expansion, there should be limitation of the number of clusters that are used for the expansion due to limitation in the number of DFT input energies. Details of how to select clusters and structures are described in our previous paper [40–42]. In brief terms, we select an optimal set of the clusters based on the genetic algorithm in order to minimize the uncertainty of predicted  $e_d^{\text{Pt}}$  by the ECIs, which is called a cross-validation (CV) score.[43] An optimal set of input structures are chosen so that resultant ECIs can predict higher as well as lower values of  $e_d^{\text{Pt}}$  [44]. For calculation of CO adsorption energy, a single CO molecule is initially placed on the top site of Pt atoms, and then, structure optimization is performed with the same calculation condition for isolated Pt-Rh nanoparticle as describe above.

## 3. Results and discussion

Following the procedure described in Sec. II, we determine eleven clusters consisting of one empty, three point, one pair, two triplet, and four quartet clusters, which is illustrated in Fig. 2. It is clear from Fig. 2 that band center of electronic density of states for Pt atom,  $e_d^{\text{Pt}}$ , is not simply determined by neighboring on-site contributions (i.e., cluster no. 2 and 3), and multi-site contributions near and far from the Pt atom site also contributes to the band center. These clusters give a CV score of 0.002 eV, which is sufficiently accurate to express relative  $e_d^{\text{Pt}}$  for ordered structures in the Pt-Rh nanoparticle. More quantitative contribution from individual clusters can be seen from the corresponding ECIs for point and multibody clusters, which are shown in Fig. 3.

It is clear from Fig. 3 that dominant contribution to  $e_d^{\text{Pt}}$  comes from ECIs for cluster no. 2 and 4, both exhibiting large positive value: The former means that when Rh atom is located at neighboring “edge” sites (i.e., cluster no. 2 and its symmetry-equivalent sites) to the Pt atom,  $e_d^{\text{Pt}}$  tends to move down from Fermi



**Fig. 2.** Dark circles and those connected with bold lines respectively denote optimized point and multibody clusters used in cluster expansion for  $d$ -band center. Vertex site where a Pt atom of interest occupies is omitted.

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