



Research paper

First-principles prediction of supported metal nanoparticle structures based on Wulff–Winterbottom construction

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ABSTRACT

Structures of metal nanoparticles in vacuum and on oxide supports were predicted by combining first-principles calculations with the Wulff theorem and its Winterbottom construction. For nanoparticles in vacuum, (111) and (100) facets were exposed for small nanoparticles, and high-index facets emerged as the size increased, which correlates with the stability of each facet relative to the (111) facet. For supported nanoparticles, interface energies reduce the distance from the particle center to the interface compared with vacuum nanoparticles, leading to an expansion of the surface area of the stable interface facet. These results enable realistic morphology prediction of supported nanoparticles within a first-principles Wulff–Winterbottom framework.

1. Introduction

In heterogeneous catalysis, well-defined metal surfaces and metal nanoparticles are employed as catalysts [1–3]. Metal nanoparticles provide a large surface area per unit mass, making them highly effective as catalysts. [4] Their catalytic utility arises not only from their large surface area but also from their structural characteristics. Bulk metals possess a crystalline structure in which metal atoms are periodically and regularly arranged. Crystal facets appear at the termination of the crystal, and the exposed facets vary depending on the orientation and cleavage of the crystal. Distinct catalytic activities have been reported for different crystal facets [5,6]. While well-defined metal surfaces typically expose a single facet, metal nanoparticles present multiple facets simultaneously. Structural information of metal nanoparticles, namely which facets are exposed and to what extent, is essential for interpretation, prediction, and enhancement of their catalytic behavior.

Although geometry optimization calculations of metal nanoparticles have been performed as a theoretical approach [7,8], their high computational cost remains a significant limitation, particularly for large systems. The Wulff theorem [9] provides an alternative approach to predict the thermodynamic equilibrium structures of metal nanoparticles in vacuum without full geometry optimization, based on the assumption that the surface energies of nanoparticles are equivalent to

those of well-defined surfaces. Wulff construction has been applied to the structure prediction of metal nanoparticles under particular gas conditions [10–12] and evaluation of catalytic performance through the estimation of exposed facets [13,14].

In practical catalysts, metal nanoparticles are typically supported on metal oxides for anchoring and dispersing the metal nanoparticles, preventing sintering. Moreover, the presence of the support induces changes in their electronic structure through interactions between metal nanoparticles and support, and also includes structural changes [15–18]. The Winterbottom construction, an extension of the Wulff theorem, predicts the thermodynamic equilibrium structures of supported metal nanoparticles by incorporating particle–support interactions [19]. Winterbottom construction has been utilized in structure prediction of supported metal nanoparticle and catalytic activity assessments [20,21].

For catalyst design, elucidating how metal species and supports influence nanoparticle structures is crucial for understanding catalytic properties. Although the Wulff theorem and Winterbottom constructions provide a theoretical framework for determining exposed facets, their practical application remains limited because interface energies between metal nanoparticles and supports are difficult to determine experimentally. Previous theoretical studies have attempted to evaluate such energies, but they are often restricted to small models or simplified

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approximations [20,22]. In the present study, we address this limitation by evaluating surface and interface energies using large-scale first-principles calculations and applying them to the Wulff–Winterbottom framework for structure prediction. In particular, we treat the interface contribution within the Winterbottom construction as an effective “pseudo-surface energy” for practical structure prediction. This approach enables systematic analysis of structural variations arising from differences in the metal species, support materials, and exposed facets. For metals, Rh and Pd, and for metal oxides, rutile TiO₂ or α -Al₂O₃, and MgO were employed. By combining large-scale density functional theory calculations with the Winterbottom construction, we demonstrate that realistic morphology prediction of supported metal nanoparticles becomes feasible.

The remainder of this paper is organized as follows. Section 2 describes the theoretical aspects, where the explanation of Wulff theorem and its expansion by Winterbottom, and computational details are explained. Section 3 presents results and discussion of structure of metal nanoparticles in vacuum and supported on metal oxides. Finally, Section 4 concludes this paper.

2. Theoretical aspects

2.1. Structure prediction of nanoparticles

Wulff theorem [9] provides a method to predict the structure of nanoparticles in vacuum. A crystal in thermodynamic equilibrium takes a structure such that the total surface energy of exposed surfaces is minimized under constant volume:

$$\frac{h_{hkl}}{\gamma_{hkl}} = \text{const.} \quad (1)$$

where h_{hkl} is the distance from the center of the crystal to the (hkl) facet, and γ_{hkl} is the surface energy of the (hkl) facet per unit area. The equilibrium shape of the crystal satisfies that the surface energy of each surface is proportional to the distance from the center of crystal to the (hkl) facet. The effects of edges and corners are neglected in this theorem. A local analysis is important to properly assess these effects. Assuming that the surface energies of well-defined metal surfaces are equivalent to those of metal nanoparticle facets, the structure of metal nanoparticles in vacuum can be predicted by calculating the surface energy of well-defined metal surfaces.

The extension of the Wulff theorem to supported metal nanoparticles was proposed by Winterbottom [19]. A single-crystal particle supported on a substrate satisfies the following relation:

$$\frac{h_{hkl}}{\gamma'_{hkl}} = \text{const.} \quad (2)$$

where γ'_{hkl} is given by

$$\gamma'_{hkl} = \begin{cases} \gamma_{PV} = \gamma_{hkl} \\ \gamma_{SP} - \gamma_{SV} = \gamma_{hkl}^* \end{cases} \quad (3)$$

where γ_{PV} is the interfacial energy between particle and vacuum, γ_{SP} is the interfacial energy between particle and substrate, and γ_{SV} is the interfacial energy between substrate and vacuum. The first term in Eq. (3) corresponds to the energy in contact with vacuum, whereas the second term in Eq. (3) corresponds to the interface with the substrate. For metal nanoparticles supported on oxide, γ_{PV} corresponds to the metal surface energy and γ_{SV} corresponds to the oxide surface energy. The quantity γ_{hkl}^* can be interpreted as an effective surface energy of the facet in contact with the support, and is hereafter referred to as a pseudo-surface energy. Assuming that the interfacial energy is independent of nanoparticle size, the structure of supported nanoparticles can be predicted within this framework.

2.2. Method for energy calculation

Surface and pseudo-surface energies of well-defined surfaces were calculated using first-principles methods and used to predict nanoparticle structures for several systems. Rh and Pd as metal, and as supporting metal oxide, rutile TiO₂, α -Al₂O₃, and MgO were used.

Cohesive energy, E_{coh} , is given by the following formula.

$$E_{\text{coh}} = \sum E_{\text{free}} - \frac{E_{\text{bulk}}}{N_{\text{bulk}}} \quad (4)$$

where E_{free} is the energy of one atom, E_{bulk} is the total energy of bulk model, N_{bulk} is the number of atoms in the bulk model.

The surface energy per unit area of a well-defined surface, γ_{hkl} , is calculated as

$$\gamma_{hkl} = \frac{E_{\text{slab}} - N_{\text{slab}}\epsilon_{\text{bulk}}}{2S_{\text{slab}}} \quad (5)$$

where E_{slab} is the total energy of slab model, N_{slab} is the number of atoms in slab model, ϵ_{bulk} is the energy of bulk model per atom, and S_{slab} is the surface area of slab model surface.

The interfacial energy is derived from the layered bulk models consisting of alternating metal and oxide regions, shown in Fig. S1. The interfacial formation energy, E_f , is obtained by subtracting the energies of the corresponding bulk models from that of the layered system, which is given by the following equation:

$$E_f = E_{\text{SP}} - N_S\epsilon_{\text{bulk-S}} - N_P\epsilon_{\text{bulk-P}} \quad (6)$$

where E_{SP} is the total energy of layered bulk model, N_S is the number of metal oxide molecules in layered bulk model, $\epsilon_{\text{bulk-S}}$ is the energy of metal oxide bulk model per molecule, N_P is the number of metal atoms in layered bulk model, and $\epsilon_{\text{bulk-P}}$ is the energy of metal bulk model per atom. The interfacial formation energy includes both interfacial and strain contributions arising from lattice mismatch. The interfacial energy per unit area, γ_{SP} , was extracted by linear fitting [23,24] to separate the strain contribution:

$$\frac{E_f}{N_{\text{SP}}} = \frac{2S_{\text{SP}}\gamma_{\text{SP}}}{N_{\text{SP}}} + \zeta \quad (7)$$

where N_{SP} is the number of atoms in layered bulk model, S_{SP} is the surface area of the interface in layered bulk model, and ζ is the strain energy per atom in layered bulk model. Interfacial and strain contributions are separated by analyzing E_f/N_{SP} as a function of $1/N_{\text{SP}}$. The slope of the linear fit yields the interfacial energy, whereas the intercept provides the strain energy. The layered bulk models were constructed to minimize lattice mismatch between metal and metal oxide bulk: details are shown in Table S1.

2.3. Computational details

Density functional theory (DFT) calculations were performed using CONQUEST code [25–27] and Vienna Ab initio Simulation Package (VASP) [28–31]. Some surface energies were calculated using both CONQUEST and VASP, while the others were evaluated using only CONQUEST due to computational cost. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [32] was used with Hamann’s optimized norm-conserving Vanderbilt Pseudopotential [33] and pseudo atomic orbital (PAO) basis set in CONQUEST, and with a projector augmented wave (PAW) pseudopotential and plane wave basis set for VASP. A PBE standard PAW potential was employed, with the semi-core p states of Rh and semi-core s and p states of Ti were treated as valence states. Double- ζ plus single polarization (DZP) PAO basis sets were employed, with the radii listed in Table S2. Spin polarization was not considered in this study.

In CONQUEST calculations, cutoff energy for the charge density was set to 70 Ha for Rh, 80 Ha for Pd, 120 Ha for rutile TiO₂, 140 Ha for

α -Al₂O₃, and 130 Ha for MgO. In VASP calculations, the cutoff energy for plane wave basis set was set to 500 eV for Rh and Pd, 700 eV for MgO, 800 eV for rutile TiO₂, and 850 eV for α -Al₂O₃. For CONQUEST calculations, Monkhorst–Pack k-point meshes of $8 \times 8 \times 8$ were used for Rh and Pd bulk structures, $5 \times 5 \times 5$ for rutile TiO₂ and MgO, and $7 \times 7 \times 7$ for α -Al₂O₃. For VASP calculations, $5 \times 5 \times 5$ for rutile TiO₂ and MgO, $7 \times 7 \times 7$ for α -Al₂O₃, $9 \times 9 \times 9$ for Rh, and $10 \times 10 \times 10$ for Pd. For other structures, k-point meshes were chosen inversely proportional to the system size. In CONQUEST, ghost atoms were introduced in the slab models to improve the description of electronic states extending outside the surface region. Atoms of the same species were employed as ghost atoms and placed in two additional layers outside the surface. For geometry optimizations in CONQUEST, we used the conjugate-gradient method for bulk structure, and quasi-Newton method for the other structures. For layered bulk models of Rh/MgO, the multi-site method in CONQUEST was employed with a cutoff radius of 13.0 bohr.

3. Results and discussion

3.1. Surface energy

Cohesive energies of Rh, Pd, rutile TiO₂, α -Al₂O₃, and MgO were calculated by both CONQUEST and VASP for evaluating the accuracy, and are shown in Fig. 1. The horizontal axis represents the experimental values [34–37] and the vertical axis represents the calculated values. Orange, blue, and green represent CONQUEST, VASP, and previous results [38–41], respectively. Red line represents perfect agreement between experimental and calculated values.

To accurately evaluate cohesive energies using localized orbital basis sets, isolated atoms require more delocalized basis functions than bulk systems because of their spatially extended electronic tails. In contrast, such tail regions are much less important in bulk solids, where the electronic states are embedded in a periodic environment. Therefore, we employed triple-zeta triple-polarization (TZTP) PAOs for isolated atoms and double-zeta plus polarization (DZP) PAOs for bulk systems, as

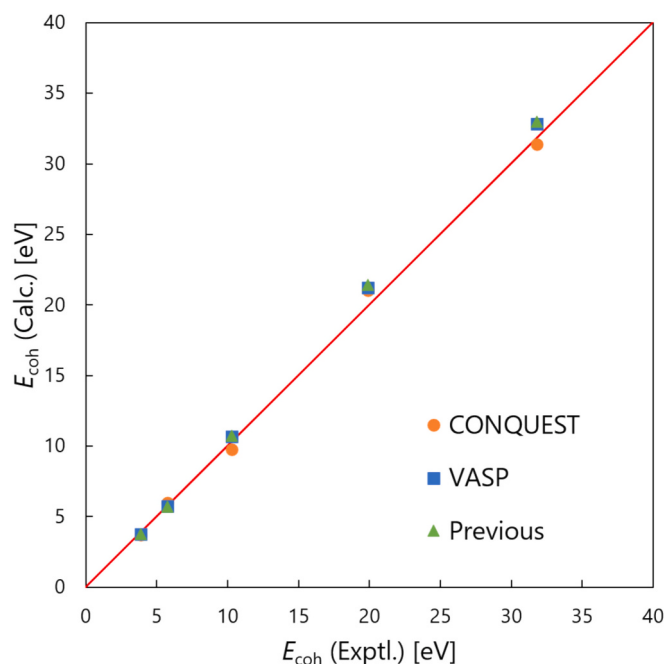


Fig. 1. Comparison of cohesive energies with experimental values. Orange, blue, and green correspond to results of CONQUEST, VASP, and reference values, respectively. Red line represents perfect agreement between experimental and calculated values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

summarized in Table S2. To assess the uncertainty associated with this mixed basis-set treatment, additional calculations using both DZP and TZTP basis sets for the bulk systems were performed, and the results are summarized in Table S3. Although the use of DZP basis sets for both isolated atoms and bulk systems leads to relatively large deviations from the TZTP/TZTP results, the deviations introduced by using DZP only for the bulk systems are much smaller. In particular, the largest deviation in the average cohesive energy per atom is only 0.160 eV, supporting the use of the DZP basis set for bulk calculations and, consequently, for the surface energies evaluated from these bulk reference energies.

These results support the use of the DZP basis set for bulk calculations and, consequently, for the surface energies evaluated from these bulk reference energies. With this basis-set combination, the cohesive energies obtained by CONQUEST are in excellent agreement with both the experimental data and the VASP calculations, confirming the reliability of the present computational setup.

Fig. 2 shows the ratio of surface energy of each facet to that of (111) facet. The horizontal axis represents the VASP values and the vertical axis represents the CONQUEST values. Red line represents perfect agreement between VASP and CONQUEST values. Panels (a) and (b) correspond to Rh and Pd, respectively. The comparison of the VASP values with the previous VASP calculations are shown in Fig. S2. Fig. 2 indicates good correlation between the VASP and CONQUEST values. Comparing Rh and Pd, the surface energy ratios relative to the (111) facet exhibit a narrower range for Pd, reflecting smaller energetic differences among the facets.

The surface energies of the metal oxide supports calculated using CONQUEST and VASP are summarized in Table 1. Assuming that metal nanoparticles are supported on the facet with the largest exposed area, only the surface energy of the most stable facet was calculated. To ensure charge neutrality, O-terminated surfaces were chosen for rutile TiO₂, and Al-terminated surfaces were selected for α -Al₂O₃. The results obtained using CONQUEST and VASP are in good agreement with the previously reported values.

3.2. Structure of metal nanoparticles in vacuum

Fig. 3 illustrates the structures of (a) Rh and (b) Pd nanoparticles in vacuum obtained using surface energy ratios calculated by VASP. The distance from the center of nanoparticles to the (111) facet, h_{111} , was varied from 0.3 to 50 nm (0.3, 1.5, 3.0, 10, and 50 nm from left to right). The corresponding structures obtained using CONQUEST are presented in Fig. S3. Both Rh and Pd nanoparticles adopted truncated octahedral structures. As the size of nanoparticles increased, additional facets appeared at the edges and corners. Pd exhibited a greater variety of facets exposed at the edges than Rh.

The distributions of surface areas of exposed facets are shown in Figs. 3 (c) Rh and (d) Pd. The horizontal and vertical axes represent h_{111} and the distribution of surface areas, respectively. For small nanoparticles, only (111) and (100) facets are exposed, whereas additional high-index facets emerge at the edges and corners with increasing size. The types of exposed high-index facets depend on the metal. For Rh, the exposed facets are (311), (331), (310), (211), (110), and (221). For Pd, (210), (221), (311), (322), (331), (211), and (332). High-index facets first appear at $h_{111} \approx 3.0$ nm for both Rh and Pd. As the size of nanoparticles increases, the fraction of the (111) facets decreases, reaching approximately 60% of the total surface area for Rh and about 40% for Pd. Compared with Rh, Pd exhibits a greater variety of edge facets and larger surface areas of these facets, resulting in a smaller fraction of the total surface area occupied by the (111) facet. In addition, a greater number of high-index facets appear at smaller nanoparticle sizes for Pd than for Rh. This behavior can be attributed to the fact that the ratios of the surface energies of each facet relative to the (111) facet are smaller for Pd. These results suggest that metals with relatively stable non-(111) facets tend to expose a wide variety of facets at the edges and corners. This difference may be related to the electronic structure of the metals.

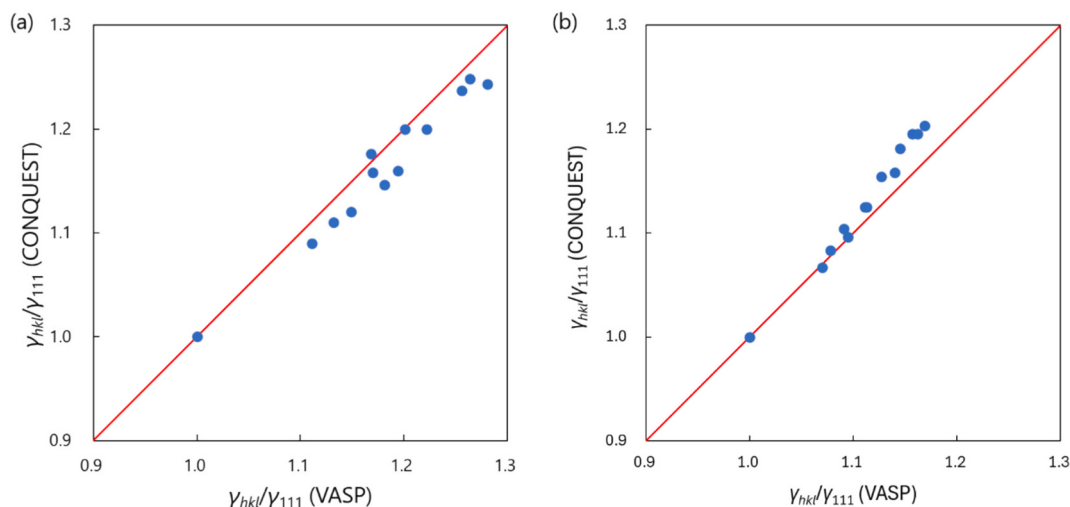


Fig. 2. Comparison of (a) Rh and (b) Pd surface energies with VASP and CONQUEST values. Red line represents perfect agreement between VASP and CONQUEST values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Surface energies of metal oxide supports calculated using CONQUEST and VASP.

Surface	γ_{sv} [eV Å ⁻²]			
	CONQUEST	VASP	Previous	
			Calc.	Exptl.
Rutile				
TiO ₂ (110)	0.0320	0.03196	0.019 ^a , 0.043 ^b , 0.056 ^c	0.0174, 0.0237 ^d
α -Al ₂ O ₃ (0001)	0.0970	0.1211	0.0992 ^e , 0.0961 ^f	0.165 ^g
MgO(001)	0.04796	0.08197	0.040 ^h , 0.061 ⁱ , 0.064 ^j	0.072 ^k

^a Calculated with ultrasoft pseudopotentials and PBE, Ref. [39,42].

^b Calculated with PAW potentials and PBE, Ref. [43].

^c Calculated with ultrasoft pseudopotentials and local density approximation (LDA), Ref. [44].

^d Ref. [45].

^e Calculated with PW91, Ref. [40].

^f Calculated with PBE, Ref. [46].

^g Ref. [47].

^h Calculated with local density functional (LDF), Ref. [41].

ⁱ Calculated with GGA, Ref. [48].

^j Calculated with ultrasoft pseudopotentials and PBE, Ref. [49].

^k Ref. [50].

Pd, with a nearly filled d¹⁰ configuration, tends to exhibit more isotropic bonding, whereas Rh, with partially filled d orbitals, may show stronger directional character, leading to larger anisotropy in surface energies.

3.3. Pseudo-surface energy

Interfacial energies of Rh(111)/rutile TiO₂, Rh(100)/rutile TiO₂, Rh(111)/ α -Al₂O₃, Rh(111)/MgO, and Pd(111)/rutile TiO₂ were calculated with Eq. (7), based on linear fitting for the interfacial formation energies of N_{SP}-atom supercells as a function of 1/N_{SP}, as illustrated in Fig. S4. The layered bulk models were calculated using CONQUEST due to computational cost. Table 2 summarizes the fitting parameters and interfacial energies. The slope and the intercept correspond to the interfacial energy and strain energy, respectively. The interfacial energy indicates interface stability, with lower values corresponding to more stable interfaces. Focusing on the effect of support, the interfacial energy is highest for Rh(111)/ α -Al₂O₃ and lowest for Rh(111)/rutile TiO₂. The interfacial energy correlates with the surface energy of the support, suggesting that interfaces formed with more stable supports are also more stable. Since the surface energy of the (111) facet of Rh is larger

than that of Pd, i.e., 0.1249 and 0.08563 eV Å⁻², respectively, the relative stabilization due to the support becomes more pronounced for Rh. Such a trend is less pronounced for Pd, reflecting its smaller variation in surface energies among different facets.

Pseudo-surface energies were calculated from interfacial and surface energies, listed in Table 2. The pseudo-surface energy reflects the stability of the metal surface in contact with the support, with lower values corresponding to metal surfaces that are less stable in vacuum. The ratio of the pseudo-surface energy to the surface energy of the (111) facet is used as a measure of the relative stabilization at the metal-support interface, where smaller values indicate stronger stabilization. In all systems, the ratio is less than 1.0, indicating stabilization upon contact with the support.

When comparing the supports, the Rh(111) surface in contact with MgO is the most stable, whereas rutile TiO₂ and α -Al₂O₃ exhibit similar pseudo-surface energies. To compare the different metal oxide supports, the number of oxygen and metal atoms in metal oxides coordinated to an individual Rh atom, CN, were determined using the following:

$$CN = \begin{cases} 1 & \text{if } x < 0 \\ 1 - 6x^5 + 15x^4 - 10x^3, & \text{if } 0 \leq x \leq 1 \\ 0 & \text{if } x > 1 \end{cases}, x = \frac{r - r_0}{r_c - r_0} \quad (8)$$

where r is the interatomic distance, r_0 is the ideal nearest neighbor distance, and r_c is the cutoff distance. The ideal nearest neighbor and cutoff distances are listed in Table S4. The average numbers of coordinating oxygen and metal atoms were calculated for Rh atoms located at the interface in the layered bulk model, presented in Table 3. The total of average CN of oxygen and metal atoms is the largest for the system in contact with MgO, suggesting that interaction with MgO helps maintain the structure of the Rh(111) surface and thereby stabilizes it, resulting in lower pseudo-surface energy.

The degree of stabilization induced by contact with the support is expressed by the difference between the pseudo-surface energy and the metal surface energy, $\Delta\gamma$, which is also listed in Table 2; larger values correspond to greater stabilization of the metal surface. In other words, $\Delta\gamma$ represents how much more stable the metal surface becomes upon interface compared to the metal surface in contact with a vacuum. When comparing metal species on the same support, the Pd(111) facet is more stable than the Rh(111) facet. When comparing Rh facets, the Rh(100) facet is more stable than the Rh(111) facet. A correlation with the metal surface energy is observed, suggesting that less stable metal surfaces are more readily stabilized by contact with the support. The magnitude of the pseudo-surface energy is governed by multiple factors, including both electronic and structural contributions at the interface. The support

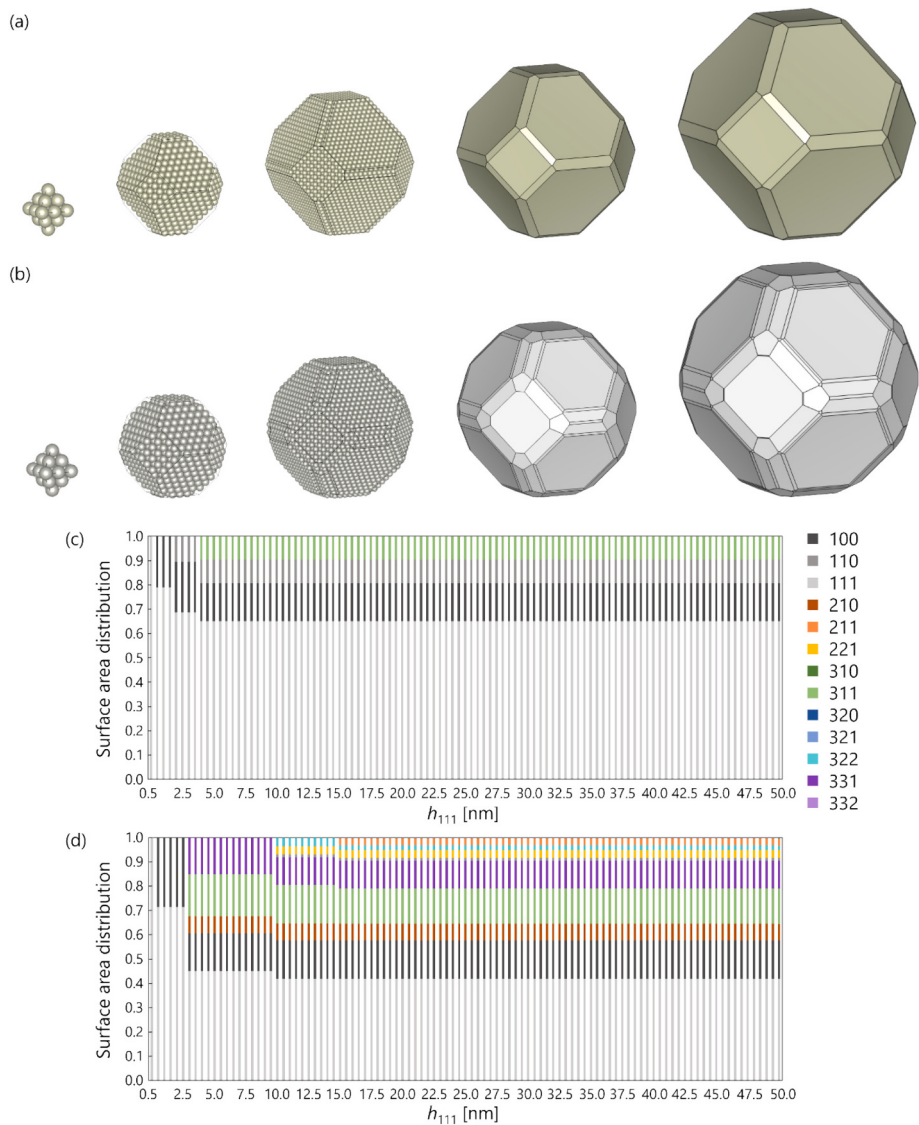


Fig. 3. Structures of (a) Rh and (b) Pd nanoparticles in vacuum with $h_{111} = 0.3, 1.5, 3.0, 10,$ and 50 nm from left to right, and distributions of surface area for (c) Rh and (d) Pd nanoparticles in vacuum, calculated using VASP.

Table 2

Fitting parameters obtained from the linear dependence of the interfacial formation energy on the inverse of the number of atoms in layered bulk model, together with the resulting pseudo-surface energies.

Metal/support	Slope $2S_{SP}\gamma_{SP}$ [eV]	Intercept ζ [eV]	R^2	γ_{SP} [eV $\text{\AA}^{-2}$]	γ_{hkl}^* [eV $\text{\AA}^{-2}$]	$\gamma_{hkl}^* / \gamma_{111}$	$\Delta\gamma$ [eV $\text{\AA}^{-2}$]
Rh(111)/rutile TiO_2 (110)	127.2	0.02872	0.8972	0.1355	0.1034	0.828	0.0215
Rh(100)/rutile TiO_2 (110)	57.97	0.03874	0.9865	0.1235	0.0915	0.733	0.0532
Rh(111)/ α - Al_2O_3 (0001)	16.23	0.01557	0.9864	0.2008	0.1039	0.832	0.0210
Rh(111)/MgO(001)	182.8	0.06248	0.9994	0.1383	0.0904	0.723	0.0346
Pd(111)/rutile TiO_2 (110)	58.24	0.01140	0.9500	0.09925	0.0672	0.785	0.0184

Table 3

The average numbers of coordinating oxygen and metal atoms to an individual Rh atom located at the interface.

Support	O atom	Metal atom in metal oxide
Rutile TiO_2	0.43	0.22
α - Al_2O_3	0.00	0.67
MgO	0.46	2.80

Rh(111), suggests that structural compatibility at the interface also contributes to stabilization. At the same time, the correlation between $\Delta\gamma$ and the metal surface energy implies that the intrinsic stability of the metal facet influences the extent of stabilization upon support contact. These results indicate that the pseudo-surface energy reflects a complex interplay of structural and energetic factors at the metal-support interface.

dependence discussed above, together with the coordination analysis for

3.4. Structure of supported metal nanoparticles

Structures of supported metal nanoparticles with $h_{111} = 3$ nm were obtained using surface and pseudo-surface energies and illustrated in Fig. 4: (a) a Rh nanoparticle supported on rutile TiO₂ with a Rh(111) interface, (b) a Rh nanoparticle with a Rh(100) interface, (c) a Rh nanoparticle supported on α -Al₂O₃ with a Rh(111) interface, (d) a Rh nanoparticle supported on MgO with a Rh(111) interface, and (e) a Pd nanoparticle supported on rutile TiO₂ with a Pd(111) interface. Compared with metal nanoparticles in vacuum, the distance from the nanoparticle center to the interface is shorter, due to the ratios of the pseudo-surface energy to the surface energy being smaller than 1.0. The distance from the center to the interface decreases relative to that of metal nanoparticles in vacuum by two layers for Rh(111)/rutile TiO₂, three layers for Rh(111)/ α -Al₂O₃ and Pd(111)/rutile TiO₂, four layers for Rh(111)/MgO, and seven layers for Rh(100)/rutile TiO₂. Although differences between metals may reflect effects of atomic radius and lattice constant, the structural change is particularly large for Pd compared with Rh. When comparing support species, MgO shows the largest reduction in the number of layers, whereas rutile TiO₂ and α -Al₂O₃ exhibit similar values. Focusing on metal facets, the reduction in the number of layers is larger for Rh(100) than for Rh(111). These results indicate that smaller pseudo-surface energies, i.e., more stable metal surfaces in contact with the support, lead to a larger reduction in the number of layers. Accordingly, the nanoparticle structure changes so as to increase the surface area of the stable interface facet.

Fig. 5 shows the surface area of supported Rh and Pd nanoparticles as a function of the number of atoms. The horizontal axis represents the number of atoms in nanoparticle, and the vertical axis represents surface area of the nanoparticle, S_{NP} . Blue, light blue, purple, orange, and gray correspond to Rh(111)/rutile TiO₂, Rh(100)/rutile TiO₂, Rh(111)/ α -Al₂O₃, Rh(111)/MgO, and Pd(111)/rutile TiO₂, respectively. The surface area was approximated by a power function of the number of atoms, as expressed in Eq. (9), the coefficients and exponents are listed

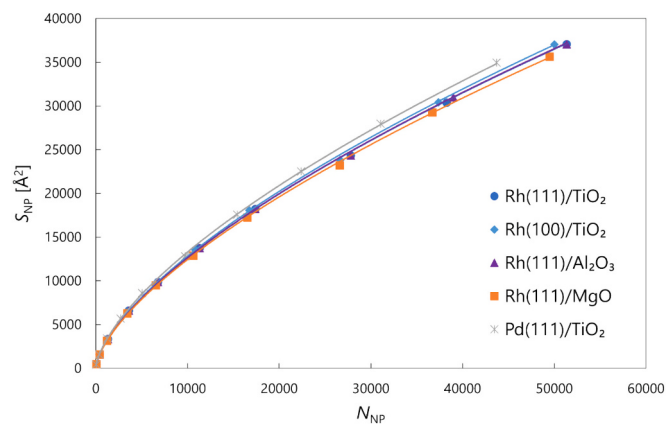


Fig. 5. Surface areas of supported metal nanoparticles. Blue, light blue, purple, orange, and gray correspond to Rh(111)/rutile TiO₂, Rh(100)/rutile TiO₂, Rh(111)/ α -Al₂O₃, Rh(111)/MgO, and Pd(111)/rutile TiO₂, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in Table S5.

$$S_{NP} = aN_{SP}^b \quad (9)$$

The surface area increases in the order of Pd(111)/rutile TiO₂, Rh(100)/rutile TiO₂, Rh(111)/rutile TiO₂, Rh(111)/ α -Al₂O₃, and Rh(111)/MgO. When comparing different supports, the surface area becomes larger as pseudo-surface energy increases. A lower pseudo-surface energy promotes the formation of a larger interfacial area, which in turn reduces the remaining free surface area. Focusing on the interface facet of Rh, Rh(100)/rutile TiO₂ has a larger surface area due to the increased number and area of exposed Rh(111) facets. Pd nanoparticles have larger surface areas than Rh nanoparticle, reflecting the larger lattice constant of Pd. The exponent in the power-law approximation is

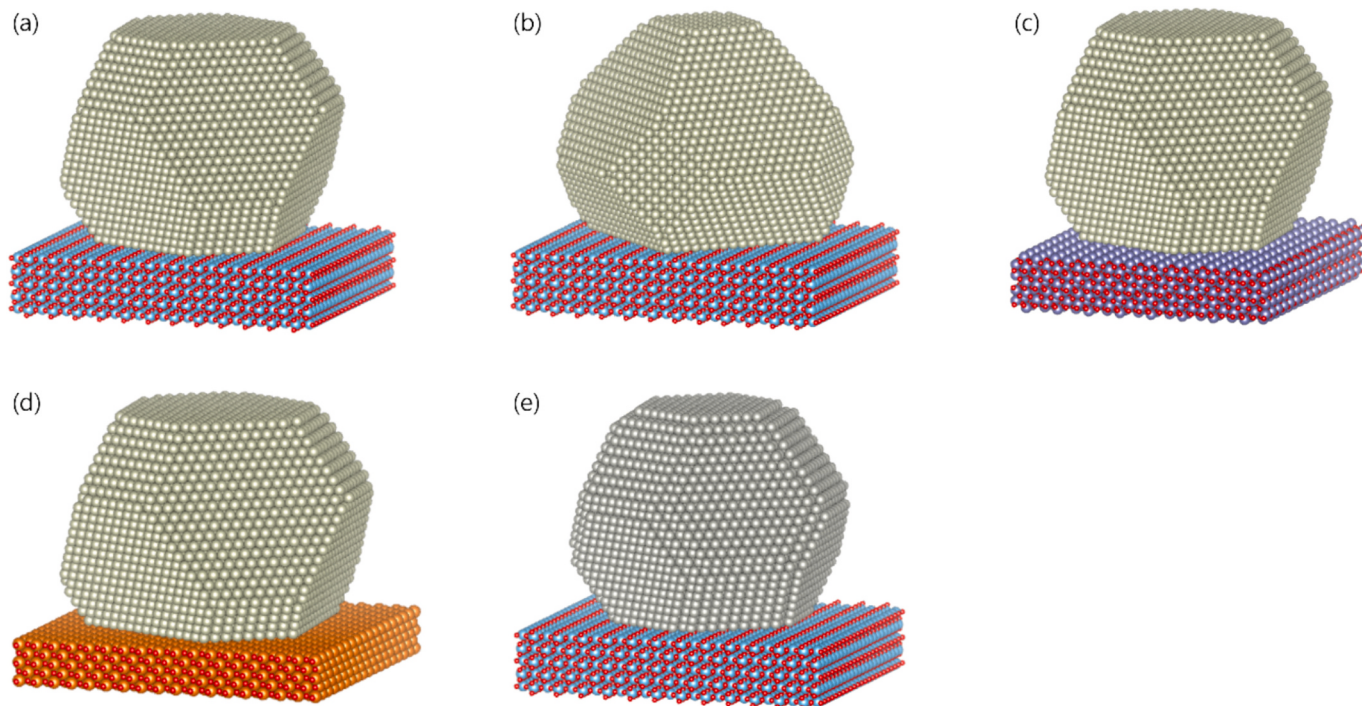


Fig. 4. Structures of (a) a Rh nanoparticle supported on rutile TiO₂ with a Rh(111) interface, (b) a Rh nanoparticle supported on rutile TiO₂ with a Rh(100) interface, (c) a Rh nanoparticle supported on α -Al₂O₃ with a Rh(111) interface, (d) a Rh nanoparticle supported on MgO with a Rh(111) interface, and (e) a Pd nanoparticle supported on rutile TiO₂ with a Pd(111) interface. The equilibrium shapes were constructed based on the Wulff–Winterbottom framework using first-principles-derived energies.

approximately 2/3 for all systems, consistent with the fact that the number of atoms scales with the cube of the nanoparticle size, whereas the surface area scales with the square. These results demonstrate that the morphology of supported metal nanoparticles is governed by the balance between surface and pseudo-surface energies, reflecting both energetic and structural factors at the metal–support interface.

4. Conclusions

In this study, we predicted the structures of Rh and Pd nanoparticles in vacuum and on rutile TiO₂, α -Al₂O₃, and MgO by combining first-principles calculations with the Wulff theorem and its Winterbottom extension.

For nanoparticles in vacuum, (111) and (100) surfaces are predominantly exposed for small particles, whereas high-index facets emerge with increasing particle size, with the exposed facets depending on the metal species. The fraction of the total surface area occupied by the (111) facet correlated with the ratios of the surface energies of other facets relative to that of the (111) facet. These results support that smaller energetic differences among facets facilitate the exposure of high-index facets as edges and corners.

The interfacial energies were evaluated using layered bulk structures to incorporate interactions between the metal and the support. The interfacial energy reflects the stability of the metal–support interface and is governed by both the metal and the support surfaces. Pseudo-surface energies were defined from interfacial and surface energies. In all systems, the pseudo-surface energies are lower than the corresponding surface energies, suggesting that the metal surfaces are stabilized upon contact with the support. A correlation with the CNs of oxygen atoms and metal atoms in the metal oxide surrounding interfacial Rh atoms suggests that such coordination contributes to the stabilization and structural preservation of the Rh(111) facet. The pseudo-surface energy also correlates with the metal surface energy, indicating that less stable metal surfaces are more strongly stabilized upon contact with the support.

For supported nanoparticles, the distance from the particle center to the interface is shorter than vacuum nanoparticles. Accordingly, the number of layers from the nanoparticle center to the interface decreases. The extent of this reduction depends on the system, leading to an increase in the surface area of the energetically stable interface facet. As a result, the structures of supported metal nanoparticles depend on the metal species, support material, and interface facet, which is reflected in systematic differences in nanoparticle surface area. Overall, this study demonstrates that the morphology of supported metal nanoparticles can be systematically understood and predicted within a first-principles-based Wulff–Winterbottom framework.

CRedit authorship contribution statement

Miyu Onishi: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Ayako Nakata:** Validation, Software, Methodology, Data curation. **Hiromi Nakai:** Writing – review & editing, Validation, Supervision, Software, Resources, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2026.142957>.

Data availability

Data will be made available on request.

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