

Article

Vacancy Formation Energy as an Effective Descriptor for the Catalytic Oxidation of CO by Au Nanoparticles

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Abstract: Gold nanoparticles (AuNPs) have attracted wide attention in the field of catalysis because of their excellent stability and electrical properties. Herein, an accurate vacancy formation energy model based on nanothermodynamics theory is developed, the intrinsic correlation between vacancy formation energy and CO oxidation activity is investigated in detail, and the relationship between vacancy formation energy and activity-influencing factors such as particle size, temperature, and crystal surface is analyzed. The results show an excellent linear relationship between vacancy formation energy and CO oxidation activity, with an accuracy of up to 95%. In addition, the vacancy formation energy also corresponds well to the influencing factors of size, temperature, and crystal surface, and its correspondence is particularly accurate when the size is below 20 nm and the temperature is below 500 K. It can serve as a normalized expression of the three influencing factors. Moreover, the present research reveals that the essence of the vacancy formation energy descriptor is the chemical bond energy, and gives its correspondence with the coordination number, diffusion activation energy, and adsorption energy (with a decrease in vacancy formation energy, the adsorption effect of AuNPs is stronger), further demonstrating the feasibility and accuracy of the vacancy formation energy as a descriptor. This research not only overcomes the problem that traditional single-influence descriptors are difficult to apply in complex environments but also has considerable potential for defect modulation.



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Keywords: vacancy formation energy; descriptors; catalysis; gold nanoparticles; nanothermodynamics

1. Introduction

In recent years, noble metal catalysts have captured substantial attention in energy conversion and environmental remediation [1–3]. In particular, gold nanoparticles (AuNPs) are considered a potential catalytic material due to their remarkable electrical properties and stability [4–7]. However, investigators have pointed out that AuNPs have to escape from the limitations of size, crystal surface, and temperature to exhibit highly efficient catalytic activity [8–11]. Therefore, it is essential to consider influencing factors to facilitate research into high-activity catalysts, utilizing practical descriptors and modulation tactics [12].

Two strategies have been proposed to optimize the catalytic activity of AuNPs lately. One notable approach is structural design involving dimensional modification and crystal surface engineering. Several studies have suggested that the catalytic activity of AuNPs is negatively correlated with the particle size, and the preferred particle radius is around 4 nm [13–15]. In addition, the binding energy of 4-nitroaniline is most remarkable on the Au (110) crystal surface, which is conducive to absorbing this molecule and fulfilling its catalytic hydrogenation [16]. The other promising method is interaction with the external environment; specifically, a critical variable for a reaction rate is temperature, and the majority of processes accelerate with increasing temperature [17]. Nevertheless, the relationship

between particle size, crystal surface, and temperature is poorly clarified, which restricts the execution of schemes for enhancing the catalytic activity of AuNPs. A tiny particle size is unfavorable to the thermal stability of AuNPs and also degrades their catalytic activity due to the particles agglomerating into clusters during the catalytic process [18]. More than that, the optimal particle size and reaction temperature in triggering catalytic activity vary with the crystal orientation [19]. For such reasons, it is valuable to identify the intrinsic mechanisms of interaction between these factors and catalytic properties.

To decipher the code of regulating catalytic activity, scholars have conducted systematic studies and drawn numerous fruitful conclusions. Sun et al. [20] found that an elevated temperature weakens the surface energy and vacancy formation energy, thus improving the catalytic properties of AuNPs. Wang et al. [21] concluded that enhancement of material activity is attributed to a decrease in particle size, which drives the growth of low-coordinated atoms on the surface to reduce the binding energy and vacancy formation energy. Furthermore, Zhang et al. [22] studied the catalytic activities of AuNPs coated with different index crystal surfaces for the hydrogenation of 4-nitrothiophenol; they revealed that the catalytic activity is strictly determined by the distribution densities of vacancies on AuNPs' surfaces. These results imply that temperature, particle size, and the crystal surface index of AuNPs may have an influential relationship with binding energy and vacancy formation energy. However, studying this using traditional density functional theory (DFT) is generally a time-consuming and labor-intensive process [23]. Meanwhile, the inherent correlations between temperature, particle size, and crystal surface index are complicated to verify experimentally [24–26]. It is speculated that the application of nanothermodynamics to examine the association of vacancy formation energy with activity has potential [27].

In our study, vacancy formation energy descriptors for the catalytic properties of AuNPs were constructed based on the theory of nanothermodynamics. We explored the interrelationship between vacancy formation energy and size, temperature, and the crystal surface in AuNPs and demonstrated that the vacancy formation energy can unify the above three influencing factors. In addition, the study of 18 kinds of different metal nanoparticles accurately revealed the nature of the vacancy formation energy as chemical bond energy. Lastly, we investigated the relationship between vacancy formation energy and adsorption energy to directly show the effect of vacancy formation energy on catalytic activity. The presented research strategy of the descriptors is expected to overcome the limitations of conventional noble metal catalyst research regimes and propose a fresh course for the design of high-efficiency catalytic systems.

2. Nanothermodynamic Model

As Cahn pointed out [28], the vacancy model is empirically self-consistent and watertight, in that it can interpret a wide range of distinct phenomena. In addition, Gorecki [29] offered extensive evidence to demonstrate the existence of correlations between the vacancy formation energy and the bonding energy of metals. The correlation between vacancy formation energy, vacancy migration energy, and Debye temperature is given as follows:

2.1. The Relationship between the Vacancy Transfer Energy and Debye Temperature

For simplicity, we consider monatomic cubic crystals [30]. A diffusion jump occurs when (a) a given atom has a large displacement from its equilibrium position in the correct direction, and (b) the surrounding atoms move so that the atom may pass to the adjacent (vacant) site. The probability of an atomic displacement $P(u_a)$, along axis a , at thermal equilibrium and in the harmonic approximation, is

$$P(u_a) = \left(2\pi \langle u_a^2 \rangle\right)^{-\frac{1}{2}} \exp \left[-\frac{1}{2} \frac{u_a^2}{\langle u_a^2 \rangle} \right] \quad (1)$$

According to normal coordinate $q_j(k)$ and mean square displacement $\langle u_a^2 \rangle$,

$$\langle u_a^2 \rangle = \frac{1}{3Nm} \sum_{k,j}^{1N} \langle q_j^2(k) \rangle \quad (2)$$

where n is the number of atoms, and M is the mass of atoms. Based on the vibration frequency $\omega_j(k)$ and vibration energy $E_j(k)$, Equation (2) can be further rewritten as

$$\langle q_j^2(k) \rangle = \frac{E_j(k)}{\omega_j^2(k)} = \hbar \omega_f(k) \times \left[\exp \frac{\hbar \omega_f(k)}{kT} - 1 \right] + \frac{1}{2} / \omega_j^2(k) = kT / \omega_j^2(k) \quad (3)$$

where $\hbar$ is the Planck constant, K is the Boltzmann constant, and T is the temperature. If we introduce the Debye function, then we can get

$$g(\omega) = 9N\omega_D^{-3} \omega^2 (\omega \leq \omega_D) \quad (4)$$

In that case,

$$\langle u_a^2 \rangle = \frac{1}{3Nm} \int \frac{E(\infty)}{\omega^2} g(\omega) d\omega = \left(\frac{\hbar}{k} \right)^2 \frac{3kT}{m\Theta^2} \quad (5)$$

Therefore,

$$P(u_a) = \left[\frac{6\pi kT}{m\Theta^2} \left(\frac{\hbar}{k} \right)^2 \right]^{-\frac{1}{2}} \exp \left[-\frac{\frac{1}{6} \left(\frac{k}{\hbar} \right)^2 m\Theta^2 u_a^2}{kT} \right] \quad (6)$$

When the lattice constant is a , $u_a = a/2$

$$E_f = a^2 \frac{1}{24} \left(\frac{k}{\hbar} \right)^2 m\Theta^2 \quad (7)$$

It can be seen that the vacancy transfer energy E_f is proportional to the square of Debye temperature Θ at a lower temperature.

2.2. The Relationship between the Vacancy Formation Energy and Debye temperature

According to the number of atoms n , the atomic distance r_i , and the potential energy $\phi(r_{ij})$, the potential V of a solid can be expressed as

$$V(r_1 \cdots r_N) = \frac{1}{2} \sum_{ij} \phi(r_i - r_j) \quad (8)$$

For symmetry, Equation (8) should be divided by 2. At the same time, the atomic potential energy can also be expressed in the following form

$$\phi(r) = \varepsilon f(r/a) \quad (9)$$

where ε is the elastic constant, and a is the lattice constant. It is worth noting that the potential V of a solid can be expanded by the Taylor series under the simple harmonic approximation

$$V = NV_0 + \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V}{\partial \mu_i \partial \mu_j} \right)_0 \mu_i \mu_j = N \frac{\varepsilon}{2} \sum_i f(r_i/a) + \frac{\varepsilon}{2} \sum_{ij} \frac{1}{a^2} f''(r_{ij}/a) \mu_i \mu_j \quad (10)$$

where V_0 is the zero potential, and μ_i is the displacement vector, which deviates from the equilibrium position. In the Debye model, each solid has the same spectrum, and the spectrum of different solids is only different with the cut-off value ω_D

$$\mu_i = m^{-(1/2)} \sum_k \lambda_{ik} q_k \quad (11)$$

In this way, the maximum cut-off value w_D can be expressed as

$$\omega_D^2 = \sum_{ij} \lambda_{K_D i} A_{ij} \lambda_{j K_D} = \frac{\varepsilon}{2ma^2} \sum_{ij} \lambda_{K_D i} f''(r_{ij}/a) \lambda_{j K_D} A_{ij} \equiv \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V}{\partial \mu_i \partial \mu_j} \right)_0 \quad (12)$$

That is to say,

$$\varepsilon = 2ma^2 \omega_D^2 \left[\sum_{ij} \lambda_{K_D i} f''(r_{ij}/a) \lambda_{j K_D} \right]^{-1} \quad (13)$$

If a vacancy is formed, the volume of the crystal will not shrink

$$E_v = V_0 = \frac{\varepsilon}{2} \sum_i f(r_i/a) = ma^2 \omega_D^2 \left[\sum_{ij} \lambda_{K_D i} f''(r_{ij}/a) \lambda_{j K_D} \right]^{-1} \sum_i f(r_i/a) \quad (14)$$

According to the definition of Debye temperature $\Theta_D = \hbar \omega_D / k$,

$$E_v = \left\{ \left[\sum_{ij} \lambda_{K_D i} f''(r_{ij}/a) \lambda_{j K_D} \right]^{-1} \sum_i f(r_i/a) \right\} a^2 \left(\frac{k}{\hbar} \right)^2 m \Theta^2 \quad (15)$$

Obviously, the vacancy formation energy is approximately proportional to the square of the Debye temperature.

2.3. The Size Effect of the Debye Temperature

According to previous studies considering the effect of vacancy defects on the chemical activity of nanomaterials, the binding energies and the Debye temperature of nanomaterials of different sizes can be written as [31–34]

$$\frac{E_v(r,0)}{E_v(b,0)} = \frac{\Theta^2(r,0)}{\Theta^2(b,0)} = \frac{E_m(r,0)}{E_m(b,0)} = 1 - \frac{CN}{4} \cdot \frac{r_0}{R} \cdot \frac{\rho_b}{\rho_n} \cdot \frac{1}{\eta} \quad (16)$$

where $E_v(r,0)$ is the vacancy formation energy of AuNPs at 0 K, and $E_v(b,0)$ is the vacancy formation energy of the corresponding Au bulk material at 0 K. Similarly, Θ is the Debye temperature, and E_m is the binding energy. In addition, ρ is the density, CN is the coordination number, η is the packing coefficient, r_0 is the atomic radius, and R is the nanoparticle radius (for the detailed derivation process and experimental details, see the Supplementary Materials). The equation applies not only to vacancy formation energy; for any form of defect, the energy can be calculated in relation to the binding energy method.

To study the temperature effect on the vacancy formation energy of AuNPs, a functional model of vacancy formation energy, binding energy, and temperature can be established in constant-pressure specific heat capacity:

$$\frac{E_v(r,T)}{E_v(b,0)} = \frac{E_m(r,T)}{E_m(b,0)} = 1 - \frac{\int_0^T C_p(T) dT}{U_m(b,0)} \quad (17)$$

where $U_m(b,0)$ is the internal energy at 0 K, and C_p is the specific heat capacity at constant pressure.

Vacancy, as one of the important melting criteria, is related to properties such as surface energy, Young's modulus, the Debye temperature, and the diffusion activation energy. Its intrinsic correlation can be expressed by the following equation [35–37]

$$\frac{E_v(r,T)}{E_v(b,T)} = \frac{\sigma(r,T)}{\sigma(b,T)} = \frac{Y(r,T)}{Y(b,T)} = \frac{Q(r,T)}{Q(b,T)} = \frac{\Theta^2(r,T)}{\Theta^2(b,T)} \quad (18)$$

where $E_v(r, T)$ and $E_v(b, T)$ are the vacancy formation energy of nanoparticles and bulk materials, respectively; $\sigma(r, T)$ and $\sigma(b, T)$ are the surface energy of nanoparticles and bulk materials, respectively; $Y(r, T)$ and $Y(b, T)$ are Young's moduli of nanoparticles and bulk materials, respectively; $Q(r, T)$ and $Q(b, T)$ are the diffusion activation energy of nanoparticles and bulk materials, respectively; and $\Theta^2(r, T)$ and $\Theta^2(b, T)$ are the Debye temperature of nanoparticles and bulk materials, respectively.

In addition, we also found that the vacancy formation energy has the following relationship with the coordination number [31,38]

$$\frac{E_v(r)}{E_v(b)} = \frac{Z_b N_c + \sum_{i=1}^2 N_i Z_i / c_i}{Z_b (R^3 / r^3)} \quad (19)$$

where Z_b is the coordination number of the Au bulk material, N_c is the number of interior atoms ($N_c = R^3 / r^3 - \sum_{i=1}^2 N_i$), and N is the number of atoms. This relationship can be used to connect vacancy formation energy with the coordination number.

3. Results and Discussion

Vacancy formation energy is a zero-dimensional thermodynamic defect, which not only shows the change in binding energy and coordination number, but also describes the influence of size, temperature, and the crystal plane. It provides more comprehensive structural and energy information than simple reaction descriptors (such as particle size and the ratio of a specific plane). Therefore, it is reasonable to believe that the vacancy-forming energy descriptor will show advantages in the design of metal catalysts such as Au.

3.1. Relationship between Vacancy Formation Energy and Catalytic Activity

There have been many studies on the catalytic oxidation of CO by AuNPs, the best known of which are those of D. Goodman. The researcher has achieved many important results by studying the catalytic oxidation of CO by AuNPs supported by different carriers [39,40]. For example, he investigated MgO-supported AuNP catalysts and found that the MgO surface F center plays a key role in the activation of Au in Au/MgO catalysts. In addition, Goodman investigated TiO₂-supported AuNP catalysts and found the importance of defect sites in determining the Au cluster shape and electronic properties. Therefore, we examine in detail the intrinsic relationship between vacancy defects and AuNPs. Figure 1 shows the relationship between CO oxidation activity and the magnitude of vacancy formation energy for AuNPs on different carriers. It can be seen from the figure that the oxidation activity of CO decreases continuously as the vacancy formation energy increases. In addition, by comparing the data for reducible (TiO₂, Fe₂O₃) and non-reducible (Al₂O₃, MgAl₂O₄, SiO₂) carriers, it can be seen from Figure 1 that the oxidation activity of CO is still linearly related to the vacancy formation energy, despite the different carriers. Therefore, it is known that although different carriers have an effect on the catalytic activity of AuNPs, the activity is mainly determined by the vacancy concentration. If we include only a few different supports, then it is possible that the fact that the AuNPs have roughly the same activity is a coincidence because the different effects are cancelled out by chance, but the large number of different supports gathered in Figure 1 should rule this out. As such, we speculate that the vacancy formation energy is a promising descriptor, reflecting the activity of AuNPs with excellent accuracy.

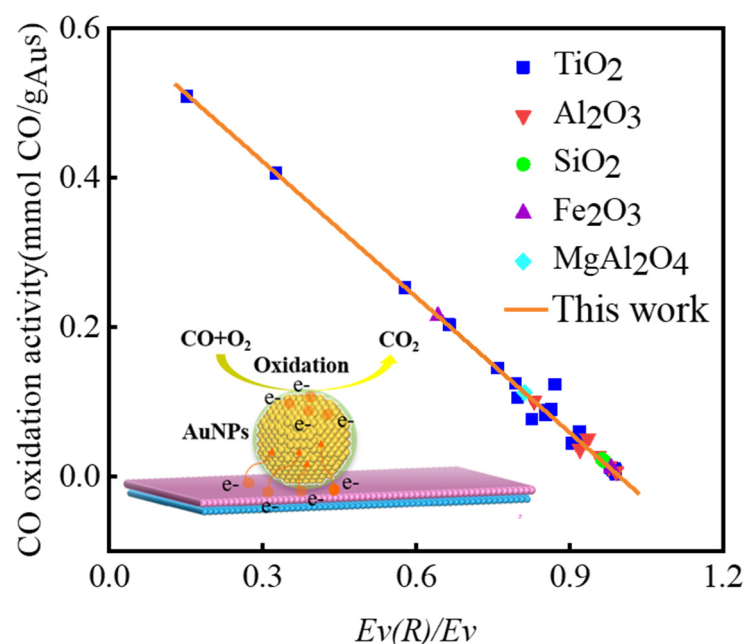


Figure 1. Measured activities for CO oxidation at 273 K over different Au-based catalysts as a function of the vacancy formation energy. (The black dashed line in the graph is the fitted trend line. The points are collected from [41–46].)

3.2. Vacancy Formation Energy Model

Recently, George [47] and Yu [27] have shown that the size effect of nanomaterials depends mainly on the number of atoms on the surface and the percentage of atoms in the bulk phase from the perspective of continuum media theory and statistical thermodynamics, respectively. Herein, we present how we calculated the atomic number of particles of different sizes of AuNPs by using the formula $N = \eta R^3 / r_0^3$, for which the result is shown in Figure 1a. Throughout the calculations, density and lattice distortion were not considered due to the small variation in size. It is clear from Figure 2a that the number of nanoparticles increases with increasing particle size. Furthermore, the calculated results are in good agreement with the molecular dynamics simulations; at 2.21 nm, the maximum difference ratio is 0.086, whereas at 4.31 nm, the difference ratio is only -0.005 , which indicates that our model is able to accurately characterize the structure of the particles.

Vacancies are the smallest and most fundamental form of defect in crystals, and many physical properties of solids are closely related to the presence of vacancies [48]. The detailed study of vacancy formation and properties is of great importance for understanding the microscopic and macroscopic properties of materials. In conjunction with Equation (1), we further investigated the effect of particle size on vacancy formation energy and compared it with the simulation results, as shown in Figure 2b. The results of the theoretical calculations agree well with the molecular dynamics simulations, indicating that our thermodynamic model is accurate and reliable and can provide a convenient method for predicting the formation of size-dependent vacancies. It can be seen from Figure 2b that the vacancy formation energy of AuNPs reduces with decreasing particle size, which suggests that vacancies can be formed more easily in nanoparticles than in the bulk material. In addition, with particle sizes greater than 20 nm, Au nanoparticles have properties similar to those of solid materials, with vacancies forming in an almost horizontal straight line. This finding suggests that 20 nm may be the threshold for the size effect of the vacancy formation energy of Au nanoparticles. Meanwhile, when the particle size is less than 20 nm, the effect of size on vacancy formation energy is a smooth curve. Furthermore, our previous models developed general relationships between thermodynamic and mechanical properties of nanomaterials and could well replicate experimental results. Overall, our

vacancy formation energy model can effectively reflect the pattern of particle size effects on catalytic performance.

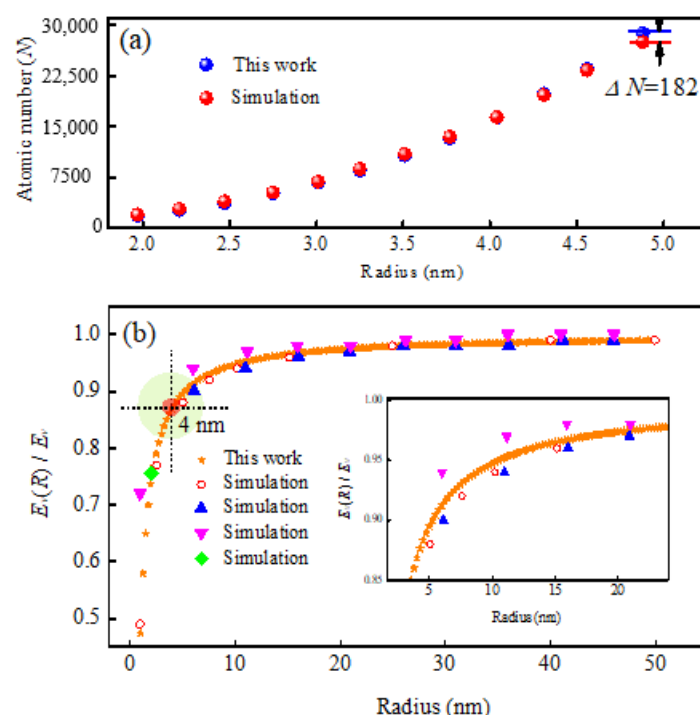


Figure 2. Relationship between particle size and (a) atomic number or (b) vacancy formation energy. (The detailed calculation parameters: CN is the coordination number 12, η is the packing coefficient 0.74, r_0 is the atomic radius 0.1442, R is the nanoparticle radius, ρ_b/ρ_n is density ratio 0.9, and the relevant data can be found in the Supplementary Materials Tables S1–S5.)

The effect of the crystal surface of AuNPs on catalytic properties has been reported in some cases, but studies in which the crystal surface and particle size together affect catalytic properties are rare [38]. It is well-known that crystals with high indices often have a large number of active sites on their surfaces, which significantly influence catalytic performance. Here, we calculate in detail the size effect of the vacancy formation energy on the (111) crystal surfaces of Au, Ag, and Cu nanoparticles (same calculation method for different crystal surfaces), as shown in Figure 3a–c. As can be seen from the figure, the vacancy formation energies of the Au, Ag, and Cu nanoparticle (111) crystalline surfaces are strongly consistent with the molecular dynamics simulations and also have a similar size effect as in Figure 2b. Furthermore, it can be seen from Figure 3d that the vacancy formation energy of the (111) surface of the Au, Ag, and Cu nanoparticles is approximately 1/4 of the overall vacancy formation energy [38]. This is attributed to the fact that the face-centered cubic (FCC) structure has a coordination number of 12, while the number of atomic bonds that need to be broken for atoms to break away from the (111) surface is 3. This conclusion is identical to that described in Equation (4), suggesting that the vacancy formation energy has a similar descriptive effect to that of the coordination number, and can also describe the effect of a reduction in coordination number on the catalytic properties [49–51]. In summary, the common effect of different particle sizes and crystal surfaces on catalytic properties can be described by the vacancy formation energy.

Temperature is an additional important factor affecting the catalytic properties of AuNPs, and we further investigate the law of temperature influence on the vacancy formation energy of AuNPs. As can be seen in Figure 4, the energy of vacancy formation decreases with increasing temperature and shows a linear relationship. In addition, the calculations of our model fall in-between those of the local harmonic method, the extensions of the local harmonic method, and the quasi-harmonic method, with an accuracy

comparable to that of Li [24]. Classical thermodynamics state that vacancies are a thermodynamic equilibrium defect and that the vacancy formation energy decreases and the concentration of vacancies increases with increasing temperature. However, the method of using coordination numbers to describe the catalytic properties at different temperatures seems less intuitive than the method of vacancy formation energy. Additionally, previous research by the team led us to point out that the nature of vacancy formation energy is bond energy, which is linearly related to vacancy migration energy and diffusion activation energy [31], a conclusion that is consistent with the mathematical description given in Equation (3). Therefore, the effect of temperature on catalysis can be well-described by the vacancy formation energy.

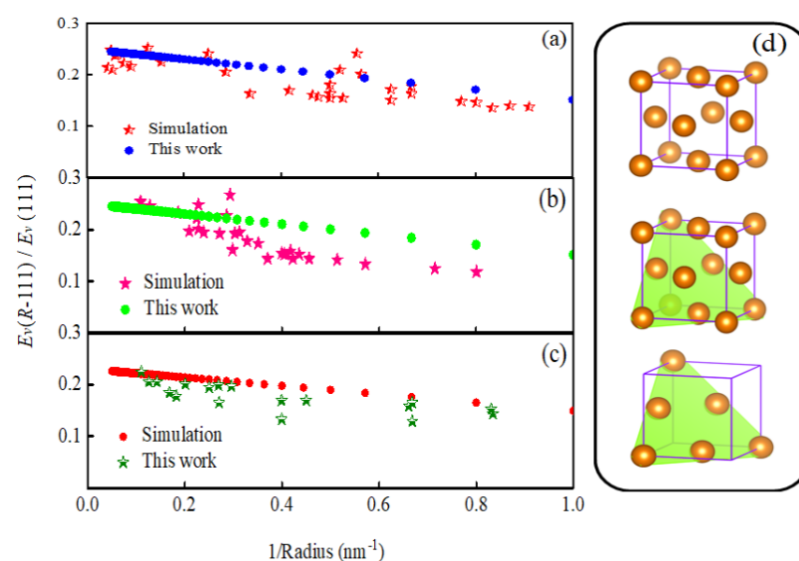


Figure 3. Size effect of the vacancy formation energies on (a) Au, (b) Ag, and (c) Cu nanoparticle (111) crystal surfaces, and (d) changes in the coordination numbers of (111) crystal surfaces of face-centered cubic crystals. (The detailed calculation parameters: CN is the coordination number 12, η is the packing coefficient 0.74, r_0 is the atomic radius 0.1442, and R is the nanoparticle radius, ρ_b/ρ_n is density ratio 0.9, k is the ratio factor of the surface to the whole 0.25, the relevant data can be found in the Supplementary Materials Tables S7–S9.)

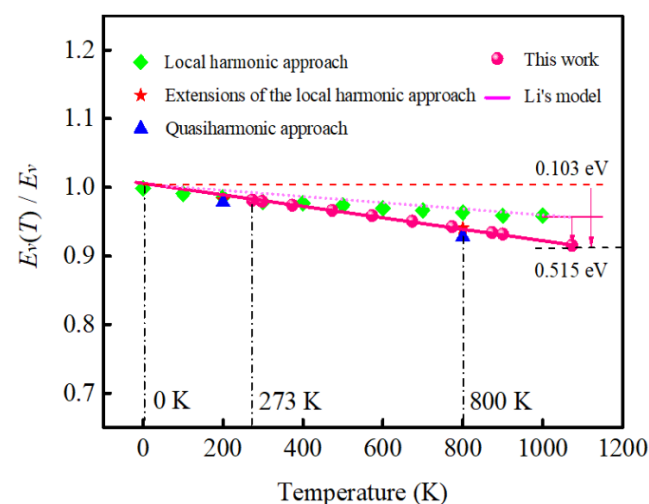


Figure 4. Temperature effect on the vacancy formation energy of AuNPs. (The detailed calculation parameters: $Um(b,0)$ is the internal energy at 0 K, C_p is the specific heat capacity at constant pressure, and the relevant data can be found in the Supplementary Materials Tables S10 and S11.)

The combined effect of temperature and particle size on the vacancy formation energy of AuNPs is shown in Figure 5. The effect of particle size is small when the particle size is greater than 4 nm, while the effect of particle size is significant when the particle size is less than 4 nm. In addition, when the temperature is too high, the atoms move violently and tend to break away from their initial positions, creating vacancies and thus leading to drastic changes in vacancy formation energy. These patterns can be accurately predicted and described using the mathematical equations of Equations (2) and (3). We compared the calculated results with the models of Li [24] and Ouyang [43] and found that Equations (2) and (3) are close to the Li model, with a maximum difference of only 0.01 at 0 K. The report by Li et al. [24] claims that the accuracy of their calculation method is the highest available; therefore, the use of vacancy formation energy to describe the effect of temperature and particle size on catalytic properties is accurate and appropriate.

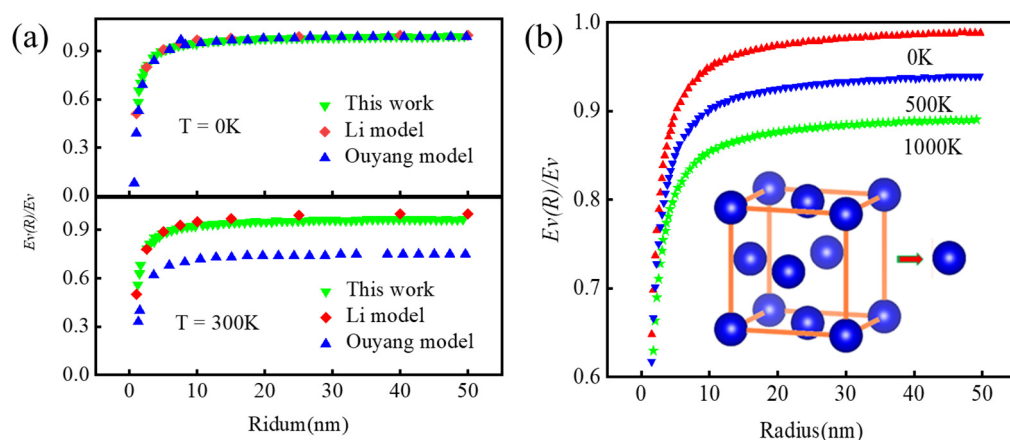


Figure 5. Effect of particle size and temperature on the vacancy formation energy of AuNPs: (a) comparison with other models at 0 K and 300 K; (b) predicted trends at 500 K and 1000 K. (The detailed calculation parameters: $U_m(b,0)$ is the internal energy at 0 K, C_p is the specific heat capacity at constant pressure, and the relevant can be found in the Supplementary Materials Tables S12–S14.)

3.3. Essence of Vacancy Formation Energy

Figures 2–5 have demonstrated that vacancy formation energy is highly correlated with particle radius, reaction temperature, and crystal surface orientation and can be used as a uniform scale for these influences. To clarify the physical essence of this description, we have studied the relationship between vacancy formation energy and bond energy for 18 common metals, and the results are shown in Figure 6. It can be seen that the vacancy formation energy of the 18 common metals is proportional to the bond energy, with a slope of 0.00255. Previous research by the team noted that the removal of one atom from a crystal would sever the chemical bond attached to that atom, and the surrounding atoms would undergo contraction (contraction ratio of 1.06), along with a decrease in coordination number [28]. Hence, the essence of vacancy formation energy is bonding energy, similar to the mechanism described for the coordination number, but it is able to reflect the combined effects of particle size, crystal surface, and temperature on catalytic properties at the same time. Notably, Jiang et al. [52] pointed out that the surface of nanomaterials has a large number of low-coordinated atoms, which makes the chemical bonds of surface atoms short and strong, resulting in a series of special physical phenomena. Qi et al. [53] also argued that the core of nanothermodynamics is bonding energy, which is lower in nanomaterials than in bulk materials, so physical quantities such as phase transition temperature, Debye temperature, surface energy, surface stress, vacancy formation energy, diffusion activation energy, heat capacity, and Young's modulus are also reduced.

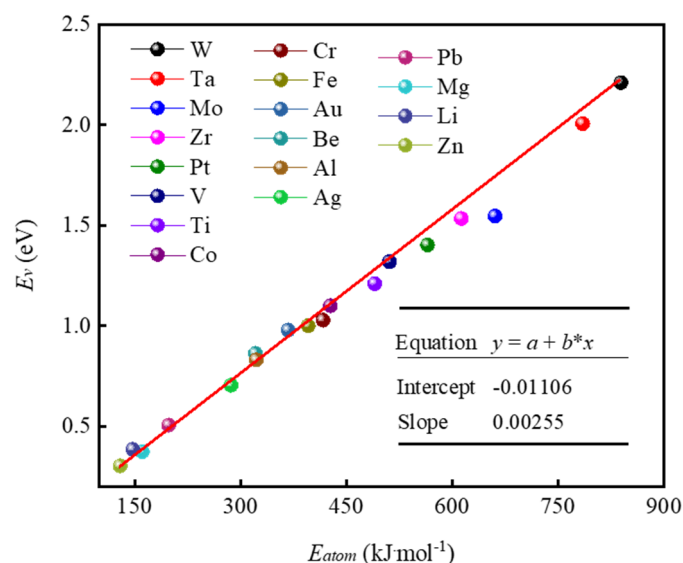


Figure 6. Relationship between vacancy formation energy and chemical bonding energy of common metals. (The red line in the graph shows the fitted trend line, and detailed data can be found in the Supplementary Materials Table S15.)

3.4. Relationships between Vacancy Formation Energy, Diffusion Activation Energy, and Adsorption Energy

Vacancy formation energy is related to bonding energy and the number of ligands but also the diffusion activation energy and the adsorption energy. While the adsorption energy has the theoretical advantage of high accuracy as a descriptor, the vacancy formation energy is also informative in terms of its application to defect modulation. In order to investigate the intrinsic link between vacancy formation energy and diffusion activation energy, we calculated the relationship between vacancy formation energy and diffusion activation energy for different bulk metals, and the results are shown in Figure 7. It can be seen that the vacancy formation energy is linearly related to the diffusion activation energy. Additionally, we further investigated the relationship between vacancy formation energy and diffusion activation energy for AuNPs at 4, 8, and 12 nm and found that the relationship was also linear, with a slope of 0.3571. This is because AuNPs have a large number of unsaturated bonds and weak interatomic forces when the vacancy formation energy is small, so the energy required to overcome the atomic motion is low. This suggests that vacancy formation energy can respond well to atomic activation on the surface, to describe catalytic performance.

Adsorption energy is an important indicator of catalytic performance, and understanding the relationship between vacancy formation energy and adsorption energy will contribute to the development of vacancy formation energy descriptors. Figure 8 shows the vacancy formation energy of the AuNPs' (111) crystal faces in relation to the O and CO adsorption energies. It can be seen from the figure that the adsorption energy stabilizes when the vacancy formation energy is greater than 0.79 eV, due to the low concentration of vacancies at this point, meaning the properties of the AuNPs are similar to those of the bulk material. Furthermore, the adsorption energy increases with decreasing vacancy formation energy when the vacancy formation energy is less than 0.79 eV. This is because at low vacancy formation energies, a large number of defects tend to form on the surface of the nanoparticles, enhancing surface adsorption. The finding again suggests that vacancy formation energy is a good catalytic descriptor.

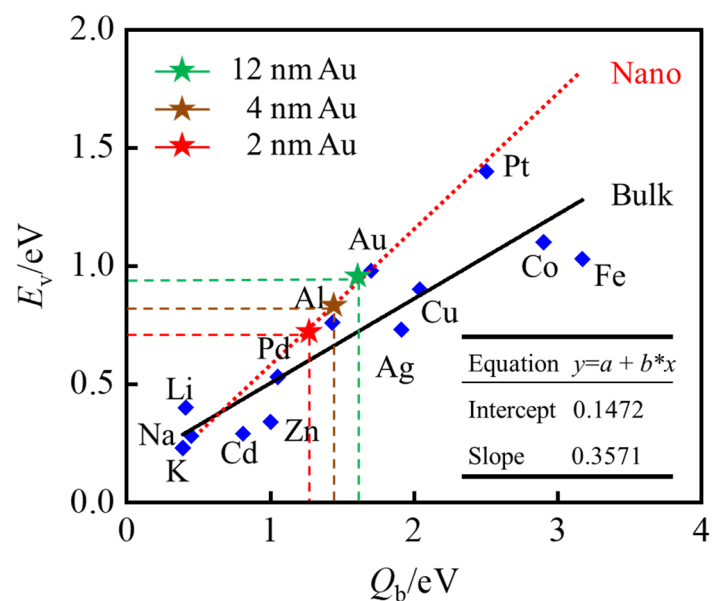


Figure 7. Relationship between vacancy formation energy and diffusion activation energy. (The black line in the figure is the trend line fitted to the bulk material, the red dashed line is the trend line fitted to the calculated values of Au nanoparticles, and detailed data can be found in the Supplementary Materials Table S16.)

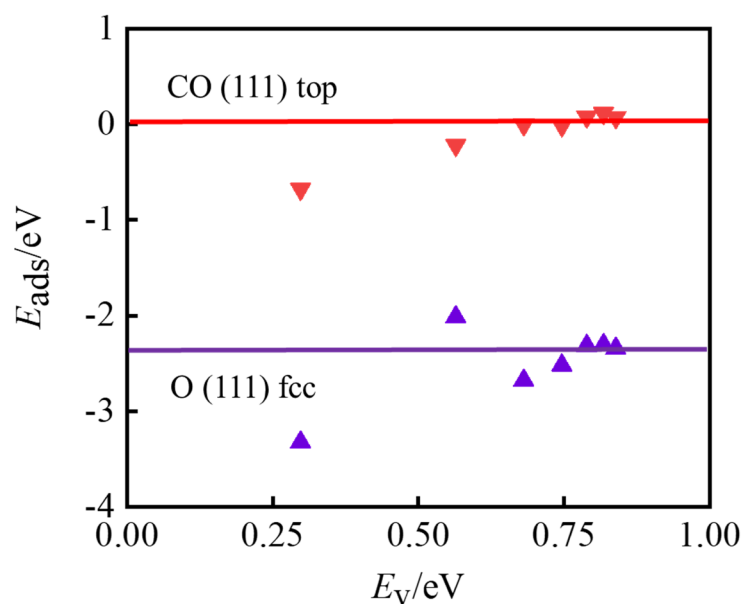


Figure 8. Relationship between vacancy formation energy and adsorption energy. (The red and blue lines in the diagram, respectively, indicate the adsorption energy of the block Au for CO and O for slab surface calculations. The points are collected from [54].)

4. Conclusions

In summary, a reactivity descriptor for AuNP electrocatalysts, vacancy formation energy, has been proposed based on nanothermodynamics theory. To begin with, we investigated the intrinsic correlation between vacancy formation energy and size, crystal surface, and temperature, and found that there is an accurate correspondence between vacancy formation energy and these three factors, which can well reflect the influence of the three on the catalytic activity of AuNPs. In addition, a mechanism has been given for correlating vacancy formation energy with bond energy, diffusion activation energy, surface energy, binding energy, and coordination number, revealing that the physical essence of

vacancy formation energy as a descriptor is bond energy. Ultimately, the relationship between vacancy formation energy and adsorption energy has been further examined, demonstrating that vacancy formation energy is a good descriptor. This research not only provides new insights into the prediction of catalyst properties but also contributes significantly to defect regulation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/met13020362/s1>, Table S1: The molecular dynamics simulation data and calculation results of Au nanoparticles; Table S2: The simulation data of Au nanoparticles; Table S3: The simulation data of Au nanoparticles; Table S4: The simulation data of Au nanoparticles; Table S5: The calculation parameter of the vacancy formation energy of Au nanoparticles; Table S6: The size effect of the vacancy formation energy of Au nanoparticles (111) crystal surface; Table S7: The size effect of the vacancy formation energy of Ag nanoparticles (111) crystal surface; Table S8: The size effect of the vacancy formation energy of Cu nanoparticles (111) crystal surface; Table S9: The calculation parameter of the vacancy formation energy of Au, Ag and Cu nanoparticles (111) crystal surface; Table S10: The constant pressure heat capacity (C_p (J.mol⁻¹K)) simulation data of Au nanoparticles; Table S11: The calculation parameter of the constant pressure heat capacity (C_p (J.mol⁻¹K)) of Au nanoparticles; Table S12: The simulation data from Li' model of Au nanoparticles; Table S13: The simulation data from Ouyang' model of Au nanoparticles in 0 K; Table S14: The simulation data from Ouyang' model of Au nanoparticles in 300 K; Table S15: The Linear relationship between the chemical bond energy and vacancy formation in common metal materials; Table S16: Linear relationship between vacancy forming energy and diffusion activation energy in common metal materials.

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