

# DFT Study of Pt/TiO<sub>2</sub> Single Atom Catalyst with Oxygen Vacancy Rich Surface

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## Research Article

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# Abstract

The titanium dioxide (TiO<sub>2</sub>) surface is suitable as a substrate for single-atom catalysts (SACs). As a common defect on TiO<sub>2</sub>, oxygen vacancy may have significant impact on the adsorption and activity of the adatoms. This work aims to investigate whether titanium dioxide containing surface oxygen vacancies is more suitable as a base material for SACs. This paper calculates the changes in the adsorption energy of Pt atoms and the energy of the d-band center on the perfect surface and the surface containing oxygen vacancies. With respect to perfect surface, the surface containing oxygen vacancies fixes Pt atom more firmly, and increases the center energy of the d-band of Pt, thereby improving the performance of Pt atom as SACs. Consequently, the (110) surface of Rutile TiO<sub>2</sub> with oxygen vacancies may be the best substrate for SACs.

## 1. Introduction

Oxygen reduction reaction (ORR) plays a vital role in various energy conversion and storage systems (such as fuel cells and metal-air batteries), and understanding which electronic factors are involved in the oxygen reduction reaction is a top priority. With the advent of single-atom catalysts (SACs), using a single metal atom to promote chemical reactions has become a more efficient method. The interaction between the substrate (holding materials) and the active metal atoms may have significant impact on the catalytic activity of the metal. On one hand, to obtain a stable contact, the adsorption energy of the metal atom on the substrate needs to be high. On the other hand, the influence of the substrate on the electronic structure of the metal needs to be taken into account. Hammer and Nørskov<sup>[1-3]</sup> proposed the d-band center theory, which claims that the adsorption energy of the molecule is mainly determined by the occupancy rate of the bonding and anti-bonding states formed by the hybridization of the d-state electrons wave function of the adsorbate and the substrate. If the anti-bonding state lies below the Fermi level (E<sub>F</sub>), the interaction between the adsorbate and the metal surface will become repulsive, resulting in weak chemical adsorption. This situation can be well characterized by the position of the d-band center of the metal. The down shift of the d-band center will lead to a stronger chemisorption. In addition, Stamenkovic et al.<sup>[4]</sup> found that ORR activity is correlated with the d-band center of platinum crystal. As the center of the d-band moves away from the E<sub>F</sub>, the observed ORR activity of Pt is higher. Lu et al.<sup>[5]</sup> also observed a strong correlation between the d-band center and oxygen adsorption energy on the surface of various single crystal metals, which is consistent with the d-band center model.

The choice of the substrate has an effect on the adsorption energy and the center of the d-band. Tianyi Wang et al.<sup>[6]</sup> calculated the d-band centers of different transition metals loaded on the perfect (001) surface and (101) surface of TiO<sub>2</sub>, including Pt single atom, and obtained the relationship between the different adsorption energies and the center of the d-band center. It is believed that the (001) and (101) faces of Anatase TiO<sub>2</sub> are suitable for single-atom catalyst substrates. However, the rich surface defects structure is more likely to affect the d-band center and further affect the ORR performance<sup>[7-9]</sup>. Therefore, it is necessary to study the influence of surface defects of the TiO<sub>2</sub> substrates on the d-band center.

In this study, we systematically calculated the adsorption energy of the single Pt adatom on the (001) and (101) surface of Anatase TiO<sub>2</sub> and (100), (011), (101) surface of Rutile TiO<sub>2</sub> in the presence of oxygen vacancy, and the d-band center of the Pt adatoms by Density functional theory(DFT) method. It is found that the relationship between the adsorption energy and the d-band center with and without oxygen vacancies are different. Furthermore, clear dependence of the d-band center of the Pt atom on the adsorption energy was found. This behavior is attributed that the oxygen vacancy changes the electron cloud density of adjacent Ti atoms, making the d electrons of Pt atom and Ti atoms overlap.

## 2. Computational Method

We used the DFT method by Vienna initio Simulation Package (VASP) to calculate the single-point energy and spin polarization geometry calculations, and used GGA to process the corrected Perdew-Burke Ernzerhof (RPBE) electronic correlation function. The cutoff energy for geometric optimization and self-consistent calculation is set to 520eV, and the K point is selected as 3×3×1.

For adatom-TiO<sub>2</sub> system, a single Pt atom is adsorbed on the (2 × 2) supercell of Anatase TiO<sub>2</sub> (001) (101) surface and (2 × 2) supercell of Rutile TiO<sub>2</sub> (100),(011),(101) surface. A vacuum space of 15Å is applied in the vertical direction to eliminate non-physical interactions between adjacent images. All geometric structures were optimized until the residual force is less than -0.001 eV /Å.

The interaction between Pt atom and TiO<sub>2</sub> surface is described as average adsorption energy (E(ads)). The calculation formula is defined as:  $E(\text{ads}) = E(\text{Pt+TiO}_2) - E(\text{TiO}_2) - E(\text{Pt})$ , where  $E(\text{Pt+TiO}_2)$  is the total energy after adsorption of Pt atom,  $E(\text{TiO}_2)$  is the energy of the TiO<sub>2</sub> surface without Pt atom,  $E(\text{Pt})$  is the energy of a single platinum atom.  $E(\text{ads})$  is usually calculated to check the adsorption stability, and a negative value indicates exothermic adsorption<sup>[10]</sup>. The greater the negative value of  $E(\text{ads})$ , the more stable the system should be. Therefore, negative  $E(\text{ads})$  means that the single metal can be stably fixed on TiO<sub>2</sub>. In addition, the calculation formula of cohesive energy  $E(\text{coh})$  is defined as:  $E(\text{coh}) = E(\text{metal}) - E(\text{single})$ , where  $E(\text{metal})$  and  $E(\text{single})$  represent the total energy derived from bulk Pt metals and single Pt metal .

## 3. Results And Discussion

The stability of SACs largely depends on the adsorption location and surface defects. The oxygen vacancies on the surface of TiO<sub>2</sub> not only provide active sites for fixing metal atoms, but also affect the catalytic performance. Single metal atom is introduced on perfect and oxygen vacancies surface of Anatase(001), (101) and Rutile(100), (011), (101) in supporting information Fig.S1 and Fig.S2. We calculated the adsorption energy of possible adsorption sites to find the most stable energy in supporting information Table S1. We calculated the most stable adsorption energy ( $E(\text{ads})$ ) and d-band center energy of different oxygen vacancies and different perfect surfaces for comparison in Fig. 1 and Fig. 2. We found that the adsorption energy we calculated always shows the same trends on these surfaces: the

adsorption energy of the surface containing oxygen vacancies is significantly higher than that of the perfect surface. It is speculated that the oxygen vacancies change the electronic distribution state of the surrounding Ti atoms, which makes the binding force of Pt and Ti atoms stronger.

The d-band center energy of (001) and (101) surface of Anatase  $\text{TiO}_2$  and (100), (011), (110) surface of Rutile  $\text{TiO}_2$  have been calculated in supporting information Table S2. We plot the d-band center energy with the most stable adsorption energy on surface in Fig. 3. We found from Fig. 3 that for the five types of  $\text{TiO}_2$  surfaces, the movement of the center energy of the d-band also shows the same trend: for a surface containing oxygen vacancies, the d-band center energy of Pt atom will be closer to the Fermi level. This shows that the surface containing oxygen vacancies may be more suitable for the substrate of Pt atom than the perfect surface for SACs.

The partial Density of States of perfect surface and oxygen vacancies surface of Anatase (001),(101) and Rutile (100), (011), (101) are given in Fig. 4 and Fig. 5. We can clearly see the change of the d-band energy of Pt atom on different surface. For the five types of surfaces, the d-band energy of Pt after introducing oxygen vacancies has increased significantly. At the same time, the hybridization between O atoms and Pt atom becomes weak, and the hybridization between Pt atom and Ti atoms increases. The interaction between Pt atom and Ti atoms may be the reason for increasing the d-band energy of Pt atoms.

Otherwise, We calculated the d-band center energy of the Pt atom on the Pt metal bulk, which is -2.22eV, consistent with -2.23 eV which calculated by Tianyi Wang et al.<sup>[6]</sup>. We found that the d-band centers of Pt atom on selected  $\text{TiO}_2$  surfaces are closer to the Fermi level than the d-band centers of Pt atom on the metal bulk. According to the d-band center theory of transition metals, the Pt atom on the surface containing oxygen vacancies are more conducive to adsorbing other atoms than the Pt atom on the metal bulk. Fig. 6. shows the relationship between the adsorption energy and the center of the d-band of Pt atom on different surfaces. under the line is the perfect surface, above the line is oxygen vacancies surface. Compared with the perfect surface, it is much easy to obtain a larger adsorption energy or a higher d-band center for the containing oxygen vacancy surface.

Generally, the adsorption energy and cohesive energy was compared to evaluate the thermodynamic stability of SACs. The cohesive energy of Pt is -5.48 eV calculated in our work in supporting information Table S3, consistent with 5.53 eV which calculated by Philipsen P H T<sup>[11]</sup>. Fig. 7 shows the relationship between adsorption energy and cohesive energy of different  $\text{TiO}_2$  surfaces. We found that on the surface of Rutile(110) and Rutile(011) with oxygen vacancies, the adsorption energy of Pt atom is higher than the cohesive energy of Pt metal. This means that its thermodynamic stability is much better than the that of those perfect surface whose adsorption energy is much smaller than their cohesive energy which may not be stable enough as SACs except Rutile(110).

## 4. Conclusion

The calculation shows the effect of oxygen vacancy on the adsorption energy and d-band center energy of Pt atom on the surface of Anatase and Rutile TiO<sub>2</sub>. On one hand, the introduction of oxygen vacancies will make the adsorption energy of TiO<sub>2</sub> for a single Pt atom increase, so that Pt atom can be more stably adsorbed on TiO<sub>2</sub>. On the other hand, it will also cause the d-band center of the Pt atom toward the Fermi level, which will make it possible to have better catalytic performance. After introducing oxygen vacancies, the increase of adsorption energy makes the adsorption energy on some surfaces higher than the cohesive energy of Pt, which improves the thermodynamic stability of loading Pt atom on TiO<sub>2</sub> as SACs. The calculation results show that the (110) surface of Rutile TiO<sub>2</sub> with oxygen vacancies has the best balance between the adsorption energy and the center of the d-band among the five common surfaces calculated, and is more suitable for SACs.

## Declarations

### **\*Funding:**

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### **\*Conflicts of interest/Competing interests:**

Not applicable

### **\*Availability of data and material:**

All data are calculated by the author and attached to the supporting materials.

### **\*Code availability**

Not applicable

### **\*Authors' contributions**

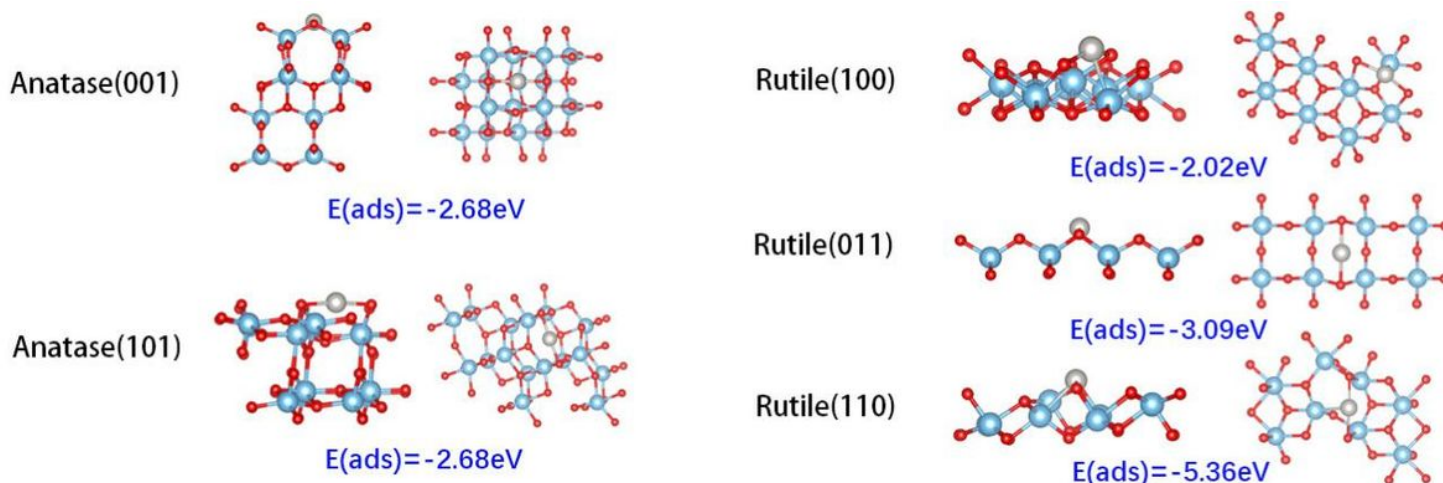
The first author calculates and analyzes all the data in the manuscript, and completes the writing of the manuscript. The second author and the corresponding author provide the use of the copyright of the VASP software and put forward suggestions for improvement.

## References

1. Hammer, B., Nørskov, J. K. Nature 1995, 376, 238.
2. Hammer, B., Morikawa, Y., Nørskov, J. K. Phys. Rev. Lett. 1996, 76, 2141.
3. Hammer, B. Top. Catal. 2006, 37, 3.
4. Stamenkovic, V., Mun, B. S., Mayrhofer, K. J. J., Ross, P. N., Markovic, N. M., Rossmeisl, J., Greeley, J., Nørskov, J. K. Angew. Chem., Int. Ed. 2006, 45, 2897.

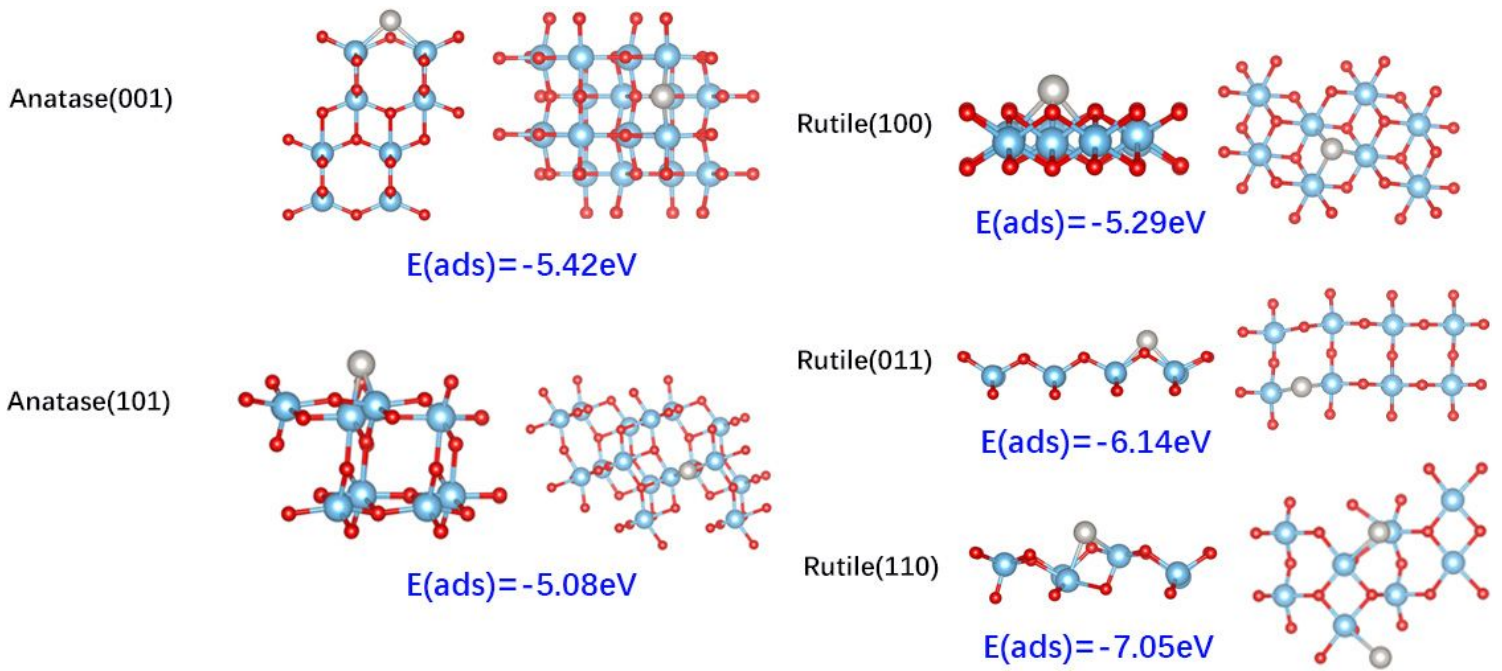
5. Lu, C., Lee, I. C., Masel, R. I., Wieckowski, A., Rice, C. J. Phys. Chem. A 2002, 106, 3084.
6. Tianyi Wang, Siyao Qiu, Zhongxu Dai, Rosalie Hocking, Chenghua Sun, Applied Surface Science 2020, 533,147362
7. T. Wei, Y. Zhu, Y. Wu, X. An, L. Liu, Effect of single-atom cocatalysts on the activity of faceted TiO<sub>2</sub> photocatalysts, Langmuir. 35 (2019) 391–397.
8. T. Sun, Y. Wang, H. Zhang, P. Liu, H. Zhao, Adsorption and oxidation of oxalic acid on Anatase TiO<sub>2</sub> (001) surface: A density functional theory study, J. Colloid. Interf. Sci. 454 (2015) 180–186.
9. S. Nong, W. Dong, J. Yin, B. Dong, Y. Lu, X. Yuan, X. Wang, K. Bu, M. Chen, S. Jiang, L. Liu, M. Sui, F. Huang, Well-dispersed ruthenium in mesoporous crystal TiO<sub>2</sub> as an advanced electrocatalyst for hydrogen evolution reaction, J. Am. Chem. Soc. 140 (2018) 5719–5727.
10. C. Liu, Q. Li, C. Wu, J. Zhang, Y. Jin, D.R. MacFarlane, C. Sun, Single-boron catalysts for nitrogen reduction reaction, J. Am. Chem. Soc. 141 (2019) 2884–2888.
11. Philipsen P H T , Baerends E J .. Phys Rev B Condens Matter, 1996, 54(8):5326-5333.
12. B. Hammer, J. K. Nørskov, Catalysis-calculation and concepts, Adv. Catal. 45 (2000) 71–129.
13. A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, J. K. Nørskov, Surface electronic structure and reactivity of transition and noble metals, J. Mol. Catal. A: Chem. 115 (1997) 421–429.

## Figures



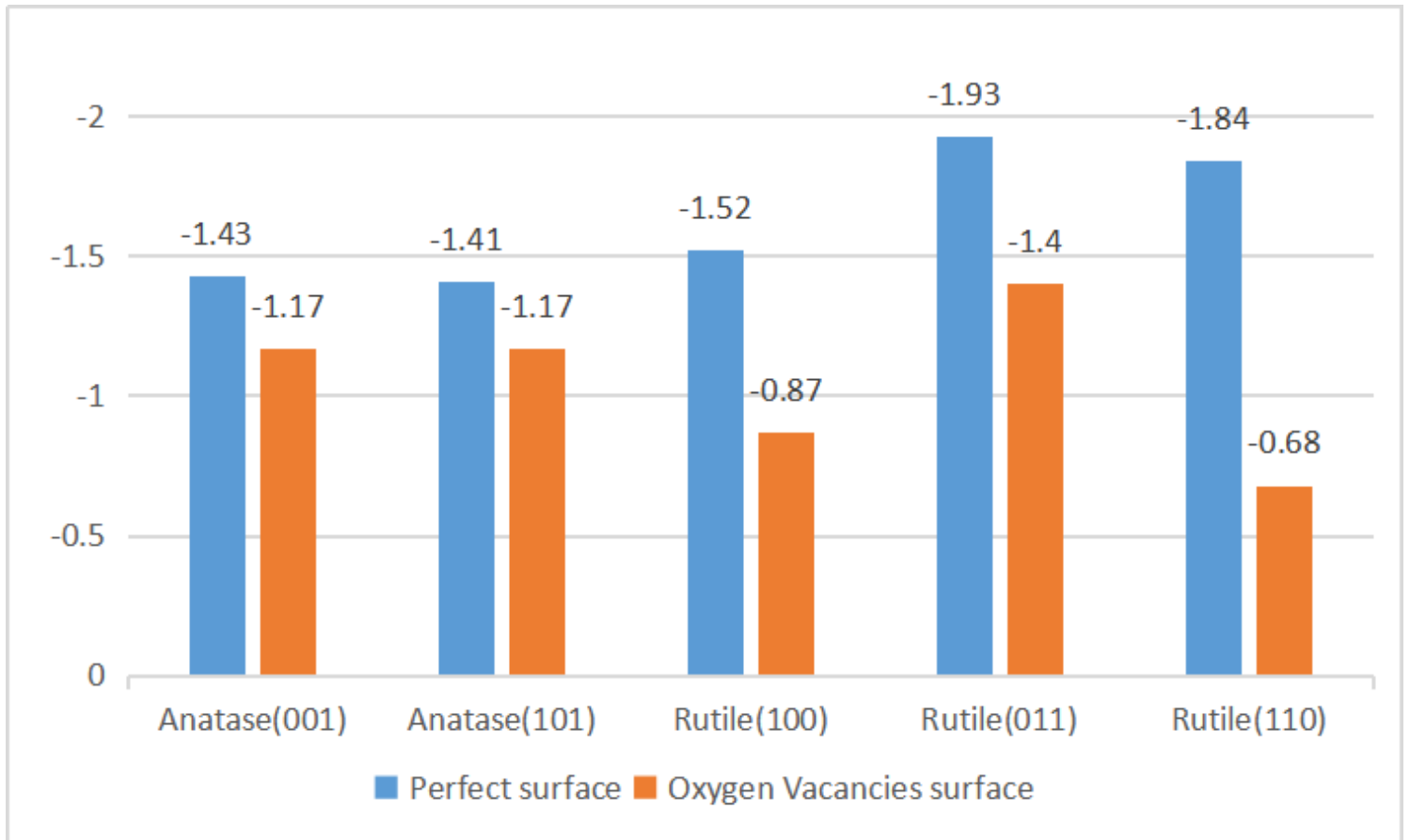
**Figure 1**

The adsorption energy ( $E(\text{ads})$ ) of single Pt atom on perfect surface of Anatase(001),(101) and Rutile(100), (011), (101). Ti, O and Pt are indicated as blue, red and grey.



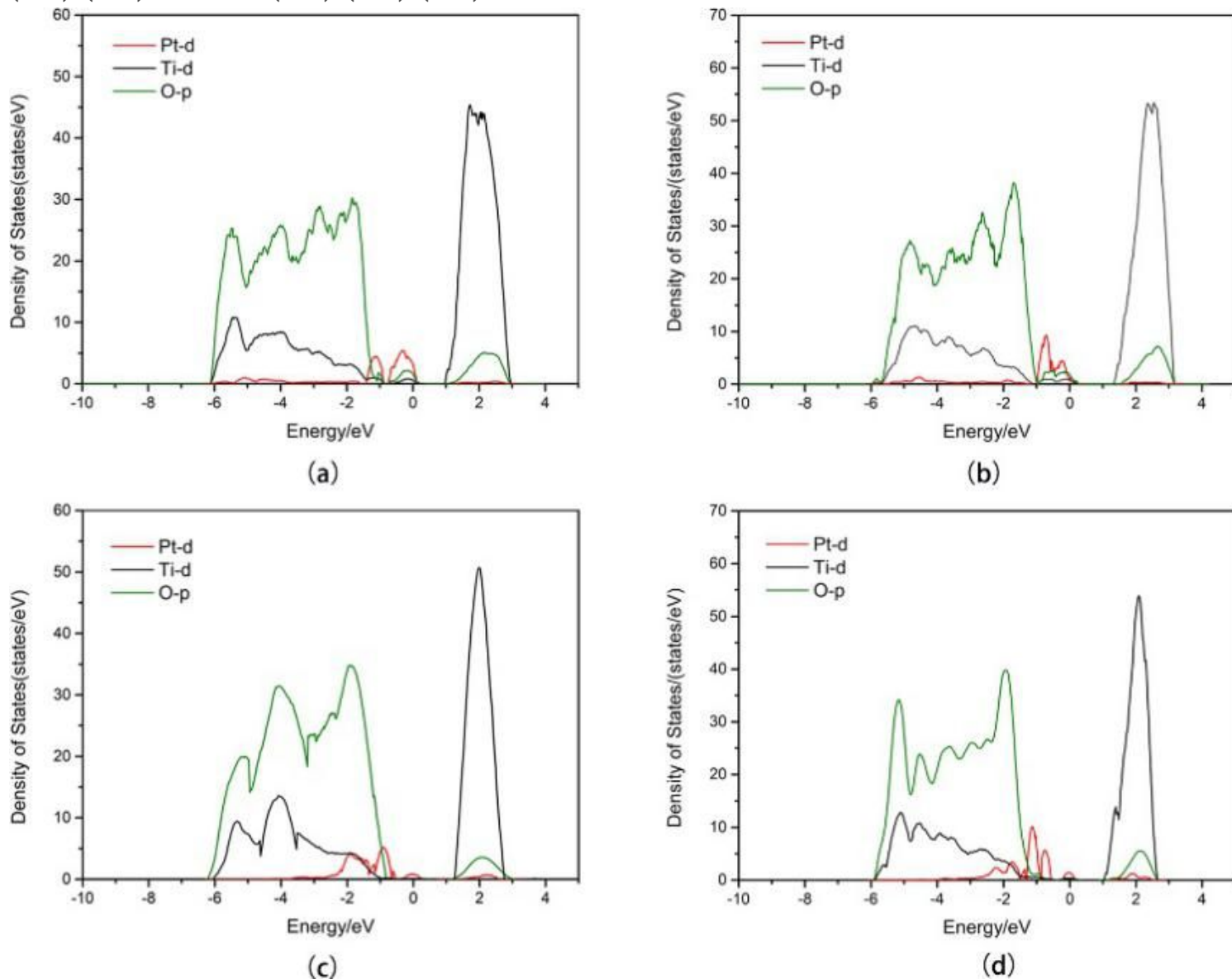
**Figure 2**

The adsorption energy ( $E(\text{ads})$ ) of single Pt atom on oxygen vacancies surface of Anatase (001), (101) and Rutile (100), (011), (101). Ti, O and Pt are indicated as blue, red and grey.



**Figure 3**

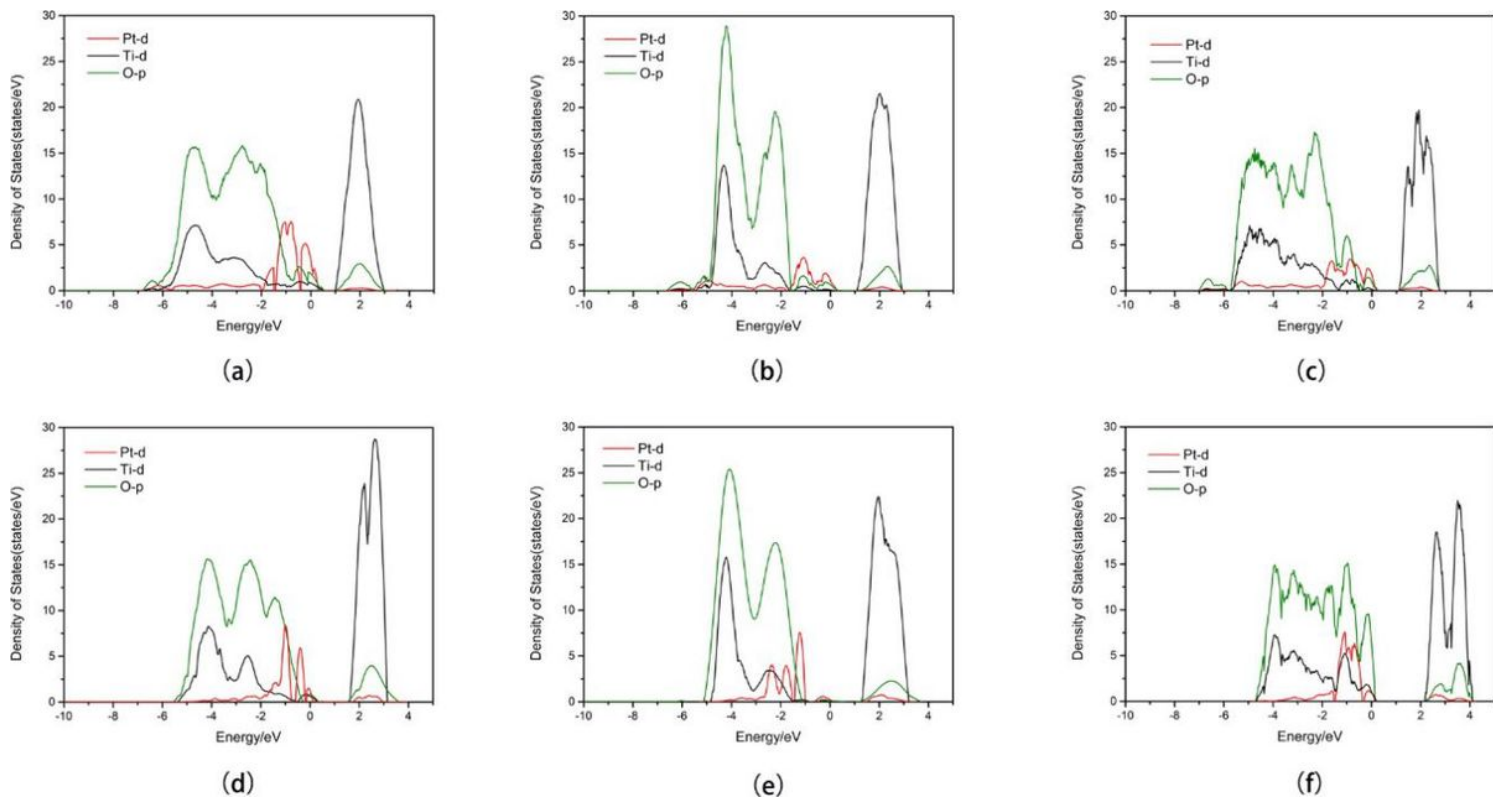
The d-band center energy of single Pt atom on perfect surface and oxygen vacancies surface of Anatase (001), (101) and Rutile (100), (011), (101). Unit is eV.



**Figure 4**

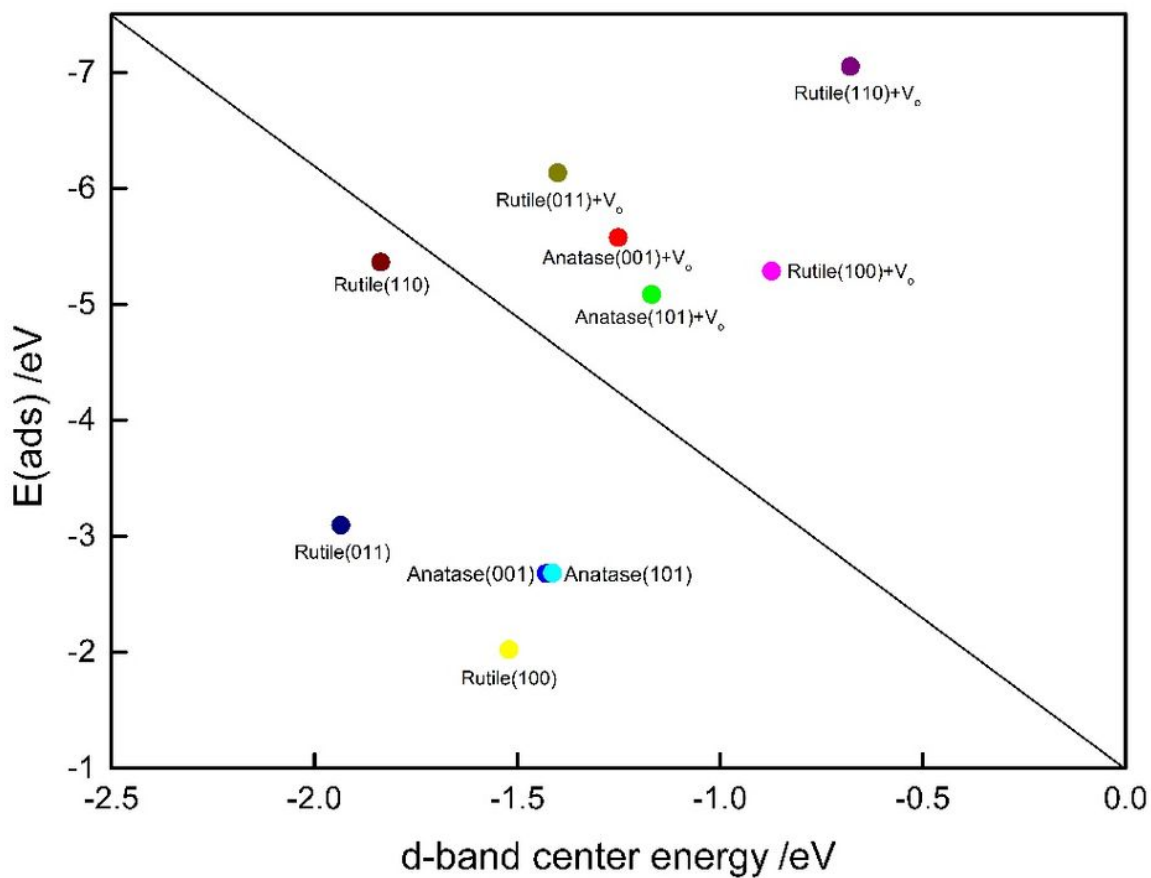
Partial Density of States of Anatase TiO<sub>2</sub> (001) perfect surface (a) and (101) perfect surface (b), compared with Anatase TiO<sub>2</sub> (001) oxygen vacancies surface (c) and (101) oxygen vacancies surface (d). The energy in the figure has subtracted the Fermi level.





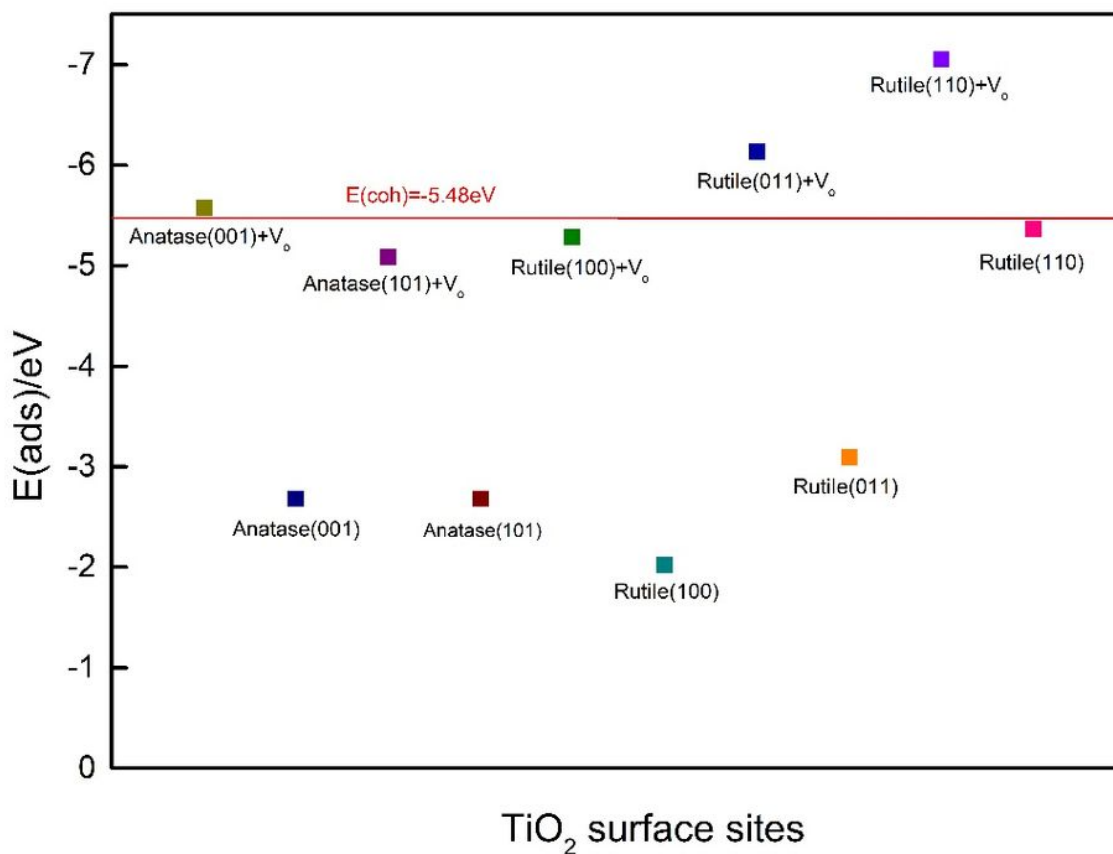
**Figure 5**

Partial Density of States of Rutile TiO<sub>2</sub> (100) perfect surface(a), (011) perfect surface(b) and (110) perfect surface(c), compared with Rutile TiO<sub>2</sub> (100) oxygen vacancies surface (d), (011) oxygen vacancies surface(e) and (110) oxygen vacancies surface(f). The energy in the figure has subtracted the Fermi level.



**Figure 6**

The schematic diagram of the d-band center energy and the adsorption energy of the Pt atom on different adsorption surface modes. Surfaces containing oxygen vacancies are represented by V<sub>o</sub>.



**Figure 7**

relationship between adsorption energy and cohesive energy of different surfaces. The red line indicates the cohesive energy ( $E(\text{coh})$ ) of Pt. Surfaces containing oxygen vacancies are represented by V<sub>o</sub>.

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