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First-principle study of O vacancy on LaNiO₃ (001) surface

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ABSTRACT

In the paper, based on the first principle of density functional theory, it is easier to form O vacancy on the surface by calculating vacancy formation energy, from which the adsorption problems of H₂ molecule on LaNiO₃ (001) surface with O vacancy are calculated and analyzed. By calculating the adsorption energy and dissociation energy of LaNiO₃ (001) surface with O vacancy, it is found that there are two kinds of chemical adsorption modes on the surface of LaNiO₃ (001): The first one is that two H atoms are adsorbed to the same O atom to form H₂O molecules, which is the best adsorption position where the PBE and PBESOL functionals are applied to perform geometry optimization and property analysis, and it is found that the application of PBESOL functional is less ideal than the application of PBE functional and takes longer. At this point, the effects of H and O atoms result from the orbital hybridization effects of H 1s and O 2p, and there is a typical covalent bond between H and O. The second one is that two H atoms are respectively adsorbed to the two O atoms, forming two –OH groups. Furthermore, H₂ molecules on the surface of LaFeO₃ (010) can also set off physical adsorption. The results show that the existence of O vacancy will lead to the increasing of adsorption energy of H, which is easier to reserve hydrogen; it also will reduce the conductivity of the surface, however, the surface conduction band with O vacancy will increase after absorbing H and its electrical conductivity will be enhanced; to appropriately increase the quantity of O vacancy of the surface will accelerate the decomposition of H₂, but it does not have much effect on the electrical conductivity of the surface.

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Introduction

ABO₃ perovskites are a group of materials that possess many interesting physical properties and functional behaviors, such

as good metallic ground state, electrochemical properties, high discharge capacity and conductivity [1,2]. So far, it has been observed that the properties and functional behaviors of the perovskites are heavily influenced by the presence of oxygen vacancies (VO) in these materials [2–5], and so the

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problem of VO has been extensively studied both theoretically and experimentally. For example, several point defects in VO in LaAlO₃ (LAO) film have been studied theoretically [6–18]. Zhang et al. [8] have recently shown that VO preferably forms at the AlO₂ surface of the LaAlO₃ overlayer on SrTiO₃ (STO) by using density functional theory, Zhong et al. [9] have discussed the similar position dependence of formation energy of an VO in the LAO/STO superlattice, Seo et al. [10] use density functional theory to investigate the influence of surface vacancies on the surface stability of a stoichiometric free-standing LaAlO₃ (001) thin film. Pavlenko et al. [11] and Lin et al. [12] found that VO at SrTiO₃ is responsible for a strong orbital reconstruction, Ref. [13] performs density functional theory (DFT) calculations for a number of SrTiO₃ slabs with various concentrations of oxygen vacancies and analyze the origin of the unusual metallic state appearing at the surface of the slabs. Lee et al. [14] and Ref. [15] discuss an approach to performing ab initio studies on these materials for SOFC applications and applies the approach to calculate oxygen vacancy formation energies in LaBO₃ (B=Mn, Fe, Co, Ni) compounds, the result shows that LaBO₃ oxygen vacancy formation energies are predicted to be in the order Fe > Mn > Co > Ni (where the largest implies most difficult to form a vacancy). And then, in experiment, Kagomiya et al. [16] investigate the characteristic of oxygen vacancy formation in layered perovskite (Sr, La)_{n+1}Fe_nO_{3n+1} with the perovskite layer number: n = 3, oxygen vacancy content δ of the (Sr_{0.775}La_{0.225})₄Fe₃O_{10-δ} (SLF4310) by a titration technique and a thermogravimetric analysis, the result find that distribution of vacancy sites in the SLF4310 changes at approximately 775 °C, accompanying no structural phase transition, and the vacancy distribution change affects to the ion conductivity of the SLF4310. Hu et al. [17] find that the electrical and optical properties of LaNiO₃ films are strongly dependent on the oxygen vacancies induced in the sputtering process. Using X-ray photoelectron spectroscopy, Qiao et al. [18] directly observe the oxygen vacancies in various LaNiO₃ films by O 1s core-level deconvolution method and also investigate the process (deposition and annealing) dependent electronic and transport properties of LaNiO₃ films on Si substrates, the result shows that oxygen vacancies formation during oxygen deficient deposition or vacuum annealing will lead to decrease of conductivity. Gupta et al. [19] find that Vacancy defects are known to play an important role in the structural and chemical properties of metallic and semiconductor nanoparticles. Zhu et al. [20] find that defect of the LaNiO₃ crystal structure as O vacancies promote charge localization and decrease conductivity of the LaNiO₃ along with the strain. Rodriguez et al. [21] discuss that the interaction between H₂ and O vacancies can be complex, O vacancies affect the chemistry of H₂ on the oxide surface, and at the same time, the adsorbate can affect the distribution of O vacancies in the surface and subsurface regions of the sample. In previous work, the process of hydrogen storage for LaNiO₃ (001) has been researched by the density functional theory (DFT), due to low resistivity and high chemical stability of LaNiO₃ make it an ideal template for epitaxial growth of all-oxide parallel plate capacitors with highly tunable oxide ferroelectric layers [22–24], and VO can greatly influence the mechanical, electrical and conductive properties of LaNiO₃ [25], and then the O vacancies play a key

role in the dissociation of H₂ [20], so it is important to research the influence of VO for hydrogen storage in this paper.

Calculation

Calculation parameters

All calculations are carried out with the Cambridge serial total energy package (CASTEP) [26] of Material Studio 6.1 software base on the DFT level and use periodic boundary conditions and plan-wave expansion of the wave function. The exchange-correlation functional based on generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Eruzerhof (PBE) [27] are used in optimization procedure, accurate describe the interaction between electron and ion by ultrasoft pseudo potential (USPP) [28] formalism. LaNiO₃ belongs to a rhombohedral perovskite (R-3c). All calculations are done with an energy cutoff of 600 eV and a 2 × 2 × 1 k-point mesh in the Brillouin zone [29], which is used for a 2 × 2 supercell of LaNiO₃ (001) with an oxygen vacancy containing 59 total atoms (Fig. 1A), considering the calculation accuracy and computational efficiency with self consistent converges to 2.0 × 10⁻⁵ eV/atom and the vacuum region is 10 Å-thick to ensure that the vacuum thickness is large enough to avoid spurious interactions between the slabs. Optimizing the cubic lattice constants of LaNiO₃ (001) with an oxygen vacancy and the results are presented in Table 1, the appearance of oxygen vacancy enlarge the lattice constants of LaNiO₃, Oxygen deficiency in LaNiO₃ will reduce Ni element transformation from normally high-valence state to a low valence state, which often exhibits a relatively larger ionic radius, thus the distorted Jahn–Teller effect will expand the volume of NiO₆ oxygen octahedral and results in an enlarged lattice constant. Qiao et al. [18] find the oxygen vacancy related dilation of lattice volume (or lattice constant) for ABO₃ perovskite oxide is not rare, and Similar expansion of lattice volume had been also observed by Mi et al. [30] and Cai et al. [31] in sputtered ferroelectric BaTiO₃ and molecular beam epitaxial dielectric SrTiO₃, respectively.

The calculation of vacancy formation energy

According to the definition about the surface oxygen vacancy formation energy [14,32]:

$$E_{vf} = E_{vac} - E_0 + 1/2 (E_{O_2} + \Delta h_{O_2}^0), \quad (1)$$

where E_{vac} and E_0 are the energies of the LaNiO₃ (001) with and without an oxygen vacancy, respectively. E_{O_2} is the calculated energy of the O₂ molecule and $\Delta h_{O_2}^0$ is a correction term, which accounts for errors that do not cancel between the treatment of oxygen in the gas and solid phases, Wang et al. [33] calculate $\Delta h_{O_2}^0 = 0.33\text{eV}/O_2$.

The different positions of O vacancy in all atomic layers and vacancy formation energies of the corresponding locations that are calculated from Fig. 2A and B. As can be seen in Fig. 2B, the O vacancy formation energy of surface is small than inner, O vacancy in crystal has a migration tendency

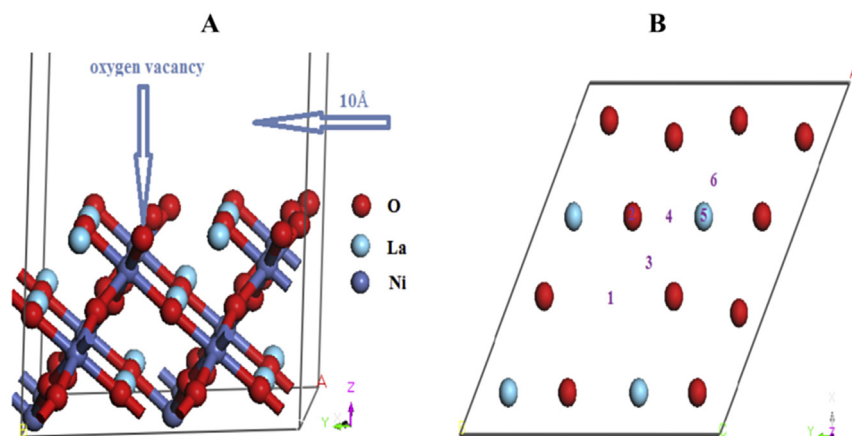


Fig. 1 – A: The structure of LaNiO_3 (001) with O vacancy, all the possible adsorption positions for H_2 in A are shown in B (●: O, ●: La, ●: Ni, 1–6 mean different adsorption positions, 1: O vacancy(V), 2: top-O (T1), 3: short-bridge-O(B1), 4: bridge-La-O(B2), 5: top-La (T2), 6: long-bridge-O(B3)).

Table 1 – It lists optimized the cubic lattice constants of LaNiO_3 (001) with an oxygen vacancy/Å (Exp. [28] and theoretical results are presented in it).

	Exp. [28]	Theory	VO
a = b	5.4534	5.3098	5.4832
c	13.1369	13.1074	13.1597

towards film surface in order to make the system stable and the energy lowest. Therefore, the O vacancy is easier to appear to the crystal surface. In calculation, the vacancy formation energy of (001) surface is lower than bulk, which comes from Fig. 2C and Table 2. In Ref. [32], the largest implies most difficult to form a vacancy, (001) surface have 1–2 eV lower vacancy formation energies and therefore far higher vacancy concentrations than the bulk, the paper results $\Delta E = 1.12$ eV (where ΔE is difference of formation energy

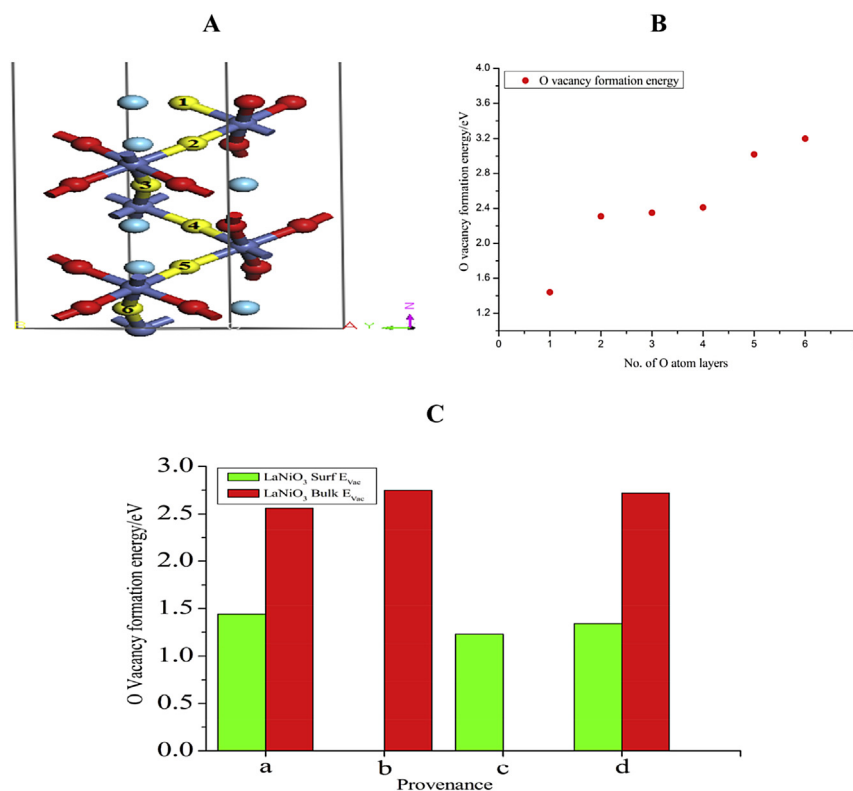


Fig. 2 – The different positions of O vacancy in all atomic layers and vacancy formation energies of the corresponding locations that are calculated from A and B. C displays the vacancy formation energy of (001) surface and bulk (a: This work b: Ref [14] c: Ref [15] d: Ref [31]).

Table 2 – The vacancy formation energy of (001) surface and bulk, ΔE is difference of formation energy between bulk and surface (The Ref. [14,15] and Ref. [31] are also listed).

	E_{bulk}	E_{surf}	ΔE
Our work	2.56	1.44	1.12
Ref. [14]	2.75		
Ref. [15]		1.23	
Ref. [31]	2.72	1.34	1.38

between bulk and surface), which is consistent with Ref. [32]. So, LaNiO₃ (001) surface is more likely to form O vacancy relative to bulk.

Calculations of adsorption energy and dissociation energy on LaNiO₃ (001) surface with oxygen vacancy

Based upon the analysis of adsorption and dissociation energies on LaNiO₃ (001) surface with oxygen vacancy, the most stable adsorption position and related properties on LaNiO₃ (001) surface with oxygen vacancy are researched. The adsorption energy is defined as the following equation [34]:

$$E_{ads} = E_{clean} + E_{H_2} - E_{slab/H_2}, \quad (2)$$

Here, E_{clean} and E_{slab/H_2} are total energy of the LaNiO₃ (001) and LaNiO₃ (001)/H₂ with oxygen vacancy, respectively. E_{H_2} signifies total energy of a H₂ molecule. In terms of this definition, a positive value corresponds to an exothermic process and indicates a stable structure. Moreover, E_{dis} is dissociation energy and the dissociation energy can be expressed as the following equation:

$$E_{dis} = -(E_{H_2} - 2E_H), \quad (3)$$

where E_H is a H atom energy. The dissociation energy of H₂ is smaller than a free H₂ by calculating, which indicates H₂ presents a dissociation phenomenon. A negative value shows that the H₂ molecule has been dissociated completely and the smaller value demonstrates dissociation more abundant for H₂.

Results and discussion

The analysis about surface adsorption positions

All the possible adsorption positions for H₂ in Fig. 1A are shown in Fig. 1B. The calculated adsorption energy and dissociation energy of different positions for LaNiO₃ (001) surface with oxygen vacancy are taken from Table 3, and also list the minimum distance between H atom and surface atoms after adsorption and adsorption energy and dissociation energy of perfect surface. Table 3 displays adsorption of different sites. When H₂ molecule is located on T1 (top-O), applying PBE and PBESOL functional geometry optimization for this position, the results present the application of PBE functional than PBESOL ideal and the application of PBE functional takes less time from the energy point of view. The calculated adsorption energy is larger than 40 kJ mol⁻¹ significantly (the adsorption

energy of a H₂ molecule is 0.415 eV), which indicates that this adsorption is a strong chemical adsorption [35] on this position (T1), and then energy of system is the lowest, which means that LaNiO₃ (001)/H₂ with oxygen vacancy system achieve a most stable structure on T1. The calculated bond length of H–H is larger obviously than the experimental value of Kresse et al. [36] and dissociation energy changes little after geometry optimization, which shows that H₂ molecule has been dissociated and two H atoms approach to a same O atom and form a H₂O molecule (Fig. 3A), the structure is almost in agreement with the value that Lie et al. [37] calculate geometric parameters of H₂O molecule (the bond length of H–O and H–H are 0.978 Å and 1.545 Å, respectively). When H₂ molecule locate on B1, B2 and B3 (bridge-O), respectively, The bond length of H–H is larger obviously and dissociation energy changes little after geometry optimization, which indicates H₂ molecule has been dissociated and two H atoms approach to two O atoms finally and then form two –OH with O atom (Fig. 3B). When H₂ molecule lists on V position (O vacancy), the calculated adsorption energy (0.01 eV) is smaller than 0.415 eV on V, which manifest that the adsorption manner is a physical adsorption. When H₂ molecule put on T2 (top-La), adsorption energy is negative value (the reaction is an endothermic reaction) on T2, therefore, its adsorption manner is instability.

However, when H₂ is located on same position, the adsorption energy of containing O vacancy is larger than perfect as can be observed Table 3. Therefore, the surface with O vacancy is more easy to adsorb H than perfect surface, which is principally similar to the conclusion of Zhu et al. [20] “the presence of O vacancy leads to increase the adsorption energy of H”.

Increasing greatly the number of O vacancy in (001) surface (Fig. 4) and then discussing the influence of O content on surface for adsorption H properties. When H₂ put T1(O-top), comparing the change of vacancy1-4 after geometry optimization. As can be shown in Table 4, the dissociation energies change large and the dissociation energies have become negative value with increasing the number of surface vacancy, which displays H₂ molecule has been dissociated completely and two H atoms approach to O-top finally and form two –OH with O atom (Fig. 4). However, the surface with an O vacancy form a H₂O molecular, H₂ dose not dissociated completely. Therefore, with increasing the number of vacancies make H₂ molecular dissociate quickly. Rodriguez et al. [21] Hold that an amount of O vacancy has a influence for H₂ dissociation.

The analysis about charge population

The bonding strength among atoms is quantitative analyzed by charge population, and the formation of chemical bond is electron gas redistribution among atoms so that the whole system achieves a lowest energy state [38]. When H₂ adsorbs on LaNiO₃ surface with O vacancy, which must contain charge transfer and the change of electronic structure. Therefore, the information about interaction of H and surface could be revealed by analyzing the Mulliken charge before and after adsorption. Table 5 lists the charge and bond populations with PBE and PBESOL functional on T1. In Table 5, the negative net charges of O1 that combine with H get large, the positive

Table 3 – The calculated parameters of geometry and energy about LaNiO_3 (001)/ H_2 with O vacancy and perfect surface after geometry optimization. Applying PBE and PBESOL functional geometry optimization on T1, the experimental value [35,36] are also included. (T, B and V represent top, bridge and vacancy site, respectively. T1 indicate top-O, T2 is top-La, B1–B3 show bridge, V means O vacancy. The specific positions are shown in Fig. 1B. $r_{\text{H-H}}$, $r_{\text{H-O}}$, $r_{\text{H-Ni}}$, $r_{\text{H-La}}$ remark the smallest length of H and H, O, Ni, La, respectively. $E_{1\text{ads}}$ and $E_{0\text{ads}}$ mean that the adsorption energy of the surface with O vacancy and perfect, respectively. $E_{1\text{dis}}$ and $E_{0\text{dis}}$ signify the dissociation energy of the surface with O vacancy and perfect, respectively).

Initial position (H_2)		$r_{\text{H-H}}$	$r_{\text{H-O}}$	$r_{\text{H-Ni}}$	$r_{\text{H-La}}$	$E_{1\text{ads}}$	$E_{0\text{ads}}$	$E_{1\text{dis}}$	$E_{0\text{dis}}$
T1	PBE	1.598	0.991	2.500	3.234	2.392	2.074	1.242	1.105
	PBESOL	1.635	0.999	2.305	3.062	1.796		1.691	
T2		0.755	3.176	4.433	3.022	−0.024	−0.045	4.518	4.525
B1		1.947	0.986	2.495	2.875	2.151	2.106	0.109	−1.678
B2		1.185	1.119	2.580	2.491	0.171		1.903	
B3		2.669	0.982	2.252	3.067	0.682		−1.198	
V		0.758	2.842	3.454	3.073	0.010		4.518	
Exp.	H_2 [35]	0.752						4.480	
	H_2O [36]	1.545	0.978						

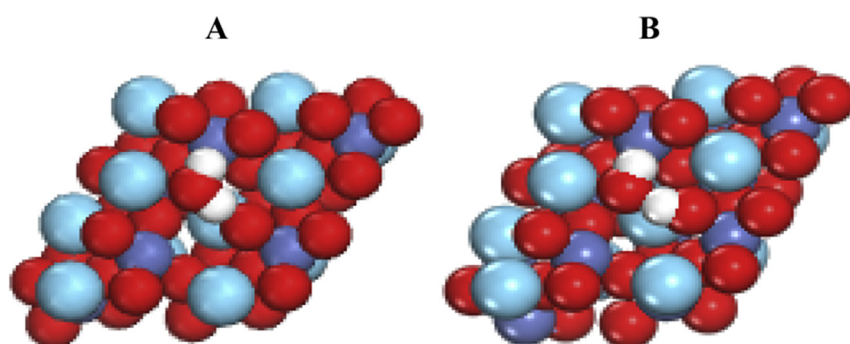


Fig. 3 – A and B show the adsorption results of LaNiO_3 (001)/ H_2 with O vacancy on T1 and B after geometry optimization (c: H).

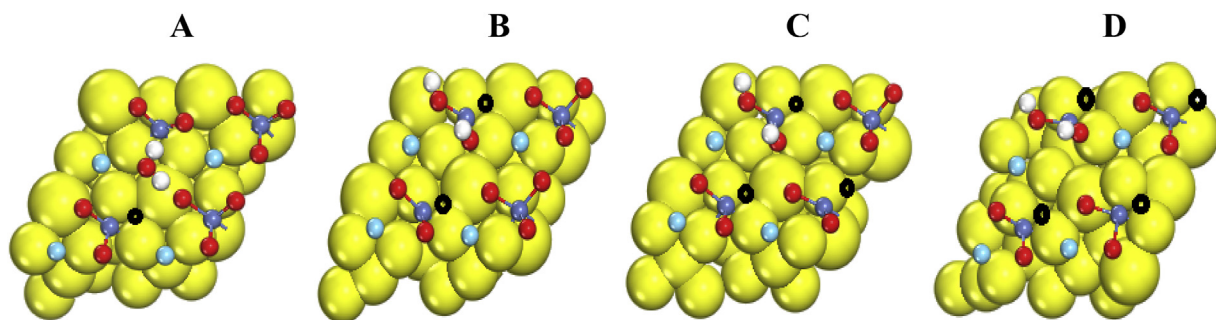


Fig. 4 – A-D represent the adsorption results of LaNiO_3 (001)/ H_2 system with an to four O vacancies on T1, respectively (c: all atoms of not the first surface).

charge of H increase significantly. The charges of Ni that combine O1 decreasing obviously and the O1–Ni bond population become small and O1–Ni bond length get long and the bond populations of H1, H2 and O1 change big. Which signifies

that the affection of O1–Ni and H–O1 get weaken and strengthen, respectively, that is to say, H and O1 make bonding enlargement. The difference of applying PBE and PBESOL functional from the point of electronic structure is small, but application of PBESOL functional take too much time.

Table 4 – It displays the dissociation energy of LaNiO_3 (001)/ H_2 with O vacancy on T1 (VO-1-4 represent the number of O vacancy in surface).

	VO-1	VO-2	VO-3	VO-4
Dissociation energy (H_2)/eV	1.242	−1.797	−1.793	−1.641

The analysis about electron localization function

Electron localization function (ELF) is also a tool of discussing charge transfer. Becke et al. [39] put forward a calculation method about local electronic distribution, which is signified

Table 5 – The calculated charge and bond populations of LaNiO_3 (001)/ H_2 with O vacancy base on PBE and PBESOL functional on T1 (A and B mean after and before adsorption, respectively. P and L illustrate population and the length of bond, respectively).

	PBE		PBESOL	
	A	B	A	B
O1	-0.85	-0.72	-0.83	-0.69
O2	-0.71	-0.67	-0.68	-0.65
O3	-0.79	-0.69	-0.76	-0.66
H1	0.38	0.00	0.38	
H2	0.35	0.00	0.35	
La	1.50	1.49	1.46	1.45
Ni	0.40	0.57	0.39	0.54

Bond	P		L/Å		P		L/Å	
	A	B	A	B	A	B	A	B
H1–O1	0.65	–	0.99	–	0.65	–	0.99	–
H2–O1	0.58	–	1.03	–	0.59	–	1.03	–
O1–Ni	–	0.37	3.13	1.91	-0.08	0.39	2.89	1.87
H1–H2	-0.12	0.88	1.59	0.75	-0.11	–	1.64	–

by graphs. Analyzing the electron near nuclear area, combination bonding area and lone pair electrons of a system, and then further to analyze the characteristics and types for chemical bond. The electron density distribution of H–O on T1 after geometry optimization is showed in Fig. 5, it is illustrate that electron gas intense between H and O and the value of ELF is close to 1 and exist electron gas overlap between H and O obviously, which shows the bond of H–O is typical covalent bond.

The analysis about density of states

Density of states (DOS) reflects the number of states for the unit energy and it is important to analyze the bonding among

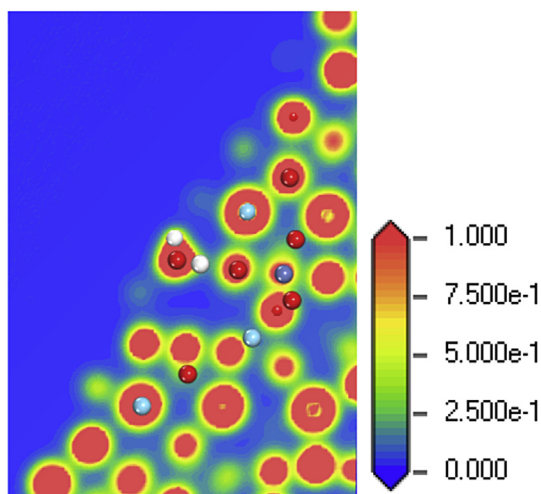


Fig. 5 – The electron localization function of LaNiO_3 (001)/ H_2 with O vacancy on T1 after optimize geometrical structure. (Highly localized electrons show the strongest covalent bond on $\text{ELF} = 1$, metallic bond on $\text{ELF} = 0.5$ and more stronger ionic bonding on $0 \leq \text{ELF} < 0.5$, respectively).

atoms and material properties. Therefore, the analysis of DOS can further understand the interaction of H and atoms of surface. Fig. 6A and B demonstrate the total and partial densities of states of LaNiO_3 (001) with O vacancy after and before adsorption, respectively. Fig. 6B (before adsorption) remarks there is the highest occupied state of the surface occur in range of -7 – -5 eV, because of the O 2p and Ni 3d orbits mainly. After adsorption (Fig. 6A), the DOS of H has highly dispersed and the highest occupied state move toward deep level slightly, which illustrate that the interaction between H and surface exists. Moreover, the energy levels of H 1s and O 2p orbits are broadened in density of states, which indicates the interaction of H and crystal face comes from H and O atom of surface. In addition, H 1s and O 2p orbits overlap and existence of apparent resonance after adsorption show that it is a covalent bond between H and O. The total DOS of perfect surface and the surface with O vacancy base on PBE and PBESOL functional before and after adsorption are shown in Fig. 6C, the results note that the DOS peaks of the surface with O vacancy weaker than perfect surface before adsorption, but after adsorption, on the contrary near the Fermi level. Which manifests that the electrical conductivity of LaNiO_3 (001)/ H_2 with O vacancy system strengthen after adsorption, this is because electronic contribution of H 1s and O 2p orbits so that it enhances electron orbital hybridization and rearrange the distribution of electron gas. Therefore, H is more easier to adsorb on the surface with O vacancy.

The conductivity of material can be judged through density of states. The conduct band of the surface with O vacancy is smaller than perfect surface before adsorption (Fig. 6C), which holds that the emergence of O vacancy reduce the electronic conductivity of surface, it is consisted with the conclusion of Ref. [18]. However, the conductive band of surface with O vacancy become big so that the electronic conductivity of system get strengthen after adsorption. With the amount of vacancy increasing in surface (Fig. 6D), the conductive band change little, which shows that the change of surface vacancy quantity have little influence on its electronic conductivity.

Conclusions

- 1, The appearance of O vacancy increases the lattice constant of LaNiO_3 , and the formation energy of surface vacancies is lower than that of 1.12 eV; so compared to lattice unit, the surface is easier to form O vacancy.
- 2, There are two types of adsorption for H_2 when it is adsorbed on LaNiO_3 (001) surface with O vacancy: The first one is that two H atoms are adsorbed to the same O atom to form H_2O molecules, which is the best adsorption position; The second one is that two H atoms are respectively adsorbed to the two O atoms, forming two $-\text{OH}$ groups. These two types of adsorption methods are both chemical adsorption, and H_2 molecules on the surface of LaFeO_3 (010) can set off physical adsorption.
- 3, In the same position of normal surface adsorption, it is found that the absorption energy of O vacancy is larger than that of the normal surface. Therefore, we can confirm

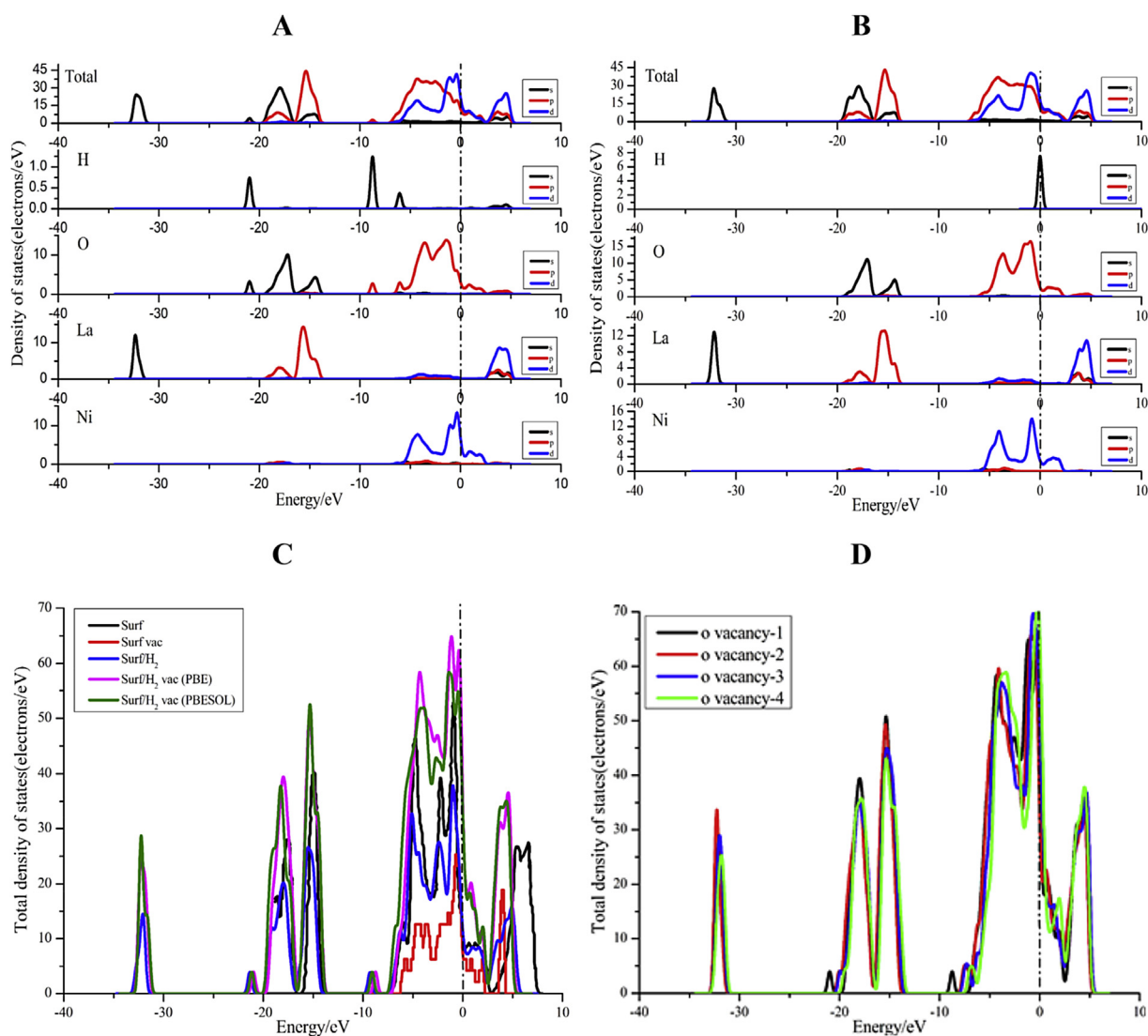


Fig. 6 – A and B demonstrate the total and partial densities of states of LaNiO₃ (001) with O vacancy after and before adsorption, respectively. The total DOS of perfect surface and the surface with O vacancy base on PBE and PBESOL functional before and after adsorption are shown in C, D illustrates the DOS of containing one to four vacancies in surface.

that the surface of O vacancy is easier to absorb hydrogen; and with the increasing of the surface oxygen vacancies, the decomposition of H₂ is accelerated.

- 4, On the most stable adsorption site T1, PBE and PBESOL functionals are applied to perform geometry optimization and property analysis on its structure. From the viewpoint of the energy, the application of PBESOL functional is less ideal than the application of PBE functional. From the viewpoint of the electronic structure, the application gap between PBE and PBESOL functional is very small, but functional PBESOL increases the computation time. At this point, the effects of H and O atoms result from the orbital hybridization effects of H 1s and O 2p, and there is a typical covalent bond between H and O.
- 5, Before H absorption, the existence of O vacancy reduces the electric conductivity of the surface; after that, the

surface conduction band with O vacancy increases, which enhances its electric conductivity. In addition, the number of surface O vacancy has little influence on the electric conductivity.

Acknowledgments

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