A DFT study of Hg⁰ adsorption on Co₃O₄ (1 1 0) surface

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Abstract: Spin polarized density functional theory calculation combined with periodic slabs were employed to reveal the elemental mercury (Hg⁰) adsorption mechanism on Co₃O₄ (1 1 0) surface. The adsorption energies and possible adsorption sites were investigated. To understand the adsorption interaction more directly, the electronic structural changes of before and after adsorption were compared. The hybridization of orbitals was studied by the partial density of states (PDOS) analysis. In addition, the temperature effects toward equilibrium constants of Hg⁰-Co₃O₄ system were taken into consideration. The results manifested that the interaction between Hg⁰ and Co₃O₄ (1 1 0) surface is chemisorption with -74.037 kJ/mol. Co³⁺ sites, the highest oxidation state of Co atoms, are crucial in this process which can accept the electrons after Hg oxidation. The redundant electrons transfer to O and other Co atoms nearby. PDOS analysis indicates the hybridization of s orbitals (Hg⁰) and p, d orbitals (Co atom). And d orbitals of Hg interacts with s, p orbitals of Co atom strongly. The trends of equilibrium constants suggest that Hg⁰ adsorption on Co₃O₄ (1 1 0) surface is favorable at low temperature.

Keywords: Elemental mercury, Co₃O₄, Adsorption energy, Equilibrium constants, PDOS¹

1. Introduction

The utilization of traditional energy source of coal has led to severe pollution to the environment, such as the emission of SO_x, NO_x, CO₂ and mercury [1-3]. Particularly, mercury has drawn great environmental concern for its persistence, toxicity and bio-accumulation[4]. The control of mercury is on the agenda of many countries in the world. In December 2011, Mercury and Air Toxics Standards(MATS)[5], the first national standards, was issued by the United States protection agency. It aims to limit the release of mercury, acid gases and other toxic matters from coal-fired power plants. In January 2013, the Minamata Convention on Mercury[6] was agreed at the fifth session of the Intergovernmental Negotiating Committee, which is a global treaty to protect human health and the environment from the adverse effects of mercury. Therefore, the removal of mercury is always a worldwide issue with great significance.

Since the elemental mercury (Hg⁰) is volatile and water insoluble, removing it from the environment is of great difficulty in all species of mercury[7]. To date, activated carbon[8], calcium-based sorbents[9], fly ash[10], noble metals[11] and metal oxides[12-14] have been used for Hg⁰ removal. Among these sorbents and catalysts, Co₃O₄-based materials capture researchers' attention because of high efficiency on mercury removal[15]. From the aspect of Co₃O₄, it has been applied in combustion of CO and organic compounds and for waste gases treatment[16]. It exhibits very high activity for CO oxidation in CO/O₂ mixtures at low temperature. The spinel structure of Co₃O₄ crystal has Co³⁺ in octahedral coordination and Co²⁺ in tetrahedral coordination. Co³⁺ has been

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regarded as the active site for CO oxidation, while Co^{2+} is almost inactive regarding the oxidation of CO[17]. The oxidation character of Co_3O_4 is essential to adsorbate which incites the research of Hg^0 adsorption and oxidation.

Experimental studies have demonstrated that Co_3O_4 -based sorbent exhibits excellent performance for adsorption and oxidation of Hg^0 . Mei et al[18] prepared Co_3O_4 loaded activated carbon (AC), which achieved high Hg^0 removal efficiency of 91.5% and good regeneration ability. Hg capture experiment found that Co_3O_4 -AC has relative high activity in the temperature range of 80-250 °C. Co_3O_4 loaded on $\gamma\text{-Al}_2\text{O}_3$ was used to remove Hg^0 in a packed-bed reactor with removal efficiency of 72.3%[15]. These studies were conducted in a catalyst testing system which consisted of Hg^0 permeation tube, a packed-bed reactor, an on-line cold vapor atomic absorption spectrophotometer, and a data acquisition system. Hg^0 permeation tube ensures certain concentration of Hg^0 in simulation gas. High purity nitrogen was used as carrier gas and balance gas. The simulation gas also contained 5.0 vol. % oxygen. Mercury removal efficiency represented the interaction strength. During this process, N_2 was very stable with no effect on mercury adsorption and oxidation. Oxygen content was too low to effect the oxidation on Hg^0 . Importantly, Hg^0 adsorption process was a pre-condition of its oxidation. Good performance of Hg^0 adsorption determined the capacity adsorbents. Hence, Co_3O_4 is a very important sorbent/catalyst which is alternative to noble metal catalyst for Hg^0 control. Nevertheless, the interaction mechanism was not clarified clearly in previous studies. Related theoretical studies are very essential for Hg^0 and Co_3O_4 interaction.

Density functional theory (DFT) is commonly used in evaluating the mechanism of mercury on sorbents/ catalysts surface. This method has revealed adsorption/oxidation mechanism of Hg^0 on metal surface [19], metal oxide surface [20], binary alloys[21] and carbonaceous surface[22]. However, Hg^0 on Co_3O_4 surface has not been investigated theoretically. The actual interaction mechanism is of great importance in Hg^0 removal sorbents design and theoretical support.

We focus on the adsorption/oxidation mechanism of Hg^0 on Co_3O_4 (1 1 0) surface. Several properties such as geometry structure, adsorption energies and possible sites, Hirshfeld population and the density of states (PDOS) were calculated and analyzed. Additionally, temperature effects on equilibrium constants of Hg^0 were also investigated to testify reaction character and stability of Co_3O_4 . This method is crucial to develop and reveal mechanism of effective Hg^0 capture materials based on transition metal compounds.

2. Models and computational methods

2.1 Surface models

Fig.1 Primary crystal structure of Co_3O_4

Co_3O_4 is a spin type oxide, with Co^{2+} in tetrahedral interstices and Co^{3+} in octahedral interstices of the cubic close-packed lattice. As shown in **Fig.1**, It is a facet-centered cubic lattice with space group FD-3M ($a=b=c=8.084\text{\AA}$, $\alpha=\beta=\gamma=90^\circ$, ICSD # 28158)[23]. Co_3O_4 (1 1 0) surface was modeled by a periodically repeated slab with four layers. The top view and side view of the surface are shown in **Fig.2**. The surface is terminated by Co^{3+} , Co^{2+} , O^{3f} in octahedral coordinate and O^{4f} in four coordination atoms. The vacuum region thickness of $13\text{\AA}$ was chosen to eliminate interaction effects of neighboring slab. The bottom layer was fixed and the other three layers were relaxed.

Fig.2 Top view and side view of clean Co_3O_4 (1 1 0) surfaces

2.2 Computational methods

All calculations were performed with the DMol³ package in Materials Studio 70[24, 25]. The accuracy of local density approximation (LDA)[26] and the generalized gradient approximation (GGA)[27] methods were studied before the calculation. By comparing with experimental lattice parameters, the GGA in forms of Perdew-Burke-Ernzerhof (PBE) shows best accuracy. Hence, GGA-PBE method was adopted to calculate the electronic structure in this system. A double numerical basis with polarization functions (DNP) were used in all calculations. All electron basis

set were used for O atoms. Density functional semi-core pseudopotentials (DSPP)[28] were used for Co and Hg atoms, whereby the outer electrons of these atoms ($3d^7 4s^2$ of Co and of $5d^{10} 6s^2$ of Hg) were treated as valence electrons and the inner electrons were as a simple potential including some degree of relativistic effects. In addition, a cutoff energy of $4.5\text{\AA}$ and $4.6\text{\AA}$ were used in Co_3O_4 surface and Hg- Co_3O_4 system, respectively. The self-consistent field convergence criterion was set to an energy change of 10^{-6}Ha . The Brillouin Zone integrations were performed using a $3 \times 4 \times 1$ Monkhorst-Pack grid. The convergence tolerance of geometry optimization based on energy, max.force and max.displacement were $1 \times 10^{-5}\text{Ha}$, $2 \times 10^{-3}\text{Ha/\AA}$ and $5 \times 10^{-3}\text{\AA}$, respectively. During all calculations, the spin polarization was applied.

For adsorption energy, it was calculated according to the following equation:

$$E_{ads} = E_{Hg^0 + surface} - E_{Hg^0} - E_{surface} \quad (\text{Eq. A})$$

where E_{ads} is the adsorption energy, $E_{Hg^0 + surface}$ represents the energy of the adsorption system, E_{Hg^0} is the energy of the element mercury, $E_{surface}$ is the energy of periodic surface, all energies are in kJ/mol. By this definition, negative value corresponds to exothermic adsorption process.

To investigate exothermicity of adsorption processes and favorability of the spontaneous reaction as a function of temperature, the equilibrium constants (K_{eq}) were calculated based on the thermodynamic data from frequency calculation[25, 29]. The method has been applied to study the equilibrium constant of mercury adsorption on CaO [30] and CoCl_2 [31] surfaces. We used general relationships for statistical thermodynamic partition functions (translational, rotational, and vibrational partition functions)[32]. Contributions from electronic motion are neglected due to the electronic ground state of the adsorption systems. The equilibrium constants are calculated by $\ln(K_{eq}) = -\Delta G / RT$, where ΔG is the Gibbs free energy change, R is the ideal gas constant, and T is the temperature. The change of Gibbs free energy during the adsorption process (ΔG) is defined as:

$$\Delta G \approx \Delta E_{ads} + \Delta E_0 + T(\Delta S_{vib} + \Delta S_{trans,rot}) - kT \ln\left(\frac{P}{P_0}\right) \quad (\text{Eq. B})$$

where ΔE_{ads} is the change of adsorption energy, ΔE_0 represents the change of zero-point energy, ΔS_{vib} and $\Delta S_{trans,rot}$ are the changes of the vibrational and translational, rotational entropy during adsorption, respectively.

The entropy and zero-point energy data of Hg^0 and Co_3O_4 surface were available in the temperature between 25K and 1000K. Nonetheless, the equilibrium constant was investigated in temperature range of 250-1000K which was more relevant for Hg^0 experimental adsorption system.

3. Results and discussion

3.1 Choice of DFT methods

In order to know which DFT methods can provide more reliable calculation results, the primary Co_3O_4 crystal was optimized by different functional methods (LDA-PWC, GGA-PBE and GGA-BLYP). It has been reported that the lattice parameters calculated by DFT methods were in good agreement with experimentally measured values[33, 34]. Accordingly, the most suitable method

was confirmed by comparing with the experimental values. All lattice parameters of bulk Co_3O_4 using different methods are given in **Table 1**.

Table 1 The optimized lattice parameters of different DFT methods

Lattice parameters	Experiment al value (Å)	LDA-PWC		GGA-PBE		GGA-BLYP	
		Values (Å)	Relative tolerance (%)	Values (Å)	Relative tolerance (%)	Values (Å)	Relative tolerance (%)
a	8.084	7.921	2.015	8.125	0.502	8.019	0.804
b	8.084	7.921	2.015	8.125	0.502	8.019	0.804
c	8.084	7.921	2.015	8.125	0.502	8.019	0.804

It is clear that LDA-PWC and GGA-BLYP methods have underestimated in lattice parameters. The LDA-PWC method has the biggest relative tolerance of 2.015% in all direction of cell lengths. GGA-BLYP method obtains 0.804% relative tolerance with length error of 0.065 Å. On contrary, GGA-PBE method overestimates the lattice parameters. The relative tolerance is only 0.502% with length error of 0.041 Å. It provides most accurate results with experimental values. Hence, GGA-PBE method was chosen in the following computation.

A reasonable vacuum thickness is very important in eliminating related effects between slabs. In previous research, the result indicated a suitable height of 13 Å [17]. The vacuum height of 13 Å and 18 Å were investigated using the GGA-PBE method above, and the energy difference is 0.019 eV which is acceptable. In consequence, the final vacuum height was set to 13 Å, which is sufficient to ignore neighboring slab interaction.

3.2 Adsorption energies

Two surface areas are taken into consideration. Surface I was constructed as following parameters: $a=8.125\text{Å}$, $b=5.745\text{Å}$. Surface II area was twice than surface I's which was made of 8.125Å (a) and 11.490Å (b). The optimized adsorption energy of Hg on surface I was -74.037 kJ/mol. The corresponding adsorption energy on surface II was -74.179 kJ/mol. The comparison is shown in **Table 2**. Only 0.20% relative difference occurred on two surfaces. It indicates that surface I is large enough for this system. Nevertheless, the surface II calculation amount has increased nearly twice than surface I. Based on the calculation cost and calculation accuracy, surface I was chosen as the research model.

Table 2 The comparison of Hg^0 adsorption on different surfaces

Surface	Surface I	Surface II
Length a (Å)	8.125	8.125
Length b (Å)	5.745	11.490
Adsorption energy (kJ/mol)	-74.037	-74.179

To confirm the most stable configuration for adsorbed Hg^0 , several different sites on Co_3O_4 (1 1 0) were investigated. The exposure feature of cleaved surface is demonstrated in **Fig.2**. There are four types of lattice atom on the surface, Co sites (Co^{3+} , Co^{2+}) and two types of lattice O sites (O^{3f} and O^{4f}). The adsorption energies and final distance between Hg^0 and Co_3O_4 (1 1 0) surface are summarized in **Table 3**. After adsorption, Co^{3+} site has distance of 2.725Å with the surface, O^{4f} site corresponds to 2.457Å . When Hg located on Co^{2+} and O^{3f} sites, it moved to O^{4f} site at final adsorption configuration. The adsorption energies, ranging from -63.073 kJ/mol to -74.037 kJ/mol, have positive correlation with the distance values. It indicates that the interaction between Hg and Co_3O_4 (1 1 0) surface attributes to chemisorption. Co^{3+} site is less stable than O^{4f} site

according to adsorption energies. The configuration of Hg on O^{4f} site is shown in **Fig.3**.

Compared to previous DFT study, Hg⁰-CaO (1 0 0) system was physical interaction with adsorption energy from -9.16 to 11.78kJ/mol[35] which is much smaller than that on Co₃O₄ (1 1 0) surface. It is found that the adsorption energy of Hg⁰ on MnO₂ (1 1 0) surface (-63.51-78.32kJ/mol)[14] is almost in the same level. It indicates that Co₃O₄ can also have strong ability in capturing Hg⁰. Moreover, the favorable adsorption sites are oxygen and bridge-oxygen for CaO (1 1 0) and MnO₂ (1 1 0) surfaces, respectively. The active site in this study is O^{4f} from the stable adsorption configuration, which is similar with surfaces mentioned above.

Table 3 Adsorption properties of Hg⁰ on various adsorption sites of Co₃O₄ (1 1 0) surface

Adsorption sites	Distance(Å)	Adsorption energies(kJ/mol)
Co ³⁺	2.725	-63.037
Co ²⁺ , O ^{3f}	N/A ^[a]	--
O ^{4f}	2.457	-74.037

[a]Moved to O^{4f} site.

Fig.3 The distances of Hg⁰ and Co₃O₄ (1 1 0) surface.

- (a)- The geometry structure before adsorption; (b)-The geometry structure after adsorption on Co³⁺ site;
(c)-The geometry structure after adsorption on O^{4f} site.

3.3 Electronic structure

Fig.4 Atomic indices for Hg⁰ adsorption on Co₃O₄ (1 1 0) surface.

The adsorption mechanism depends on the variation of system electronic structure. The charge transfer of all atoms and related PDOS analysis were studied systematically. Atomic charges with Hirshfeld atomic population analyses were conducted in this system, which is based on deformation density on the free atom electron density[36]. Compared to Mulliken method, it provides an accurate partitioning of the electron density. The atomic charges for clean Co_3O_4 surface and $\text{Hg}^0\text{-Co}_3\text{O}_4$ slabs were calculated by Hirshfeld method. The charge transfer were based on the difference between original state and adsorption state (**Table 4**). Positive value means the atom obtains electrons after adsorption and negative value means the atom loses electrons after adsorption. **Fig.4** shows the atomic indices of $\text{Hg}^0\text{-Co}_3\text{O}_4$ (1 1 0) interaction system.

Table 4 Atoms charge transfer calculated by Hirshfeld method

Atom indexes	Hirshfeld atomic charges		
	Before	After	Electron transfer
Co(1)	0.363	0.339	0.024
Co(2)	0.316	0.304	0.012
Co(3)	0.316	0.305	0.012
Co(4)	0.363	0.338	0.025
Co(5)	0.356	0.342	0.014
Co(6)	0.204	0.196	0.009
Co(7)	0.204	0.198	0.006
Co(8)	0.200	0.193	0.007
Co(9)	0.200	0.193	0.007
Co(10)	0.240	0.155	0.085
Co(11)	0.356	0.344	0.012
Co(12)	0.240	0.154	0.086
O (13)	-0.140	-0.151	0.011
O (14)	-0.244	-0.251	0.007
O (15)	-0.257	-0.265	0.008
O (16)	-0.243	-0.252	0.009
O (17)	-0.156	-0.161	0.005
O (18)	-0.156	-0.161	0.005
O (19)	-0.243	-0.252	0.009
O (20)	-0.140	-0.149	0.009
O (21)	-0.244	-0.251	0.007
O (22)	-0.192	-0.196	0.004
O (23)	-0.257	-0.264	0.008
O (24)	-0.243	-0.257	0.014
O (25)	-0.156	-0.161	0.005
O (26)	-0.243	-0.257	0.014
O (27)	-0.156	-0.161	0.005
O (28)	-0.192	-0.197	0.004
Hg(29)	0.000	0.224	-0.224

As shown in **Fig.4**, Co(1), Co(4), Co(10), Co(12), O(13), O(16), O(19), O(24) and O(26) atoms are distributed in the first layer. Hg^0 , on the top site of O^{4f} , has the biggest charge transfer

of 0.224 electrons after adsorption. It indicates that Hg has been oxidized after adsorption. As for Co_3O_4 (1 1 0) surface, all atoms have positive charge transfer. Co (10) and Co (12) obtain the highest electron number of 0.085 and 0.086, respectively. Co (1) and Co (4) accept nearly equal number of electrons (0.024 and $0.025e^-$). The electron transfer of O atoms range from $0.004e^-$ to $0.014e^-$. It is interesting that the most stable adsorption O^{4f} site has only $0.009e^-$ charge transfer corresponding to O (20) atom. Obviously, O (20) is not the active site atom in Hg^0 adsorption system. From the respect of charge transfer, the Co^{3+} site is active site that obtain much electrons from Hg atom. O^{4f} is a middle position between Co (10) and Co (12) at the next layer. The strong interaction of Hg and the surface depends on the two Co^{3+} atoms. They obtain most electrons for Hg and then deliver surplus electrons to related atoms. The charge transfer follows the routes below. Co (10) and Co (12) accept electrons from Hg then transfer some to linked O atoms. O (24), O (26), O (16), O (19), O (13), O (20) and O (28) atoms obtain $0.014e^-$, $0.014e^-$, $0.009e^-$, $0.009e^-$, $0.011e^-$ and $0.004e^-$, respectively. The other Co^{3+} atoms on the first layer, Co (1) and Co (4), accept 0.024 and $0.025e^-$, respectively. Co^{3+} atoms are in the highest oxidation state which have strong ability to obtain electrons from other atoms. There are two kinds of O atoms (O^{3f} and O^{4f}) exposing on the surface. O^{4f} achieves electronic saturated state more easily. Therefore, the charge transfer of O^{3f} atoms are higher than that of O^{4f} . Some delicate differences in charge transfer are due to the distance between Co^{3+} active site atoms. Long distance leads to lower charge transfer and vice versa. Consequently, Hg adsorption system is in a very stable state.

Fig.5 PDOS of Hg and Co (Co^{3+} site) for surface system before and after adsorption on Co_3O_4 (1 1 0) surface.

The Fermi level (E_f) is set to be zero (dashed line in the figure).

The plots of PDOS characterizes the electronic interactions of Hg^0 with Co_3O_4 (1 1 0) surface in **Fig.5**. Co^{3+} sites of Co (10) and Co (12) have the same PDOS change before and after the

interaction. Before adsorption, the s orbitals of Hg locates at 0 Ha and 0.50 Ha. The p orbitals of Hg has maximum PDOS at 0.28Ha in the conduct band state. Two peaks of d orbitals distributed at -0.11 and 0.58Ha, respectively. After adsorption, the s orbitals shift to 0.08Ha with greatly decreasing of PDOS. Meanwhile, the peak at 0.05Ha disappeared. The p orbitals turn to flat with no distinct peak plot. The d orbitals shift to lower energy states of -0.20Ha. All of these changes confirm that strong interaction occurred between Hg^0 and Co_3O_4 surface. The orbitals of Co atoms were analyzed to investigate possible interaction with Hg^0 . As shown in **Fig.5**, the s, p and d orbitals change slightly after adsorption. Specifically, s and p orbitals become much higher in PDOS value and overlap with s and d orbitals of Hg atom. It indicates the hybridization of s orbitals (Hg^0) and p, d orbitals (Co atom). The d orbitals of Hg interacts with s, p orbitals of Co atom strongly. From respect of PDOS, Hg^0 and Co_3O_4 surface can form a very stable system after adsorption and oxidation process. It is consistent with the experimental results of metal oxide-loaded activated carbon (AC) in the simulated gases (5.0 vol.% O_2 , 1.26 ppm Hg^0 , balance gas & carrier gas N_2). Hence, the real interaction occurred between pure Hg^0 and adsorbent. Hg^0 removal efficiency of Co_3O_4 modified AC reached 91.5%[18]. It has been testified that AC had no obvious capture and oxidation ability in related research[8]. The DFT calculation results in this study indicates that Co_3O_4 has strong interaction with Hg^0 . Additionally, it has certain oxidation ability in Hg^0 removal. Both chemical adsorption and oxidation ability of Co_3O_4 contribute to good performance in Hg^0 removal process.

3.4 Temperature effect on equilibrium constants of Hg^0

Fig.6 Equilibrium constants for adsorption of Hg^0 on Co_3O_4 (1 1 0) surface as a function of temperature.

Temperature plays an important role in adsorption process, so it is necessary to study the effect of temperature on the equilibrium constants for Hg^0 interaction with Co_3O_4 (1 1 0) surface. Based on the thermodynamics analysis in DFT, the calculated entropy, Gibbs free energy changes, and equilibrium constants of Hg^0 adsorption on the Co_3O_4 surface in temperature range of 250-1000K are listed in **Table S1** in the supplementary material. According to the results, negative Gibbs free

energy difference is obtained, which indicates a spontaneous adsorption process in this system. As shown in **Fig.6**, the equilibrium constants have negative correlation with the temperature. High temperature corresponds to low equilibrium constants and vice versa. This trend is consistent with the previous studies of Hg^0 adsorption on CaO [30], MnO_2 [14] surfaces. Specifically, $\ln(K_{\text{eq}})$ decreases with the rising of temperature. The highest $\ln(K_{\text{eq}})$ value reaches 39.057 at 250K and the minimum value is 16.511 at 1000K. It decreases by 57.73% during the temperature increase process. It has been reported that the maximum $\ln(K_{\text{eq}})$ of CaO was below 20. The decrease amplitude was 33.33%. As for Hg^0 adsorption on MnO_2 (1 1 0) surface, the peak and lowest value of $\ln(K_{\text{eq}})$ were about 60 and 5, respectively. It has the highest deduction rate of 91.71% among three adsorbents. MnO_2 exhibits relative high performance in equilibrium constants. However, it is the most temperature sensitive adsorbent for Hg^0 . The equilibrium constants of Co_3O_4 is higher than that of CaO which indicates the former one is more effective. In conclusion, Co_3O_4 is temperature durable and effective in Hg^0 adsorption process.

4. Conclusions

The adsorption mechanism of Hg^0 on Co_3O_4 (1 1 0) surface was investigated by density functional theory and the periodic slab model. The interaction between Hg^0 and Co_3O_4 (1 1 0) surface is chemisorption with adsorption energy of -74.037kJ/mol. The optimal adsorption configuration is on the top of O^{4f} site. However, Hirshfeld population analysis indicated that the charge transfer of Co^{3+} atoms near O^{4f} is the highest. It reveals that Co^{3+} is the most direct interaction sites to form a stable adsorption system for Hg^0 . This high reactivity of Co_3O_4 surface to Hg^0 is due to the hybridization of s orbitals (Hg^0) and p, d orbitals (Co atom). The d orbitals of Hg interacts with s, p orbitals of Co atom strongly as well. Besides, the equilibrium constants of Hg^0 - Co_3O_4 (1 1 0) surface have negative correlation with the temperature. Hence, Hg^0 adsorption is more favorable at low temperature.

Acknowledgement

This work was supported by the National Science Foundation of China (Project No. 21177083, and the program for New Century Excellent Talents in Shanghai Jiao Tong University, and Wyoming Clean Coal Program.

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