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QUANTUM-CHEMICAL CONSIDERATION OF NITROGEN DOPING ON Co_3O_4 FOR WATER DISSOCIATION

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We report the results of theoretical investigations of nitrogen doping on Co_3O_4 (100) bulk by means of the plane-wave periodic density functional theory (DFT) calculations combined with the Hubbard- U approach and statistical thermodynamics. Using accurate DFT+ U calculations, we have shown that bulk Co ions denote charges in value 0.017 – 0.57e. For further water adsorption process studies was selected structures with most changes in charges in Co ions: (3) structure for $n=25\%$, (2) structure for $n=12.5\%$ and structure for (1) structure.

Key words: Co_3O_4 , spinel oxide, dopant, concentration, DFT+ U calculation, Bader charges

1. Introduction

Today, we observe worldwide significant progress in the development of the transition to "green" energy. Such development in the countries is connected not only with the strongest negative impact on the environment from emissions, but also with the advanced strategic development of the economies of these countries in this area. Possession of such technologies makes the country's economy more attractive to investments in the energy sector.

Consuming growth not - renewable fossil energy resources of which "thermal pollution", bursts in the atmosphere of products of burning and fast exhaustion of power sources is result do perspective creation of highly effective technologies of use of sustainable that first of all includes development of methods of conversion of solar energy.

Process splitting of water takes place with energy absorption as a result of which the free energy of Gibbs increases by 237 kJ of mole⁻¹. This additional energy necessary for photocatalytic and photoelectrochemical decomposition of water is provided by means of energy of sunlight. For this purpose in photoelectrochemical cells as the cathode noble metals on which there is a restoration of the hydrogen formed in the course of water expansion, and as the anode on which there is a decomposition of water under the influence of sunlight are used, semiconductors in which under the influence of sunlight are excited an electron - hole couples are used. These excited charge carriers in the process of a relaxation are transferred to surface-active parts where participate in water splitting process. For achievement of the greatest efficiency process of diffusion of photoexcited charge carriers on the surface of the catalytic agent shall prevail over process of a recombination an electron - hole couples. Besides, the semiconductor anode shall absorb an electromagnetic radiation in a visible part of a range to be effective for sunlight absorption. Taking into account the specified requirements one of perspective semiconductors for practical application as material of the anode are oxides of transition metals. One of such stable and cheap materials is the cobalt oxide having, in addition, the narrow width of the forbidden band.

Co_3O_4 -based materials are widely used for Lithium-Ion Batteries [1], Zink-Air Batteries, treatment of waste gases [2,3] and other energy applications. In particular, Co_3O_4 is known as a low-cost high-performance catalyst for Oxygen Reduction Reaction (ORR) [4] and Oxygen Evolution Reaction (OER) [5].

Oxygen Reduction Reaction and Oxygen Evolution Reaction also are main stage of the catalyst processes in metal-air membranes and water splitting. Numerous attempts have been made in order to decrease the energetic efficiency of these reactions maintained on the different catalysts by various dopants. Obtained data are in a good agreement with experimentally obtained results [6]. Another promising doping material for Co_3O_4 is nitrogen. Xu et.al in their experimental work discuss production of N-doped Co_3O_4 nanosheets [7]. Increased surface area in combination with oxygen vacancies lead to enhancement of electrocatalytic activity for OER.

2. Method and Model

Co_3O_4 is easily available and thermodynamic stable oxide in a wide interval of temperatures and conditions with rich concentration of oxygen. Crystal Co_3O_4 has structure of spinel (space group) with the half-filled sites in an octahedral environment of Co^{3+} , and cobalt ions in a tetrahedral environment of Co^{2+} . Ion Co is the transition element having incomplete configurations of d-orbitals. For the transition elements existence of a set of the connections having a number of physical and chemical properties is peculiar. It is caused by presence at the transition elements of incomplete d-electron shells, and, as a result, a wide set of the valence states of atoms. A specific place among all compounds of d-metals is held by oxides and complex connections on their basis. Ability of the transition elements to change the valence state, presence of the lone couples of electrons at oxygen atoms, ease of exchange of oxygen with the environment, different impurity centers create variety of defects which, forming the discrete levels in the forbidden band, significantly influence physical and chemical properties of the considered substances [8]. Schematic view of the crystal structure of Co_3O_4 presented in Figure 1.

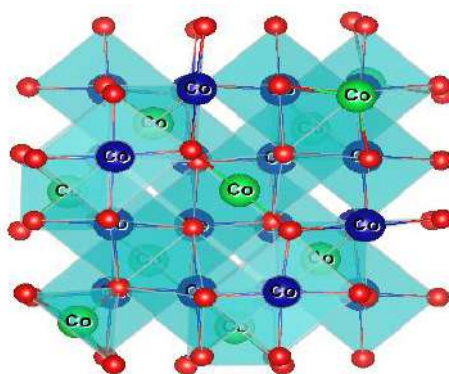


Figure 1. Schematic image of the crystal structure of Co_3O_4 . Green and blue balls indicate Co^{2+} and Co^{3+} ions respectively, red ball indicate O ion.

Calculations were performed using the DFT method [9] as implemented in the computer code VASP 5.4 [10]. Core electrons were substituted with the US potentials with the PAW method [11]. In Table 1 presented US PAW potentials of Co and O.

Table 1. US PAW potentials of Co and O.

| Element | Free electrons | E_{cutoff} , eV |
|---------|----------------|--------------------------|
| Co | $4s^1 3d^8$ | 267.968 |
| O | $2s^2 2p^4$ | 400.000 |
| N | $2s^2 2p^3$ | 400.000 |

Exchange-correlation described by the PBE functional. The Hubbard correction $U-J=3\text{eV}$ was applied to d -electrons of Co_{tet} as well as Co_{oct} atoms. For defects modeling cubic 56-atom supercell model has been used. For Brillouine zone was sampled with the $2 \times 2 \times 2$ Monkhorst-Pack scheme.

Plane-wave basis set has the kinetic energy cut-off of 550 eV. Charge redistribution was analysed by the Bader method, as implemented by Henkelmann et al. [12].

Doping by nitrogen was performed by substitution of oxygen atoms. Four concentrations have been tested – 1, 2, 4 and 8 N per 32(O+N) atoms. There are five nonequivalent distances between 32 e sites in the supercell – 1-4 and 6NN. Some coordination spheres are split to the subspheres with a small deviation in distances as shown in Figure 2.

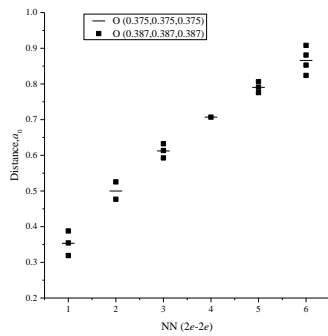


Figure 2. Nearest Neighbors of $2e-2e$ sites of Co_3O_4 structure, symmetry group 227.

Two N atoms were placed at each subsphere of the 1NN coordination sphere. For the 2NN single calculation was performed, since there is no subspheres. Also two N atoms were placed at the largest possible distance within the model supercell – 6NN. Four N atoms were arranged in three different configurations, as shown in Table 2.

Table 2. 12.5% N concentration configurations. Distances between N_O in NN (32e-32e)

| Conf.1 | N_O | N_O | N_O | N_O | Conf.2 | N_O | N_O | N_O | N_O | Conf.3 | N_O | N_O | N_O | N_O |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| N_O | 0 | 6 | 4 | 2 | N_O | 0 | 1 | 4 | 1 | N_O | 0 | 4 | 4 | 4 |
| N_O | | 0 | 2 | 4 | N_O | | 0 | 1 | 4 | N_O | | 0 | 4 | 4 |
| N_O | | | 0 | 6 | N_O | | | 0 | 1 | N_O | | | 0 | 4 |
| N_O | | | | 0 | N_O | | | | 0 | N_O | | | | 0 |

Nanorod was created, by placing N atoms in line, along the [110]. All N atoms in the same line are the 1NN. The smallest distance between the parallel rods is 3NN (Table 3).

Table 1. 25% N concentration configurations. Distances between N_O in NN (32e-32e)

| | N_O | N_O | N_O | N_O | N_O | N_O | N_O | N_O |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| N_O | 0 | 1 | 4 | 1 | 4 | 3 | 3 | 4 |
| N_O | | 0 | 1 | 4 | 3 | 4 | 4 | 3 |
| N_O | | | 0 | 1 | 4 | 3 | 3 | 4 |
| N_O | | | | 0 | 3 | 4 | 4 | 3 |
| N_O | | | | | 0 | 1 | 1 | 4 |
| N_O | | | | | | 0 | 4 | 1 |
| N_O | | | | | | | 0 | 1 |
| N_O | | | | | | | | 0 |

3. Results

The adsorption energy of N was calculated by means of this formula:

$$E_{\text{(ads)}} = E_{\text{(bulk-N)}} - E_{\text{(bulk)}} - N \cdot (E_{\text{(O)}} - E_{\text{(bulk)}})$$

where $E_{\text{(bulk-N)}}$ - energy of bulk with N dopants of nitrogen, $E_{\text{(bulk)}}$ - energy of bulk, N- number of dopants, $E_{\text{(O)}}$ - energy of bulk with one nitrogen atom. After nitrogen doping the slab structure was reoptimized. The calculations predict no essential lattice relaxation around the substitutional N ion: the change of the equilibrium bond length between O and catalytic active cobalt, $\text{Co}_{2c}^{\text{T}} - \text{O}_{3c}$ is larger than $\text{Co}_{2c}^{\text{T}} - \text{F}$ bond by $\Delta l = 0.001 \text{ \AA}$ only. In Table 4 listed energy of adsorption and Bader charges of nitrogen dopants in Co_3O_4 bulk.

Table 4. Energy of adsorption and Bader atomic charges on N (q, e).

| | Energy of adsorption, eV | Location * First Number indicate number of N dopants | Charge on N, $\Delta q(e)$ |
|----|--------------------------|---|----------------------------|
| 1 | -0,06 | 1 structure | 0,02 |
| 2 | -0,04 | 2 (1) structure | 0,02 |
| 3 | 0.01 | 2 (2) structure | 0,03 |
| 4 | 0,07 | 2 (3) structure | 0,5 |
| 5 | 0,17 | 2 (4) structure | 0,03 |
| 6 | 0,10 | 2 (5) structure | 0,03 |
| 7 | 0.5 | 4 (1) structure | 0,03 |
| 8 | -0.12 | 4 (2) structure | 0,02 |
| 9 | 0.37 | 4 (3) structure | 0,04 |
| 10 | -0,15 | 8 structure | 0,3 |

In Table 5 listed Bader charges of Co, nearest to atom N, for different concentration n (%) of dopants.

Table 5. Bader charges of Co²⁺ and Co³⁺, nearest to atom N, for different concentration n (%) of dopants

| Atom | $n=25\%$ | | $n=12.5\%$ | | $n=6.25\%$ | |
|---------------|------------------|---------------|------------------|---------------|------------------|---------------|
| | Type of Co ions | $\Delta q(e)$ | Type of Co ions | $\Delta q(e)$ | Type of Co ions | $\Delta q(e)$ |
| (1) structure | Co ²⁺ | -0,017 | Co ²⁺ | -0,017 | Co ²⁺ | -0,056 |
| | Co ³⁺ | -0,02 | Co ³⁺ | -0,026 | Co ³⁺ | -0,022 |
| (2) structure | Co ²⁺ | -0,016 | Co ²⁺ | -0,057 | Co ²⁺ | - |
| | Co ³⁺ | -0,21 | Co ³⁺ | -0,026 | Co ³⁺ | - |
| (3) structure | Co ²⁺ | -0,018 | Co ²⁺ | -0,031 | Co ²⁺ | - |
| | Co ³⁺ | -0,047 | Co ³⁺ | -0,026 | Co ³⁺ | - |
| (4) structure | Co ²⁺ | -0,016 | Co ²⁺ | - | Co ²⁺ | - |
| | Co ³⁺ | -0,024 | Co ³⁺ | - | Co ³⁺ | - |

4. Conclusion

Using accurate DFT+ U calculations, we have shown that bulk Co ions denote charges in value 0.017 – 0.57e. For further water adsorption process studies was selected structures with most changes in charges in Co ions: (3) structure for $n=25\%$, (2) structure for $n=12.5\%$ and structure for (1) structure. So, in the case of oxygen substitution with N leads to anion doping effects for Co₃O₄. In the forthcoming paper we will discuss water dissociation process on (100) surface of N-doped Co₃O₄.

Acknowledgements

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СУДЫ ҮДЫРАТУ ҮШІН Co_3O_4 КОБАЛЬТ ОКСИДІН АЗОТПЕН ҚОСПАЛАУДЫ КВАНТТЫ-ХИМИЯЛЫҚ ЗЕРТТЕУ

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Мақалада түйіндегі Хаббард жуықтауымен электрон-электрондық корреляцияны ескере отырып тығыздық функционалы теориясы (ТФТ) аясында кобальт оксидінің Co_3O_4 (100) бетінде судың адсорбциялануы мен ыдырауын теориялық зерттеу үшін көлемдік кобальт оксидін азотпен қоспалаудың нәтижелері баяндалған. Қоспаның әртүрлі 6.25%, 12.5% және 25% концентрацияларындағы қоспаға көршілес Со иондарындағы заряд шамалары анықталған.

Түйін сөздер: Co_3O_4 , кобальт шпинелі, қоспа, концентрация, DFT+U есептеулер, Бадэр зарядтары

КВАНТОВО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ ДОПИРОВАНИЕ АЗОТОМ ОКСИДА КОБАЛЬТА Co_3O_4

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В статье представлены результаты теоретического исследования внедрения примеси азота в объемную структуру оксида кобальта в целях его применения в качестве катализатора для адсорбции и расщепления молекулы воды. Представлены значения заряда на соседних ионах Со при различных значениях концентрации допанта.

Ключевые слова: Co_3O_4 , шпинель кобальта, допант, концентрация, DFT+U вычисления, Бадэровские заряды