Final Report for PHYS3042

The Property and Application of Metastable Materials–IrO2

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Abstract

Metastable nanomaterials exhibit unique physical and chemical properties that are increasingly important for the development of next-generation emerging technologies. Metastable catalysts have a high-energy structure and high reactivity, and present a non-equilibrium metallic surface, which is a promising high-performance catalytic material.Iridium oxide (IrO_2) is considered to be the most advanced anode oxygen evolution reaction catalyst. In this paper, we will study the properties of iridium oxide nanomaterials and the application of this material in engineering.

1 Introduction

In this article, we obtained monoclinic iridium oxide nanoribbons with space group C2/m, which is a metastable structure. [4]According to the characteristic properties of the metastable structure, this has a relatively stable energy state, but its energy is higher than the most stable state of the system Metastable nanomaterials exhibit unique physical and chemical properties that are increasingly important for the development of next-generation emerging technologies. Metastable catalysts have a high-energy structure and high reactivity, and present a non-equilibrium metallic surface, which is a promising high-performance catalytic material.[4] (i.e., the equilibrium state. This is different from rutile iridium oxide which has a stable tetragonal phase (P42/mnm). In Under acidic conditions, the OER activity is much higher than that of tetragonal IrO_2.

For this material with a miraculous structure, we briefly introduce its material characteristics and properties next. The (010) and (100) Crystal planes are identified as marked, we know that the structure of this material is FCC (Face-Centered Cubic) through the figure (1).In this structure, the ratio of oxygen atoms to atoms is exactly 2 to 1. This means that for each square lattice, its arrangement must be very neat.

It is precisely because the FCC structure has a high degree of symmetry. The arrangement of atoms in a crystal remains the same, both in terms of position in space and in different orientations of the crystal. In the case of iridium oxide, this symmetry makes the physical properties of the material essentially the same in all directions. At the same time, iridium oxide has good electrical properties, because the highly symmetrical lattice in the FCC structure can provide good electron transport channels, so that the material has good electrical conductivity.

2 Research direction and purpose

2.1 Our Objectives and Goals

The goal of this paper is to explore the optimization application of metastable monoclinic iridium oxide(IrO_2) nanometer high-efficiency electrocatalytic oxygen evolution properties in electrochemical aspects, and to explore its development and application.

2.2 Problems to be discussed

1. Due to the particularity of this material, we will first discuss the preparation process of this nanomaterial and its material characterization properties.We will also analyze its energy band structure through density functional calculation, and at the same time study the lower part of the monoclinic phase structure, so as to know its unique physical properties and energy band structure properties.

2. We analyze its unique chemical properties, especially for applications in electrochemistry and energy.We will also analyze its energy band structure through density functional calculation, and at the same time study the lower part of the monoclinic phase structure, so as to know its unique physical properties and energy band structure properties.

3. We will explore the application of this material in sustainable development in the future, and study what advantages it will bring to the production of human life.

3 Main Content including Research and Analysis

3.1 Preparation Process

Its preparation process is not very complicated, and it is mainly obtained through chemical methods. As shown in the figure(2), it is divided into two steps and procedures. We first select the hydrate of iridium chloride, dissolved in a solution of 1,2,3,4-tetrahydronaph- thalene (tetralin) and oleylamin at 60°C. Then we heat it up to 200 degrees Celsius and operate it in an argon atmosphere. will dissociate iridium atoms. Put it in an oxygen environment at a high temperature of 500°C, and a chemical reaction will occur to obtain iridium oxide crystals. But for the iridium oxide we want to study, its crystal structure is very complex and diverse, so we need to adjust and rearrange the crystal lattice.[3] The authors successfully synthesized monoclinic iridium oxide nanobelts with space group C2/m from monoclinic $K_{0.25}IrO_2(2/m_{12}$ precursors by using molten alkali mechanochemistry.

3.2 Analysis of its structure

After we complete the preparation of the material, we need to study its structure from the perspective of nanoscience. The intrinsic activity of the rutile phase IrO_2 is closely related to the [Ir-O6] unit connection structure and lattice distortion. Therefore, the rational design of metastable nanostructured IrO_2 with different unit connections may be one of the keys to

improve the catalytic efficiency. As shown in Figure (3).[1] We now know that iridium oxide exists in a total of four crystal forms, and we apply what we have learned here to describe it. However, through the efforts of many scientists, we have discovered more and more lattice forms, among which, what we need to study in this paper is the metastable monoclinic iridium oxide nanostructure of C2/m.[1] If we analyze its metastable configuration, for n=1, the most stable state is the P3m1 structure, for n=2/4, then P42-IrO_2 is the most stable form, and so on. A number of different configurations are available, each with associated advantages, as shown in the table. This table(Figure(5)) shows us the properties of iridium oxide in different lattice configurations. The most important for the application include its energy band structure and enthalpy. Through the analysis of these data, we selected a metastable material with a structure of C2/m, and we started the research on its properties and physical laws.

3.3 Properties and research

The author used the comparative analysis method throughout the article, and he selected two kinds of iridium oxide with lattice structure, Rutile and the nanobelts metastable iridium oxide we studied in this paper. First, the mechanism by which they react is different, The main difference originates from the different geometric configurations of the Ir-O octahedr.[4]

The following figure (4) tells us the free energy evolution of these two different forms of iridium oxide structures during the reaction process. In the gen evolution reaction (OER), there is no obvious difference in the reaction of *OOH, but the nanobelts metastable structure we selected has a high efficiency throughout the cycle.We can choose the following formula when analyzing its Gibbs free energy.[1]

$$\Delta \mathrm{G} = \Delta \mathrm{E} + \Delta \mathrm{E_{ZPE}} - \mathrm{T}\Delta \mathrm{S}$$

$$\mathrm{ZPE} = \sum_{\mathrm{i}} \frac{1}{2}\, \mathrm{h}\nu_{\mathrm{i}}$$

$$S = k_B \sum_i \left(\frac{h_{\nu_1}}{k_B T \left(\exp\left(\frac{\mathrm{h}\nu_1}{k_{\mathrm{B}} T} \right) - 1 \right)} - \ln\left(1 - \exp\left(\frac{-\mathrm{h}\nu_i}{k_B T} \right) \right) \right)$$

The geometric and electronic analyses in this study were carried out using the density functional theory (DFT) framework for all theoretical simulations. We chose to use the revised Perdew-Burke-Ernzerhof (PBE) function to describe the electronic exchange-correlation energy in our study, as it has been shown to provide more accurate treatment of surface adsorption systems. Density functional theory calculations show that when IrO_2 nanobelts are used as electrocatalysts for OER under acidic conditions, the intrinsic catalytic activity of IrO_2 nanobelts is much lower due to the lower d-band center of Ir in this special monoclinic phase structure. Higher than the tetragonal phase IrO_2.[2]

3.4 Result and Conclusion

In summary, the authors successfully synthesized a metastable IrO_2 with nanoribbon morphology by a strong base-assisted mechanothermal process. This study once again demonstrates the superiority of the two-dimensional layered structure in the form of nanosheets in the field of catalysis. The combination of nanoribbons and layered structures may have a significant impact on future applications. With rational design and fabrication techniques, this combination may generate unusual phases that do not exist in bulk materials, thereby generating new active sites for electrocatalytic energy conversion reactions. With the rapid development in the fields of surface science, nano science, and nanotechnology, as well as advances in theoretical studies, well-defined metal oxide ribbon nano structures will pave the way for the design of next-generation solid catalysts. At the same time, this study also provides a new basis for in-depth understanding of the structure-activity relationship.

4 Proposals for development

The invention of metastable iridium oxide is a great achievement, especially in the fields of electrochemistry and nanomaterials.

In the research field of nanomaterials, this is undoubtedly a major breakthrough. We know that we can improve the properties of other aspects by changing the structure and arrangement of nanomaterial crystal lattices. For example, the problems discussed in this paper, we can get inspiration and enlightenment from this, we can design a variety of nanomaterial templates with different configurations, so as to achieve different requirements.

In the field of application and development, this promotes the development of new energy sources and sustainable development strategies. This undoubtedly reflects that the discovery and improvement of nanomaterials are gradually being put into our daily life. The development of our society and the progress of science cannot be separated from the improvement of nanomaterials science. The advancement of science and technology and the development of science and technology have promoted the development of society.

References

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[2] Danilo González et al. "Metal coordination determines the catalytic activity of IrO2 nanoparticles for the oxygen evolution reaction". In: *Journal of Catalysis* 412 (2022), pp. 78–86. ISSN: 0021-9517. DOI: https://doi.org/10.1016/j.jcat.2022.05.023.

[3] Youngmin Lee et al. "Synthesis and Activities of Rutile IrO2 and RuO2 Nanoparticles for Oxygen Evolution in Acid and Alkaline Solutions". In: *The Journal of Physical Chemistry Letters* 3.3 (Feb. 2012), pp. 399–404. DOI: 10.1021/jz2016507.

[4] Fan Liao, Kui Yin, Yanchun Ji, et al. "Iridium oxide nanoribbons with metastable monoclinic phase for highly efficient electrocatalytic oxygen evolution". In: *Nature Communications* 14 (2023), p. 1248. DOI: 10.1038/s41467-023-36833-1.

Figures and Tables are located in the next several pages

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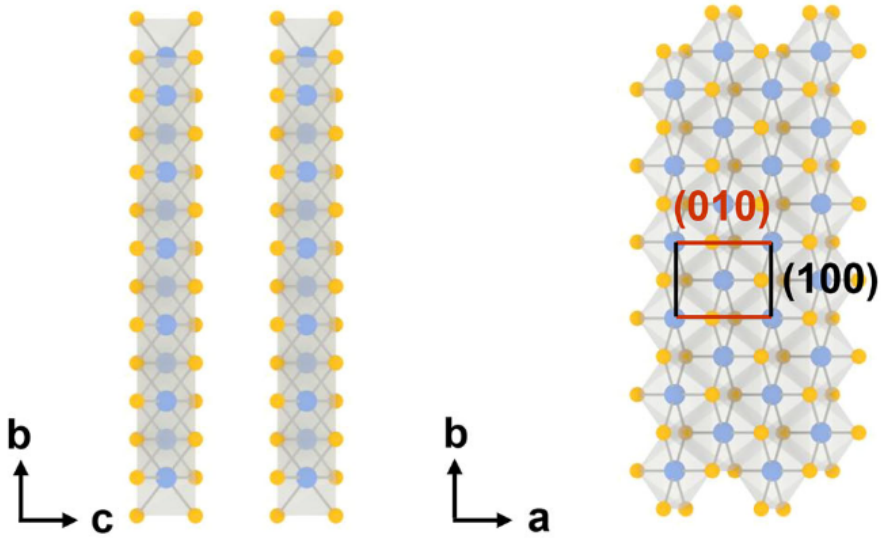

Figure 1: This is the basic model of the material

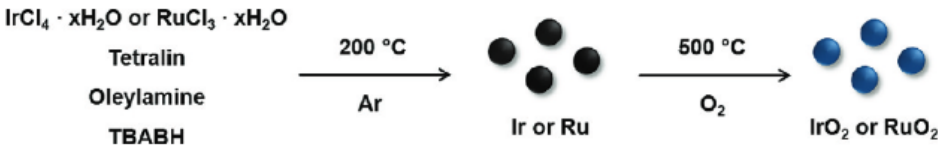

Figure 2: This is the equation for the reaction.

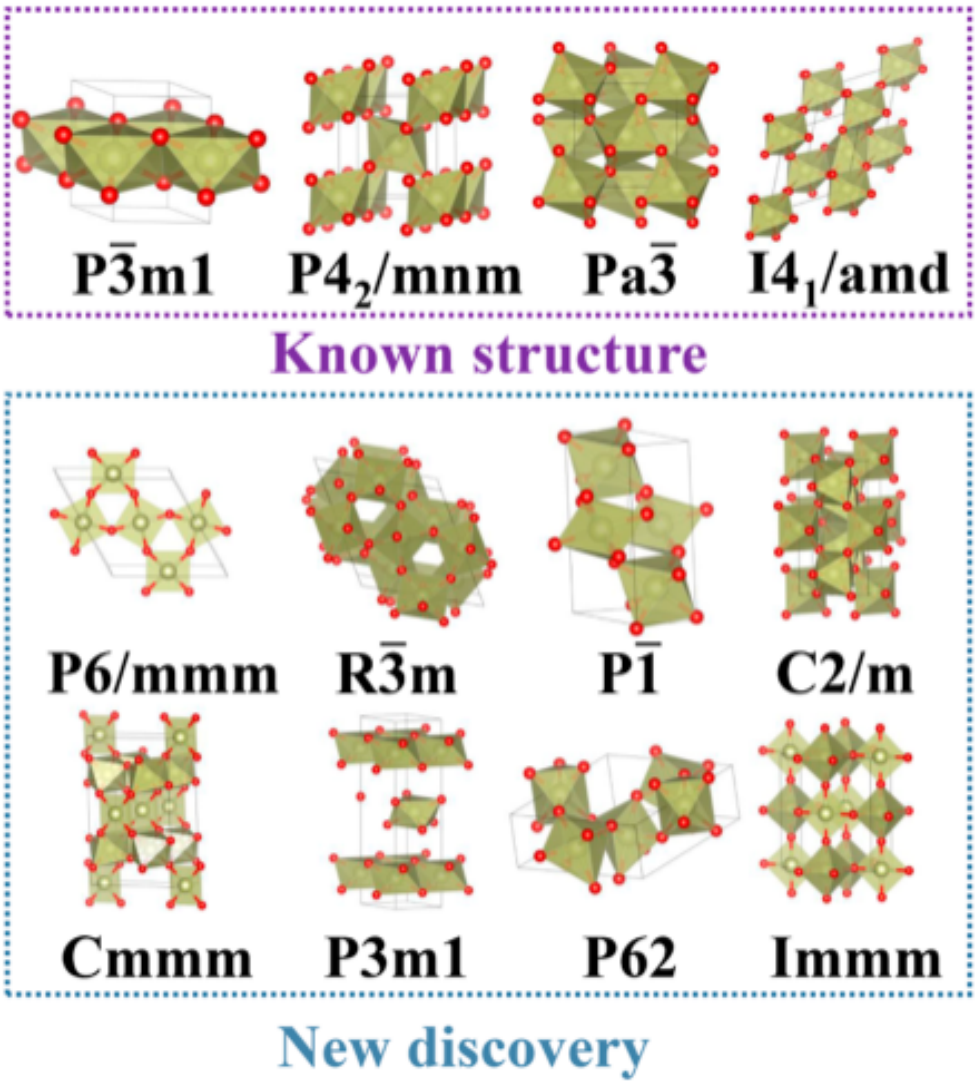

Figure 3: different models.

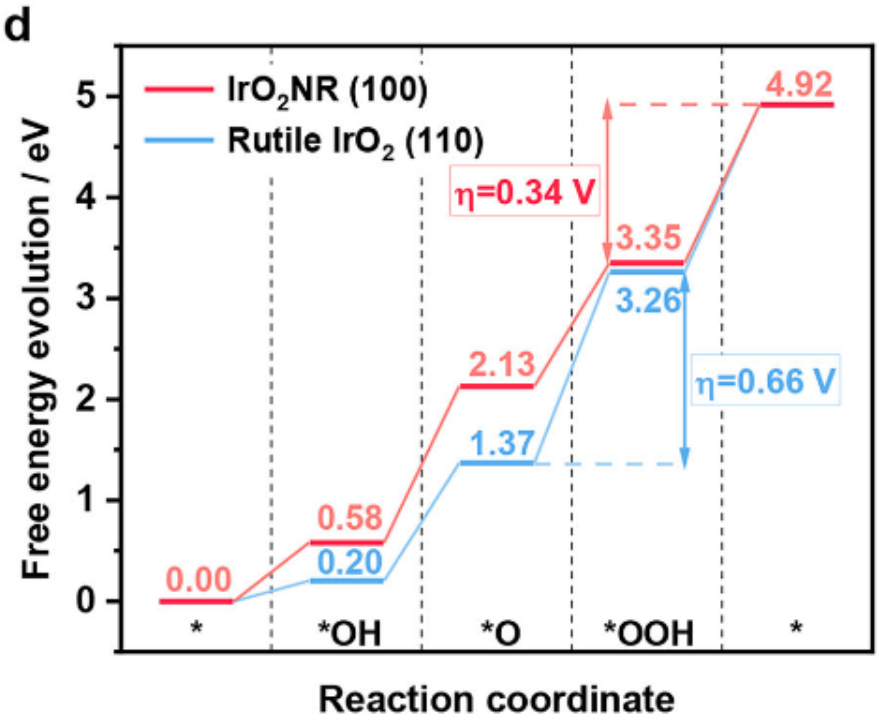

Figure 4: This plot tells us the relation for energy.

space group	n	a	b	c	enthalpy	Ir−O coordination	band gap
$P\bar{3}m1$	1	3.14	3.14	4.11	−6.81	6	1.94
$P4_2/mnm$	2	4.54	4.54	3.19	−7.05	6	0
$Pa\bar{3}$	4	4.94	4.94	4.94	−6.93	6	0.53
$I4_1/amd$	4	5.62	5.62	5.62	−6.69	6	0
$P6/mmm$	3	7.22	7.22	2.80	−6.83	4	1.04
$R\bar{3}m$	3	4.86	4.86	4.86	−6.82	6	0.52
$P\bar{1}$	3	3.18	4.42	7.36	−6.80	6	0.64
$C2/m$	3	5.23	8.39	4.36	−6.79	6	0.24
$Cmmm$	3	10.36	7.14	3.08	−6.77	6, 4	0.29
$P3m1$	3	3.14	3.14	12.74	−6.77	6	1.74
$P62$	3	6.31	6.31	3.10	−6.75	6	1.00
$Immm$	4	7.17	7.40	3.09	−6.78	6, 4	0

[a] n represents the number of formula units in the simulation cell. a, b, and c represent the lattice constants. The enthalpies (eV) and band gap (eV) of these structures were obtained by DFT calculations.

Figure 5: This table is for different models.