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PREFACE

Tungsten trioxide (WO_3) is a kind of multifunctional semiconductor materials, and it has been widely used in different fields including photochromism, electrochromism, chemical sensors and so on, for its unique physical and chemical properties. In this work, the electronic structure and surface chemical reactivity of tungsten trioxide semiconductor are systematically investigated by using DFT method. It is hoped that this book would provide reliable theoretical foundation to get deep insight into the origin of the characteristic of WO_3-based material, as well as designing the new heterogeneous catalysts. The main conclusions of this book are as listed in following.

1. The structural and electronic properties of seven WO_3 bulk phases have been studied. Our calculations indicate that, among these phases the simple cubic structure is the least stable, but the energy difference between different WO_3 phases is small (< 0.1 eV per WO_3 unit). When the unit cell is distorted from the cubic structure, the reducing of the symmetry results in the increasing of the band gap. According to our theoretical results, the band gaps of simple cubic, tetragonal, hexagonal, orthorhombic, RT-monoclinic, triclinic, and LT-monoclinic phases are 1.42 eV, 1.46 eV, 1.55 eV, 2.13 eV, 2.47 eV, 2.54 eV and 2.75 eV, respectively.

2. Geometries and electronic structures of a series of reconstructed $WO_3(001)$ surfaces have been systematically investigated. Our calculations demonstrate that the reconstructed $(\sqrt{2} \times \sqrt{2})R45°$ surface has the lowest surface energy and is thermodynamically most stable. According to the electronic structure, the bridging oxygen at surface is the main component of the top maximum of the valence band, while the contributions of the top oxygen atom locate at lower energy region. Comparing with the structural and electronic properties of a series of $(WO_3)_n$ clusters,

the similarities in the structural and electronic properties between cluster and surface can be found when $n = 6$, thus W_6O_{18} can be viewed as the smallest molecular model to understand the complex processes happened on the WO_3 surface.

3. The oxidation reactions of CO on perfect, defective and O_2-preadorbed $WO_3(001)$ have been systematically investigated. A possible full catalytic cycle is proposed to make the perfect $WO_3(001)$ surface as catalyst for CO oxidation, which contains three steps: (a) CO reacts with the top oxygen of the perfect WO_3 (001) surface to form a CO_2 molecule and the corresponding defective surface is formed; (b) the O_2 molecule is activated after adsorbing on the defective surface, because of the formation of O_2^{2-} species; (c) another CO molecule reacts with the pre-adsorbed O_2 to form the second CO_2 molecule, and meanwhile the initial perfect surface is subsequently regenerated. The NEB calculations indicate that all steps are exothermic strongly; however, the first step is the rate-limiting step from the kinetics viewpoint.

4. Geometries and electronic structures of $WO_3(001)$ surface doped by ⅤB, ⅥB, and ⅦB transition metals have been systematically explored. According to the doping energy, only the Ta doping is energetically favorable. By analyzing the electronic structures of four Ta-doped configurations, the distribution of terminal-oxygen radical as observed in $W_3O_9^+$ can be reproduced only when a Ta atom replaces a six-coordinated W atom on the surface. After doping, the top oxygen just above Ta atom is activated, and the CO oxidation reaction on the $WO_3(001)$ surface is enhanced. With respect to the undoped surface, the activation energy of the corresponding rate-determining step is reduced obviously about 0.64 eV.

In addition, we have also simulated the photo-oxidation mechanism of water on the WO_3 surface by using positively charged and neutral W_6O_{18} cluster models. The results obtained by two models are consistent with each other, and the rate-limiting step for the water oxidation on the WO_3 surface is related to the breaking of the O—H bond.

CONTENT

Chapter 1

Introduction

1.1 Applications of Tungsten Trioxide

Transition metal oxide is an important material that possesses various interesting properties in the field of catalyst, electrochromism, memory devices, and sensors. Among them, tungsten trioxide (WO_3) shows extensive application potential and has been receiving much attention due to its unique physical and chemical properties.

1.1.1 Coloration

The main interest in tungsten trioxide is its coloration properties, which may be induced by a variety of methods such as electrochromism, photo-chromism, and thermo-chromism. WO_3 is a kind of cathode coloration material, and the coloration process is carried out through double inserting of the electrons and cations, which can be described as:

$$xM^+ + xe^- + WO_3 \rightarrow M_xWO_3 (M = H, Li, Na, K) \qquad (1-1)$$

On the one hand, it is considered that WO_3 crystal changes from original semiconductor to conductor after the introduction of M atom, which can be proved by the corresponding band structures as shown in Figure 1 – 1. The appearance of W^{5+} cation in tungsten bronze (M_xWO_3) is the main reason of the coloration phenomenon. On the other hand, fully oxidized WO_3 crystal does not show any

coloration; however, the reduction of transparent WO_3 single crystal or yellow-green WO_3 powder causes blue coloration, implying that the oxygen vacancy plays a key role in this phenomenon. Therefore, the coloration of WO_3 can be attributed to the electron excess localized on the W^{5+} ions. Furthermore, the oxygen vacancies have been postulated as the color center and the corresponding experimental evidence for its significance to electrochromic performance has been extensively studied. The coloration properties of tungsten trioxide are strongly dependent on the concentrations of oxygen vacancies.

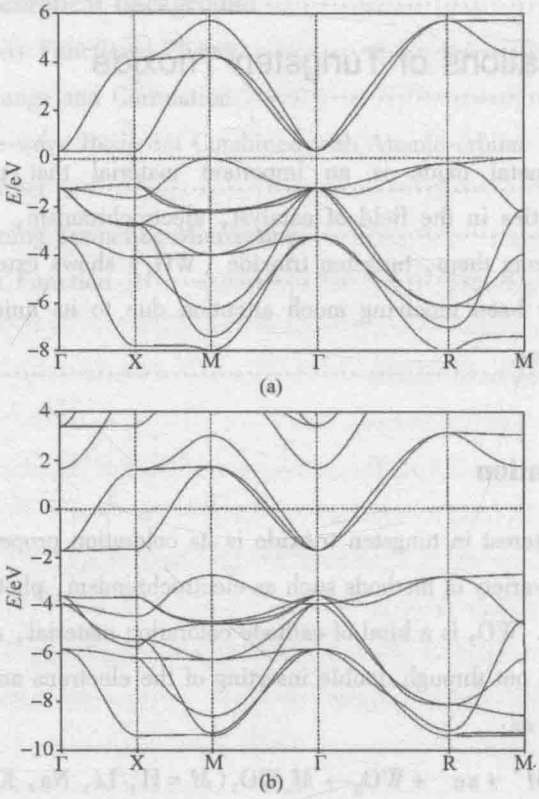

Figure 1 – 1 Band structures of (a) WO_3 and (b) $NaWO_3$ along a path in typically reciprocal space for the cubic structure [All the energies are corresponding to the Fermi level.]

According to the experimental research, WO_{3-x} surfaces exhibit various chromic properties at different levels of oxygen deficiency: when $x < 0.3$, the

surface remains transparent and dielectric; when $0.3 < x < 0.5$, it exhibits blue and conductive; when $x > 0.5$, the surface is metallic and conductive.

1.1.2 Gas Sensors

Metal oxides are generally used as gas sensitive materials due to their reproducibility and typical surface properties are suitable for gas detection. WO_3 is one potential candidate of gas sensors. Stoichiometric WO_3 turns into non-stoichiometric WO_{3-x} under high-temperature treatment with some lattice oxygen taking off, forming a typical *n*-type semiconductor that the majority charge carrier is electrons. The sensor performance of WO_3 material is directly related to the chemical adsorption of gas molecules on its surface. For instance, when WO_3 is exposed in the air, the O_2 molecules adsorb on the surface and the chemically adsorbed oxygen species O_2^-, O_2^{2-} and O^{2-} are produced at different temperatures. The charge transfer between the adsorbed oxygen and the WO_3 surface can be expected, and in the meanwhile the surface conductivity changes.

Shaver et al. first reported the gas sensing properties of WO_3 to H_2 and other gases including N_2H_4, NH_3, and H_2S, etc. In addition, it has been found that WO_3 material is also sensitive to other gases, especially shows excellent response to the toxic gas NO_x— typically NO_2 and NO, because the W atom in WO_3 surface is found to be with different oxidation states (W^{5+}, W^{6+}) which can improve the oxidizing ability of NO_x molecules on the WO_3 surface. Tomchenko et al. prepared WO_3 film sensor with different thickness that contains Bi_2O_3 dopant by using traditional screen printing technology, and their tests demonstrate that WO_3 exhibits good response to low-concentration of NO at the temperature of 100 ~ 300 ℃. The prominent sensitivity of tungsten trioxide to the toxic gases (NO, H_2S and so on) makes it possible to detect those environmentally-unfriendly gases. Thus, the tungsten trioxide has an important application in the field of trace gas treatment and environmental monitoring.

1.1.3 Photo-catalytic Degradation

In recent years, there has been growing interest in the heterogeneous photo-catalysis of semiconductor catalyst as a promising technology for the environmental purification and solar energy conversion. Compared with other methods, photo-catalysis has some advantages such as high efficiency, energy saving, non-toxic, no secondary pollution, etc.; as well as it exhibits wide applications in the fields of wastewater treatment and water advanced treatment.

Previous studies mainly focus on the titanium dioxide (TiO_2) due to its high efficiency and stability; however, since it has a large band gap (about 3.2 eV), the transformation efficiency of the visible light is lower than 4%. With respect to TiO_2, WO_3 may have higher transformation efficiency due to the lower band gap (2.4 ~ 2.9 eV). Wang et al. reported the photo-catalysis properties of nanocrystal and amorphous WO_3. Their results indicate that the productivity of photo-catalytic degradation increases along with the presence of oxygen vacancy and the reduction of amorphous amount in WO_3 film. Additionally, WO_3 shows high efficiency and selectivity to many catalytic reactions and it has wide applications in the fields of chemical and petroleum chemical industry. For example, it can oxidize benzene and toluene into maleic anhydride and benzaldehyde, respectively. Many studies indicate that the WO_3 exhibits good catalytic performances in hydrogenation, dehydrogenation, hydrocarbon isomerization, alkylation and many other reactions, etc. However, because the band gap of WO_3 is not large, the redox capacity and photo-catalytic activity are not good enough. Therefore, many efforts have been paid to improve the catalytic activity of this important material.

1.1.4 Water-splitting Electrode

There has been considerable interest in using solar energy to produce hydrogen by photo-electrolysis of water for a long time. Especially, Fujishima and

Honda found the generation of hydrogen in the process of illuminating TiO_2 to split water, which reveals the possibility of producing hydrogen by means of decomposing water. There are several factors involved in the choice of a semiconducting anode: (1) it must be chemically inert; (2) the most important factor is that the semiconductor must have an appropriate band gap which makes the best use of the solar energy (Figure 1 - 2); (3) it must match with the cathode to form a system which allows an effective conversion of solar energy to electrical or stored chemical energy. Up to date, many semiconductors have been investigated in the photo-electrolysis of water, including TiO_2, $SrTiO_3$, SnO_2, and so on. However, none of them provide a good match to the solar spectrum due to their big band gap (larger than 3.1 eV). Therefore, new classes of semiconductor materials have been taken into account in order to make better use of the visible light. Among them, tungsten trioxide (WO_3) is a potential candidate since it can capture approximately 12% of the solar spectrum and can adsorb light in the visible spectrum up to 500 nm. Given its band gap (E_g =2.6 eV), WO_3 is a more suitable material for photo-electronic water splitting than TiO_2 (E_g =3.0 ~3.2 eV). TiO_2 adsorbs only in the ultraviolet region of the spectrum and captures approximately 4% of solar irradiation. The theoretical maximum conversion efficiency of solar energy into H_2 is only 2.2% in a photo-electro-chemical water-

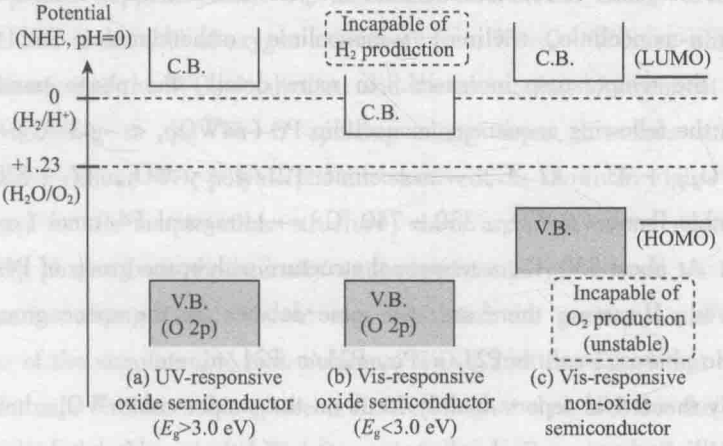

Figure 1 - 2 Energy levels of various semiconductors

splitting device using TiO_2 as a photo-anode and is approximately 4.8% using WO_3 as a photo-anode. WO_3 exhibits high resistance against photo-corrosion and good chemical stability in acidic aqueous solutions ($pH < 4$) under solar illumination. Therefore, in recent years, much effort has been focused on to improve the incident photo-to-electron conversion efficiency of WO_3 photo-anode.

1.2 Research Progress in WO_3 Bulk

Similar to the structure of ReO_3, the ideal cubic WO_3 crystal is originated from the cubic perovskite ABO_3 structure with the missing of A atom. The basic building block of WO_3 bulk is a simple cubic perovskite-type unit with W atom occupying the center of an octahedron, and the octahedron is corner-sharing with another one. All the W and O atoms are six- and two-coordinated in various WO_3 crystals. Figure 1 - 3 displays the crystalline structure of WO_3. Some studies based on X-ray diffraction measurements demonstrate that WO_3 prepared in experiments is usually a series of polymorphs. Like other metal oxides, the phase transitions of WO_3 crystal take place during annealing and cooling. The distortion of the WO_6 octahedron is observed, and as a result of the displacement of W atom away from the center of octahedron, bulk WO_3 exhibits at least five different phases including ε-monoclinic, triclinic, γ-monoclinic, orthorhombic, and tetragonal phase as the temperature increased. In more detail, the phase transformation occurs in the following sequence: monoclinic Pc (ε-WO_3, < -43 ℃) → triclinic P1 (δ-WO_3, -43 ~ 17 ℃) → monoclinic P21/*n* (γ-WO_3, 17 ~ 330 ℃) → orthorhombic Pmnb (β-WO_3, 330 ~ 740 ℃) → tetragonal P4/nmm (α-WO_3, > 740 ℃). At aboat 830 ℃, a tetragonal structure with space group of P4/ncc may be observed. However, there are still some debates for the space groups of the monoclinic phases, such as P21/a, Pc, P21/c, P21/n, etc.

Early theoretical reports mainly focus on the simple cubic WO_3; however, in this crystalline phase, a single electron occupies in the e_g orbital, which gives rise to a second-order Jahn-Teller distortion and therefore the cubic WO_3 structure is

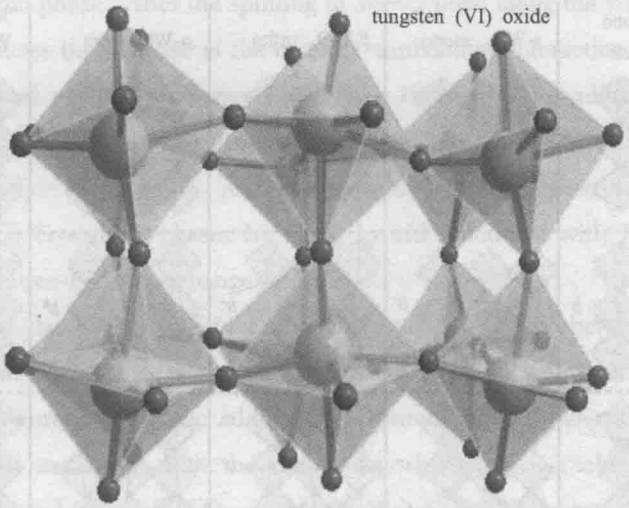

Figure 1 – 3 Schematic structure of corner-sharing network of WO_6 octahedron in WO_3 crystal [The big spheres stand for the W atoms, while the small spheres denote the O atoms.]

unstable. Actually, this simple cubic WO_3 crystalline phase is difficult to be observed in the experiment, except in the WO_3 film. Theoretically, we will see that the energy differences between the simple cubic WO_3 and other distorted phases are very small, indicating that the structural transformation between different phases happens easily. As mentioned above, the energy divergence is mostly related to the shift of oxygen atom away from W—O—W line, which results in the distortion of the WO_6 octahedron and the alternating arrangement of W—O bond. According to the W—O splitting along three directions at different temperature, various WO_3 polymorphs are observed, as shown in Figure 1 – 4.

Except for the simple cubic structure, there are also several reports on the other WO_3 phases both theoretically and experimentally, as well as the phase transformation among them. Corà et al. calculated the geometry and electronic structures of the simple cubic and tetragonal WO_3, and they found that the energy of WO_3 formula unit for cubic phase is 0.8 eV higher than that for the tetragonal one, owing to the elongating of W—O covalent bond. Experimentally, Vogt el al. investigated the high-temperature phases (orthorhombic β-WO_3 and tetragonal

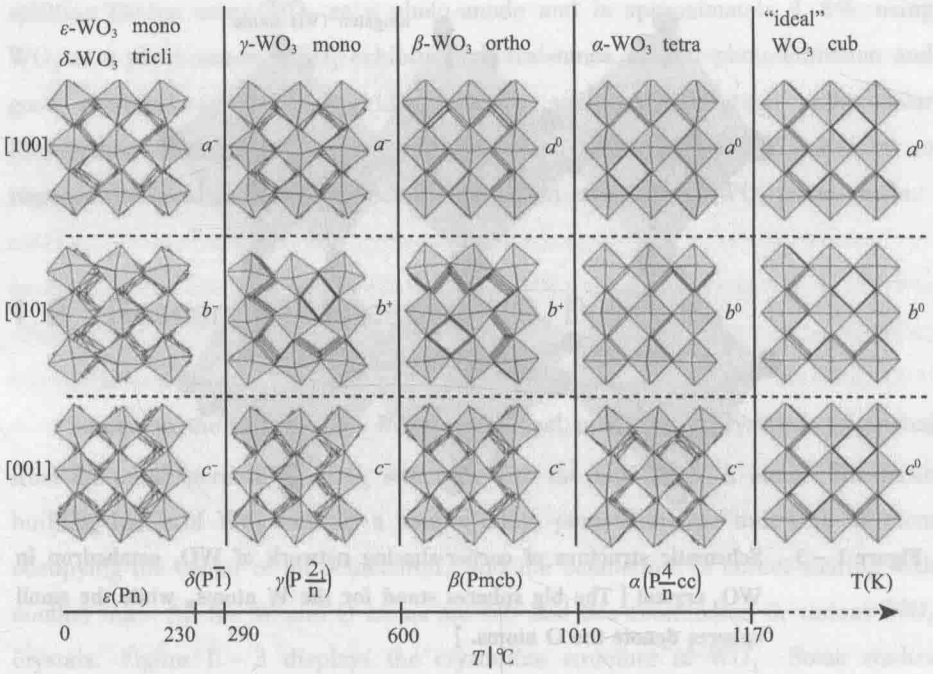

Figure 1-4 Tilt patterns and stability temperature domains of the different polymorphs of WO_3

α-WO_3) of WO_3 with the help of high-resolution neutron powder diffraction. Their results further confirmed that the temperature induced phase transitions in WO_3 can be rationalized in terms of the changes in the tilt direction of WO_6 octahedron and/or off-center displacements of the tungsten cations.

Besides, the structural distortion has a major impact on the electronic properties, such as the band gap of WO_3 bulk. First-principles studies of Chatten et al. illustrated that the electronic structure of WO_3 bulk is critically dependent on the splitting of W—O bond along each direction. The cubic WO_3 has a small band gap of 0.69 eV; while the W—O bond only splits along z axis, i.e. in the tetragonal phase, the band gap enlarges slightly (0.71 eV); as for the orthorhombic one, the W—O bond further splitting along the y direction, making its band gap increase to 1.50 eV. Therefore, the obvious splitting of W—O bond along the y direction is the dominant factor in determining the band gap of WO_3