Enhancing Photocatalytic Performance of Strontium Titanate Nanomaterials through Defects and Band Gap Engineering

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Enhancing Photocatalytic Performance of Strontium Titanate Nanomaterials through Defects and Band Gap Engineering

Bolin Qu

A thesis in fulfilment of the requirements for the degree of Master of Engineering

School of Materials Science & Engineering
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Photocatalysis as an efficient and green solution to produce highly efficient and renewable energy H₂ has attracted more attention recently. Among many photocatalyst materials, perovskite oxides have shown high efficiency and excellent stability under light irradiation due to their unique crystal structures and electronic properties. SrTiO₃ as one of the perovskite oxides is a promising photocatalyst because of its low cost, high photochemical stability, and catalytic efficiency. However, the wide band gap of SrTiO₃ (3.2eV) makes it active only under UV light irradiation instead of visible light which means more harsh reaction conditions and more energy consumption. Therefore, it is a big challenge for modifying SrTiO₃ to improve photocatalytic performance. In this work, a hydrothermal method was used to synthesize pristine SrTiO₃ nano-cubic particles with high crystallinity. Then a novel strategy is applied through creating more oxygen vacancies and doping with chromium in the pristine SrTiO₃ to improve photocatalytic performance respectively. A molecular dynamic simulation method was first used to investigate the oxygen vacancies diffusion mechanism for a better understanding of experimental directions. The simulation part concludes that creating more oxygen vacancies and elevate the temperature would increase the oxygen vacancies diffusion in SrTiO₃. Then, the annealing method was used to create oxygen vacancies mixing SrTiO₃ with strong reductant NaBH₄ in the tube furnace with Argon gas flow. After creating more vacancies in SrTiO₃, H₂ production efficiency has been improved for three times. For the doping chromium part, a similar method has been used to synthesize cubic Cr-doped SrTiO₃ nanoparticles. The colour of the product turns to yellow-green and the analysis of energy dispersive X-ray spectroscopy and inductively coupled plasma concludes that Cr element doped in SrTiO₃ successfully. It is observed that the degree of crystallization of the products increased with increasing reaction time according to the XRD result. UV-visible spectroscopy indicates that the band gap of Cr-doped SrTiO₃ is 2.30eV, much lower than pristine SrTiO₃ of 3.32eV. Photocatalytic performance efficiency of Cr-doped SrTiO₃ is eight times better than pristine SrTiO₃, three times better than annealing SrTiO₃.

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Abstract

Photocatalysis as an efficient and green solution to produce highly efficient and renewable energy H₂ has attracted more attention recently. Among many photocatalyst materials, perovskite oxides have shown high efficiency and excellent stability under light irradiation due to their unique crystal structures and electronic properties. SrTiO₃ as one of the perovskite oxides is a promising photocatalyst because of its low cost, high photochemical stability, and catalytic efficiency. However, the wide band gap of SrTiO₃ (3.2eV) makes it active only under UV light irradiation instead of visible light which means more harsh reaction conditions and more energy consumption. Therefore, it is a big challenge for modifying SrTiO₃ to improve photocatalytic performance. In this work, a hydrothermal method was used to synthesize pristine SrTiO₃ nano-cubic particles with high crystallinity. Then a novel strategy is applied through creating more oxygen vacancies and doping with chromium in the pristine SrTiO₃ to improve photocatalytic performance respectively. A molecular dynamic simulation method was first used to investigate the oxygen vacancies diffusion mechanism for a better understanding of experimental directions. The simulation part concludes that creating more oxygen vacancies and elevate the temperature would increase the oxygen vacancies diffusion in SrTiO₃. Then, the annealing method was used to create oxygen vacancies mixing SrTiO₃ with strong reductant NaBH₄ in the tube furnace with Argon gas flow. After creating more vacancies in SrTiO₃, H₂ production efficiency has been improved for three times. For the doping chromium part, a similar method has been used to synthesize cubic Cr-doped SrTiO₃ nanoparticles. The color of the product turns to yellow-green and the analysis of energy dispersive X-ray spectroscopy and inductively coupled plasma concludes that Cr element doped in SrTiO₃ successfully. It is observed that the degree of crystallization of the products increased with increasing reaction time according to the XRD result. UV-visible spectroscopy indicates that the band gap of Cr-doped SrTiO₃ is 2.30eV, much lower than pristine SrTiO₃ of 3.32eV. Photocatalytic performance efficiency of Cr-doped SrTiO₃ is eight times better than pristine SrTiO₃, three times better than annealing SrTiO₃.
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Chapter 1 Introduction

1.1 General background and research objectives

SrTiO$_3$ as one of the perovskite oxides which has unique regular arrangement of atoms is a promising photocatalyst because of low cost and high photochemical stability. However, the photocatalytic performance of pure SrTiO$_3$ stays in a low level for several reasons. Modified SrTiO$_3$ which can improve the efficiency of photocatalysis could be practical and interesting. Therefore, creating more defects and doping with Chromium element in pure SrTiO$_3$ are adopted to achieve the goal in this research respectively and compare with each other. Moreover, before creating defects in SrTiO$_3$, oxygen vacancy diffusion is investigated by computational simulation method in order to instruct the experiment.

The research outlines are listed below:

- To investigate the oxygen vacancy diffusion by computational simulation in SrTiO$_3$
- To improve the photocatalytic performance by making defects in pure SrTiO$_3$
- To synthesize Cr-doped SrTiO$_3$ for enhancement of photocatalysis efficiency

1.2 Thesis outline

This thesis contains six chapters in total. Chapter one shows a brief background of the research topic, general research objectives and outlines for each part. Chapter two supplies the quantum mechanics background for simulation and review of previous research on properties, synthesis and applications of SrTiO$_3$. Chapter 3 investigates the oxygen vacancy diffusion by computational simulation method in SrTiO$_3$. In Chapter 4, pure SrTiO$_3$ is synthesized by hydrothermal method and more defects are introduced in pure SrTiO$_3$ for improvement of photocatalysis efficiency. In Chapter 5, Chromium element is doped in pure SrTiO$_3$ for enhancement of photocatalysis and compared with the performance of annealing SrTiO$_3$. Chapter 6 is the summary of whole thesis and the outlook of the future research.
Chapter 2 Literature Review

2.1 Experimental method for investigation in SrTiO$_3$

2.1.1 Photocatalytic Hydrogen Production for semiconductor

Research Background for Energy and Environmental issue

At present, the biggest problem and challenge facing mankind is energy shortage and environmental pollution. As is known to all, the reserves of fossil fuels on the earth are limited and non-renewable. Besides the gas like CO$_2$, SO$_2$ and dust released by the combustion of fossil fuels will cause serious environmental problems. Therefore, it is urgent to find new clean energy to solve the problems such as energy shortage and environmental pollution. H$_2$ is the most abundant element in the universe. It is safe, secure, simple to store and transport as a fuel, and can also be used for direct electricity generation in fuel cells. At present, H$_2$ has been commonly recognized as an optimal source of energy and has gained high interest. Due to the low density and active chemical properties of H$_2$, there is no pure H$_2$ on the earth's surface. Therefore, it is important to decompose from compounds with H element. Because there are abundant water resources on the earth, the decomposition of H$_2$ from water will essentially solve energy and environmental problems.

In 1972, Fujishima and Honda[1] discovered that, in the electrode system consisting of TiO$_2$ and Pt, when the TiO$_2$ electrode was irradiated with light, the Hydrogen and Oxygen could be decomposed from the water. This is a seminal finding which promises to use solar energy to generate clean H$_2$ fuel from the water through semiconductor catalysis. Since then, the semiconductor photocatalytic decomposition of water has attracted extensive attention from scientists in the field of condensed matter physics and materials science.
Semiconductor photocatalysis mechanism

Semiconductors can be used as catalysts because of their unique band structure. The semiconductor band consists of a valence band filled with electrons and an empty conductor band. The region between them is called the prohibited band. The photocatalytic property of the semiconductor is determined by its unique band structure. As a photon with an energy greater than or equal to the band gap width is absorbed by the electrons of the valence band, the electrons of the valence band will leap to the conduction band to form free electrons and at the same time leaving corresponding holes in the valance band, resulting in electron-hole pairs. At this point, the electron hole pair disappears in two ways. One is that the electron hole pair will combine to emit photons or heat energy which cannot be used. The second is electron-hole separation, which transitions to the surface of the semiconductor and converts to chemical energy through catalytic reactions which is called photocatalysis or converts to electricity energy through external power supply which is used to make solar cells.

Water is a very stable substance and free energy will increase when breaking down water to create hydrogen and oxygen. The chemical equation for photocatalytic water splitting is as below.

$$2H_2O + 4\nu = O_2 + 2H_2O$$  \hspace{1cm} (2-1)

A normal state breakdown of a mole of water takes at least 285.5 KJ energy. From the electrochemical perspective, since the energy difference between oxygen evolution potential and oxygen evolution potential in H$_2$O is 1.23eV, that is to say, when the electric field energy increases to more than 1.23eV, electrons have the ability to reduce H$^+$ to H$_2$, and holes can oxidize H$_2$O to produce O$_2$. Therefore, theoretically the band gap of the catalyst needs to be wider than 1.23eV, but considering the energy loss, the most suitable band gap width should be 2.0-2.2eV, otherwise it cannot provide enough REDOX energy.
In order to decompose water molecules, the band structure of semiconductor is also required from the electrochemical aspect. The conduction band edge and valence band edge positions of semiconductor must match the hydrogen evolution potential and oxygen evolution potential of water molecules. The position of the conduction band bottom represents the limit of electron reduction ability. Only materials with lower conduction band bottom than reduction potential can be reduced. Besides, the lower the conduction band bottom is, the stronger the reduction ability of the conduction band electrons. Similarly, the position of the valence band top represents the limit of the oxidation capacity of the hole. Only materials with a higher valence band top than the oxidation potential can be oxidized. The higher the valence band top is, the stronger the oxidation capacity of the hole in the valence band is. Therefore, the conduction band bottom of photocatalytic semiconductor has the ability to reduce H+ in water molecules only when the hydrogen evolution potential is lower than that in water molecules, while the valence band top has the ability to oxidize O2- in water molecules only when the oxygen evolution potential is higher than that in water molecules. The role of catalyst is to provide sufficient REDOX potential in the process of water molecule decomposition.
Except that the band gap of the semiconductor should be wider than the threshold of water decomposition, the valence band top of the semiconductor should be higher than the oxygen evolution potential and the conduction band should be lower than the hydrogen evolution potential. Otherwise, additional bias voltage will be needed to drive the precipitation of hydrogen or oxygen, thus affecting the catalytic effect. Therefore, semiconductor materials can be used as photocatalytic materials as long as the band gap size and the appropriate location of guide and valence bands theoretically.

2.1.2 Strontium Titanate

Perovskite Crystal

Perovskite is actually the name of a naturally occurring mineral found in the 19th century in the Ural Mountains. It attracts attention simply because the arrangement of atoms within its crystal which three atoms of Calcium, Titanium and Oxygen are arranged in a specific order that repeats itself. Since then, Perovskites refer to a class of ceramic oxide with particular ABO₃ crystalline structure in which different cations could be surrounded in this structure to develop various materials. Fig.1[4] represents the original ABO₃ cubic structure. In general, A as the larger cations with O cations form the FCC lattice in the
meanwhile B as the smaller cations take the position of octahedral sites center surrounded by O cations only.[5][6]

Fig 2.1.2.1 The cubic perovskite structures shown with A, B, O atoms[4]

The B-site cation is a transition metal element and the A-site cation often consists of an alkaline-earth metal element or a rare earth element. The properties are determined by cations occupying A and B sites collectively. As perovskite-type oxides research continues, ABO₃ family exhibit a wide range of ferro-, piezo-, and pyroelectrical properties and electro-optical effects. Due to these properties, they have been used in numerous technological applications as the part of electronic, structural, magnetic and refractory materials.[7]

**Strontium Titanate**

Strontium Titanate(SrTiO₃) as a typical perovskite-type crystal is widely studied recently with good insulating properties, excellent optical transparency, superconductivity, and high dielectric constants.[8] In addition, SrTiO₃ shows resistive switching properties which refers to the physical phenomenon when the dielectric changes the terminal resistance under strong electric field or current.[9][10] Moreover, SrTiO₃ is one of promising materials of Titanate perovskites family for photocatalytic processes due to their excellent insulating properties and excellent resistance to photocorrosion. It has been widely studied as an important n-type semiconductor with an indirect band gap of 3.1-3.7[11] and used in a variety of applications such as H₂ production[12], solar cells[13],...
oxide electronics[14] and the formation of two-dimensional electron gas.[15]

**SrTiO₃ Synthesis Methods and Applications**

The properties of SrTiO₃ are determined by crystal structure and morphology which means it is vital to control these two factors for desired properties when synthesizing SrTiO₃. There are several synthesis methods to obtain pristine and doped SrTiO₃ such as sol-gel method[16], solid-state reaction method[17] and hydrothermal synthesis method[18][19].

Sol-gel method developed in the 1960s for preparing ceramics, glass, fiber, bulk solids and thin films. The basic principle is to hydrolyze the inorganic salt in the organic solvent and obtain the gel by polycondensation reaction. The desired materials are obtained by aging, drying and calcining the gel. In the whole sol-gel process, the added water amount, system PH value, alcohol salt concentration and system temperature all have important effects on the gelation time, morphology, particle size and yield of the final products. Liu[20] prepared the transparent sol in the glove box with ethanol as the organic solvent, and then used ammonia water to slowly adjust the sol PH value to help the amorphous precursor nanoparticles in the sol slowly grow. After 3-5 days, nanocrystalline with diameter of 17nm was obtained by heat treatment under 500-600°C from amorphous nanoparticles which is an ideal material for investigating nano-size effect. O’Brien[21] presented a universal injection-hydrolysis method for synthesis of monodisperse oxide nanoparticles. Rapid injection of H₂O₂ was used instead of slow addition of ammonia to promote the sol to gel process which greatly improved synthesis efficiency. The final diameter of BaTiO₃ nanoparticles ranged 6-12nm. Sol-gel method could synthesize ideal size nanoparticles. However, this method also has obvious disadvantages, such as complex preparation process, trying different types of organic molecules, some of which are even toxic.

Solid-state reaction method is a relatively simple method to synthesize ceramic powders.
Solid state reactions are performed in the absence of solvents by either grinding or melting the starting materials together or simply applying heat to a mixture of starting materials for new ideal materials. The basic principle is to use the high temperature environment of molten salt to provide energy and reaction medium for the dissolution of reactants, precipitation and crystallization. When ceramic powders are prepared by NaOH and KOH as solid-state method, molten salt not only provides the required high temperature environment for the reaction, but also acts as a mineralizing agent to promote the reaction. In recent years, molten salt method has been used to prepare nanostructures of complex oxides including perovskite structure materials. Mao[22] synthesized BaTiO$_3$ nanowires with diameter of 50-80nm and SrTiO$_3$ nanocubes with diameter of 80nm by solid state reactions successfully. Solid state reaction has many advantages such as easy operation and low cost, however, it is hard to control morphology of ideal materials.

Hydrothermal method refers to preparing compounds by reaction in a special closed reaction vessel, in which some kind of water or organic solvent is used as the reaction medium. The reaction vessel is heated to produce a high-temperature and high-pressure reaction environment which dissolves normally insoluble or insoluble substances to make synthesis reaction occur. The powder can be controlled by optimizing the reaction conditions such as temperature, reactant concentration and solution value. To understand and design hydrothermal methods, Lencka[23] and Riman provided a thermal dynamic model to simulate reactants phase change under hydrothermal process. They showed that phase diagrams can be rigorously generated for your ideal materials under hydrothermal process. More importantly, they found that PH value is a vital variable for morphology control by hydrothermal synthesis. Deng[24] obtained 5-10nm diameter nanoparticles by hydrothermal methods with severe aggregation. With the widespread use of hydrothermal method, some research groups began to explore the introduction of organic molecules into the hydrothermal system or the use of solvent thermal method to regulate the reaction process to achieve the controllable morphology, size and dispersion of product particles. Monodisperse and polysized nanoparticles are ideal materials to study the size
dependence of nanoparticle properties.

Among these, hydrothermal method is more widely used due to not only low temperature and short reaction time which means energy-efficient, but also stable structure synthesized. The term hydrothermal origins from geography which was described the formation of various rocks and minerals when water bring out of earth at elevated temperature and pressure. Geologists aiming at simulation in laboratory of natural hydrothermal phenomena was original hydrothermal research. Recently, it is well known to synthesize nanocrystals with the development of technology. Moreover, with an increasing demand for composite nanostructures, various compounds were coated on metals, polymers and ceramic bodies by hydrothermal method. Fig.2 indicates many applications aspects of hydrothermal synthesis method which links most vital technologies including geotechnologies, biotechnologies, advanced materials technologies and nanotechnologies.[25]
Oxygen Vacancy in SrTiO$_3$

Oxygen vacancy as intrinsic defects in the materials makes significantly contribution to the properties of SrTiO$_3$.[26] In general, the formation of oxygen vacancies is caused by the growth of crystals and chemical reaction with the heat treatment in the external environment which lead to the separation of oxygen. The defect equation can be shown as below:
$$O = \frac{1}{2}O_2 + V_O$$  \hspace{1cm} (2-2)

In SrTiO$_3$, the electronegativity of oxygen is the highest so that when losing oxygen, it will take away an oxygen atom plus two positive-electron holes which produce the positive oxygen vacancy.[27] As is known to all, oxygen vacancy formation is determined by two reasons which are the electronic Fermi level and oxygen chemical potential.[28]

Oxygen vacancy diffusion mechanism as the reason for conductivity is crucial to fully understand the properties of SrTiO$_3$ such as resistive switching and high charge storage capacity.[29][30] Unlike the Fick empirical equations, oxygen vacancy diffusion mechanism is based on random walk theory on the microscopic scale.[31] The advantage of microscopic way is to suppose the fundamental of theoretical analysis and examine the diffusion coefficients according to atomic quantities in order to explain and predict the properties of materials better.[32][33] Sawa and co-workers found the relationship between resistance and oxygen vacancy concentration in the STO/Ag cells which indicates that with the increase of oxygen vacancy concentration, the resistance becomes to decrease obviously. So that it is vital to make full understanding of the diffusion procedure to optimize and design the properties of materials.

2.1.3 Photocatalytic water splitting for SrTiO$_3$

Photocatalysis study in SrTiO$_3$

Photocatalytic water splitting as an efficient and green solution to the current environmental deterioration and energy crisis has attracted more attention recently. [34][35] Among many photocatalyst materials, perovskite oxides have shown high efficiency and stability under visible-light irradiation due to their unique crystal structures and electronic properties. The perovskite structure provides a good framework in which to tune the band gap values to enable visible-light absorption band edge potentials for photocatalytic reactions. Furthermore, lattice distortion in perovskite compounds strongly
influences the separation of photogenerated charge carriers.[36] SrTiO$_3$ as one of the perovskite oxides is a promising photocatalyst because of low cost, high photochemical stability and catalytic efficiency. At room temperature, SrTiO$_3$ is a typical perovskite structure with Pm3m space group. In the SrTiO$_3$ structure, transition metal Ti and O form a regular octahedral structure and Sr filling in the interstice of the regular octahedron. The ligancy of Sr$^{2+}$ and Ti$^{4+}$ are 12 and 6. The band gap of SrTiO$_3$ is 3.2eV.[37]

SrTiO$_3$ was first used as photocatalyst by Wrighton and co-workers in 1976.[38] They found that water is decomposed into H$_2$ and O$_2$ with Pt as photocathode and SrTiO$_3$ as photoanode under ultraviolet light. Mavroides and co-workers[39] found that the quantum efficiency of SrTiO$_3$ under zero bias is 10% compared to 1% in TiO$_2$ which shows great potential for photocatalysis of SrTiO$_3$. Ferre with his colleagues[40] found that water vapors were decomposed into H$_2$ when the light shines on the surface (1,1,1) of SrTiO$_3$ under high temperature and vacuum atmosphere. Avudaithai[41] found that the electrolyte with SrTiO$_3$ powder in the diameter of 40-80nm was decomposed into H$_2$ and O$_2$ under the light. Wagner[42] found that the H$_2$ production was increased when monocystal SrTiO$_3$ was coated with Pt on the surface which shows the possibility of increasing photocatalytic efficiency. Similar work by Somorjai[43] found that SrTiO$_3$ with NiO on the surface has more efficiency than pure one. Therefore, more and more researchers use metal or metal oxide to modify the surface of SrTiO$_3$ to improve the catalytic performance. After surface modification, on one hand it will form Schottky junction which helps to separate the carriers and improve the photocatalytic efficiency; On the other hand, some metal and metal oxide will help H$_2$ and O$_2$ desorption to improve the photocatalytic efficiency. NiO/SrTiO$_3$ has higher catalytic activity which can completely decompose the water to H$_2$ and O$_2$. In addition, some noble metal modified SrTiO$_3$ such as Rh/SrTiO$_3$ has the highest photocatalytic efficiency for H$_2$ production.

**Limitation and modification for photocatalysis of SrTiO$_3$**

However, the wide band gap of SrTiO$_3$(3.2eV) makes it active only under UV light
irradiation instead of visible light which means more harsh reaction conditions and more
energy consumption. Besides, photoexcited electron hole pairs from SrTiO₃ readily
recombine which lead to the electrons and holes to recombine before reaching the surface
to participate in the REDOX reaction. These two reasons affect photocatalytic efficiency
seriously. Therefore, it is necessary to improve the photocatalytic efficiency by properties
of materials, so as to make large-scale use of photocatalytic technology. In order to make
full use of the solar energy on the earth surface and improve the light absorption
performance of the semiconductor electrode, people make the semiconductor light
absorption boundary move to the visible light part possibly through various ways,
reducing the recombination between the photogenic carriers and increasing the carrier life.
The reduction of recombination can be achieved by reducing the radius of particles. The
smaller the particle radius, the more particles per unit mass, and the larger the specific
surface area, the more favorable it is for the photocatalytic reaction to be carried out on
the surface, so as to improve the photocatalytic efficiency.

In order to achieve the light-seeing response, the band gap of SrTiO₃ needs to be reduced.
The most common method to reduce the band gap is element doping due to the low cost
and reaction time of the process. Therefore, many works have been devoted to expand the
spectral response of SrTiO₃ such as combining with another semiconductor[44], doping
with metals[45] and nonmetals[46]. Modified SrTiO₃ such as doping or deposition on
nonmetals has been reported to enhance the performance for wide band gap
semiconductors. It can be concluded that the change in electronic band structures
proceeds in two different ways which are formation of a new mid-gap state between
valence band and conduction band, as seen in Cr-, Rh-, Ir- doped materials and changing
the valence band or conduction band by mixing energy levels of the dopant and host
elements, as seen in N-, F-, C- doped materials.[36]

Besides, due to the fact that the high electron-hole recombination rate of SrTiO₃ leads to
low photocatalytic efficiency, reducing the electron-hole recombination would also be an
efficient way to improve photocatalytic performance. It is well known that oxygen defect plays an important role in the processes of photocatalysis.[65] Surface oxygen vacancies can prevent the recombination of photogenerated charge carriers as charge traps or adsorption sites resulting in the improvement of the photocatalytic performance.[50] Therefore, controlling the oxygen defects on the surface of photocatalyst and increasing the oxygen vacancy diffusion could be very important for the improvement of its photocatalytic property.

2.2 Simulation method for investigation in SrTiO$_3$

Typically, computational simulation is commonly used to explore the microscopic mechanism. Computational simulation theories for oxygen vacancy diffusion are divided into two parts including quantum mechanical and molecular mechanics. Here are introductions for both theories and methods to implement the process.

2.2.1 Quantum mechanical theory applied in simulation

Fundamentals of Density functional theory

Density functional theory (DFT) is a whole systematic and mature theory to understand the electronic structure of many-body system deeply using quantum mechanical method. DFT is widely used in different areas of materials science to explore the properties under the scale of atoms, molecules and condensed matters. The core thought from DFT is to solve the Schrödinger equation.

The theory of DFT came from the model of Tomas-Fermi in 1927.[47] In comparison to the modern theory, the original one is extremely immature because of the low inaccuracy lack of the characteristic of wave function and interaction among electrons. In the same year, Born and Oppenheimer presented Born-Oppenheimer approximation to simplify the procedure of solving Schrödinger equation to calculate nuclear and electrons equations separately which accelerate the DFT development.[48]
In 1964, Kohn with his assistant Hohenberg and Sham presented two theorems which based the modern DFT theory.[49] Inhomogeneous electronic gas theory created by Kohn and Hohenberg mainly include two theorems.

Theorem I: The ground state energy is only determined by the ground state particle density for any system.

Theorem II: The energy functional of system minimizes to obtain the ground state energy in the meanwhile the ground state density is also the minimum of particle density functional.

These two theorems are called Kohn-Hohenberg theory together.[50] K-H theory illustrates that particle density functional is the basic independent variable of the physical properties of ground state in many-body systems including energy and wave functional.

In addition, if the ground state particles density functional is established, it is easy to minimize the functional to obtain the ground state particles energy.

For the confirmed local potential to all of the electrons, the energy of system $E[\rho]$ is the functional of the electrons density $\rho(r)$:

$$E[\rho] = F[\rho] + E_{ext}[\rho] + E_{N-N}$$

(2.3)

In the formula above, $F[\rho]$ stands for the inner functional in the system including the kinetic energy of electrons and interaction energy among electrons.

$$F[\rho] = T[\rho] + E_{e-e}[\rho] = T[\rho] + \frac{1}{2} \iint dr dr' \frac{\rho(r)\rho(r')}{|r-r'|} + E_{xc}[\rho]$$

(2.4)

$E_{ext}[\rho]$ stands for the interaction energy from outer field.

$$E_{ext}[\rho] = \int dr v(r)\rho(r)$$

(2.5)

$E_{N-N}$ stands for the repulsive energy among atomic nuclear.
\[ E_{N-N} = \sum_{i<j} \frac{Z_i Z_j}{|R_i - R_j|} \] (2-6)

\( E_{xc}[\rho] \) is the exchange-correlation interaction energy including all the complexity of electrons interaction which contains two parts, exchange energy and correlation energy.

\[ E_{xc} [\rho] = E_x [\rho] + E_c [\rho] \] (2-7)

It is obvious that if \( \rho(r), T[\rho] \) and \( E_{xc}[\rho] \) are confirmed, the energy functional \( E[\rho] \) could be obtained easily which means the ground state of the system and the properties of the ground state are quite clear.

Kohn and Sham solve the puzzles of \( \rho(r) \) and \( T[\rho] \), in addition, \( E_{xc}[\rho] \) is generally approximated by local density in the system.[51]

The progress of approximate functionals of exchange and correlation potential make density functional theory successful which become the most important technique to estimate the electronic structure.

Local density approximation (LDA)[52] make great success in the homogenous electronic gas model functionals. LDA supposes that \( E_{xc}[\rho] \) is only related to electron density at all points in space. In general, for a spin-unpolarized system, a local-density approximation for the exchange-correlation energy shows behind.

\[ E_{xc}^{LDA} [\rho] = \int \rho(r) \epsilon_{xc} (\rho) dr \] (2-8)

In the construction of LDA, generalized gradient approximations (GGA) mark the improvement of electronic structure calculation. In addition, LDA+U as an additional orbital-dependent interaction use the Hubbard model to minimize the error existed in the LDA.[53] Besides, hybrid functionals are also a class of approximation to the \( E_{xc}[\rho] \) which is usually constructed as a linear combination of the Hartree-Fock exchange functional.
\[ E_x^{HF} = -\frac{1}{2} \sum_{i,j} \iint \psi_i(r_1) \psi_j(r_1) \frac{1}{r_{12}} \psi_i(r_2) \psi_j(r_2) \, dr_1 \, dr_2 \] (2-9)

With the development of these approximate functionals, DFT becomes much precise and popular today.

**Brief introduction of VASP**

The Vienna Ab-initio Simulation Package(VASP) is widely-used software using projector augmented wave (PAW) method based on density functional theory.[54][55] The advantages of VASP are the abundant well-tested pseudopotentials packages used to describe the projector augmented wave interaction based on a plane wave basis set. Pseudopotentials are introduced to optimize the strong bound of electrons and the PAW method could improve the computational efficiency and make the outcomes more precise. VASP computes an approximate solution from Schrödinger equation and solve the Kohn-Sham equations to obtain the ground state energy of system from density functional theory. In general, a vasp code needs four input files including INCAR file, POSCAR file, POTCAR file and KPOINTS file to initial the parameters from crystal structure as well as choose the appropriate functionals in simulation.

**2.2.2 Molecular Mechanics Theory applied in simulation**

**Fundamentals of Molecular Dynamics theory**

In molecular simulation, the basic research object is molecules, and the system is regarded as a collection of molecules with certain characteristics. Classical or quantum mechanical methods are used to study the motion laws of microscopic molecules, and the motion states of each molecule are obtained. Then the macroscopic basic rules of the system are obtained by statistical methods. With the progress of computer software and hardware technology, molecular simulation developed fast and have wide applications. Molecular simulation is divided into Molecular Dynamic simulation and Monte Carlo method.
Monte Carlo method is a stochastic simulation or statistical experiment method based on probability statistics. To solve the specific problem, a probabilistic model or random process is established to make the desired parameters equal to the solution of the problem. Then, the statistical characteristics of the desired parameters are calculated by observing or sampling the model or process. Finally, the desired parameters are solved. Although the program structure is relatively simple and the simulation is relatively time-saving, it cannot study the motion state of each particle at a certain time. Thus, it is not suitable for simulating problems with transport phenomenon or dynamic characteristics.

Molecular dynamics simulation method is different from Monte Carlo stochastic simulation method. Molecules are the basic object of study. Solving the dynamics equation of the system of all the individual particles is to get the microscopic particles motion law using classical mechanics and quantum mechanics. At the same time, using appropriate statistical methods of statistical system of microscopic. Then the macroscopic properties of the whole system can be obtained. Molecular dynamics(MD)[56] is a systematic theory devoted to simulating the movements of molecules and atoms in the computer. During a period for interaction, it would be clear to examine the dynamic process for atoms and molecules as well as transport properties for the system.[57]

Molecular dynamics method is required to build molecular Newton motion equations. In general, the movement trails could be obtained by solving the Newton’s equations of motion. Once the system keeps balance, the properties of the system would not change when the system equilibrates. In addition, the potential for systems are determined by the molecular interacted functional and molecular force field.

Classical molecular dynamics is based on the theory which B. J. Alder et al.[58][59] presented a hard sphere model to calculate equilibrium properties. In 1967, Verlet[60] proposed a new algorithm to calculate displacement, velocity and accelerated velocity step by step which is widely used in the molecular dynamics simulation today. In 1980 and 1984, Anderson[61] and Nose presented the constant pressure and constant
temperature separately to perfect the MD theory to make it stable and practical. With the development of computer science and algorithm, molecular dynamics becomes crucial tools in the simulation areas of materials science, physics, chemicals and biology.

**Main steps in Molecular Dynamic simulation**

- Potential energy model setting or called potential function selection

The potential energy model is a reflection of the interaction potential between particles. The success of the simulation depends on whether the potential energy model can be selected correctly. For simple molecules, models such as hard ball, soft ball, lennard-Jones, Kihara and Stock Meyer are often used. For complex molecules, the multi-center interaction model can be used while the interaction between the centers still adopts the simple potential energy function. For charged molecules or ions, Coulomb interaction should also be introduced. Once the potential function model is determined, the relevant physical quantities in simulation can be obtained according to the laws of physics. Among these models, Lennard-Jones model has simple fluid structure and abundant experimental data which is perfect to use. The interaction potential shows as below.

\[ U(r) = \begin{cases} U_{LJ}(r) - U_{LJ}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases} \]  

(2-10)

\( U_{LJ} \) represents potential energy equation shown as below.

\[ U_{LJ} = 4\varepsilon \left[ \left( \frac{\sigma^{12}}{r} \right) - \left( \frac{\sigma^6}{r} \right) \right] \]  

(2-11)

\( r \) stands for molecular distance, \( \varepsilon \) and \( \sigma \) represent energy parameters and size parameters of potential energy function respectively.

- Initial condition determination

To solve the motion equation, the initial position and velocity of the particle should be given. Different algorithms require different initial conditions. For example, the Verlet
algorithm group needs zero-point coordinates and time-step-point coordinates and velocity. The initial conditions of the system are generally impossible to know. In fact, it does not require accurate selection and solution. Because when the simulation time is long enough, the system will ignore the initial conditions. Of course, reasonable initial conditions can reduce the time for the system to reach equilibrium and obtain good accuracy.

- Calculation towards equilibrium

After the boundary conditions and initial conditions are given, the motion equation can be solved, and the molecular dynamics simulation can be carried out. But the resulting system would not have the required energy of the system, and the state itself would not be an equilibrium state. In order to balance the system, a balancing process is designed in the simulation. In this process, the energy is added or removed from the system until a definite energy value is continuously given, at which time the system has reached equilibrium. This time to equilibrium is called relaxation time. In molecular dynamics, the choice of time step size is very important, which determines the time required for simulation. In order to reduce the error, the step size should be small enough, but a small-time step will increase the relaxation time of the system simulation to increase the increase computation. Therefore, the time step size should be selected according to experience.

- Macroscopic physical quantities calculation

The actual calculation of macroscopic physical quantities and transport characteristics is usually carried out in the last stage of simulation, which is calculated by averaging along the trajectory of phase space replacing the average ensemble with the average time.

**Brief introduction of LAMMPS**

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is
a scalable molecular dynamics program including long range Coulomb interactions.[62][63] Lammps uses Verlet lists to record close particles to improve the computing efficiency which repels in the short distance to make the particle density small.[64] LAMMPS can model systems with only a few particles up to millions or billions with free-available open-source code. In a nutshell, it is convenient to use LAMMPS to simulate molecular dynamics to explore the properties of systems.

2.2.3 Previous work of oxygen vacancy diffusion in Strontium Titanite

A numerous research has been studied for oxygen vacancy diffusion of SrTiO$_3$ based on the theory of DFT while less molecular dynamic simulation is investigated to explore the interactions and migration of oxygen vacancy, several studies of which are representative and significant. M. Javed Akhtar et al.[65] took the lead to computational simulation of SrTiO$_3$ in 1995. They found the energies of defects in SrTiO$_3$ and SrO disorder are very similar in the SrTiO$_3$ vacancy disorder based on Mott-Littleton methodology. Jill Crawford et al.[66] presented pair-potential study in SrTiO$_3$ using HFSCF calculations method. They calculated the kinetic energy and exchange-correlation energy by approximated by the sum of the two SCF ionic charge densities as well as the mobility of substitutes. Teruyasu Mizoguchi et al.[67] studied the atomistic migration in the SrTiO$_3$ using computer simulation method. They find that the migration energy is determined by the diffusion path and distance shown in the figure. The most important result is that Ti$^{4+}$ via the vacancies of Sr$^{2-}$ can significantly decrease the migration energy in Ti-migration which open a new space in the SrTiO$_3$ migration energy reduction.
Aron Walsh et al. [68] did the similar study with Teruyasu Mizoguchi to develop the different migration pathways to the migration energy using quantum mechanism model. In general, cations migrate between the closest lattice sites. As is shown in the figure, different pathways determine different energy in the O ion and Sr ion which means the migration energy via vacancy is lower than the ion migration directly.

B.S. Thomas et al. [69] studied the threshold displacement energy and displacement in the SrTiO$_3$ using molecular dynamics in 2006. They use their previous empirical model
presented in 2005[70] to simulate the atom scale radiation in the SrTiO\textsubscript{3}. They find that the atom sequence will change on their own sublattice and each atom type for the displacement energy is in the range of 20-250eV. J. Carrasco et al.[71] also studied the formation energy and energy barrier in the structure of cubic SrTiO\textsubscript{3} using DFT functional. They realize that the conduction band decrease by 0.5eV from 270-atom supercell to 320-atom supercell. It shows that the energy barrier could be affected by the supercell size. M. Lontsi-Fomena et al.[72] choose the 222-atom supercell to investigate the activation energy in the SrTiO\textsubscript{3} and calculate that the value is 0.6eV lower than the experiment which indicates that a low vacancy rate will prevent the oxygen diffusion. A significant research has been investigated by Lipeng. Lipeng et al.[73] tried to find the details of oxygen vacancy diffusion in SrTiO\textsubscript{3}. Due to the fact that the properties of SrTiO\textsubscript{3} are severely affected by point defects in the materials, they use density functional theory to examine the factors to determine the energy barriers. Bulk SrTiO\textsubscript{3} has been chosen with different size of supercells. The methodology they use is The Vienna Ab-initio Simulation Package[74] (VASP) code to do DFT calculations as well as the PBE form of GGA functional in addition to the exchange-correlation functionals of PBEsol for solids. They use different sizes of supercells from 2*2*2 to 5*5*5 to calculate the formation energy and energy barriers in charged and neutral oxygen vacancy. Finally, they find that with the increase of SrTiO\textsubscript{3} supercell size, the relative formation energy calculated by the model of PBEsol+U decreases sharply at first and changes a little in the large supercell ones. Also, the charged one is higher than the neutral one as shown in the figure.
In addition, the energy barrier of SrTiO$_3$ shows the similar tendency with the formation energy in the chart below from 0.39eV-0.49eV and the different DFT model also affects the results. Although in the 2*2*2 system, the values of energy barrier in SrTiO$_3$ using PBE+U functional method is far too higher than other functional model, there is little gap with the increase of supercell size.
By systematic research in the different SrTiO$_3$ supercell using density functional theory method, the SrTiO$_3$ supercell size, the vacancy with charge or not and the different DFT model can make contribution to the formation energy and energy barrier. Raied AL-Hamadany et al.[75] open a new space of the tensile strain in the SrTiO$_3$ of oxygen vacancy diffusion. They present that a huge reduction will occur in the diffusion barrier with up to 25% values in the strain structure.
Chapter 3 Computational Simulation of Oxygen Vacancy Diffusion in SrTiO₃

3.1 Brief introduction

The migration and diffusion of point defects are vital for properties for transition metal oxides. For photocatalysis application, controlling the oxygen defects on the surface of photocatalyst and increasing the oxygen vacancy diffusion could be very important for the improvement of its photocatalytic property. Thus, it is necessary to investigate oxygen vacancy diffusion mechanism in simulation for better understanding experimental directions. Besides, Simulation of oxygen vacancy diffusion on the atomic scale in SrTiO₃ demands thousands of atoms to create sufficient density of point defects. In addition, simulation timescale refers to nanosecond level. Combine the above two points, empirical models offer possibility while first principles calculation are unable to treat such large systems over such long timescales. In this study, an empirical model was employed to study certain oxygen defects diffusion. Here, molecular dynamic simulation was used as theoretical basis for oxygen vacancy investigation. In this section, several computational models from previous work were compared in order to choose the one that is closer to experimental data. Then, defect-free SrTiO₃ was examined the stability of system under chosen computational model. In the end, different contents of oxygen vacancy SrTiO₃ lattice was created to investigate the vacancy diffusion factor.

3.2 SrTiO₃ structure stability test

Molecular dynamics simulations were conducted with lammps using velocity verlet algorithm and the thermostat and barostat to establish a canonical NPT ensemble. Supercells are simulated consisting of 10*10*10 perovskite unit cells. Simulations at 300K-1600K were run for at least 100ps. During MD simulation, ion positions were collected every 100 timesteps. Run the program using constructed perfect defect-free SrTiO₃ lattice file to test stability. Fig.1 shows that all of the parameters including press,
volume, total energy, potential energy and temperature keep stable when simulation running which indicates the SrTiO$_3$ lattice parameters set before is reliable.

Fig 3.2.1 SrTiO$_3$ structure constructed stability test

### 3.3 Computational model compared

Modified Buckingham potential is widely used as classical interatomic forces model.

$$U_{ij} = A \exp\left(-\frac{r_{ij}}{\rho}\right) \ast \left(-\frac{C_6}{\sigma}\right) \ast \left(q_i q_j / r_{ij}\right) \quad (3-1)$$

Where $A$, $\rho$ and $C_6$ are parameters to be fitted. The exponential term on the right-hand side of the equation is short ranged and represents repulsive overlap interactions between pairs of ions. The second term is longer ranged and represents attractive van der Waals interactions between the ions. These first two terms together constitute the Buckingham potential. The third term is the Coulomb interaction between pairs of ions of charge $q$. Table 3.3.1 lists the parameters for each potential considered in their work.
Table 3.3.1 Interatomic potential parameters for the models being tested in this work. All the models assume fixed formal charges on the ions, except for the Thomas potential, which assumes fixed partial charges.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\mathcal{A}$(eV)</th>
<th>$\rho$(Å)</th>
<th>$C$(eVÅ$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Buckingham Potentials</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Akhtar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$–O$^{2-}$</td>
<td>776.84</td>
<td>0.35867</td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$–O$^{2-}$</td>
<td>877.20</td>
<td>0.38096</td>
<td>9.0</td>
</tr>
<tr>
<td>O$^{2-}$–O$^{2-}$</td>
<td>22764.3</td>
<td>0.1490</td>
<td>43.0</td>
</tr>
<tr>
<td>McCoy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$–O$^{2-}$</td>
<td>682.172</td>
<td>0.39450</td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$–O$^{2-}$</td>
<td>2179.122</td>
<td>0.30384</td>
<td>8.986</td>
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<tr>
<td>O$^{2-}$–O$^{2-}$</td>
<td>9547.960</td>
<td>0.21916</td>
<td>32.00</td>
</tr>
<tr>
<td>Crawford</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$–Sr$^{2+}$</td>
<td>9949.1</td>
<td>0.2446</td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$–Ti$^{4+}$</td>
<td>12708.1</td>
<td>0.2191</td>
<td></td>
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<tr>
<td>Sr$^{2+}$–O$^{2-}$</td>
<td>1805.2</td>
<td>0.3250</td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$–Ti$^{4+}$</td>
<td>16963.1</td>
<td>0.1847</td>
<td></td>
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<tr>
<td>Ti$^{4+}$–O$^{2-}$</td>
<td>854.0</td>
<td>0.3770</td>
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<td>O$^{2-}$–O$^{2-}$</td>
<td>22764.3</td>
<td>0.1490</td>
<td>20.37</td>
</tr>
<tr>
<td>Thomas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$^{1.84+}$–O$^{1.40-}$</td>
<td>1769.51</td>
<td>0.319894</td>
<td></td>
</tr>
<tr>
<td>Ti$^{2.36+}$–O$^{1.40-}$</td>
<td>14567.4</td>
<td>0.197584</td>
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<tr>
<td>O$^{1.40-}$–O$^{1.40-}$</td>
<td>6249.17</td>
<td>0.231472</td>
<td></td>
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<td><strong>Shell Models</strong></td>
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<td></td>
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<tr>
<td>Species</td>
<td>$q_i$(e$^r$)</td>
<td>$k$(eVÅ$^{-2}$)</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>Akhtar</td>
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<td></td>
<td></td>
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<tr>
<td>Sr$^{2+}$</td>
<td>1.526</td>
<td>11.406</td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>−35.863</td>
<td>65974.0</td>
<td></td>
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<tr>
<td>O$^{2-}$</td>
<td>−2.389</td>
<td>18.41</td>
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</tr>
<tr>
<td>McCoy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>−0.1</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>−2.04</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Crawford</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>7.468</td>
<td>421.9</td>
<td></td>
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<tr>
<td>Ti$^{4+}$</td>
<td>−35.863</td>
<td>30490.0</td>
<td></td>
</tr>
<tr>
<td>O$^{2-}$</td>
<td>−2.249</td>
<td>24.9</td>
<td></td>
</tr>
</tbody>
</table>
In order to test the quality of these four force-field models, the isobaric volume expansion $V(T)$ of defect-free SrTiO$_3$ were calculated and compared to the results with experiment.[76] The investigated temperature ranges from 300k to 1900k. The volume expansion data obtained shown as Fig 3.3.1 all of the experiment and theory data show a linear ascent in the normalized volume which demonstrate parameter set before is appropriate and these four computational models are in good agreement with experimental work. Compared four theory models, it is obvious that Thomas model shows the closest experimental work result which is the most reliable one. To describe SrTiO$_3$ lattice in the following part, the set of Born-Mayer potentials reported by Thomas would be adopted.[77] In contrast to other force-field models for SrTiO$_3$, this model is based on the constituent ions being possessing partial ionic charges. Moreover, this model disregards cation-cation interaction contributions. These two points might be the reason for Thomas model much closer to experimental work.

![Fig 3.3.1 Four Computational models compared with experimental work](image)

**3.4 Oxygen vacancies diffusion investigation**

The diffusion of oxygen vacancies in SrTiO$_3$ was investigated by means of MD simulation. A supercell consisting of 10*10*10 unit cell of SrTiO$_3$ was created with a side length of 39.05Å. The oxygen ions were removed randomly to create oxygen vacancies. The mean
square displacement was determined from

\[ MSD(t) = \frac{1}{N} \sum_i ([r_i(t_0) - r_i(t_0 + t)]^2) \]  \hspace{1cm} (3-2)

Where N is the number of ions and \( r_i \) refers to the position of ion. As shown in Fig 3.4.1, all of ions keep stable indicating that in the defect-free SrTiO\(_3\), there are no ions diffusion no matter how conditions changes. However, as shown in Fig 3.4.2, in the defective system, it is clear to see that oxygen ions diffuse even in the room temperature 300k. Besides, under the same vacancy fraction 1%, diffusion turns stronger with the rise of temperature. In the meanwhile, Ti and Sr show by construction no migration in the simulation cell because no cation defects were included in the simulation cell. As shown in Fig. 3.4.3, under the same temperature 1000k, the diffusion turns faster by increasing the oxygen vacancy content.

![Fig 3.4.1 MSD for perfect SrTiO\(_3\) lattice](image_url)

Fig 3.4.1 MSD for perfect SrTiO\(_3\) lattice:(300k, 700k, 1000k, 1300k for a, b, c, d respectively)
Fig 3.4.2 MSD for defective SrTiO₃ lattice:
(1%Vo, Temp=300k,700k,1300k,1700k for a, b, c, d respectively)

Fig 3.4.3 MSD for defective SrTiO₃ lattice:
(Temp=1000k, Vo%=0.5%,1%,1.5%,2% for a, b, c, d respectively)
In conclusion, creating more oxygen vacancies or elevate the temperature would increase the oxygen vacancies diffusion in SrTiO$_3$. This conclusion will apply the following experimental work for creating more oxygen vacancies at high temperature to enhance the SrTiO$_3$ photocatalytic performance.

3.5 Summary of the chapter

In this chapter, molecular dynamic method was applied for investigation of oxygen vacancy diffusion in SrTiO$_3$. The structure of SrTiO$_3$ was constructed in the input file first. After several durability tests for the structure, it was proven stable and reliable for use of next stage. In order to choose appropriate potentials for simulation, several models including Akhtar, Crawford, McCoy and Thomas were compared with experimental work and Thomas model was chosen for best fitting with experiment due to the fact that partial ionic charges were considered and cation-cation interaction contributions were disregarded in the model. In addition, to investigate oxygen vacancy diffusion in SrTiO$_3$, a supercell consisting of 10*10*10 unit cell of SrTiO$_3$ was created with a side length of 39.05Å. To create oxygen vacancies, the oxygen ions were removed randomly and mean square displacement was calculated for vacancies diffusion. The result shows that oxygen vacancies diffusion turns faster when increasing the temperature and contents of Vo which indicate that improvement of temperature is a possible way for creating more vacancies in the reduction experiment.
Chapter 4 Enhancing Photocatalytic Performance of SrTiO$_3$ through Defects Engineering

4.1 Synthesis and characterization of pure SrTiO$_3$

4.1.1 Synthesis of pure SrTiO$_3$ using hydrothermal method

Chemicals

Strontium hydroxide octahydrate(s) [Sr(OH)$_2$·8H$_2$O, ≥97%], Polyvinlypyrrolidone(s) [PVP, average Mw ~55,000], Titanium butoxide(l) [Ti(BUO)$_4$, 97%], Triethylene glycol(l) [TEG, 99%], ammonia solution(l) [25%]. For ease of writing, these complex chemical names are replaced by Sr(OH)$_2$·8H$_2$O, PVP, Ti(BUO)$_4$ and TEG in the following statement. All chemicals were purchased from Sigma-Aldrich.

Experiment details

Strontium titanate nanoparticles were synthesized by sol-precipitation method using autoclaves. The synthetic procedure was divided into four main parts including sample preparation, reaction in the autoclave, centrifugal purification and drying for the final product. During the sample preparation process, Sr(OH)$_2$·8H$_2$O (8mmol) and PVP (0.01mmol) were added into a white Teflon flask container by medicine spoon first. TEG (20ml) was added into the container by measuring cylinder and mixed with a magnetic stirrer at room temperature until completely dissolved. Then Ti(BUO)$_4$ (8mmol) was added when mixing until solution turning yellow. In the final step, ammonia solution (4ml) was added by needle tubing in circular motions. During reaction process, autoclave heater was set at 160°C with mid-range stirring for 4h. And then heater was turned off and cooled down solution to room temperature. The solution was transferred into beaker and mixed with distilled water at the volume ratio 1:4. The beaker was left overnight until obvious layer occurred which was precipitation in the bottom layer. During the centrifugal purification progress, top layer limpid solution was pumped into waste liquid tank and
bottom layer was filled with centrifuge tubes and put in high speed centrifuge which was set at 16000rpm for 4mins.

After washing for several times by distilled water and ethanol, precipitation was collected in the glass vial and dried at 60°C for 12h. In the end, white fine SrTiO₃ powder was obtained.

![Diagram of process](image)

Scheme 4.1.1.1 Process of pure SrTiO₃ synthesis by a hydrothermal method

4.1.2 Characterization method

Scanning Electron Microscope

The morphology of strontium titanate sample was analyzed by NanoSEM450 which is a field-emission scanning electron microscope. It allows the user to achieve high imaging
resolution at a range of kV, at both low (high-resolution imaging) and high (microanalytical imaging) currents. Before using NanoSEM450, SrTiO$_3$ powder should be taken pretreatment for observing. It was stuck on the special adhesive carbon dots on the 25mm pin stub by powder-free gloves and blew by nitrogen gas to leave the firm sticky powder. The SEM image of samples on the special carbon dots would have less cracks than normal ones. And then powder need coating to improve the surface conductivity of particles which makes the SEM images clearer. Carbon coating and Platinum coating are two common ways according to purpose. Carbon coating was operated by DCT Turbo-pumped Desktop Carbon Evaporator which used high electric current to make the carbon drop out of carbon cord. The voltage was set 13V and current was increased from 0 to 100 for 3s. Time of holding current changed the evaporator thickness (1s 150Å, 2s 300Å, 3s 450Å). On the other hand, Platinum coating was operated by LEICA ACE600 Sputter coater which introduces argon atoms into vacuum chamber and carries Platinum atom onto sample surface to increase particle conductivity. Once initialization process was completed, choosing coating thickness on the screen which was normally 15nm.

Transmission Electron Microscope

The morphology of strontium titanate was also analyzed by field emission transmission electron microscope (TEM, Philips CM200). It can require very high-resolution images from thin materials. In a field emission gun, a very strong electric field is used to extract electrons from a metal filament. During pretreatment process, thimbleful powder was added into 1.5ml micro centrifuge tube with 1ml ethanol. Then the tube was ultrasonicated for 10mins to make the powder uniformly dispersed. Pipette was used to transfer three drops of liquid dropwise onto tiny copper grid. At the end, it was dried at the room temperature.
X-Ray Diffraction

The crystalline phases were analyzed by X-Ray diffraction (PANalytical Xpert Multipurpose X-Ray Diffraction System, MPD). During sample pretreatment process, it was fully ground to make fine powder because of the demand of granularity of X-Ray diffraction. Squash technique was used to prepare powder sample. First, it was filled into the container and removed excess powder using glass slide. Then the slide was pressed to make sample surface flat otherwise it led to obtain wrong results due to insufficient diffraction. After squash method, it was ready for XRD measurement.

4.1.3 Results and discussion

Strontium titanate nanoparticles obtained by hydrothermal synthesis method looks white with a touch of yellow and shows good crystallinity and high hardness when grinding in apperaceny(fig.1). XRD patterns will provide some evidence in the next section.

The Scanning Electron Microscopy images of the sample are shown in Fig 4.1.3.1. Particles consisting of the sample reveal tight arrangement. Compared to carbon coating and Pt coating method under 300,000x magnification, Pt coating image is clearer than carbon one while carbon one has only pure sample without platinum impurity interference. Because the diameter of platinum is close to SrTiO$_3$ which means it cannot be distinguished from Pt and SrTiO$_3$ particles clearly. The size distribution of nanoparticles is shown by the histograms in Fig 4.1.3.2. The average size of carbon coating sample is 31.24nm among 22.83nm to 41.51nm while the average size of Pt coating sample is 21.84nm among 16.35nm to 29.72nm. Due to the adhesion of carbon, the diameter of carbon coating SrTiO$_3$ is bigger than Pt coating SrTiO$_3$ particles.
Fig 4.1.3.1 Pure SrTiO₃ SEM image by carbon coating(a) and Pt coating(b)

Fig 4.1.3.2 Size histograms of pure SrTiO₃ nanoparticles for carbon coating(a) and Pt coating(b)

The composition distribution of the sample in the cross section was measured by energy dispersive X-Ray spectroscopy analysis (EDS) attached to scanning electron microscopy. A small piece of the sample was chosen to analyze in Fig 4.1.3.3. The spectrum of line scan result shows that the sample is pure SrTiO₃ which only consists of the elements of Sr, Ti, O. The mapping result also indicates that the sample has uniform distribution of these three kinds of elements shown in Fig 4.1.3.4. In order to explore the contents of element in the sample, six random points were selected in Fig 4.1.3.5 to analyze the percentage contents of atom shown in Table 4.1.3.1. The sum element contents of Sr, Ti, O atoms equal to 100% for each point which show that the sample is pure SrTiO₃.
Fig 4.1.3.3 SEM-EDS line scan results of Sr, Ti and O distributions in the cross section of the sample. (a) Line scan image (b) line scan chart for samples (c) line scan spectrum

Fig 4.1.3.4 SEM-EDS mapping results of O, Sr, Ti distributions of pure SrTiO$_3$
Table 4.1.3.1 SEM multipoint element content for Sr, Ti, O in pure SrTiO$_3$

<table>
<thead>
<tr>
<th>element content [norm. at%]</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium</td>
<td>27.36</td>
<td>58.89</td>
<td>43.11</td>
<td>50.23</td>
<td>52.73</td>
<td>37.65</td>
</tr>
<tr>
<td>Titanium</td>
<td>30.26</td>
<td>21.62</td>
<td>29.97</td>
<td>26.52</td>
<td>26.24</td>
<td>33.32</td>
</tr>
<tr>
<td>Oxygen</td>
<td>42.38</td>
<td>19.49</td>
<td>26.91</td>
<td>23.25</td>
<td>21.03</td>
<td>29.03</td>
</tr>
<tr>
<td>sum</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Transmission electron microscope was used to explore the microstructure of SrTiO$_3$ sample. Fig 4.1.3.6 shows the uniform dispersion of SrTiO$_3$ nanocubes under TEM with average size of 17nm. A combination of dark and light features was also observed, suggesting crystalline phase in the cubes.
Fig 4.1.3.6 TEM image of pure SrTiO$_3$ under different magnification

Energy Dispersive X-Ray Spectroscopy mapping analysis with TEM was used for observing elements distribution of SrTiO$_3$. Different colors indicate the uniform existence of Sr, Ti, O element in Fig 4.1.3.7.
The crystal phase of the prepared sample was analyzed using X-Ray Powder Diffraction (XRD). Fig 4.1.3.8 shows the XRD pattern of the samples compared with the standard diffraction pattern of Strontium Titanate Oxide (ICSD code: 027045).
Fig 4.1.3.8 XRD pattern of pure SrTiO$_3$ compared with reference ICSD data

The diffraction peaks of the sample are well indexed as SrTiO$_3$ nanocube. Bragg equation is used to calculate distance between planes of atoms.

\[ d = \frac{n\lambda}{2\sin\theta} \]  \hspace{1cm} (4-1)

In this equation,

\( \lambda \)=wavelength of incident X-ray

\( \theta \)=peak position

\( n \)=order of diffraction

\( d \)=interplanar spacing

The characteristic diffraction peak occurs at 32.26 ° with the crystal plane (1,1,0) showing the d-spacing of 2.78Å, which indicates good quality of crystalline.
4.2 Introducing oxygen vacancies in pure SrTiO\textsubscript{3} by annealing

4.2.1 Annealing SrTiO\textsubscript{3} by tube furnace

To create more oxygen vacancies, Strontium titanate powder was annealed with NaBH\textsubscript{4} powder in a tube furnace under constant Argon gas flow for 1h. Before heat treatment process, SrTiO\textsubscript{3} and NaBH\textsubscript{4} powder were sufficiently grounded on the mortar at molar ratio 1:1 in the glove box for 30 mins and transferred to alumina crucible. In case of oxidation of NaBH\textsubscript{4}, crucible should be sealed tight until taken to the tube furnace. The annealing temperature varied from 300°C to 450°C with the heating time 30mins to 1h. The heating rate was maintained at 5°C/min. After annealing, sample was left in the tube furnace and cooled down until room temperature roughly around 3h. In the end, various degree of black powder was obtained and washed with DI water.

During the annealing process, NaBH\textsubscript{4} acts as an oxygen scavenger[78] which decompose and produce active hydrogen with more reactive than H\textsubscript{2}. Its high reduction power helps remove oxygen atoms from the SrTiO\textsubscript{3} surface. This creates oxygen vacancies at a relatively short time and low temperature, which helps maintain the original morphology of SrTiO\textsubscript{3}. By changing the reaction time and temperature, the oxygen vacancy concentration can be easily modified. Furthermore, washing with water and ethanol will quickly eliminate NaBH\textsubscript{4} by-products.

4.2.2 Results and discussion of characterization for annealing SrTiO\textsubscript{3}

The color of sample was changed after annealing from white to black from Fig 4.2.2.1 suggesting that more oxygen vacancies were created during annealing process.
As shown in Fig 4.2.2.2 (a), TEM images demonstrate little change in particle size and morphology of SrTiO₃ samples before and after NaBH₄ treatment. The morphology of annealed SrTiO₃ is close to cube phase and the average diameter is 21nm which exhibits high crystalline nature. More detailed information of nanostructure was provided by HR-TEM image of annealing SrTiO₃ in Fig 4.2.2.2(b). The lattice plane distances of annealing SrTiO₃ crystalline is 0.209nm which is close to 0.204nm from pure SrTiO₃ indicating good match with (2,0,0) lattice plane. Energy dispersive X-Ray spectroscopy mapping analysis with TEM was used for observing elements distribution of annealing SrTiO₃. As is shown in Fig 4.2.2.3, the uniform distribution of Sr, Ti, O elements in different color indicates the element components in the nanoparticles.
X-ray diffraction (XRD) was used to characterize the crystalline phase change of annealed sample.
Fig 4.2.3.4 shows the XRD peak pattern of annealing SrTiO$_3$ under 450°C for 1h as example and SrTiO$_3$ cubic phase pattern (ICSD:027045) as reference. It is obvious that annealing SrTiO$_3$ matches well with pure SrTiO$_3$ reference pattern which indicate that there is little change of phase composition during annealing progress. The characteristic diffraction peak occurs at 32.26 ° with the crystal plane (1,1,0) showing the d-spacing of 2.78Å, which indicates good quality of crystalline.

![XRD pattern for annealing SrTiO$_3$ with reference ICSD](image)

**Fig 4.2.3.4 XRD pattern for annealing SrTiO$_3$ with reference ICSD**

### 4.3 Photocatalytic performance of pure and annealed SrTiO$_3$ samples

The H$_2$ production from water under light irradiations was applied to evaluate the photocatalytic performance of SrTiO$_3$ and annealing SrTiO$_3$ samples. During the operation of photocatalytic test, 40 mg of the annealing SrTiO$_3$ powder was dispersed in 40 mL of deionized water. Before irradiation, the system was purged with Argon gas for 15 min and vacuumed for 15 min. Then, the solution was irradiated from the top through
a quartz window under stirring, and an external cooling jacket was used to absorb the heat. The visible-light illumination was achieved by eliminating the UV part of the spectrum from a 300 W xenon arc lamp using a 420 nm cut-off filter.

As is shown in Fig 4.3.1, H₂ production of catalysts was recorded every 30mins during the catalytic reaction for 3h. Compared to pure SrTiO₃ and annealing SrTiO₃, it is obvious that the H₂ generation was increased in total by annealing process. In addition, compared to annealing SrTiO₃ in three different conditions, improvement of annealing temperature and increase of annealing time will bring better photocatalysis performance. Fig 4.3.2 shows the efficiency of these four catalysts. The H₂ production rate of annealing SrTiO₃ under 450 °C for 1h is 458 μmol*g⁻¹*h⁻¹, which is almost three times than pure SrTiO₃(167μmol*g⁻¹*h⁻¹).

![Graph](image.png)

Fig 4.3.1 H₂ generation in 3h compared with pure and annealing SrTiO₃
According to the previous simulation results, the oxygen vacancies diffusion increases when temperature goes up as the reaction goes on which indicates more active oxygen vacancies were created during annealing process under higher temperature and longer time. It is well-known that oxygen defects can serve as electron donors[79] and contribute to semiconductor donor capacity. By increasing donor capacity, loading transfer in SrTiO$_3$ can be increased. The Fermi level of SrTiO$_3$ may also move to the conduction band. This Fermi level change will boost the SrTiO$_3$ electrolyte interface charging isolation. Therefore, the reasons for enhanced photocatalytic behavior in SrTiO$_3$ may be attributed to enhanced separation of charges through more created oxygen vacancies.

4.4 Summary of this chapter

In this chapter, pure SrTiO$_3$ was synthesized by an hydrothermal method first. Energy Dispersive analysis proved the distribution of Sr, Ti, O elements in the products. The
morphology of SrTiO$_3$ was nanocube with diameter of 17nm and the high crystalline crystal was shown in X-ray diffraction with the d-spacing of 2.78Å for main peak occurring at 32.26 °. Then the SrTiO$_3$ with defects was obtained by annealing method through tube furnace which turns from white to black in apparenpy. X-ray diffraction exhibited little phase change and high crystalline in the annealing SrTiO$_3$. The morphology of annealing SrTiO$_3$ nanostructure was still cubic phase. Moreover, compared with pure SrTiO$_3$ and annealing SrTiO$_3$ for photocatalytic performance, H$_2$ production efficiency was increased by three times after annealing treatment. For annealed samples, increasing treatment temperature and heating time would improve the photocatalytic performance due to more oxygen vacancies created which is consistent with molecular dynamic simulation results.
Chapter 5 Enhancing Photocatalytic Performance of SrTiO$_3$ by Band Gap Engineering

5.1 Preparation of Cr-doped SrTiO$_3$ by hydrothermal synthesis

5.1.1 Experiment procedures for synthesis

Chemicals

Chromium nitrate nonahydrate(s) [Cr(NO$_3$)$_3$·9H$_2$O, 99%], Strontium hydroxide octahydrate(s) [Sr(OH)$_2$·8H$_2$O, ≥97%], Polyvinylpyrrolidone(s) [PVP, average Mw ~55,000], Titanium butoxide(l) [Ti(BUO)$_4$, 97%], Triethylene glycol(l) [TEG, 99%], ammonia solution(l) (25%). For ease of writing, these complex chemical names are replaced by Cr(NO$_3$)$_3$·9H$_2$O, Sr(OH)$_2$·8H$_2$O, PVP, Ti(BUO)$_4$ and TEG in the following statement. All chemicals were purchased from Sigma-Aldrich store.

Experiment details

Chromium doped strontium titanate nanoparticles were synthesized by sol-precipitation method using autoclave. The synthetic procedure was also divided into four main parts including sample preparation, reaction in the autoclave, Centrifugal purification and drying for the final product. During the sample preparation process, Sr(OH)$_2$·8H$_2$O (8mmol) and PVP (0.01mmol) were added in a white Teflon flask container by medicine spoon first. TEG (20ml) was added in the container by measuring cylinder and mixed with a magnetic stirrer at room temperature until completely dissolved. Then Ti(BUO)$_4$ (8mmol) and Cr(NO$_3$)$_3$·9H$_2$O (8mmol) were added in the Teflon container when mixing until solution turning dark green. In the final step, ammonia solution (4ml) was added by needle tubing in circular motions. During reaction part, autoclave heater was set 160°C with mid-range stirring for 24h. And then heater was turned off and cooled down solution until room temperature. The solution was transferred into beaker and mixed with distilled water at the volume ratio 1:4. The beaker was left overnight until obvious layer occurred.
which was precipitation in the bottom layer. During the centrifugal purification progress, top layer limpid solution was pumped into waste liquid tank and bottom layer was filled with centrifuge tubes and put in high speed centrifuge which was set at 16000rpm for 4 mins. After washing for several times by distilled water and ethanol, precipitation was collected in the glass vial and dried at 60°C for 12h. At the end, yellow green fine SrTiO₃ with 5 at% chromium doped powder was obtained.

Scheme 5.1.1.1 Process of Cr-dope SrTiO₃ synthesis by a hydrothermal method

5.1.2 Characterization method

Scanning Electron Microscope

The morphology of Strontium Titanate powder was analyzed by NanoSEM450 which is
a field-emission scanning electron microscope. Carbon coating was operated by DCT Turbo-pumped Desktop Carbon Evaporator which used high electric current to make the carbon drop out of carbon cord. Platinum coating was operated by LEICA ACE600 Sputter coater which introduces argon atoms into vacuum chamber and carries Platinum atom onto sample surface to increase particle conductivity.

**Transmission Electron Microscope**

The morphology of Strontium Titanate was also analyzed by field emission transmission electron microscope (TEM, Philips CM200). During pretreatment process, thimbleful powder was added into 1.5ml micro centrifuge tube with 1ml ethanol. Then the tube was put in ultrasonic for 10mins to make the powder uniformly disperse. Pipette was used to transfer three drops of liquid dropwise onto tiny copper grid. In the end, it could be used until drying in the room temperature.

**X-Ray Diffraction**

The crystalline phases were analyzed by X-Ray diffraction (PANalytical Xpert Multipurpose X-Ray Diffraction System, MPD). During sample pretreatment process, it was fully ground to make fine powder due to the demand of granularity of X-Ray diffraction. Squash technique was used to prepare powder sample. First, It was filled into the well and removed excess powder using glass slide. Then the slide was pressed to make sample surface flat otherwise it led to obtain wrong results due to insufficient diffraction. After squash method, it was ready for XRD measurement.

**Raman Microscopy**

Raman microscopy was also used as an auxiliary of XRD to make sure the phases. All of Raman data was obtained with an 830nm laser beam, static mode, exposure time 5, laser power 100 and accumulation 20.
**Energy Dispersive X-ray Spectroscopy**

The distribution of elements was obtained by the energy dispersive X-ray spectroscopy (EDS) attached to SEM and TEM machine.

**Inductively Coupled Plasma**

The more precise distribution of elements was measured by inductively coupled plasma (PerkinElmer Optima as ICP-OES). Samples digested with heated Hydrochloric acid for Titanium Oxide.

**5.2 Results and discussion**

**5.2.1 Morphology analysis**

Chromium doped strontium titanate sample was synthesized by hydrothermal method. The dark green precursor turns to yellow green after reaction in the autoclave and the yellow green powder of different reaction time with 6h, 24h, 48h was obtained after centrifuge as shown in Fig 5.2.1.1.

![Fig 5.2.1.1 The precursor of Cr-doped SrTiO₃ (a), product after reaction (b), powders after centrifuge and dry (c).](image-url)
SEM was used to determine the morphology of Cr-doped SrTiO$_3$. It is clear to see the tight arrangement of nanoparticles in Fig 5.2.1.2. Compared to carbon coating and Pt coating samples, Pt coating image is clearer than carbon one while carbon one has only pure sample without platinum impurity interference. Due to the adhesion of carbon, the diameter of carbon coating sample is much larger than Pt coating one, which is around 65.89nm and 43.88nm respectively. Compared to pure SrTiO$_3$ nanoparticles shown in last chapter which is 31.24nm and 21.84nm respectively, the diameter of nanoparticles expand after doping method. The addition of Chromium element may cause the expansion of particles.

Fig 5.2.1.2 SEM image of Cr-doped SrTiO$_3$ for carbon coating (a), and Pt coating (b)

The composition distribution of the sample in the cross section was measured by Energy Dispersive X-Ray Spectroscopy analysis (EDS) attached to scanning electron microscopy. A small piece of sample was selected for analysis in Fig 5.2.1.3 (a). Line scan test spectrum (Fig 5.2.1.3 C) shows that the sample consists of Sr, Ti, O and Cr elements which indicate the Chromium element was doped in SrTiO$_3$ successfully.
Fig 5.2.1.3 SEM-EDS line scan results of Sr, Ti and O distributions for Cr-doped SrTiO$_3$ (a) line scan image (b) line scan chart for samples (c) line scan spectrum

The SEM mapping analysis reveals that the sample has the uniform distribution of these four kinds of elements in Fig 5.2.1.4 which demonstrate Chromium element has been doped in the sample successfully from other side.
Fig 5.2.1.4 SEM-EDS mapping results of O, Sr, Ti and Cr distributions of Cr-doped SrTiO$_3$

To investigate the element distribution, six random points were chosen in Fig 5.2.1.5 to examine the atom percentage content shown in Table 5.2.1.1. The total element contents of Sr, Ti, O and Cr atoms equal to 100% for each stage indicating that the sample is pure Cr-doped SrTiO$_3$.

Fig 5.2.1.5 SEM multipoint image for Cr-doped SrTiO$_3$
Table 5.2.1.1 SEM multipoint element content for Sr, Ti, O and Cr in Cr-doped SrTiO$_3$

<table>
<thead>
<tr>
<th>Element content [norm. at.%]</th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
<th>P6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strontium</td>
<td>27.32</td>
<td>26.94</td>
<td>24.19</td>
<td>26.20</td>
<td>20.84</td>
<td>23.09</td>
</tr>
<tr>
<td>Titanium</td>
<td>27.52</td>
<td>26.99</td>
<td>25.32</td>
<td>26.56</td>
<td>22.32</td>
<td>24.12</td>
</tr>
<tr>
<td>Chromium</td>
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<td>1.49</td>
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<td>1.41</td>
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<td>1.32</td>
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<td>Oxygen</td>
<td>43.62</td>
<td>44.58</td>
<td>49.10</td>
<td>45.83</td>
<td>55.63</td>
<td>51.47</td>
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<td>100%</td>
</tr>
</tbody>
</table>

In addition, to make the element distribution more accurate, Inductively coupled plasma (ICP) spectroscopy is used to detect and measure elements to analyze Cr-doped and pure SrTiO$_3$ samples. Samples digested with heated hydrochloric acid for titanium oxide. Digests with SrTiO$_3$, Cr-doped SrTiO$_3$ and reference solution were prepared in Fig 5.2.1.6 and analyzed by ICP-OES (PerkinElmer Optima). The chromium element was detected 1.36 wt% which verify the existence in the doped sample.

Fig 5.2.1.6 digests with SrTiO$_3$, Cr-doped SrTiO$_3$ and reference solution
Table 5.2.1.2 ICP results of elements contents for Cr-doped SrTiO$_3$

<table>
<thead>
<tr>
<th>ID</th>
<th>Cr Wt%</th>
<th>Sr Wt%</th>
<th>Ti Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>0.00</td>
<td>37.3</td>
<td>27.0</td>
</tr>
<tr>
<td>Cr-doped SrTiO$_3$</td>
<td>1.36</td>
<td>40.0</td>
<td>21.7</td>
</tr>
<tr>
<td>LOR</td>
<td>0.10</td>
<td>1.00</td>
<td>0.10</td>
</tr>
</tbody>
</table>

LOR-Limit of Reporting - The lowest concentration of a substance that can be reliably

Transmission electron microscope was used to explore the microstructure of SrTiO$_3$ sample. Fig 5.2.1.7 shows the uniform dispersion of Cr-doped SrTiO$_3$ nanocubes under TEM with the diameter of 16nm. A mixture of dark and light patterns was also found, indicating crystalline phase in cubes which keeps almost the same morphology with pure SrTiO$_3$. Fig 5.2.1.7 (d) HRTEM picture reveals the interface between two crystals. Clear lattice fringes show strongly crystalline with 0.242 nm d-spacing that fits well with (1,1,1) lattice plane with reference of ICSD 027045.
Fig 5.2.1.7 TEM image of Cr-doped SrTiO$_3$ under different magnification

Spectroscopy mapping technique with TEM was used to detect SrTiO$_3$ distribution of elements. Different colors imply Sr, Ti, O and Cr element's uniform presence in Fig 5.2.1.8 which shows the evidence of Cr doping successfully.
5.2.2 Crystalline phase analysis

The crystal phase of the prepared sample was analyzed using X-Ray Powder Diffraction (XRD). Three different synthesis conditions of Cr-doped SrTiO$_3$ were compared with 6h, 24h, 48h in Fig 5.2.2.1. From the XRD pattern, it is seen that a well-crystallized Cr-doped SrTiO$_3$ with synthesis reaction time of 6h at least. In addition, with the increase of reaction time, the diffraction peak amplitude was higher and finer, suggesting that the product's degree of crystallization increased by extending reaction time.
Fig 5.2.1.1 XRD patterns compared with reaction time 6h, 24h, 48h for Cr-doped SrTiO$_3$

Compared to Cr-doped and pure SrTiO$_3$ in Fig 5.2.1.2, doped sample shows good matches with pure sample which indicate that there is little phase change during doping process. The characteristic diffraction peak occurs at 32.26° with the crystal plane (1,1,0) showing the d-spacing of 2.78Å, which indicates good quality of crystalline.
To explore the nanostructure in more details, Raman spectroscopy analysis was used to compare pure SrTiO₃ and Cr-doped SrTiO₃. Raman is a light-scattering technique that scatters incident light from a high-intensity laser light source. A small amount of light (typically 0.0000001%) is scattered at different wavelengths (or colors) is Raman Scatter which depend on the chemical structure of the sample. The incident light chose 830nm because of severe fluorescent effect under 830nm after several attempts. During the process of analysis, static mode was chosen, exposure time set 5, laser power set 100 and accumulation was set 20. Fig 5.2.1.3 shows the Raman spectra ranging from 90 to 1150cm⁻¹. The broad structure is observed from 465 to 650cm⁻¹ in SrTiO₃ which is also observed from 465 to 675cm⁻¹ in Cr-doped SrTiO₃.

As shown in figure, there is good match between SrTiO₃ and Cr-doped SrTiO₃ which indicate little phase change after doping Chromium. In addition, the main distinct peaks of Cr-doped SrTiO₃ show 10cm⁻¹ offset to the left compared to the pure SrTiO₃ consistently which suggest the Chromium element is at work.
5.3 Photocatalysis compared with pure, annealing and Cr-doped SrTiO$_3$

H$_2$ production from light-irradiation water was used to test the photocatalytic efficiency of Cr-doped SrTiO$_3$ sample compared with pure and annealing SrTiO$_3$ samples. As is shown in Fig 5.3.1, H$_2$ production of catalysts was recorded during the catalytic reaction for 3h. The yellow line increase rapidly indicating that the H$_2$ production of Cr-doped SrTiO$_3$ is much higher than other four catalysts which is 3961.2 μmol/g in total. In addition, yellow line increases sharply showing that Cr-doped SrTiO$_3$ sample have more H$_2$ production efficiency than other catalysts. The production efficiency was described in Fig5.3.2. The production rate of Cr-doped SrTiO$_3$ is 1321μmol/g/h, which is almost three times than the best annealing one(458μmol/g/h) and eight times than pure one(167μmol/g/h). The catalytic performance was improved dramatically by doping Chromium element in pure SrTiO$_3$. 

Fig 5.2.1.3 Raman patterns compared with pure and Cr-doped SrTiO$_3$
Fig 5.3.1 H₂ generation in 3h compared with pure, annealed and Cr-doped SrTiO₃

Fig 5.3.2 H₂ production efficiency compared with pure, annealing and Cr-doped SrTiO₃
To explore the reason for incredible photocatalytic improvement of Cr-doped sample, UV-vis diffuse reflectance analysis was used. During the process of preparing sample, an ten tonne Enerpac was used to squeeze the powder into thick wafers as shown in Fig 5.3.3 which make sure 100% diffuse reflection without transmission in the course of analysis.

Fig 5.3.3 Sample preparation for UV-vis analysis: ten tonne Enerpac (a), thick wafers for pure and Cr-doped SrTiO₃ (b)

Fig 5.3.4 shows that pristine SrTiO₃ exhibits the absorption onset at 348 nm. Cr-doped SrTiO₃ includes initiation of absorption at 396nm first and starts to reflectance at 536nm then continues to absorption at 612nm.
Fig 5.3.4 UV-vis spectra compared with pure and Cr-doped SrTiO$_3$

Tauc Plot method was used to calculate band gap of nanomaterials from UV-Vis Absorption data. The Tauc and Davis-Mott relation equation shows as below.

\[
(\alpha h \gamma)^n = K(h \gamma - E_g)
\]  \hspace{1cm} (5-1)

$\alpha$=absorption coefficient

$h\gamma$=incident photon energy

$K$=energy independent constant

$E_g$=optical band gap energy of nanomaterials

$n$=the nature of transition ($n=2$ For direct band gap)

The optical band gap was obtained after calculation as shown in Fig 5.3.5. SrTiO$_3$ sample exhibits the band gap absorbance of 3.32eV while Cr-doped SrTiO$_3$ shows 2.30eV which decrease dramatically.
It is well known that SrTiO$_3$ band gap refers to the energy difference between valance band which is full of low-energy electrons, and an empty high energy conduction band. If the semiconductor is illuminated with light, it absorbs a photon and if the photon energy is equal to or exceeds the band gap energy, an electron is transferred from the VB to the CB and leave a hole in situ. The electron-hole pair then migrates to the photocatalyst surface where it can recombine and dissipate energy as heat and react with adsorbed electron donors or acceptors as the photocatalytic water splitting is a surface phenomenon. Besides, the chromium was probably introduced as dopants to substitute lattice Ti atoms because of a ionic radius relations as Sr$^{2+}$ (1.18Å) > Cr$^{3+}$ (0.615Å) > Ti$^{4+}$ (0.605Å).[80] Therefore, lattice distortion caused by Cr$^{3+}$ substituting Ti$^{4+}$ narrow the band gap of SrTiO$_3$ nanocubes which lead to enlarge light absorption properties. Therefore, the excellent charge carriers mobility and narrowed band-gap energy lead to an enlarged light-harvesting property, and improved charge conductivity and separation efficiency.

Fig 5.3.5 Band gap energy compared with pure and Cr-doped SrTiO$_3$
In conclusion, the electronic structure has a major contribution in the SrTiO$_3$ photocatalysis and lower band gap needs lower energy for photoexcitation, which could increase the photocatalytic performance.

5.4 Summary of the chapter

In this chapter, Cr-doped SrTiO$_3$ was prepared by hydrothermal method. Energy dispersive spectrum and ICP analysis proved the uniform distribution of Sr, Ti, O and Cr elements in the products. The morphology of Cr-doped SrTiO$_3$ was nanocubic with average size of 16nm which is close to pure SrTiO$_3$. There was little phase change in Cr-doped SrTiO$_3$ through X-ray diffraction and the crystalline increased as the synthesis time increasing. In addition, the main distinct Raman spectra peaks of Cr-doped SrTiO$_3$ shows 10cm$^{-1}$ offset to the left compared to the pure SrTiO$_3$ consistently which suggest the Chromium element is at work. Moreover, the photocatalytic performance of Cr-doped SrTiO$_3$ highly improved compared to pure and annealing SrTiO$_3$. H$_2$ production efficiency was increased by three times compared to annealing SrTiO$_3$ and eight times compared to pure SrTiO$_3$. In addition, the band gap of Cr-doped SrTiO$_3$ was 2.30eV compared to pure SrTiO$_3$ with 3.32eV. The huge decrease of band gap could be the main reason for high enhancement of photocatalytic performance.
Chapter 6 Conclusions and Future Prospects

In this dissertation, creating more oxygen vacancy defects and doping with chromium element in pure SrTiO₃ are adopted to improve the photocatalytic performance by comparing H₂ production. The research accomplishments are listed below:

- Pure SrTiO₃ nanocubes were synthesized by a hydrothermal method. A series of characterization results indicate that the SrTiO₃ nanocubes are quite uniform and good crystallinity with average size of 17nm which are expected to be a good support for creating vacancies. Before introducing oxygen vacancies into pure SrTiO₃ nanocubes, computational simulation by molecular dynamic method used for investigating oxygen vacancies diffusion showed that increasing the temperature and contents of oxygen vacancies would improve the diffusion of oxygen vacancies which suggest controlling temperature and reaction time in experiments as variables. Then, a facile annealing method was introduced to increase oxygen vacancies on pure SrTiO₃ nanoparticles with NaBH₄ by a solid-state reaction. A series characterization results indicate that there is little phase change and good quality of crystalline in the annealing SrTiO₃ which was expected to be good support for photocatalytic experiment. In the catalysis experiment, H₂ production was increased three times after annealing process. Besides, raising the annealing temperature and prolonging reaction time would make annealing catalysts better which could improve the photocatalytic performance.

- Cr-doped SrTiO₃ was fabricated successfully by a revised hydrothermal method. Transmission electron microscope analysis verified that the morphology of Cr-doped SrTiO₃ is nanocubes with high dispersibility and good crystalline quality. Energy dispersive X-ray spectroscopy and Inductively Coupled Plasma showed that Chromium element is doped in pure SrTiO₃ successfully. X-ray diffraction analysis determined that there is little phase change and high crystalline compared with pure SrTiO₃ which showed favorable potentials for photocatalysis. In the photocatalytic
experiment, \( \text{H}_2 \) production efficiency for Cr-doped SrTiO\(_3\) was 1321\( \mu \text{mol/g/h} \) which was almost improved eight times compared to pure SrTiO\(_3\) (167\( \mu \text{mol/g/h} \)) and three times compared to annealing SrTiO\(_3\) at 450°C for 1h (458\( \mu \text{mol/g/h} \)).

By adopting vacancies-introduced method and doping chromium method, there is obvious improvement of photocatalytic performance compared with pure SrTiO\(_3\). However, some problems still remain unsolved. For example, it is hard to get exact number of oxygen vacancies during annealing method in order to compare the vacancies and photocatalytic performance quantitatively. This might be conducted in the future research work. In addition, due to the high photocatalytic performance of Cr-doped SrTiO\(_3\), there is large space to modify doped sample for better performance including creating vacancies. This study may contribute to synthesize stable and high crystalline SrTiO\(_3\), Cr-doped SrTiO\(_3\) and offer a train of thoughts to improve photocatalytic performance by making oxygen vacancies and doping with other elements.
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