MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
KYIV NATIONAL UNIVERSITY OF TECHNOLOGIES AND DESIGN
Faculty of Chemical and Biopharmaceutical Technologies
Department of Biotechnology, Leather and Fur

QUALIFICATION THESIS

on the topic **Research on the antibacterial effect of zinc oxide-based tungstate nanocomposites against *Escherichia coli***
First (Bachelor's) level of higher education
Specialty 162 "Biotechnology and Bioengineering"
Educational and professional program "Biotechnology"

Completed: student of group BEBT-21
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KYIV NATIONAL UNIVERSITY OF TECHNOLOGIES AND DESIGN

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«___»_______________2025

ASSIGNMENTS
FOR THE QUALIFICATION THESIS
Liu Jiaming

1. Thesis topic **Research on the antibacterial effect of zinc oxide-based tungstate nanocomposites against *Escherichia coli***

Scientific supervisor Dr. Sc., Prof. Tetiana SHCHERBATIUK

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WORK CALENDAR

№	The name of the stages of the qualification thesis	Terms of performance of stage	Note on performance
1	Introduction	until 11 April 2025	
2	Chapter 1. Literature review	until 20 April 2025	
3	Chapter 2. Object, purpose, and methods of the study	until 30 April 2025	
4	Chapter 3. Experimental part	until 11 May 2025	
5	Conclusions	until 15 May 2025	
6	Draw up a bachelor's thesis (final version)	until 25 May 2025	
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8	Submission of bachelor's thesis to the department for review (14 days before the defense)	28 May 2025	
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10	Submission of bachelor's thesis for approval by the head of the department (from 7 days before the defense)	04 June 2025	

I am familiar with the task:

Student _____________ Liu Jiaming

Scientific supervisor _____________ Tetiana SHCHERBATIUK

Abstract

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The purpose of this study is to explore the antibacterial effect of zinc oxide-based tungstate nanocomposites on Escherichia coli and some other potential future application values. Bacterial resistance has become a major challenge in the field of global public health. Developing new antibacterial materials is one of the key strategies to address this issue. In this study, different concentrations of $FeWO_4$@ZnO nanocomposites were successfully synthesized by hydrothermal method, and their physical structure and optical properties were characterized and tested by techniques such as ultraviolet-visible spectroscopy (UV-Vis). The test results show that the composite material exhibits significant light absorption characteristics in the ultraviolet-visible light region, and the band gap values of the three samples are all between pure ZnO and tungstate, which confirms the formation of the heterojunction structure. The formation of the heterojunction structure can effectively promote the separation of photogenerated electron-hole pairs, thereby enhancing the photocatalytic activity of the samples in this study. The antibacterial experiment shows that the samples of this experiment have a significant inhibitory effect on Escherichia coli, especially the antibacterial effect is more prominent under light conditions. Among them, sample FZ-3 completely inhibited bacterial growth within 120 minutes. Then, the antibacterial mechanism of the samples was analyzed. It was believed that under light conditions, the composite samples produced reactive oxygen species (ROS) through photocatalysis, which destroyed the structure of bacterial cells, while under dark conditions, the release of Zn^{2+} and W^{6+} ions interfered with the normal metabolism and growth of bacteria. With the increase of tungstate content, it was found that the antibacterial performance of the samples was also significantly improved, which indicates that the synergistic effect plays a key role in the antibacterial process.

Key words: zinc oxide tungstate, nanocomposite, escherichia coli, antibacterial mechanism, photocatalysis.

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INTRODUCTION

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The relevance of this research lies in its close integration with the actual demands of antibacterial material innovation, enhancing photocatalytic performance through material modification, and conducting in-depth mechanism analysis. It has a clear thematic focus and application potential.

The purpose of the study is to synthesize and optimize $FeWO_4$ @ZnO nanocomposites, evaluate their photocatalytic antibacterial properties, reveal the bactericidal mechanism, and promote their application in the field of anti-drug-resistant bacterial infections and related areas.

The objectives of the study is to synthesize and optimize $FeWO_4$ @ZnO nanocomposites and promote their application in the field of anti-drug-resistant bacterial infections and related areas.

The object of the study focus on the synthesis, characterization of zinc oxide-based tungstate nanocomposites ($FeWO_4$@ZnO), as well as their antibacterial properties and mechanisms against Escherichia coli.

Research methods: Material synthesis, material characterization and antibacterial experiments.

The scientific novelty: It was confirmed for the first time that the formation of $FeWO_4$@ZnO heterojunctions significantly improves the separation efficiency of photogenerated electron-hole pairs, enhances photocatalytic activity, clarifies the dual antibacterial pathways of ROS-mediated oxidative damage under light conditions and the release of Zn^{2+} and W^{6+} ions under dark conditions, reveals the linear positive correlation between tungstate content and antibacterial effect, and provides a theoretical basis for the optimization of material composition.

The practical significance of the results obtained is: The zinc oxide-based tungstate nanocomposite ($FeWO_4$@ZnO) developed in this study has important practical application value. This material, through a dual antibacterial mechanism of photocatalysis and metal ion release, can effectively inhibit the growth of drug-resistant Escherichia coli, providing an innovative solution to the increasingly severe problem of bacterial drug resistance. In the medical field, this material can be used as an antibacterial coating on the surface of medical devices, significantly reducing the risk of nosocomial infections. In the food industry, its excellent antibacterial performance can extend the shelf life of food and ensure food safety. In terms of environmental governance, the photocatalytic properties of the material make it suitable for the purification and treatment of drinking water and wastewater. In addition, the low toxicity and environmentally friendly properties of the material are in line with the concept of sustainable development, providing an important reference for the development of new green antibacterial materials. These application potentials fully demonstrate the practical value and social benefits of the research results in multiple fields such as medical health, food safety and environmental protection.

CHAPTER I

LITERATURE REVIEW

1.1 INTRODUCTION TO *ESCHERICHIA COLI*

Escherichia coli is a type of Gram-negative, facultative anaerobic short rod-shaped bacteria belonging to the Enterobacteriaceae family. As common normal microbiota members in the intestines of humans and warm-blooded animals, most *Escherichia coli* strains are non-pathogenic. Sometimes, they also have probiotic effects on the host, such as participating in the synthesis of vitamin K and inhibiting the colonization of pathogenic bacteria [1]. However, some of these pathogenic strains can also cause severe intestinal or exenteral infections, including diarrhea, urinary tract infections, sepsis and meningitis, etc. [2].

From the perspective of biological characteristics, the genome size of *Escherichia coli* is approximately 4.6 Mb and contains about 4,300 genes [3]. According to its pathogenicity, it can be divided into two major categories: symbiotic type and pathogenic type. Pathogenic *Escherichia coli* can be further classified into enteropathogenic *Escherichia coli* (DEC) and extraintestal pathogenic *Escherichia coli* (ExPEC). Among them, DEC includes six main types: Enteropathogenic *Escherichia coli* (EPEC), Enterotoxigenic *Escherichia coli* (ETEC), Enteroinvasive *Escherichia coli* (EIEC), Enterohemorrhagic *Escherichia coli* (EHEC), enteroaggregative *Escherichia coli* (EAEC), and diffusive adhesive *Escherichia coli* (DAEC) [4]. These pathogenic strains cause diseases through different virulence factors and pathogenic mechanisms. For example, EPEC destroys intestinal microvilli through the "adhesive-smoothing" mechanism, while EHEC produces shiga toxin (Stx), leading to hemolytic uremic syndrome[5].

In recent years, the problem of drug resistance of *Escherichia coli* has become increasingly serious. Strains producing extended-spectrum β -lactamase (ESBL) have developed resistance to penicillin and cephalosporin antibiotics[6], and the emergence of carbapenem-resistant *Escherichia coli* (CRE) has posed significant challenges to clinical treatment[7]. According to statistics, the resistance of multi-drug resistant (MDR) strains to more than three types of antibiotics has significantly increased, posing a serious threat to public health[8].

In terms of detection and prevention and control, the traditional MacConquet AGAR culture method remains the basic detection approach[9], while molecular detection techniques such as PCR can specifically detect virulence genes[10]. Prevention and control measures include strengthening food safety management, avoiding raw consumption of contaminated meat and vegetables, and strictly implementing infection control measures in medical institutions[11].

As an important model organism, *Escherichia coli* holds an irreplaceable position in molecular biology research[3]. Meanwhile, its clear pathogenic mechanism and increasingly serious drug resistance problem make it an important object for the research of new antibacterial materials and alternative therapies. This study selected *Escherichia coli* as the experimental strain, aiming to evaluate the antibacterial effect of zinc oxide-based tungstate nanocomposites and provide a new solution for dealing with drug-resistant bacterial infections.

1.2 INTRODUCTION TO ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES

1.2.1 THE BASIC PROPERTIES OF ZINC OXIDES AND TUNGSTATE SALTS

Zinc oxide, as an inorganic compound, is generally a white solid at room temperature. Its crystal structure mainly consists of two types: hexagonal wurtzite and cubic sphalerite. The physical and chemical properties of zinc oxide are closely related. It is precisely due to this unique physical structure that zinc oxide exhibits excellent photoelectric and catalytic properties. For instance, zinc oxide can effectively absorb ultraviolet light when the wavelength is less than 400 nanometers. This characteristic has enabled zinc oxide to be widely applied in photocatalysis and optoelectronic devices[12, 13]. In terms of antibacterial applications, zinc oxide has demonstrated excellent antibacterial activity. Relevant studies have found that the antibacterial mechanism of ZnO is to effectively inhibit bacterial growth by continuously releasing zinc ions. When the size of ZnO is reduced to the nanometer level, its specific surface area increases, which leads to a stronger antibacterial effect. Moreover, because ZnO nanoparticles have obvious inhibitory effects on various common pathogenic bacteria such as Staphylococcus aureus and Escherichia coli, this makes ZnO an ideal material for new antibacterial drugs [14].

Tungstate salts are a class of compounds containing tungstate ions and are usually acidic. Common tungstate salts include sodium tungstate and ammonium tungstate, etc. This type of compound has excellent thermal stability, high melting point and strong corrosion resistance, and is widely used in fields such as catalysis, materials and biomedical engineering [15]. In antibacterial research, tungstate also shows potential. The antibacterial mechanism of tungstate is mainly achieved by releasing tungsten ions, which can interfere with the metabolic processes of bacteria and inhibit their growth. Studies have shown that tungstate has inhibitory effects on both Gram-positive and Gram-negative bacteria, making it an effective component for the synthesis of new antibacterial materials.

From this perspective, zinc oxides and tungstate salts, due to their excellent basic properties and antibacterial activities, have shown profound application potential in the field of antibacterial. Future research focus can be placed on exploring the combined application of the two to develop new antibacterial materials. Meanwhile, in-depth research on their antibacterial mechanisms and interactions in different biological systems will help promote the practical application of these materials in fields such as medical care and environmental governance.

1.2.2 THE CONCEPT AND ADVANTAGES OF ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES

Nanocomposites are materials composed of two or more different materials, among which at least one component has a size within the nanoscale range (1-100 nanometers). By combining nanomaterials with traditional materials, nanocomposites can exhibit comprehensive performance superior to their components in multiple aspects. The construction of this kind of material often utilizes the combination of nano-fillers (such as metals, oxides or carbon-based materials) with polymers, metals or ceramic matrices. Nanocomposites have been widely applied in many fields due to their outstanding physical, chemical and biological properties, including catalysis, medicine and environmental governance, etc. [16].

The unique advantages of nanocomposites in the field of antibacterial mainly lie in their large surface area and scattering effect, synergistic effect, multiple antibacterial mechanisms, and enhanced mechanical strength and thermal stability. Due to the extremely small size of nanomaterials, they usually have a large specific surface area, which means they offer more active surfaces for interaction with microorganisms. A larger contact area is more conducive to enhancing the antibacterial activity of the material[17], When different nano-components (such as zinc oxides and tungstate salts) are used in combination, a synergistic effect may be produced. This effect makes the antibacterial performance of the composite material stronger. For example, the combination of ZnO and tungstate can further enhance the ability to release metal ions, thereby improving the antibacterial effect[18]. Nanocomposites usually can exert antibacterial effects through multiple mechanisms. For instance, zinc oxides can cause damage to bacteria by generating reactive oxygen species (ROS), while tungstate salts can interfere with the metabolic pathways of bacteria by releasing tungsten ions [19]. This combined effect can make the antibacterial effect more significant. Nanocomposites usually exhibit better mechanical properties and thermal stability, which enables them to maintain good antibacterial effects under various environmental conditions[20].

Nanocomposites of zinc oxet-based tungstate have attracted a great deal of research attention in recent years. Since both zinc oxides and tungstate salts exhibit excellent antibacterial properties, their composites show great potential in antibacterial applications. Studies show that the combination of zinc oxides and tungstate salts can not only enhance the antibacterial activity, but also improve the mechanical properties and thermal stability of the materials. For instance, studies have shown significant inhibitory effects on Staphylococcus aureus and *Escherichia coli* through nanocomposites synthesized from ZnO and silver tungstate [21]. In addition, this composite material can also be used in the surface coating of medical devices, which helps prevent bacterial infections.

Further research results show that Zno-based tungstate nanocomposites maintain high antibacterial performance under various environmental conditions and can provide continuous antibacterial effects by slowly releasing metal ions, making them have a long service life in medical applications [22]. The combination of this persistence and antibacterial activity makes zinc oxide-based tungstate materials have good cost-effectiveness in the field of antibacterial.

From this perspective, zinc oxide-based tungstate nanocomposites exhibit excellent antibacterial performance and good physical properties, and have great potential in the research and application of antibacterial materials. The application of such materials may offer new development directions for future antibacterial solutions and provide technical support in fields such as medical care and environmental governance.

1.3 THE ANTIBACTERIAL EFFECT AND PRACTICAL SIGNIFICANCE OF ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES ON *ESCHERICHIA COLI*

Bacterial drug resistance has become a major challenge in the field of global public health. The World Health Organization (WHO) points out that if no effective measures are taken, drug-resistant infections could cause 10 million deaths worldwide each year by 2050 [23],. The development of new antibacterial materials is one of the important strategies to deal with this challenge. The research on zinc oxet-based tungstate nanocomposites can not only provide a new antibacterial solution, but also reduce the reliance on antibiotics, thereby delaying the development of bacterial resistance. *Escherichia coli* is widely present in the environment. Some pathogenic strains cause urinary tract infections, food poisoning, etc., imposing a huge burden on public health[24]. However, zinc oxide-based tungstate nanocomposites offer new solutions to this challenge due to their unique antibacterial mechanisms and excellent physicochemical properties.

Zinc oxide (ZnO) has been widely used due to its superior antibacterial properties. However, by compounding with tungstate, its antibacterial effect can be significantly enhanced [25][25]. Studies have shown that the combination of ZnO and tungstate not only enhances its inhibitory ability against *Escherichia coli*, but also improves the biocompatibility of the material through nanoscale methods and reduces toxicity [26]. The formation of this composite material effectively enhances the effect of the antibacterial agent, making it have greater benefits and value in clinical and environmental applications.

Zinc oxide-based tungstate nanocomposites are of great significance in promoting the development of antibacterial materials. This material can not only effectively combat *Escherichia coli* but also inhibit many other bacteria by promoting the release of ZnO and enhancing the antibacterial ability of metal ions, and maintain continuous activity under many environmental conditions[27]. This offers potential possibilities for the development of new antibacterial surface coatings, especially with broad application prospects in fields such as medical devices, food packaging and water treatment.

In terms of public health security, the development of antibacterial materials is also of vital importance. In recent years, the infection rate caused by *Escherichia coli* has continued to rise. Actively promoting the research and development of nanocomposites with sustained antibacterial properties is conducive to reducing the incidence of infections in the medical environment [28] Zinc oxide-based tungstate nanocomposites reduce the risk of bacterial resistance by providing a new antibacterial mechanism, thereby enhancing the effectiveness of antibiotics [29]

In addition, the green synthesis method and environmentally friendly characteristics of this material also conform to the concept of sustainable development. For instance, both ZnO and tungstate are non-toxic or low-toxic materials, and they have good biocompatibility. They can naturally degrade in the environment, reducing the negative impact on the ecosystem Therefore, this research not only holds significant scientific value but also has profound implications for the sustainable development of the social economy and the ecological environment.

Therefore, the research on the antibacterial effect of zinc oxide-based tungstate nanocomposites on *Escherichia coli* will undoubtedly provide new solutions for addressing the increasingly severe public health challenges. The promotion of this research will make significant contributions to the development of antibacterial materials and ensuring public health security, providing sustainable solutions to address the crisis of bacterial resistance.

1.4 RESEARCH STATUS AT HOME AND ABROAD

1.4.1 RESEARCH STATUS OF ZINC OXIDES

Zinc oxide, as a multifunctional inorganic antibacterial material, has become a new hotspot in the research of antibacterial materials due to its outstanding antibacterial performance, good biocompatibility, safety and persistence. In recent years, researchers at home and abroad have conducted in-depth discussions on its antibacterial properties, mechanisms and applications. Especially at the nanoscale, zinc oxide has shown more significant antibacterial effects.

The antibacterial mechanisms of zinc oxide mainly include photocatalysis, zinc ion dissolution and the generation of reactive oxygen species. Under photocatalysis, photogenerated electron-hole pairs are produced on the surface of zinc oxide, which in turn generate reactive oxygen species with strong oxidizing properties, destroying the cell membranes and organelles of bacteria and leading to bacterial death [30]. Zinc ion dissolution affects the growth and metabolism of bacteria by interfering with their physiological functions. In addition, zinc oxide can also promote the generation of reactive oxygen species and destroy the structure of bacterial cells [31] There may be a synergistic effect among these mechanisms, jointly enhancing the antibacterial effect [32].

Nano zinc oxide has more excellent antibacterial performance due to its high specific surface area and surface active sites. It has broad-spectrum antibacterial activity against a variety of pathogenic microorganisms, including Gram-positive bacteria, Gram-negative bacteria and fungi, etc [33][33]. Moreover, factors such as particle size, crystal structure, specific surface area, light conditions and pH value all affect its antibacterial performance [34], In terms of preparation methods, zinc oxide antibacterial materials can be prepared through various approaches such as physical, chemical and biological methods. Recent studies have shown that biosynthetic zinc oxide nanoparticles have been successfully prepared through green synthesis methods and possess antioxidant and antibacterial activities [35],

Zinc oxide antibacterial materials are widely used in multiple fields such as medical care, food packaging, textiles, cosmetics and personal care products. For example, the hydrogel modified with zinc oxide has good antibacterial activity against *Escherichia coli* and Staphylococcus aureus, and can significantly accelerate the healing of infectious wounds[35],

In the field of food packaging, nano-zinc oxide can extend the shelf life of food [37].

In addition, the application of zinc oxide in the adhesive for mounting calligraphy and paintings also demonstrates its advantages in antibacterial and UV resistance [38].

Significant progress has been made both at home and abroad in the research on the antibacterial properties of zinc oxide. Several universities and research institutions in China, such as Sichuan Agricultural University and Shanghai Jiao Tong University, have conducted systematic studies on the antibacterial properties, mechanisms, safety and applications of nano-zinc oxide [39-40].

Internationally, research institutions in the United States, Europe and other countries have also made significant progress in the antibacterial mechanism of zinc oxide, nanocomposites, functional modification and other aspects [41-42]. In the future, research on the antibacterial properties of zinc oxide will focus on aspects such as nano-safety, multi-functionality, intelligent response, and sustainable development. It has broad application prospects in multiple fields such as medical health, food safety, environmental protection, and cultural protection. By strengthening basic research, technological innovation and international cooperation, zinc oxide antibacterial materials will make greater contributions to human health and sustainable development.

1.4.2 RESEARCH STATUS OF TUNGSTATE

Zinc tungstate, as an important functional material, has shown remarkable potential in the field of antibacterial. In recent years, with the increasingly severe problem of antibiotic resistance, the development of new antibacterial materials has become a research hotspot. Tungstate has received extensive attention from researchers at home and abroad due to its unique physicochemical properties and excellent antibacterial performance. Relevant studies have shown that tungstate has significant inhibitory effects on a variety of bacteria. For instance, phosphotungstate exhibits certain antibacterial effects on *Escherichia coli*, Staphylococcus aureus, yeast and Aspergillus Niger, especially its inhibitory effect on Staphylococcus aureus is particularly prominent [43].

In China, researchers have successfully synthesized zinc tungstate antibacterial composition powder through microwave heating or microwave-molten salt method, and its antibacterial effect is significantly better than that of a single component [44]. Qingdao University of Science and Technology synthesized intercalated metal oxide antibacterial agents, which have highly efficient and long-lasting antibacterial performance [45][45]. In terms of application, zinc tungstate has been used in the antibacterial modification of ceramic tiles and oral materials, and significant progress has also been made [46-47] In addition, some tungstate salts containing silver or copper can achieve contact sterilization through the release of metal ions. For instance, Ag_2WO_4 can slowly release Ag+ ions, which can combine with sulfhydryl groups (-SH) on the bacterial cell membrane, thereby disrupting membrane integrity [48].

Internationally, certain progress has also been made in the research on the antibacterial properties of zinc tungstate. Foreign researchers have developed a new type of antibacterial material based on tungstate, which has demonstrated highly efficient antibacterial activity against a variety of pathogens related to medical treatment. This study used a variety of pathogens including Staphylococcus aureus, *Escherichia coli* and Pseudomonas aeruginosa for testing. The results showed that the material could achieve effective antibacterial ability at low concentrations [49].

In addition, this material also has good safety and biodegradability, making it suitable for antibacterial applications in the medical field. This research has laid the groundwork for the application of tungstate in the medical field.

Overall, both at home and abroad, there are different focuses in the research on the antibacterial properties of zinc tungstate. In China, more attention is paid to the preparation methods and vigorous application, while international research focuses more on the in-depth exploration of the antibacterial mechanism. It is believed that long-term progress will be made in the research and development of tungstate antibacterial materials in the future.

1.4.3 RESEARCH STATUS OF ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES

Although the antibacterial properties of ZnO and tungstate have been widely studied respectively, there are still many unknown factors regarding the antibacterial mechanism of the nanomaterial system formed by their combination, the possible formation of heterojunctions, and their synergistic effects [50]. Studies have shown that the antibacterial properties of composite nanomaterials may stem from the combination of multiple materials at the interface to form heterojunctions. The band alignment at the heterojunction interface and the built-in electric field promote the effective separation of photogenerated electron-hole pairs, reduce the recombination rate, and thereby enhance the photocatalytic activity [51]. Under light conditions, $FeWO_4$@ZnO nanocomposites demonstrated excellent photocatalytic degradation of organic pollutants under visible light[52] [52]. For example, research has found that $FeWO_4$@ZnO nanocomposites can degrade rhodamine B by more than 95% [53]. The synergistic effect of zinc oxides (ZnO) and tungstate salts (such as $FeWO_4$) leads to the generation of more reactive oxygen species (ROS) on the material surface, such as superoxide radicals ($\cdot O_2^-$) and hydroxyl radicals (· OH). These reactive oxygen species can damage the cell membranes, proteins and DNA of bacteria, eventually leading to the death of bacteria [54] In addition, the release of zinc ions further enhances the antibacterial effect, interfering with the metabolic activities of bacteria through interaction with their cell membranes. Therefore, zinc oxide-based tungstate nanocomposites achieve efficient and broad-spectrum antibacterial properties through the formation of heterojunctions. At present, the research on the synergistic antibacterial mechanism is still shallow. Most of it still remains at the stage of phenomenon observation and preliminary analysis, lacking systematic exploration of the intrinsic connection between the structure and antibacterial performance and comprehensive consideration of influencing factors. As scholars such as Zhu Hao pointed out in the review, although the phenomenon of synergistic enhanced antibacterial has been observed, the in-depth mechanism analysis still needs to be strengthened [55].

In recent years, scholars at home and abroad have conducted preliminary explorations on the antibacterial properties of zinc oxide-based tungstate nanocomposites. Mao et al. confirmed through experiments that the combination of ZnO and tungstate could significantly enhance its antibacterial effect against

Escherichia coli[18]. Silvestre et al. 's research also found that the antibacterial properties of composite materials are closely related to their component ratios and preparation methods [56] Furthermore, Mahamuni-Badiger et al. applied zinc oxide-based tungstate nanocomposites to the coating of medical devices and found that they could effectively inhibit the formation of bacterial biofilms [57].

In terms of synthesis methods, the most commonly used method was to prepare $FeWO_4$@ZnO nanocomposites by hydrothermal method. By adjusting parameters such as reaction temperature, time and pH value, the morphology and size of the products could be controlled. The photocatalytic degradation performance of methyl orange was also studied. Duraimurugan et al. prepared $FeWO_4$@ZnO nanocomposites with different morphologies by hydrothermal method and investigated their photocatalytic properties [58]. The sol-gel method can be used to achieve uniform mixing at the molecular level of materials, and the prepared composite materials have good dispersion and uniformity. The coprecipitation method is simple to operate and easy to be produced on a large scale.

In terms of performance research, $FeWO_4$@ZnO nanocomposites have potential application value in areas such as lithium-ion batteries and supercapacitors. For example, $FeWO_4$@ZnO nanocomposites have high specific capacity and cycling stability as anode materials for lithium-ion batteries [59]. $FeWO_4$@ZnO Nanocomposites have sensitive responses to a variety of gases. The study found that these nanocomposites have high sensitivity and selectivity for ethanol gas[60].

1.5 EXPECTED RESULTS AND RESEARCH SIGNIFICANCE

It is expected that this study will successfully synthesize zinc oxide-based tungstate nanocomposites (such as $FeWO_4$/ZnO or $ZnWO_4$, etc.) and successfully conduct characterization tests on their morphological characteristics, structural characteristics and chemical composition, etc. Meanwhile, it is expected that the final synthesized zinc oxide-based tungstate nanocomposites will have a significant improvement in the antibacterial rate against E. coli, which should be significantly higher than that of ordinary single zinc oxide or tungstate materials. The antibacterial effect of this material may be positively correlated with factors such as the concentration of the reactive material and the reaction time, and it may have antibacterial mechanisms such as generating reactive oxygen species (ROS) and destroying bacterial cell membranes.

This research will be dedicated to developing an emerging low-toxicity and highly efficient zinc oxide-based tungstate nanocomposite material, providing a practical solution to the problem of drug resistance in pathogenic *Escherichia coli*. Meanwhile, during the experiment, the optimal synthesis method of this nanocomposite material was explored, the connection between its structural characteristics, etc. and its antibacterial effect on *Escherichia coli* was found, and the antibacterial mechanism of this material against *Escherichia coli* (ROS oxidation, metal ion release, physical damage, etc.) was clarified.

This study, by developing zinc oxide-based tungstate nanocomposites and simultaneously exploring their antibacterial ability against *Escherichia coli*, has significant theoretical and practical significance. Theoretically, this research can reveal the synergistic antibacterial mechanism of zinc and tungsten (such as reactive oxygen species generation, metal ion release, etc.), enrich the design ideas of multifunctional nano-antibacterial materials, and provide new insights for inorganic composite materials in the field of microbial inhibition. In practical applications, this material is expected to become an efficient, low-toxicity and highly biosoluble antibacterial agent, providing new solutions to the problems of infection caused by *Escherichia coli*, shocking food contamination and increasingly severe drug resistance. At the same time, it can be extended to fields such as healthcare and water resource treatment, in line with the demands of the green and sustainable development concept. It has potential socio-economic benefits.

Summary of the chapter I

1. *Escherichia coli* is a short, rod-shaped, Gram-negative, facultative anaerobic bacterium. Most strains are non-pathogenic, but some pathogenic strains can cause diarrhea, urinary tract infections and other diseases. The problem of drug resistance in *Escherichia coli* is becoming increasingly serious, especially with the emergence of ESBL-producing and carbapenem-resistant strains.
2. Zinc oxide (ZnO) has high thermal stability, good biocompatibility and antibacterial activity, and its nanoparticles have a more significant antibacterial effect. Tungstate salts (such as sodium tungstate) have anti-corrosion and antibacterial properties, mainly interfering with bacterial metabolism by releasing tungsten ions. Zinc oxide-based tungstate nanocomposites provide a new idea for solving the problem of bacterial drug resistance. This material has the characteristics of high efficiency, low toxicity and good biocompatibility, and is suitable for fields such as medical devices and food packaging.
3. Research on zinc oxides focuses on antibacterial mechanisms (photocatalysis, zinc ion dissolution, ROS generation) and applications (medical care, food packaging, etc.), while research on tungstate salts emphasizes antibacterial properties and the development of composite materials. The research on zinc oxet-based tungstate nanocomposites is still in its infancy, with a focus on exploring the synergistic antibacterial mechanism and optimizing the preparation methods.

CHAPTER II
OBJECT, PURPOSE, AND METHODS OF THE STUDY

2.1 MAIN REAGENTS AND INSTRUMENTS
2.1.1 EXPERIMENT REAGENT

Reagents for synthetic materials: Zinc oxide (ZnO, analytical grade), ammonium tungstate ($(NH_4)_2WO_4$, purity ≥99%), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, purity ≥99%), ultrapure water.

Reagents for antibacterial experiments: Tryptone, Yeast Extract, sodium chloride (NaCl), phosphate buffering solution (PBS), Standard strain of *Escherichia coli*.

2.1.2 EXPERIMENTAL APPARATUS

Material synthesis equipment: magnetic stirrer, high-pressure reactor (50 mL), oven (constant temperature drying at 60 ℃), muffle furnace (maximum temperature ≥1200 ℃), mortar and pestle (for grinding powder).

Material characterization instrument: Ultraviolet-visible spectrophotometer (UV-Vis).

Antibacterial experimental equipment: biosafety cabinet, constant temperature shaker (37 ℃ for cultivating Escherichia coli), light source system, centrifuge (for concentrating and washing bacterial liquid), constant temperature incubator (37 ℃ for cultivating AGAR plates).

Conventional laboratory consumables: sterile petri dishes, centrifuge tubes, pipettes and tips, coating rods (glass or disposable plastic), LB AGAR plates.

2.2 PREPARATION OF ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES

2.2.1 PRECURSOR SYNTHESIS

Slowly add 1 g of precise zinc oxide (ZnO) powder to 30 ml of ultrapure water, and then continuously stir magnetically for 30 minutes to ensure the formation of a stable suspension. Subsequently, 0.028g / 0.056g / 0.083g of ferrous sulfate ($FeSO_4$) were respectively added to the above solutions and stirred continuously. Then, 0.048g / 0.096g / 0.144g of ammonium tungstate ($(NH_4)_2WO_4$) were respectively added and stirred continuously to ensure their full dissolution.

2.2.2 HYDROTHERMAL REACTION AND POST-TREATMENT

The mixed solution was transferred to a high-pressure reactor and subjected to hydrothermal reaction at 180 ℃ for 12 hours. After the reaction is completed, the product is washed with centrifugal water three times and then subjected to suction filtration. The obtained precipitate is dried in an oven at 60 ℃ for 12 hours. After completion, it is ground for 1 hour to form fine powder. The powder was then placed in a muffle furnace and calcined at 500 ° C for 4 hours. After cooling, it was ground again and collected to obtain FeWO4@ZnO powder with concentrations of 5%, 10%, and 15% respectively (labeled as FZ-1, FZ-2, FZ-3).

2.3 MATERIALS CHARACTERIZATION

2.3.1 STRUCTURAL AND MORPHOLOGICAL ANALYSIS

The crystal phase of the material was analyzed by X-ray diffractometer (XRD, Bruker D8 Advance, Cu-Kα radiation), and then the surface morphology and particle size distribution were observed by field emission scanning electron microscope (SEM, FEI Nova NanoSEM 450).

2.3.2 OPTICAL PERFORMANCE TEST

The light absorption characteristics of the materials were determined by ultraviolet-visible spectroscopy (UV-Vis, Shimadzu UV-2600) to evaluate their photocatalytic activity.

2.4 ANTIBACTERIAL EXPERIMENT

2.4.1 STRAIN AND CULTURE MEDIUM

In the experiment, E. coli was selected and incubated at 37 °C in LB liquid medium (peptone 10 g/L, yeast extract 5 g/L, NaCl 10 g/L, pH 7.4) until the logarithmic growth phase.

2.4.2 EXPERIMENTAL GROUPING AND CONDITIONS

Illumination group: Xenon lamp light source (wavelength ≥420 nm, light intensity 300 mW/cm2) is adopted to simulate the visible light environment. The following groups are set up:

Blank control group: Bacterial liquid

ZnO control group: Pure ZnO (30.0 mg) + bacterial liquid

Experimental group: FZ-1, FZ-2, FZ-3 (30.0 mg) + bacterial liquid

Dark group: Repeat the above grouping under light-free conditions to distinguish between photocatalytic and non-photocatalytic effects.

2.4.3 EVALUATION OF ANTIBACTERIAL PERFORMANCE

Dilute the logarithmic phase bacterial liquid to 106 CFU/mL, mix it with the material suspension, and then act under light or dark conditions for 2 hours respectively. The reaction solution was gradient diluted (10-1 to 10-4), spread on LB AGAR plates, and after overnight culture at 37℃, the colony count (CFU) was counted. The Survival Rate (SR) of bacteria is calculated as follows:

$$\text{survival rate}(\%) = \left(\frac{N_t}{N_0}\right) \times 100$$

N_t:The colony count (CFU/mL) of the experimental group or the control group at time t.
N_0:Colony count (CFU/mL) at the initial moment (t=0).

Summary of chapter II

1. Three different concentrations (5%, 10%, 15%) of $FeWO_4$ @ZnO nanocomposites (FZ-1, FZ-2, FZ-3) were successfully prepared by the hydrothermal method. Then, the materials were systematically characterized by techniques such as XRD, SEM and UV-Vis, verifying the crystal structure, morphological characteristics and optical properties of the materials.
2. The standard strain of Escherichia coli was selected as the experimental object and cultivated in LB medium. A contrast experiment was set up between the light group (xenon lamp source) and the dark group to clearly distinguish the antibacterial effect under photocatalytic and non-photocatalytic conditions. The antibacterial performance of the material was quantitatively evaluated by the colony counting method (CFU), and the bacterial survival rate was calculated.
3. The experimental design was rigorous, and the control group was set up reasonably, ensuring the reliability of the experimental results. Standardized operation procedures

and evaluation methods were adopted, providing a scientific basis for the subsequent analysis of the experimental results.

CHAPTER III

EXPERIMENTAL PART

3.1 CHARACTERIZATION RESULTS OF ZINC OXIDE-BASED TUNGSTATE NANOCOMPOSITES

3.1.1 XRD AND SEM ANALYSIS

The XRD patterns show that the characteristic diffraction peaks of ZnO and $FeWO_4$ coexist simultaneously in all three experimental samples, confirming that all three composite materials in this experiment were successfully prepared. According to the SEM images, the material presents a nanosheet-like structure with a uniform particle size distribution, and the average particle size is approximately 100 nm. This nanostructure provides the sample with a larger specific surface area, allowing the sample's nanoparticles to have more active sites, which is more conducive to contact with bacteria and the exertion of antibacterial activity.

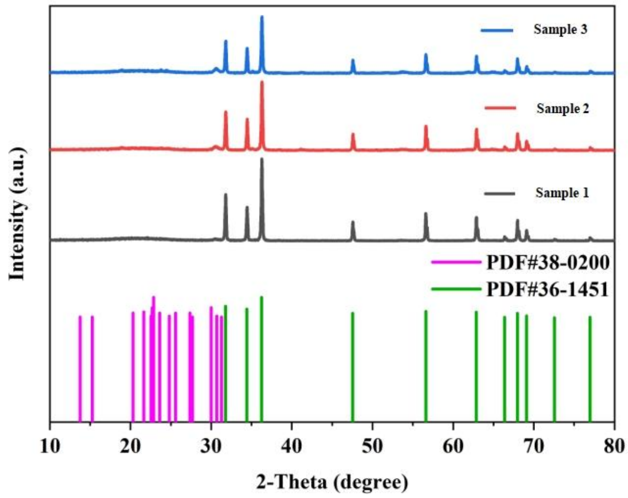

Figure 3.1 X-ray diffraction pattern of composite materials

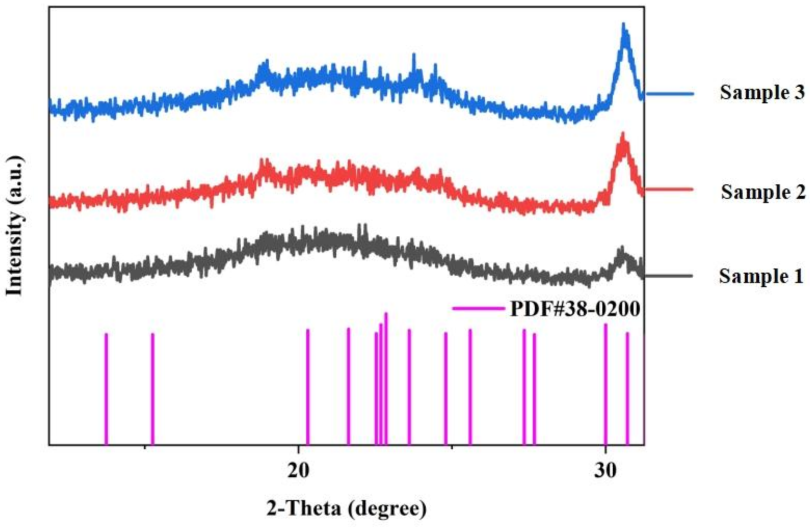

Figure 3.2 locally magnified X-ray diffraction pattern

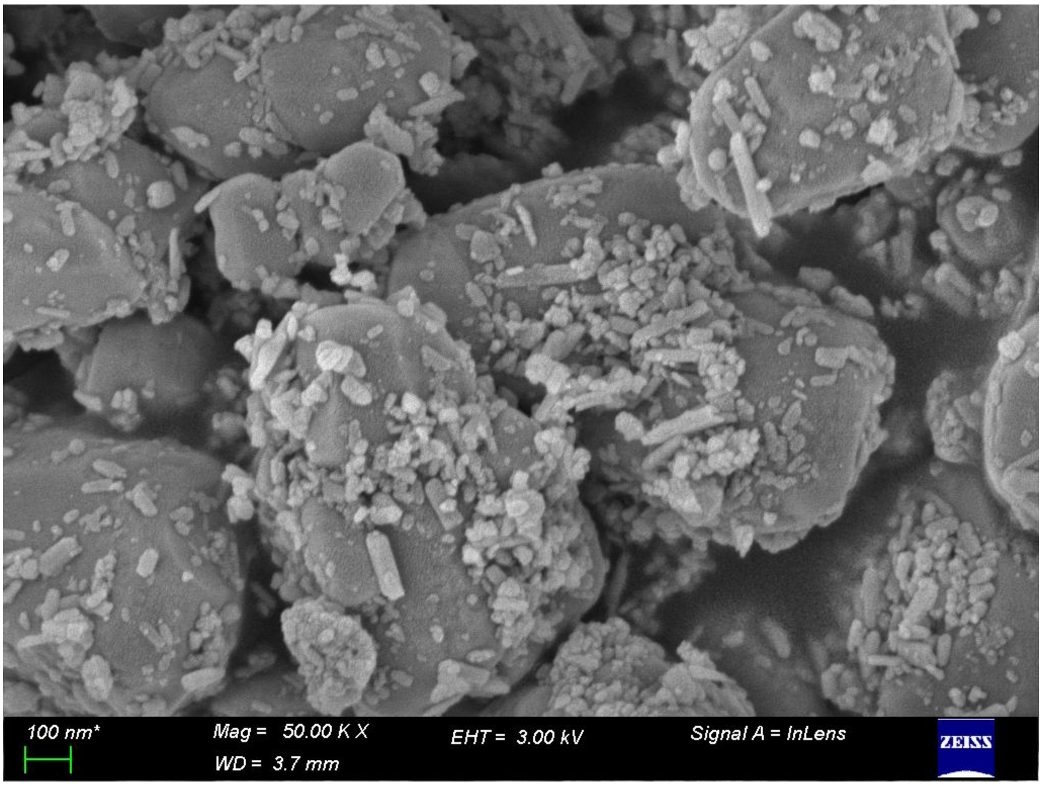

Figure 3.3 Sample magnified 50,000 times by SEM

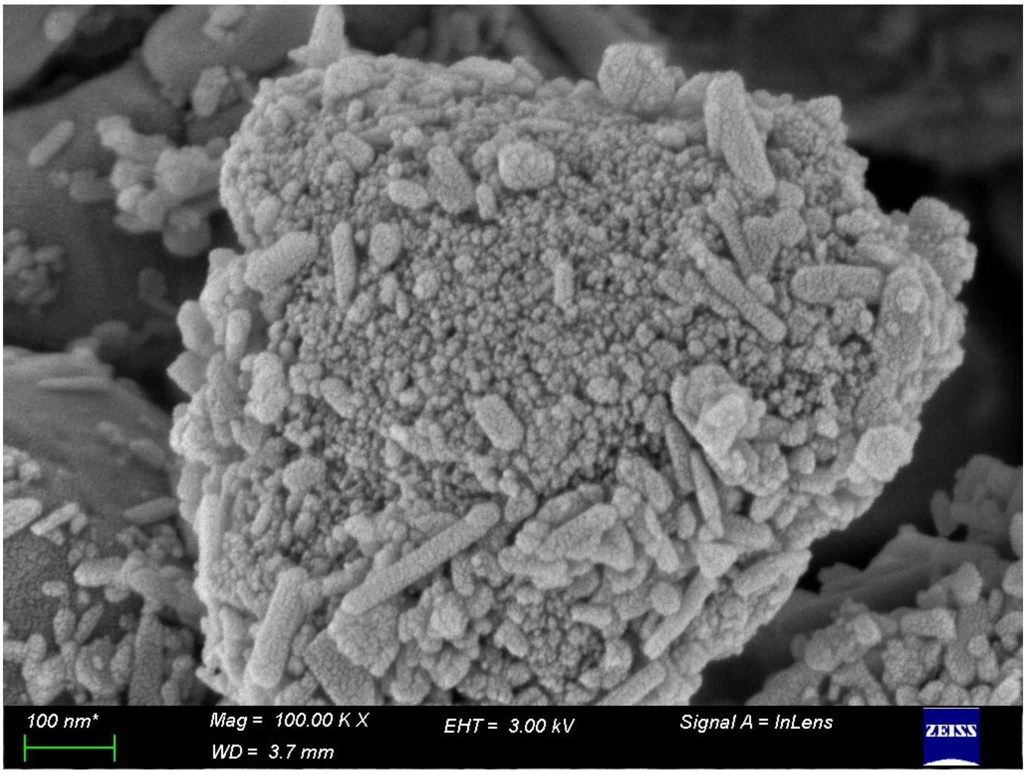

Figure 3.4 Sample magnified 100,000 times by SEM

3.1.2 ULTRAVIOLET-VISIBLE SPECTROSCOPY ANALYSIS

Through conducting ultraviolet-visible spectroscopy tests, the absorbance data of three groups of experimental samples at different wavelengths were obtained in this experiment. From these data, it can be concluded that all three groups of samples exhibit significant light absorption characteristics within the wavelength range of 220-800 nm. Particularly, the absorbance is relatively high within the wavelength range of 220-400 nm in the ultraviolet region, which is consistent with the bandgap characteristics of ZnO. The absorption within the wavelength range of 400-800 nm in the visible light region may result from the introduction of tungstate.

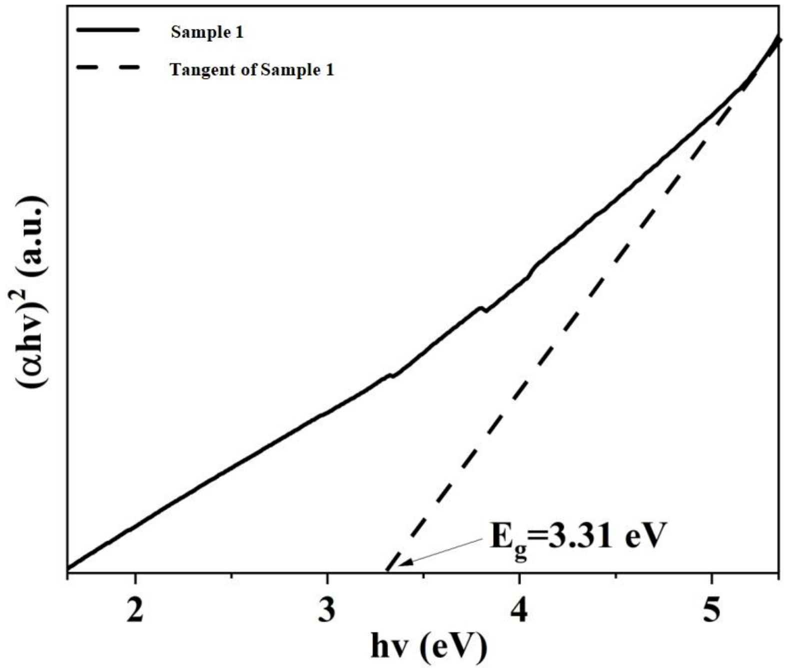

Figure 3.5 Band gap energy of Sample 1

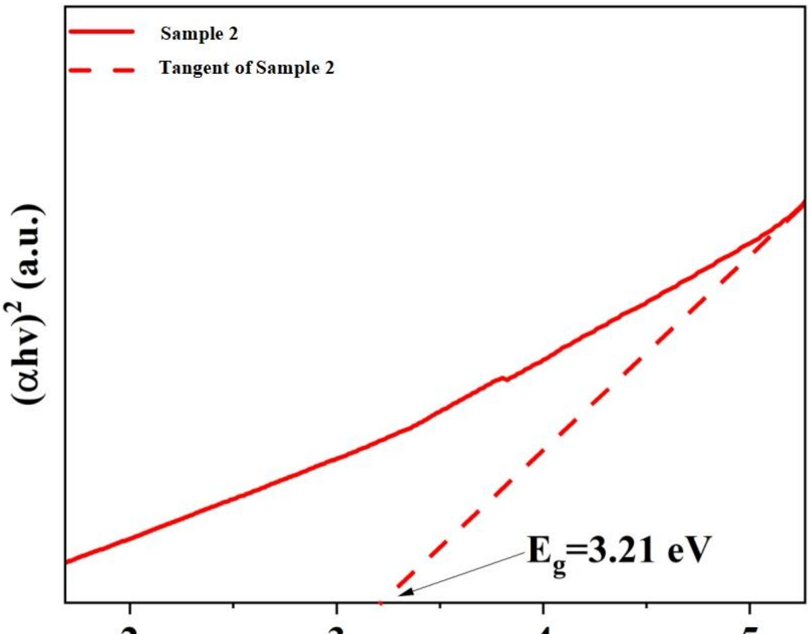

Figure 3.6 Band gap energy of Sample 2

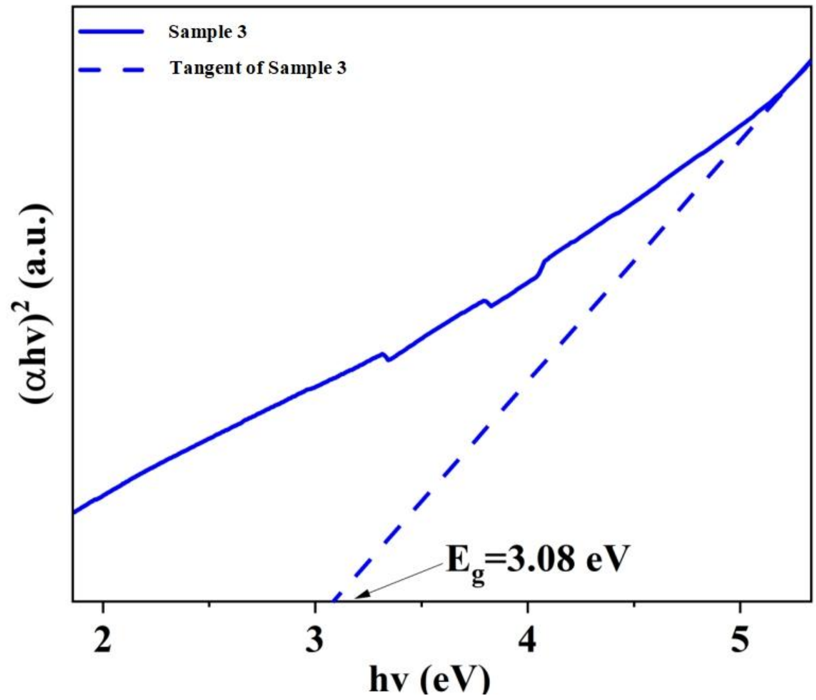

Figure 3.7 Band gap energy of Sample 3

The bandgap energies of the three samples were calculated based on the Kubelka-Munk function formula. It can be concluded that the bandgap values of the composite samples are between pure ZnO and tungstate, indicating that an effective heterojunction structure has been formed between these two substances. This structure is conducive to the separation of photogenerated electron-hole pairs, thereby enhancing the photocatalytic activity and enabling the samples to exhibit more effective antibacterial properties.

3.2 ANALYSIS OF ANTIBACTERIAL EXPERIMENT RESULTS

3.2.1 EVALUATION OF ANTIBACTERIAL EFFECT

The results of the antibacterial experiment show that zinc oxide-based tungstate nanocomposites exhibit significant inhibitory effects on Escherichia coli. It can be seen from Figures 3-8 and 3-9 that the antibacterial effect of sample 3 is the most significant when exposed to light. After 120 minutes of action, the bacterial growth is completely inhibited (with a survival rate of 0%). In contrast, although the antibacterial effects of the three groups of experimental samples were weaker under dark conditions, they were still better than those of the blank control group.

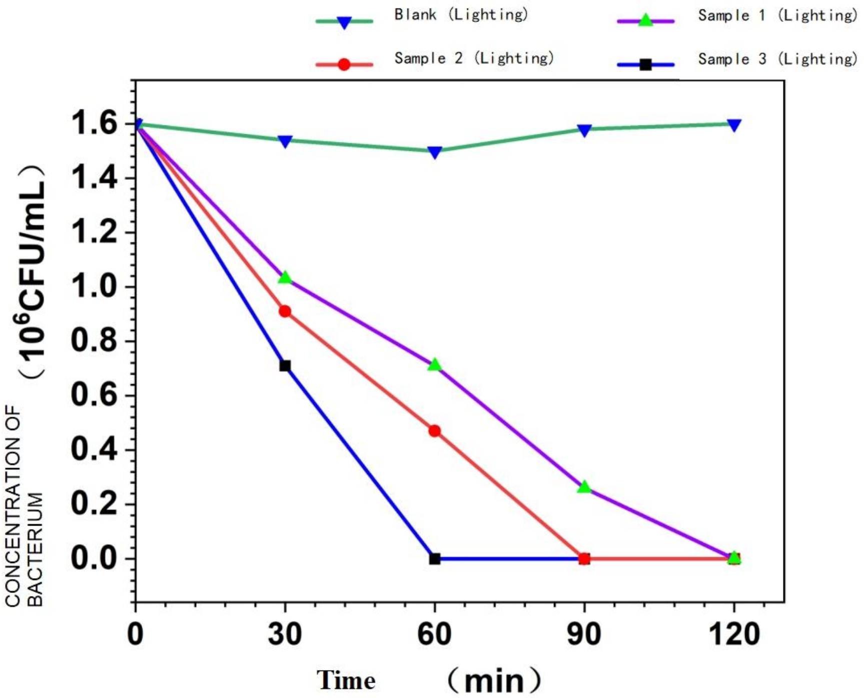

Figure 3.8 Concentration of bacterial liquid under light conditions

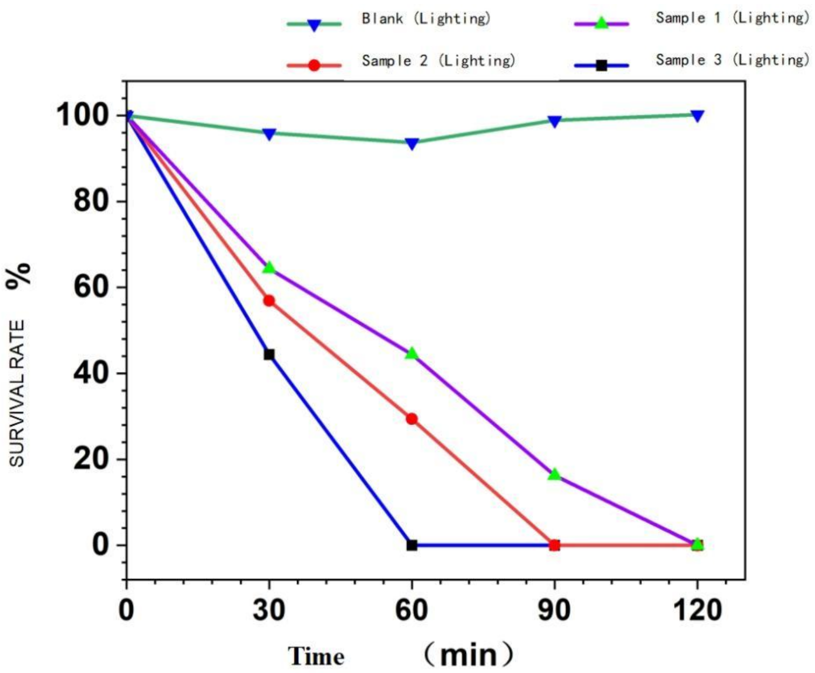

Figure 3.9 Survival rate of large Escherichia coli under light conditions

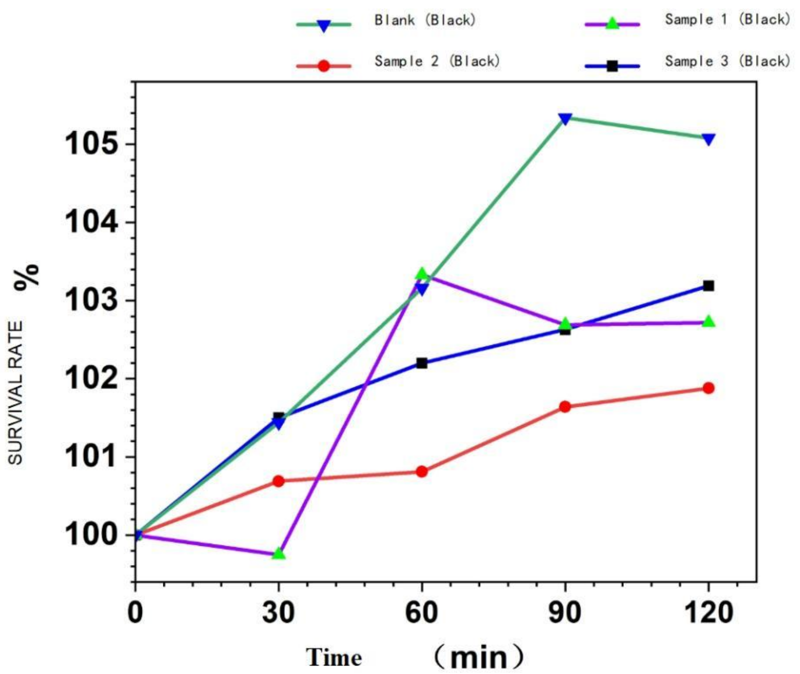

Figure 3.10 Survival rate of Escherichia coli under dark conditions

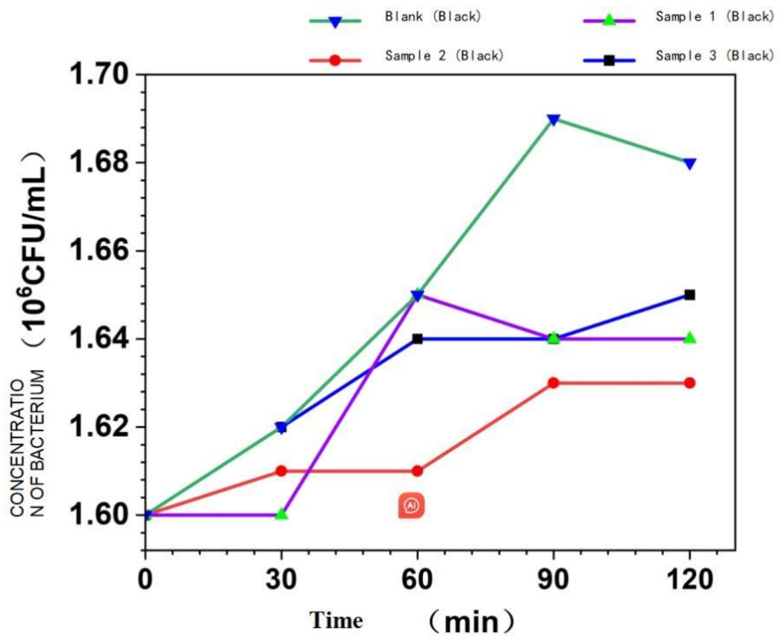

Figure 3.11 Concentration of bacterial liquid under dark conditions

3.2.2 ANTIBACTERIAL MECHANISMS UNDER LIGHT AND DARK CONDITIONS

The experimental results show that when exposed to light sources, the antibacterial effects of the three groups of experimental samples will be significantly enhanced. This is mainly attributed to the photocatalytic effect of the composite nanoparticles. ZnO generates electron-hole pairs under light exposure, thereby generating reactive oxygen species (ROS). These active substances can destroy the cell membranes and internal structures of bacteria, thereby killing the bacteria or inhibiting their normal growth. The introduction of tungstate further promotes the separation of photogenerated carriers, enhances the photocatalytic efficiency, and enables the antibacterial performance of the samples to be maximized.

When there was no light, the antibacterial effect of the three groups of samples was still better than that of the blank control group. Therefore, at this time, it is believed that the antibacterial effect of the three groups of experimental samples can still be attributed to the release of $Zn^{2+}$and W^{6+}. These ions can interfere with the normal metabolic process of bacteria and thereby inhibit their growth. In conclusion, the sample can still demonstrate a certain antibacterial ability under dark conditions, indicating that it is the metal ion release mechanism that enables the sample to exert a certain antibacterial effect in the absence of light.

3.2.3 CONCENTRATION DEPENDENCE

It can be concluded from the experimental results that as the content of tungstate in the composite material increases, the antibacterial effect of the experimental samples also shows a progressive improvement. This might be because a higher concentration of tungstate provides more active sites for the samples, thereby enhancing the photocatalytic activity and metal ion release capacity of the samples. The formation of heterojunction structures between zinc oxides and tungstate salts may also be optimized with the increase of tungstate salt content, thereby further enhancing the antibacterial performance of the experimental samples and achieving better antibacterial effects in the experiments.

3.3 DISCUSSION

3.3.1 SYNERGISTIC ANTIBACTERIAL MECHANISM

This study suggests that zinc oxides and tungstate salts have a significant synergistic effect after being compounded. This effect is the key for this nanocomposite material to exert its highly efficient antibacterial ability in this experiment. Coupled with the photocatalytic activity of ZnO, which can be combined with the metal ion release ability of tungstate salts, multiple highly efficient antibacterial mechanisms can be formed. The formation of heterojunction structures between zinc oxides and tungstate salts can promote the separation of photogenerated carriers, which reduces the recombination rate and thereby enhances the photocatalytic efficiency of the samples. The various synergistic effects in this experiment jointly constitute the synergistic antibacterial mechanism of the material, enabling the composite material to exert efficient antibacterial effects even at low concentrations.

3.3.2 FUTURE APPLICATION PROSPECTS

Based on the experimental results, this study holds that the synthesized zinc oxide-based tungstate nanocomposites have the characteristics of high efficiency, low toxicity and durability. These characteristics make the zinc oxide-based tungstate nanocomposites applicable in aspects such as medical device coatings, food packaging and water treatment. Especially under light conditions, the material can fully exert its photocatalytic sterilization ability to rapidly kill bacteria, which is of great significance for preventing hospital infections and food contamination.

Summary of chapter III

1. XRD and SEM analyses confirmed that the composite material has a uniform nanosheet structure with an average particle size of approximately 100nm. UV-Vis tests showed that the material has significant light absorption characteristics in the wavelength range of 220-800nm, and the band gap value is between ZnO and tungstate, confirming the formation of heterojunctions.
2. The FZ-3 sample exhibited the optimal antibacterial effect under light conditions, completely inhibiting bacterial growth within 120 minutes. The antibacterial effect was concentration-dependent and significantly improved with the increase of tungstate content. It still maintained certain antibacterial activity under dark conditions, but the effect was weaker than that under light conditions.
3. Under light conditions, it mainly exerts antibacterial effects by generating ROS through photocatalysis. Under dark conditions, it interferes with bacterial metabolism by relying on the release of $Zn^{2+}$and W^{6+}ions. The heterojunction structure promotes the separation of photogenerated carriers and enhances the photocatalytic activity of the material.
4. The multiple antibacterial mechanisms of the composite materials have been revealed, providing a theoretical basis for the design of new antibacterial materials. The positive correlation between the content of tungstate and the antibacterial performance has been proved, pointing out the direction for material optimization.

CONCLUSION

In this study, zinc oxide-based tungstate nanocomposites $FeWO_4$@ZnO at different concentrations were successfully synthesized by hydrothermal method. Three groups of experimental samples were labeled as FZ-1, FZ-2, and FZ-3 according to different proportions. Then, the antibacterial effects of these composites on Escherichia coli and their multiple mechanisms of action were systematically investigated.

In the characterization test of the material, the characteristic diffraction peaks of ZnO and $FeWO_4$ in the composite material were further verified by XRD analysis first, indicating that the composite material in this experiment was successfully synthesized and the crystal structure of the obtained sample was intact. Based on the SEM images, it was observed that the sample presented a nanosheet-like structure with a uniform particle size distribution, with an average particle size of approximately 100 nm. This nanostructure provided a larger specific surface area for the sample, enabling the nanoparticles to have more active sites, which was more conducive to contact with bacteria and the exertion of antibacterial activity. Finally, the samples were analyzed by ultraviolet-visible spectroscopy. It was found that the experimental samples exhibited significant light absorption characteristics within the wavelength range of 220-800 nm. Especially in the ultraviolet region, the absorbance was relatively high within the wavelength range of 220-400 nm, which was exactly consistent with the bandgap characteristics of ZnO. Then, the Kubelka-Munk formula calculation was carried out. It was found that the band gap value of the sample was between pure ZnO and tungstate, which strongly confirmed the formation of a heterojunction structure between zinc oxide and tungstate. The heterojunction can effectively promote the separation of photogenerated electron-hole pairs, improve the photocatalytic efficiency of the sample, and achieve a more ideal antibacterial effect.

In this experiment, the three groups of samples showed significant inhibitory effects on Escherichia coli, and the antibacterial effect under light conditions was significantly better than that under dark conditions. Among them, the sample with the best antibacterial effect was sample 3. Sample FZ-3 could completely inhibit the growth of bacteria around the 120_{th} minute and had superior antibacterial performance. The antibacterial effect is also concentration-dependent. With the increase of tungstate content, the antibacterial performance significantly improves, which indicates that the synergistic effect between the two substances plays a key role in the antibacterial process.

Under light conditions, the composite material generates reactive oxygen species (ROS) through photocatalysis. These substances can damage the cell membranes and internal structures of bacteria, thereby leading to their death. Moreover, the heterojunction structure formed between zinc oxide and tungstate further enhances the photocatalytic efficiency, enabling the nanocomposites to exhibit superior antibacterial properties.

Under dark conditions, although the antibacterial efficacy of the experimental samples in this experiment could not be fully exerted, the bacterial survival rates of the three groups of samples in the experiment were significantly lower than that of the blank control group after the 90th minute. It indicates that even in a dark environment, the samples of this experiment can still exert certain antibacterial properties, which mainly depends on the release of Zn^{2+} and W^{6+} ions. These ions can interfere with the normal metabolic process of bacteria, thereby inhibiting their growth.

The material studied in this thesis simultaneously possesses characteristics such as high efficiency, safety and durability. These excellent properties enable zinc oxide-based tungstate nanocomposites to be applied in aspects such as medical device coatings, food packaging, and water treatment. The nanocomposites explored in this study can provide future challenges for humanity in dealing with bacterial infections. Solving the problem of bacterial drug resistance provides new solutions and can correspondingly reduce the socio-economic costs involved.

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