

银-氧化锌-黑滑石复合材料的制备及抑菌性能

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摘 要: 为获得抗菌性能优良的材料, 选用江西广丰黑滑石作为基体材料制备了 Ag-ZnO/Talc 三元复合材料, 并采用扫描电子显微镜、透射电子显微镜、X 射线衍射和 X 射线光电子能谱等分析手段对复合材料进行表征, 以大肠杆菌和金黄色葡萄球菌为实验菌株采用平板计数法、抑菌圈法对复合材料抗菌性能进行试验。结果表明: 黑滑石的片层状结构促进纳米颗粒分散, 增大复合材料与细菌的接触面积; Ag-ZnO/Talc 三元复合材料具有高的抗菌活性, 对大肠杆菌和金黄色葡萄球菌的抑菌率可达到 99% 以上。

关键词: 黑滑石; 复合材料; 抗菌性能

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Preparation and Antibacterial Properties of Ag-ZnO/Talc

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Abstract: To obtain materials with superior antibacterial properties, Ag-ZnO/Talc ternary composite was prepared by a water-bath heating method with black talc (from Guangfeng, Jiangxi) as a matrix material. The composite was characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy, respectively. *Escherichia coli* and *staphylococcus aureus* were used as the experimental strains. The antibacterial properties of the composite were examined by a plate counting method and a bacteriostatic zone method. The results show that the layered structure of talc sheet promotes the dispersion of nanoparticles and increases the contact area between the composite and bacteria. The Ag-ZnO/Talc composite displays a high antibacterial activity, and the antibacterial rate against *escherichia coli* and *staphylococcus aureus* reaches more than 99%.

Keywords: black talc; ternary composite; antibacterial property

1 Introduction

With the remarkable improvement in people's living

standards and health awareness^[1], people are paying increasing attention to antibacterial materials^[2-4] and related products. Antibacterial materials^[5-8] have been widely used

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in many fields^[9], such as antibacterial masks, antibacterial cases, and bags. Common antibacterial materials can be divided into organic antibacterial agents (e.g. chitosan), inorganic antibacterial agents (ZnO、Ag、CeO₂)^[10-12], and compound antibacterial agents. Among them, inorganic antibacterial materials are widely used because of their good stability and excellent antibacterial performance^[13]. Inorganic antibacterial agents can be divided into photocatalytic bactericidal materials and noble metals. Nano ZnO is a common semiconductor metal oxide with abundant reserves^[14], wide raw materials, low price, and high biocompatibility^[15]. It has been used in water pollution, biomedicine, photocatalysis, and other aspects. When the light energy is larger than the bandgap of ZnO, its bound electron-hole is converted to an excited electron-hole, and the electrons and holes react with water and oxygen to produce reactive oxygen species^[16]. Reactive oxygen species react with proteins, enzymes, and other organic matters in the cell membrane and cytoplasm, affecting the normal physiological metabolism of cells, thus inhibiting bacterial growth and proliferation. As a common inorganic antibacterial agent, Ag series antibacterial materials^[17-18] have the characteristics of high biocompatibility, stable antibacterial performance, and spectral properties. Positive charge Ag⁺ is released from the surface of Ag material^[19-20] and adsorbed to the surface of negatively charged bacteria, which directly reacts with proteins and enzymes of the cell membrane and destroys cell membrane structure. At the same time, Ag antibacterial materials produce reactive oxygen species^[21], which destroy bacterial cell membrane and cytoplasm and inhibit bacterial proliferation. Due to the influence of intermolecular electrostatic attraction and van der Waals force, nanoparticles may have a certain degree of agglomeration when they are used, which hinders their antibacterial performance. At the same time, the long-term use of nanoparticles alone also has potential dangers related to nanometer size, which may have adverse effects on humans and the environment.

Silicate clay minerals have been widely used in biomedicine and sewage treatment in recent years because of their diverse chemical composition and mineral structure, excellent surface charge properties, large specific surface area, and other characteristics that can inhibit the bacteria proliferation to a certain extent. On the one hand, the silicate clay minerals containing Fe, Cu, and other elements can destroy the membrane of Gram-positive bacteria and gram-negative bacteria, and at the same time enter the cell to destroy the cytoplasm, to achieve the purpose of inhibiting bacterial proliferation. Silicate clay minerals content, on the other hand, the permanent negative surface charge caused by lattice replace, mineral edge valence bond rupture caused by variable charge, and adsorption of humic acid on the surface ionization of different factors, such as silicate clay minerals content by physical electrostatic adsorption in the surface of the bacterial cell membrane, affecting

cell permeability, hinder the material exchange between the normal bacteria and its environment. Black talc, one kind of silicate clay mineral, is abundant in China. China has five bases of Black talc deposits in Jiangxi^[22], Liaoning, Guangxi, Shandong, and Qinghai. Among them, Jiangxi Guangfeng has the world's largest reserves of high-grade talcum mines^[23-24]. It is reported that the proven reserves of Guangfeng Black talc are as high as 1 billion tons, and the content of silicon and magnesium exceeds 95%. Talc can be divided into five types according to color: black talc, grey talc, white talc, green talc, and pink talc. Black talc appears black or gray when it contains a certain amount of organic matter. Black talc is a 2:1 layered silicate clay composed of two silicon oxide tetrahedral sheets (T) and a magnesium oxide octahedral (O) with an interlayer thickness of about 0.1 Å. The main components of the black talc deposit are talc, calcite, quartz, sepiolite, and a certain amount of organic matter. As a kind of talc, black talc attracts each other with relatively weak van der Waals forces between layers, so black talc has a set of (001) extremely complete cleavage planes, with the lowest Mohs hardness and more slippery. At present, Black talc is mainly used in traditional fields, such as ceramics^[25], plastics, rubber, and other industries^[26].

In this study, Talc was combined with inorganic antibacterial materials. On the one hand, Silicate clay minerals have an excellent specific surface area, abundant surface hydroxyl groups, and special morphological structures, which provide rich loading sites for nanoparticles^[27-29]. Thus, the nanoparticles can be more evenly distributed on the mineral surface, then the composite materials can maintain excellent antibacterial performance at the reduced use of nanoparticles to some extent. On the other hand, the addition of black talc can save the cost without reducing the antibacterial performance of antibacterial materials. It also responds to the "13th Five-Year Development Plan of Non-metallic Mineral Industry"^[30], providing ideas for modification and functionalization of Talc.

2 Experimental

2.1 Experimental materials and reagents

Black Talc (from Guangfeng Jiangxi); Zn(NO₃)₂·6H₂O (Aladdin Reagent (Shanghai) Co, LTD); AgNO₃ (Aladdin Reagent (Shanghai) Co, LTD); NaOH (Aladdin Reagent (Shanghai) Co, LTD); Talc refers to black talc after calcination in a Muffle furnace at 700 °C; *Escherichia coli* (ATCC25922); *Staphylococcus aureus* (ATCC25923).

2.2 Preparation of Ag-ZnO/Talc composite

First, 1.071 g Zn(NO₃)₂·6H₂O, 0.84 g of black talc calcined at 700 °C for 2 h was dissolved into 90 mL ethanol. A homogenized and stable suspension was formed by ultrasonic agitation at room temperature for 20 min, and the suspension was heated to 75 °C. 0.72 g NaOH was weighed and dissolved in 270 mL ethanol.

Then, the NaOH solution was added to the suspension drop by drop for 60 min. After the dropping, the solution was stirred for 60 min and centrifuged for filtration. The filter cake was washed with DI water three times to remove residual $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NaOH on the surface. Then the sample was placed in an oven at 60°C and dried for 12 h to obtain $\text{Zn}(\text{OH})_2/\text{Talc}$ composite material. Further, $\text{Zn}(\text{OH})_2/\text{Talc}$ composites were calcined in a muffle furnace at 400°C for 4 h to obtain ZnO/Talc .

1.0 g ZnO/Talc 、0.3 g AgNO_3 was added to deionized water (40 mL), and stirred under dark (10 h) to form a homogeneous suspension. After the stirring, the sample was centrifuged and washed for further use. Finally, the $\text{Ag}-\text{ZnO}/\text{Talc}$ antibacterial material was obtained by grinding. Meanwhile, $\text{Ag}-\text{ZnO}/\text{Talc}$ with different silver contents of 5%, 10%, and 16% were prepared by changing the added amount of AgNO_3 . Fig. 1 is a schematic diagram of the steps for the synthesis of $\text{Ag}-\text{ZnO}/\text{Talc}$.

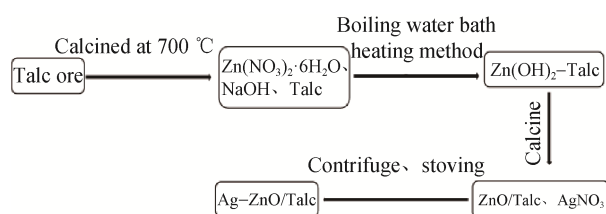


Fig. 1 Schematic diagram of the synthesis steps of $\text{Ag}-\text{ZnO}/\text{Talc}$ composite

2.3 Antibacterial experiment

2.3.1 Preparation of LB medium Preparation of LB liquid medium: 2 g sodium chloride, 2 g tryptone, and 1 g yeast extract were dissolved in 200 mL deionized water. Preparation of LB solid medium: 2 g sodium chloride, 2 g tryptone, 1 g yeast extract, and 3 g agar were dissolved in 200 mL deionized water. The prepared liquid medium and solid medium were sterilized in the autoclave at 121°C for two hours. All the experimental instruments such as centrifugal tubes needed in the antibacterial experiment have been treated aseptically.

Bacterial culture: Firstly, a tube of 1.5 mL *Escherichia coli*, *Staphylococcus aureus* was taken out from the -80°C refrigerator to thaw, then 20 μL of thawed strains was added to 20 mL of the liquid medium in an ultra-clean bench, the centrifuge tube containing bacteria liquid and liquid culture medium was sealed and placed into a shaking table with the temperature set at 37°C and speed set at 180 r/min for 13 h for a subsequent experiment. 500 μL of overnight cultured bacteria were diluted to 10^5 – 10^6 CFU/mL, so the initial colony concentration was 10^5 – 10^6 CFU/mL.

2.3.2 Antibacterial experiment All instruments used in the experiment need to be further sterilized on the ultra-clean workbench for 30 min before use. On the sterilized ultra-clean workbench, 0.5 mL of the bacteria

liquid cultured on the shaking table was added to the 4.5 mL liquid medium and stirred evenly on the stirrer. Then 0.5 mL of the bacteria liquid that was evenly stirred was added to the 4.5 mL liquid medium and stirred evenly again with the stirrer. This operation was repeated four times in total. 100 μL of the final bacterial solution was added to the liquid medium, and 0.001 g of $\text{Ag}-\text{ZnO}/\text{Talc}$ powder was added simultaneously. In the blank group, 100 μL of bacterial solution and 10 mL liquid medium were added and then placed into the shaking table with the temperature set at 37°C and speed set at 180 r/min for 4 h.

2.3.3 Bacterial coating First, the solid petri dish and instrument used for coating were put on the ultra-clean workbench for sterilization for 30 min. Then, the solid medium was heated and melted in the microwave oven and poured into the sterilized solid petri dish until it solidified and covered. After 4 h culture, the bacterial solution was added to a liquid medium, and the operation was repeated three times. 50 μL of the final diluted bacterial solution was added to the poured solid petri dish, and four sterile glass beads were added to shake to make the bacterial solution evenly coated. Three groups of experiments were set up in parallel. The coated Petri dishes were placed in a constant temperature incubator at 37°C for inverted incubation for 15 h. The antibacterial activity of ZnO was easily affected by light. All experiments were carried out under light conditions

2.4 Detection of antibacterial properties

2.4.1 Colony count The cultured plate was placed in a gel imaging system, and the colony count method was used to detect the colony count of *Escherichia coli*/*Staphylococcus aureus*.

2.4.2 Bacteriostatic ring The $\text{Ag}-\text{ZnO}/\text{Talc}$ composite powder was placed on a sterile and dry filter paper with a diameter of 5 mm. Then, DI water was dropped on the filter paper. Add 50 μL of the bacterial solution diluted four times in the antibacterial experiment to the solid medium, then add glass beads to the solid medium four times to coat the bacterial solution evenly, and let the bacterial solution dry for 3 min. At the same time, the filter paper without powder was set as blank control. Finally, the plate was placed in a constant temperature incubator at 37°C for 15 h. The diameter of the antibacterial ring was measured with Vernier calipers, and the average value was taken three times. Criteria: If the diameter of the bacteriostatic ring is greater than 7 mm, it is judged to have a bacteriostatic effect; If the bacteriostatic ring is less than or equal to 7 mm, it is judged to have no bacteriostatic effect. Three times repeated experiments have achieved the results of the bacteriostatic effect, judged as qualified. There was no change in the bacteriostatic ring in a blank group, otherwise, the experiment was invalid.

2.5 Characterization methods

The crystal phase composition of the samples was

analyzed by a Bruker D8 Advance X-ray diffractometer with a range of 10° – 80° , at a scanning speed of $10(^{\circ})/\text{min}$; the surface morphology of the sample was observed by HITACHI scanning electron microscope to judge whether the composite was successfully prepared; the morphologies and structures of the samples were observed by Thermo Fisher Scientific Talos F200x transmission electron microscope.

3 Results and discussion

3.1 Characterization of structure and morphology

3.1.1 Scanning electron microscope Fig. 2 shows the micromorphology of Talc(Fig. 2(a)), ZnO(Fig. 2(b)),

ZnO/Talc(Fig. 2(c)) and Ag–ZnO/Talc (Fig. 2(d)) under scanning electron microscope. Fig. 2 shows that when black talc is calcined to 700°C , the layers are stacked in lamellar form, the stacking is relatively close, and the particles are relatively small. ZnO(Fig. 2(b)) is uniformly spherical. When ZnO(Fig. 2(c)) is loaded on the surface of Talc, a relatively uniform spherical load can be seen on the lamellar structure, indicating that talc provides a loading site for ZnO. The EDS energy spectrum results in Fig. 2(d) show that the composite contains Ag, O, Mg, Zn, and Si. Fig. 2(d) shows the Ag–ZnO/Talc ternary composite with ZnO nanoparticles and Ag-based antimicrobial materials loaded on the Talc lamellar structure.

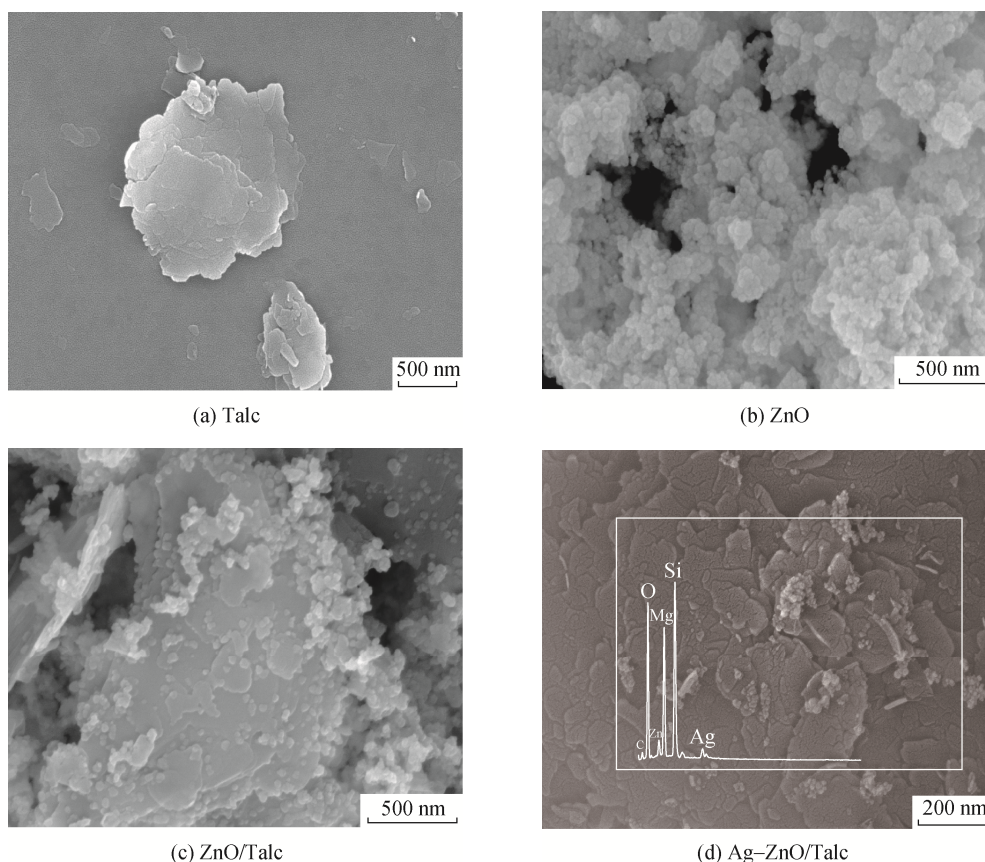


Fig. 2 SEM images of Talc, ZnO, Talc, Ag–ZnO/Talc

3.1.2 Transmission electron microscope Fig. 3 shows that TEM micrographs of Talc(Fig. 3(a)), ZnO(Fig. 3(b)), ZnO/Talc(Fig. 3(c)), Ag–ZnO/Talc(Fig. 3(d)). Fig. 3(a) shows the TEM morphology and energy spectrum of Talc calcined at 700°C . As shown in Fig. 3(a), Talc is a lamellar clay mineral, and the uneven lamellar structure of Talc can also be observed at the grain edge, mainly composed of Si, Mg, O, and other elements. Fig. 3(b) shows ZnO nanoparticles prepared by water bath in an alcohol solution. It can be seen that the size distribution of nanoparticles is relatively uniform, about 20–40 nm. Under the influence of van der Waals force and electrostatic attraction, ZnO nanoparticles agglomerate seriously. Fig. 3(c) shows

the TEM morphology of Ag–ZnO/Talc ternary composite with a silver loading of 16%. Mg and Si in the Mapping corresponded to the elements of Talc itself, and the uniformly distributed Zn, O and Ag elements can further prove that ZnO and Ag are uniformly loaded on the layered structure of talc sheet in the ternary composite. Fig. 3(c) shows the TEM morphology of the Ag–ZnO/Talc ternary composite. The Si and Mg in the figure correspond to elements of talc itself, the C element is partly derived from black talc and partly forms silver carbonate, and the Zn, O and Ag elements can be further demonstrated by the loading of ZnO, Ag and Ag_2CO_3 on the lamellar structure of talc flakes in the ternary composites.

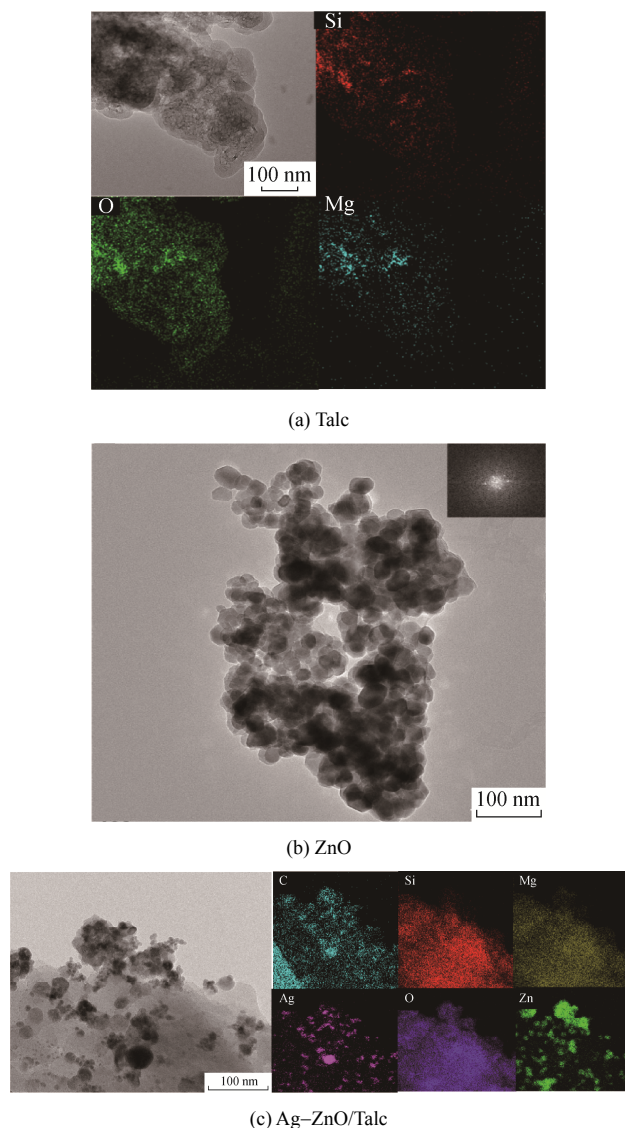


Fig. 3 TEM micrographs of Talc, ZnO, Ag-ZnO/Talc

3.1.3 X-ray diffraction X-ray diffraction patterns of Talc, ZnO, ZnO/Talc, and Ag-ZnO/Talc with different silver loading (5%, 10%, 16%) were shown in Fig. 4. When $2\theta=28^\circ$, the d value is $3.11 \text{ \AA}$. In addition, it can

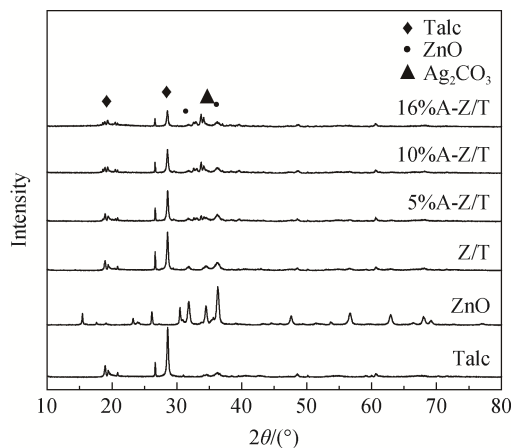


Fig. 4 XRD patterns of Talc, ZnO, ZnO/Talc, and Ag-ZnO/Talc with different silver loading

also be seen that the peak position of (221) is near $4.77 \text{ \AA}$, but the peak strength is relatively weak. In the synthesized ZnO/Talc and Ag-ZnO/Talc composites with different loadings, the characteristic peaks $2\theta=18^\circ$ and 28° for Talc, $2\theta=36^\circ$ for ZnO, and $2\theta=33^\circ$ for elemental silver were observed, which implies the successful preparation of ZnO/Talc binary composites and Ag-ZnO/Talc composites with different elemental silver loadings (5%, 10%, 16%) of Ag-ZnO/Talc ternary composites.

3.1.4 X-ray photoelectron spectroscopy To further characterize the presence of Ag nanoparticles in Ag-ZnO/Talc ternary composites, XPS characterization was carried out to verify the valence distribution of Zn and Ag elements. The full spectrum of XPS shows that the ternary materials contain Zn, Mg, O, Si, Ag, and other elements. The elements Si and Mg correspond to the elements contained in Talc itself, and the elements O and Zn correspond to the loaded ZnO nanoparticles. The symmetrical peaks at 1021.5 eV and 1044.8 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, indicating that zinc exists in the composite as divalent zinc, which is the synthesized nano-ZnO. Ag XPS results show that the characteristic diffraction peaks at 367.0 eV and 373.0 eV correspond to Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, indicating the existence of elemental Ag in the ternary composites.

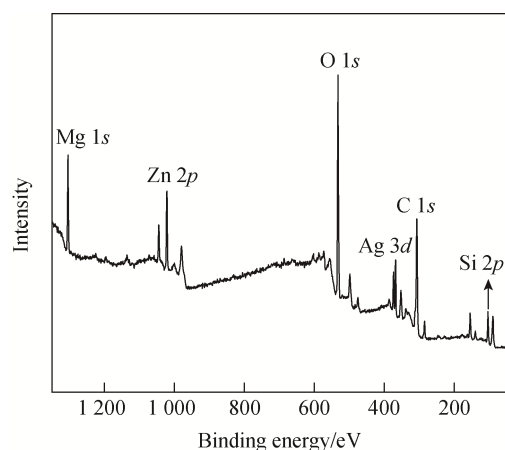
3.2 Antibacterial properties of Ag-ZnO/Talc composite

3.2.1 Colony count The antibacterial properties of Talc, ZnO, ZnO/Talc, and Ag-ZnO/Talc (5%, 10%, 16%) were studied by plate counting method by using *Escherichia coli* and *Staphylococcus aureus* as experimental strains. As shown in Fig. 6, there is no significant difference in the number of *Escherichia coli* or *Staphylococcus aureus* colonies in the Talc-treated group compared with the blank control group, indicating that Talc calcination at 700°C did not have an obvious antibacterial effect. Compared with the blank control group, the colony number of *Escherichia coli* culture plate treated with ZnO was significantly reduced, indicating that the prepared ZnO nanoparticles had a certain antibacterial effect; the colony numbers of *Escherichia coli* and *Staphylococcus aureus* after ZnO/Talc treatment were significantly reduced, and the antibacterial performance of ZnO/Talc composite was improved; the colony number of *Escherichia coli* and *Staphylococcus aureus* treated with ternary Ag-ZnO/Talc (5%, 10%, 16%) was 0, indicating that Ag-based antimicrobial materials doping could further improve the antibacterial performance of ZnO/Talc binary materials.

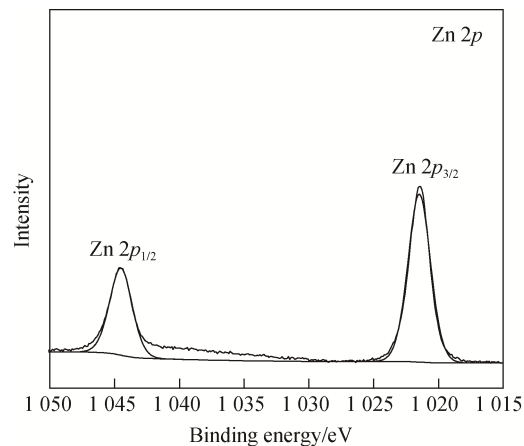
Further, colony count was carried out on Petri dishes in the experimental process by the gel imaging system and the average value was taken for statistics. Fig. 7 shows the average colonies number of *Escherichia coli* and *Staphylococcus aureus* with different treatments. Talc, ZnO, ZnO/Talc group had a slightly stronger effect on *Escherichia coli* than *Staphylococcus aureus* after

co-culture with bacteria for 15 h. Ag-ZnO/Talc (5%, 10%, 16%) ternary composites had similar antibacterial

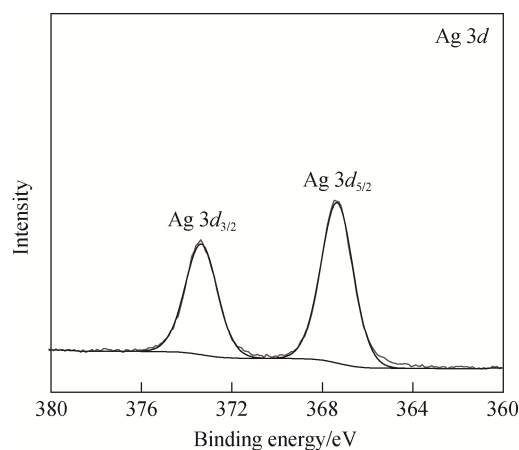
effects on *Escherichia coli* and *Staphylococcus aureus*, which reached more than 99%.



(a) Full-range XPS survey spectrum of Ag-ZnO/Talc



(b) Zn spectrum of Ag-ZnO/Talc



(c) Ag spectrum of Ag-ZnO/Talc

Fig. 5 Full-range XPS survey spectra of Ag-ZnO/Talc, Zn and Ag spectrum of Ag-ZnO/Talc

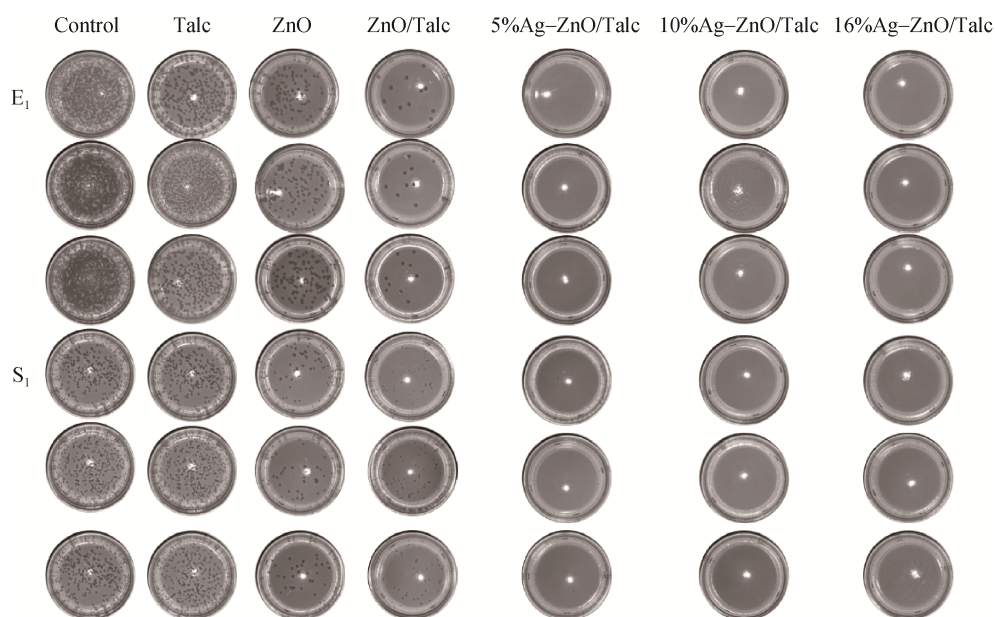


Fig. 6 Growth status of *Escherichia coli* and *Staphylococcus aureus* treated with blank control, Talc, ZnO, ZnO/Talc, Ag-ZnO/Talc

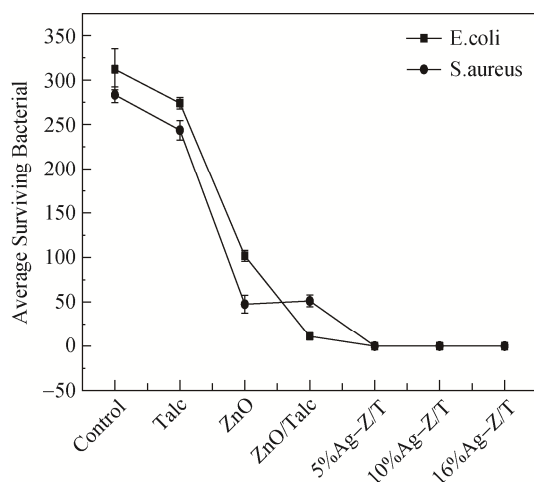


Fig. 7 Average surviving bacterial of *E.coli* and *S.aureus* treated with Talc, ZnO, ZnO/Talc, Ag–ZnO/Talc

3.2.2 Bacteriostatic ring Fig. 8 shows the effects of Ag–ZnO/Talc (5%, 10%, 16%) on *Escherichia coli*. Fig. 9 shows the effects of Ag–ZnO/Talc (5%, 10%, 16%) on *Staphylococcus aureus*. When the inhibition zone was directly larger than 7 mm, the sample was considered to be bacteriostatic. The antibacterial zones of Ag–ZnO/

Talc (5%, 10%, 16%) composites were found to be much larger than 7 mm, indicating that the composite has a strong inhibitory effect on *Escherichia coli*. Talc as a carrier improves the dispersity of ZnO nanoparticles, and effectively alleviates the problem of easy agglomeration of nanoparticles, thus improving the generation of ZnO reactive oxygen species. The layered structure and surface groups of Talc are tightly bonded with Ag-based antimicrobial materials and ZnO, which can immobilize the loaded ZnO nanoparticles and Ag-based antimicrobial materials, thus improving the antimicrobial stability of the ternary composites. In the *Escherichia coli* experiment, when the silver load reached 10%, the average diameter of the antibacterial ring was the largest, but there was no significant difference compared with the experimental results of other loads. In the *Staphylococcus aureus* experiment, the average diameter of the antibacterial ring was the largest when silver loading reached 5%, but there was no significant difference between the same and other experimental results. Considering the popularity of composite materials in the future, we recommend choosing the 5% silver-based composite materials with a similar effect but lower cost.

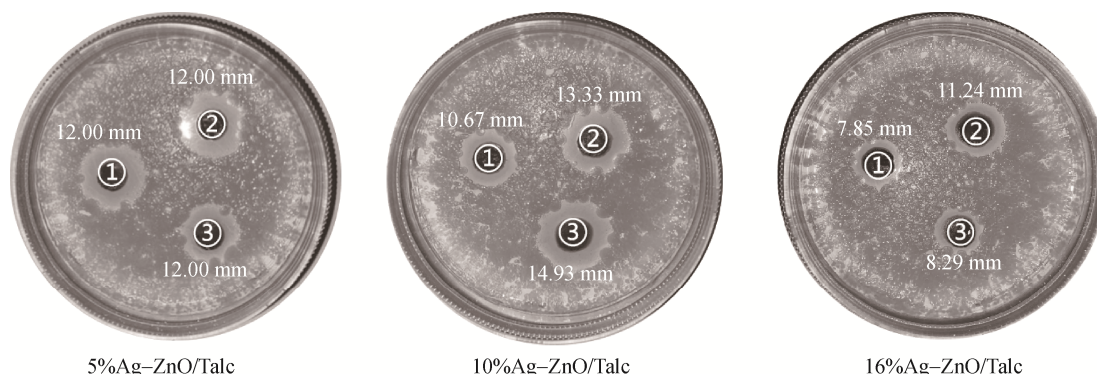


Fig. 8 Schematic diagram of the antibacterial zone of Ag–ZnO/Talc composites with different silver loading against *Escherichia coli*

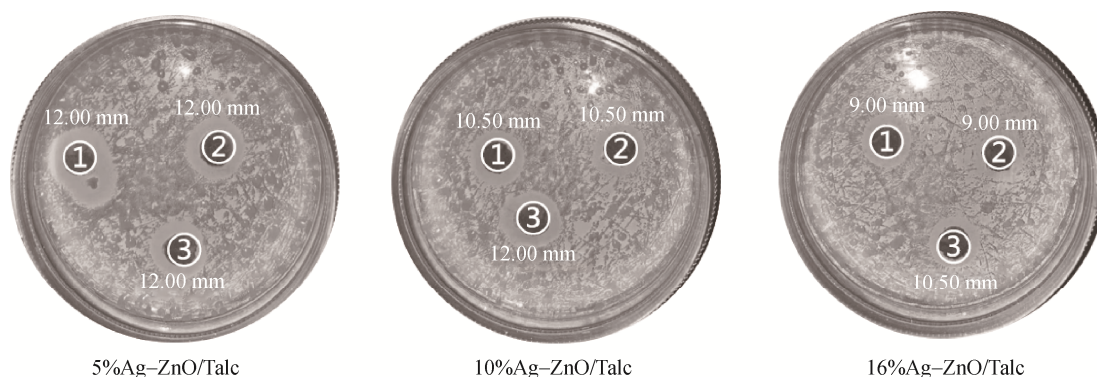


Fig. 9 Schematic diagram of the antibacterial zone of Ag–ZnO/Talc composites with different silver loading against *Staphylococcus aureus*

4 Conclusions

1) In ZnO/Talc binary composites, Talc layered structure as a carrier material can enhance the dispersion

of ZnO nanoparticles and alleviate their easy agglomeration.

2) The antibacterial experimental results show that the antibacterial performance of the composite can be greatly improved by loading Ag-based antimicrobial

materials on the ZnO/Talc surface.

3) Among Ag-ZnO/Talc (5%, 10%, 16%) ternary composites, the antibacterial rate against *Escherichia coli* and *Staphylococcus aureus* reached more than 99%, the bacteriostatic effect is obvious.

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