# Facile preparation of sepiolite-based composites and their antibacterial/rheological properties

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**Abstract** Natural sepiolite has great potential for application in wound healing, hemostasis, and medicines. This paper introduces a versatile solid-state sintering technique for preparing sepiolite-based nanocomposites with enhanced antibacterial properties, the physical, structural, rheological, and antibacterial properties of which were determined to be enhanced. The incorporation of nanosized Ag and metal oxides into sepiolite composites results in a notable improvement in their antibacterial efficacy against E. coli and S. aureus in comparison to the unmodified sepiolite. With a low silver content of just 5%, the sepiolite/Ag composite achieves an antibacterial rate of approximately 100%. Furthermore, the rheological properties exhibited by the sepiolite composites are noteworthy, suggesting their suitability for use in wound dressing applications due to their exceptional workability. The methodology employed in this research has the potential to offer a viable substitute for the production of economical and effective natural antibacterial nanocomposites.

**Keywords:** sepiolite; composites; antibacterial properties; rheological behavior; metal oxides



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## 1. Introduction

Sepiolite, a natural fibrous clay mineral, is characterized by a significant external surface area, which presents promising prospects for the development of nanocomposites (Jiang et al., 2021b; Jiang et al., 2020; Jiang et al., 2024; Kose et al., 2005). The structure of sepiolite comprises alternating blocks and channels aligned along the fiber direction(Alves et al., 2020; Zhou, Wang, et al., 2022). Within its framework, two tetrahedral silica sheets encase a central octahedral sheet that contains magnesium, forming the fundamental unit of the sepiolite structure. The presence of numerous Si-OH groups on the surface, a result of the tetrahedral silica sheets, endows sepiolite with a variety of applications in fields such as adsorption, catalysis, and energy storage and conversion (X. Huang et al., 2024; Junior et al., 2020; Vilarrasa-García et al., 2017). Nevertheless, the raw sepiolite's specific surface area was insufficient to satisfy the demands of practical applications. To address this, various methods, including acid treatment, heat treatment, and surface modification, have been utilized to increase the specific surface area and, consequently, enhance the physical properties of sepiolite (Dutta & Devi, 2021; Pang et al., 2022; Wu et al., 2017). However, the aforementioned methods for modifying sepiolite often require reactions to be carried out in a solution, which are cumbersome, time-consuming, and not environmentally friendly.

Among the techniques mentioned, acid treatment is commonly used to increase the surface area and reduce impurities in sepiolite (Franco et al., 2014; Valentín et al., 2007). However, this method is not environmentally friendly as it can generate effluents. Fabricating sepiolite composites presents an alternative approach to improve the physical properties of sepiolite. The in-situ production of crystalline nanoparticles on the sepiolite surface has been widely reported in recent literature(Aranda & Ruiz-Hitzky, 2018; Ma & Zhang, 2016). The development of sepiolite-based nanoarchitectures holds great promise for a range of applications in next-generation functional materials. Various sepiolite/metal oxide composites have been synthesized



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using methods such as the sol-gel process(Zhang et al., 2011), solvothermal synthesis(Liu et al., 2018), and other wet chemical techniques(Song et al., 2023). For example, sepiolite-$TiO_2$ nanocomposites were synthesized by microwave hydrothermal (M-H) treatment, which showed relatively uniformly distributed $TiO_2$ particles on the sepiolite surface without visible aggregation(Zhou et al., 2018). Additionally, sepiolite/$Cu_2O$/Cu ternary composites have been successfully synthesized using a hydrothermal method, with sepiolite serving as a nonremovable template(Zhou, Jiang, et al., 2022). These composites have demonstrated excellent electrochemical performance as anodes in Li-ion batteries. $Fe_2O_3$/sepiolite magnetic materials, synthesized via chemical co-precipitation, have potential applications as effective adsorbents for the removal of anionic dyes, such as Congo red, from aqueous solutions(Wang et al., 2018). However, many of these synthesis methods rely on the use of harmful chemicals and involve complex fabrication processes(Uygun et al., 2023). Consequently, there is an urgent need to develop greener techniques that are cost-effective, efficient, and environmentally friendly for the preparation of sepiolite/metal oxide composites. Nowadays increased interest has been focused on various clays groups to fabricate wound dressing materials(Dutta & Devi, 2021; Hardt et al., 2021; Xiaojuan Huang et al., 2024; Tavakoli, 2017). Sepiolite, due to its excellent absorption capacity for exudates, has a broad application prospect in wound dressings. However, powdered sepiolite cannot be directly used for wound treatment. It is reported in literature that sepiolite is commonly combined with materials such as chitosan and gelatin to prepare wound dressings(Liu et al., 2016). This process requires complex techniques and is not suitable for large-scale preparation. Therefore, developing a large-scale green preparation method for sepiolite wound dressings remains a challenge.

Recently, we reported on a sepiolite composite material for rapid hemostasis (Jiang et al., 2023). Zeolite-based nanomaterials have been proved to be one of the most effective hemostatic materials owning to the high water-adsorption capability and acceleration in the coagulation of



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the blood(Zhang et al., 2021; Zheng et al., 2023). However, zeolite-based hemostatic materials may cause potential tissue injury due to the exothermic physical effect, greatly limiting their application as hemostatic agents. Compared with the commercial zeolite materials, the sepiolite composite exhibits competitive hemostatic properties without exothermic reaction. The current key lies in developing green technologies for large-scale preparation of sepiolite composite materials. In this study, we propose a versatile solid-state sintering method for the preparation of sepiolite-based nanocomposites with improved antibacterial properties. This method is notable for its safety, cost-effectiveness, and time efficiency. Utilizing readily decomposable metal acetates, nanoparticles are generated in-situ on the sepiolite surface at low sintering temperatures. The resulting sepiolite-based composites demonstrate significantly enhanced antibacterial properties when compared to the raw sepiolite materials. By employing this method, the unique properties of sepiolite are leveraged to create nanocomposites with a broader range of applications, particularly in the field of antibacterial materials and wound dressings. The low-temperature sintering process not only ensures the safety and environmental friendliness of the procedure but also reduces the overall production costs and time, making it a viable option for large-scale applications.

## 2. Experimental

### 2.1 *Materials and chemicals*

Sepiolite (Sep) powders (purity ~70%) were provided by Xiangtan sepiolite Technology Co., Ltd. (Hunan, China). Silver acetate ($CH_3COOAg$), Copper acetate monohydrate ($C_4H_6CuO_4 \cdot H_2O$), Zinc Acetate ($C_4H_6O_4Zn$) and sodium chloride (NaCl) were purchased from Macklin Chemical Co., Ltd. Tryptone, yeast, E. coli, agar and S. aureus were provided by Xiangya Hospital (Hunan, China). All the materials and chemicals were used without further purification.

### 2.2 *Preparation of materials*



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In this paper, we proposed a universal solid-state sintering method for the preparation of sepiolite-based nanocomposites. Firstly, sepiolite powders and $CH_3COOAg$, $C_4H_6CuO_4$, and $C_4H_6O_4Zn$ were mixed in a certain proportion (9:1, 9:1.74, and 9:1.53), respectively. This mixture was then placed into a ball milling tank and further mixed for 10 minutes at 500 rpm. Subsequently, the resulting powder was transferred into a muffle furnace and heated at a rate of 4°C per minute to a final temperature of 500°C, where it was maintained for a duration of 5 hours. Upon completion of the heating process, the furnace was allowed to cool down naturally to room temperature. The final product that was obtained after this cooling process was then ball-milled for an additional 10 minutes at 500 rpm. The resulting samples were designated as Sep/Ag, Sep/CuO, and Sep/ZnO, corresponding to the respective metal oxides incorporated into the sepiolite matrix.

**2.3 *Characterization of materials***

Following gold sputtering, the samples were examined using a field-emission scanning electron microscope (FE-SEM, ZEISS Sigma-300). The structural characteristics of the composites were analyzed by X-ray diffraction (XRD) on a Rigaku SmartLab SE X system. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-F200 microscope. The antibacterial activities of the composites were evaluated using E. coli and S. aureus as model bacterial strains. Further details are provided in the Supporting Information.

**2.4 *Rheological experiments***

For medical materials and wound dressings, good rheological properties can ensure the conformity of the wound dressing to the wound surface during application, and also affect the moisture retention capability of the wound dressing. In the development of new medical materials, it is essential to consider their rheological characteristics comprehensively to achieve optimal therapeutic outcomes and patient experience. Rheological experiments on the material were performed using an Anton Paar MCR 301 rheometer. The material was mixed with water to form a sample with flow-like viscosity, and a 25 mm diameter cone-plate geometry was utilized for



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the tests. In the shear rate-viscosity test, the shear rate was varied over a range from $10^{-2}$ to 10.0 ($s^{-1}$). For the dynamic strain sweep, the strain amplitude was incrementally increased from 0.1% to 100%, with the frequency maintained at 5.0 Hz. The thixotropy test involved subjecting the sample to a 1% strain for 120 seconds, followed by an 80% strain for 60 seconds, both at a frequency of 5.0 Hz. This cyclic procedure was repeated a total of seven times. Throughout the testing, the environmental conditions were meticulously controlled, with the temperature set at 25°C and the relative humidity maintained at 50%.

## 3. Results and discussion

The schematic representation of the sepiolite-based composites' preparation process is depicted in **Fig.1**. The natural tendency of sepiolite fibers to agglomerate significantly impacts their dispersibility within composites (Chivrac et al., 2010; García et al., 2011; Zhou, Wang, et al., 2022). In this study, precursors were synthesized by ball-milling pristine sepiolite powder in the presence of solid metal acetates. The inclusion of metal acetates enhances the dispersibility of the sepiolite fibers by reducing the interactions between them. Consequently, the sepiolite fibers act to curb the growth of nanoparticles within the composites. Following the heat-treatment process, a secondary ball-milling step is conducted to further refine the particle size of the sepiolite-based composites. This methodology offers several notable advantages: Firstly, the preparation of the sepiolite-based composites does not require the use of solvents or water. Secondly, the entire preparation process is significantly more time-efficient and cost-effective compared to traditional wet chemical synthesis methods.



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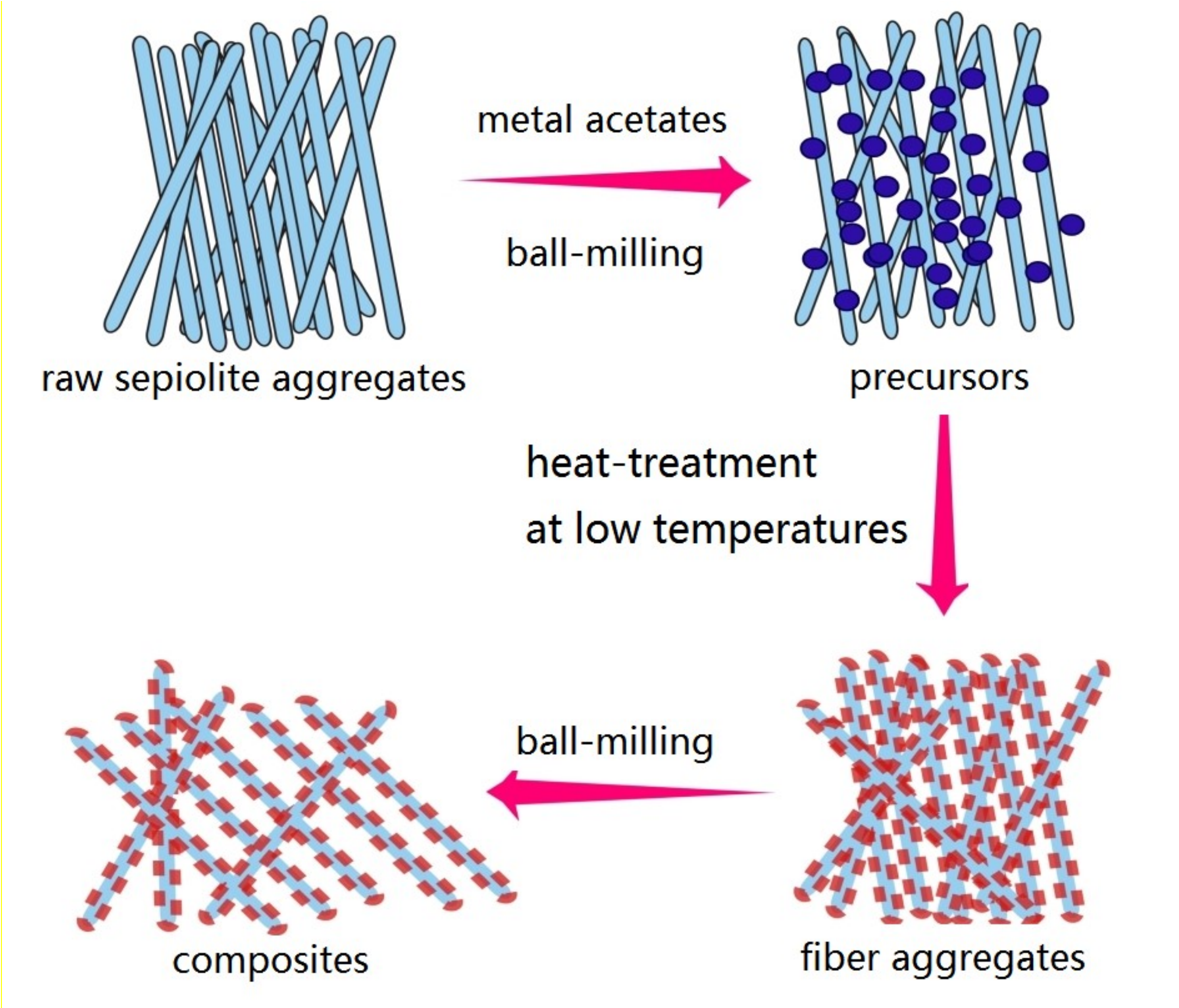


**Fig.1** Schematic diagram of preparation procedure for the sepiolite-based composites



The SEM images of the as-prepared raw sepiolite and the sepiolite-based nanocomposites are presented in **Fig.2**. The raw sepiolite displays a fibrous morphology with fiber diameters ranging from approximately 20 nm to 30 nm, as depicted in **Fig.2a**. Some of the sepiolite fibers are stacked to form sheet-like structures. The presence of impurities, primarily calcite and talc, in the sepiolite clay results in a significant number of nanoparticles observable within the raw sepiolite sample. As shown in **Fig.2b**, the sepiolite/Ag composites exhibit a fibrous morphology that closely resembles the structure of the pristine sepiolite. Following heat treatment, the fibrous morphology of the composites becomes more distinct. However, the presence or absence of Ag

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nanoparticles within the composites could be definitively ascertained. The sepiolite/CuO and sepiolite/ZnO composites, as illustrated in **Fig.2c** and **2d**, respectively, display morphological features that are similar to those observed in the sepiolite/Ag composites. This consistency suggests that the reaction mechanism proposed earlier aligns well with the observed experimental findings. TEM characterization was employed to confirm the morphology of the sepiolite-based composites. For instance, a substantial number of Ag nanoparticles are observable in the TEM images of the sepiolite/Ag composites, as depicted in **Fig.3**. The majority of these Ag nanoparticles are found to be tightly affixed to the surface of the sepiolite fibers. The particle size analysis is presented in **S2**. The average diameter of the nanoparticles, as measured from this figure, is approximately 8 nm. It is known that Ag nanoparticles with smaller particle sizes exhibit more potent antibacterial effects.The findings suggest that the sepiolite fibers effectively restricted the growth of Ag nanoparticles, as postulated in the mechanism analysis. In the high-resolution TEM image (**S1**), the lattice spacing of 0.238 nm, corresponding to the (111) plane of the Ag nanoparticles, is clearly discernible (Chen et al., 2016). These results confirm that the synthesis of ultrafine Ag nanoparticles was successful, as anticipated.



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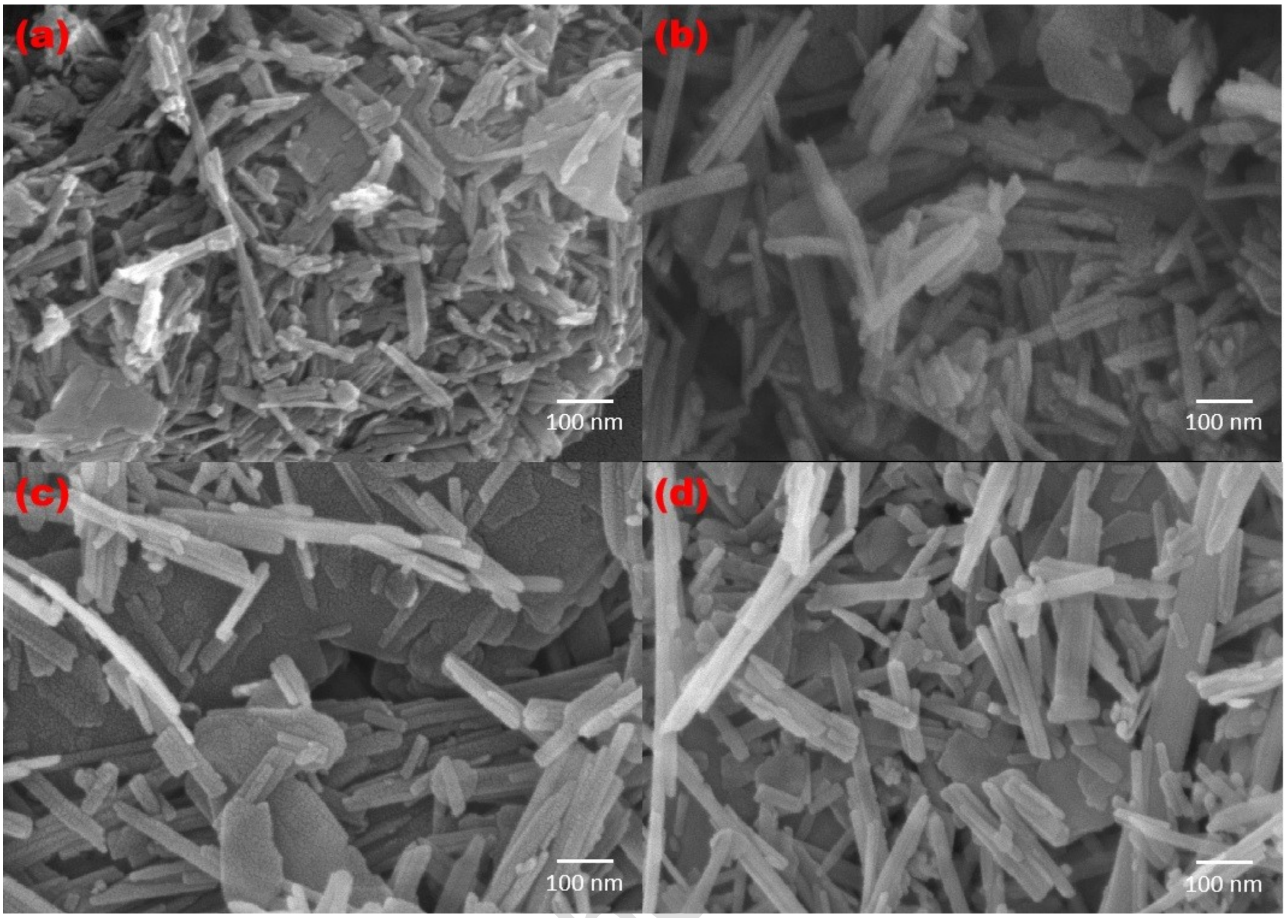


**Fig.2** SEM images of the as-prepared raw sepiolite and sepiolite-based nanocomposites. (a) Sep; (b) Sep/Ag; (c) Sep/CuO; (d) Sep/ZnO.



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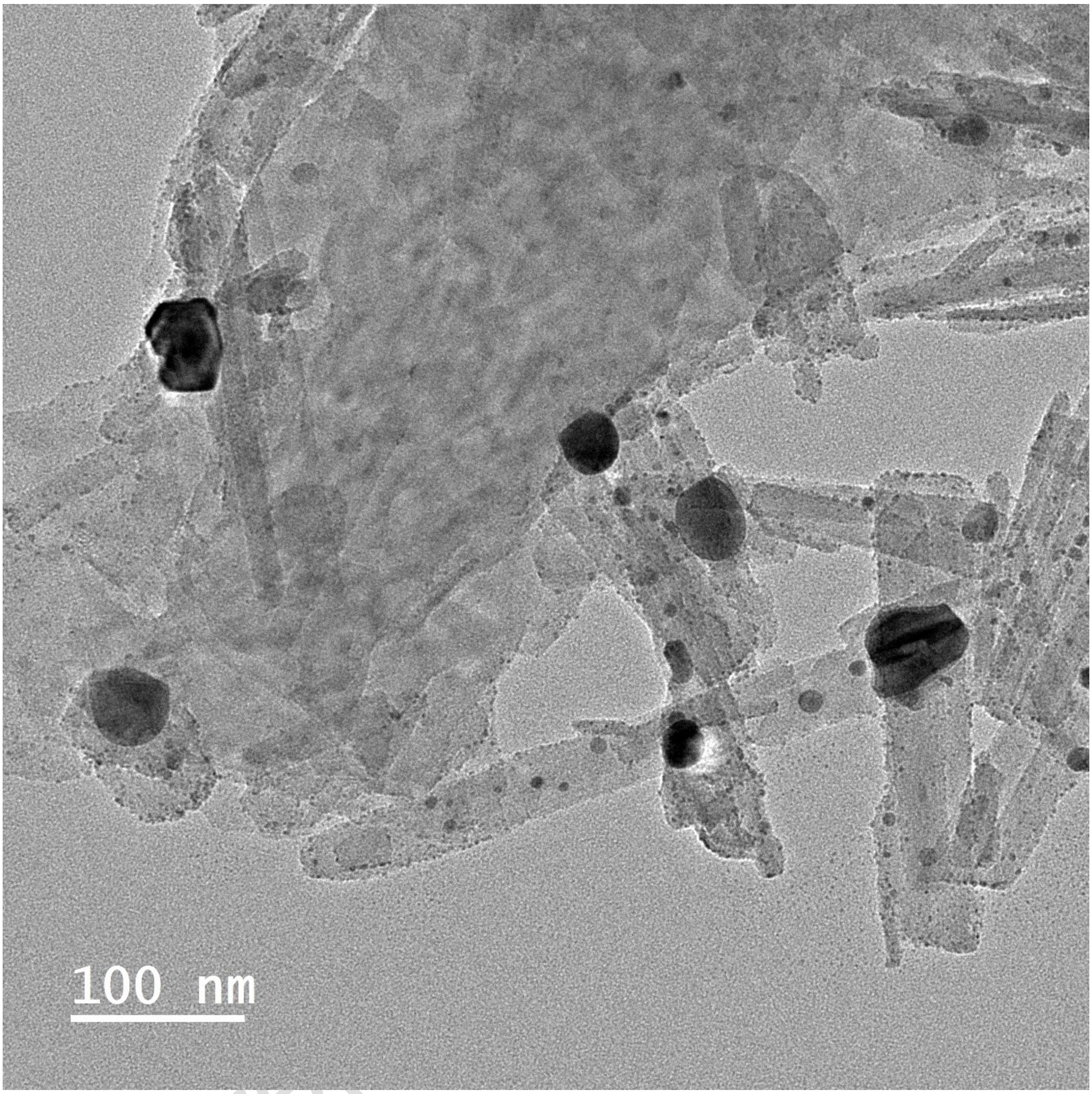




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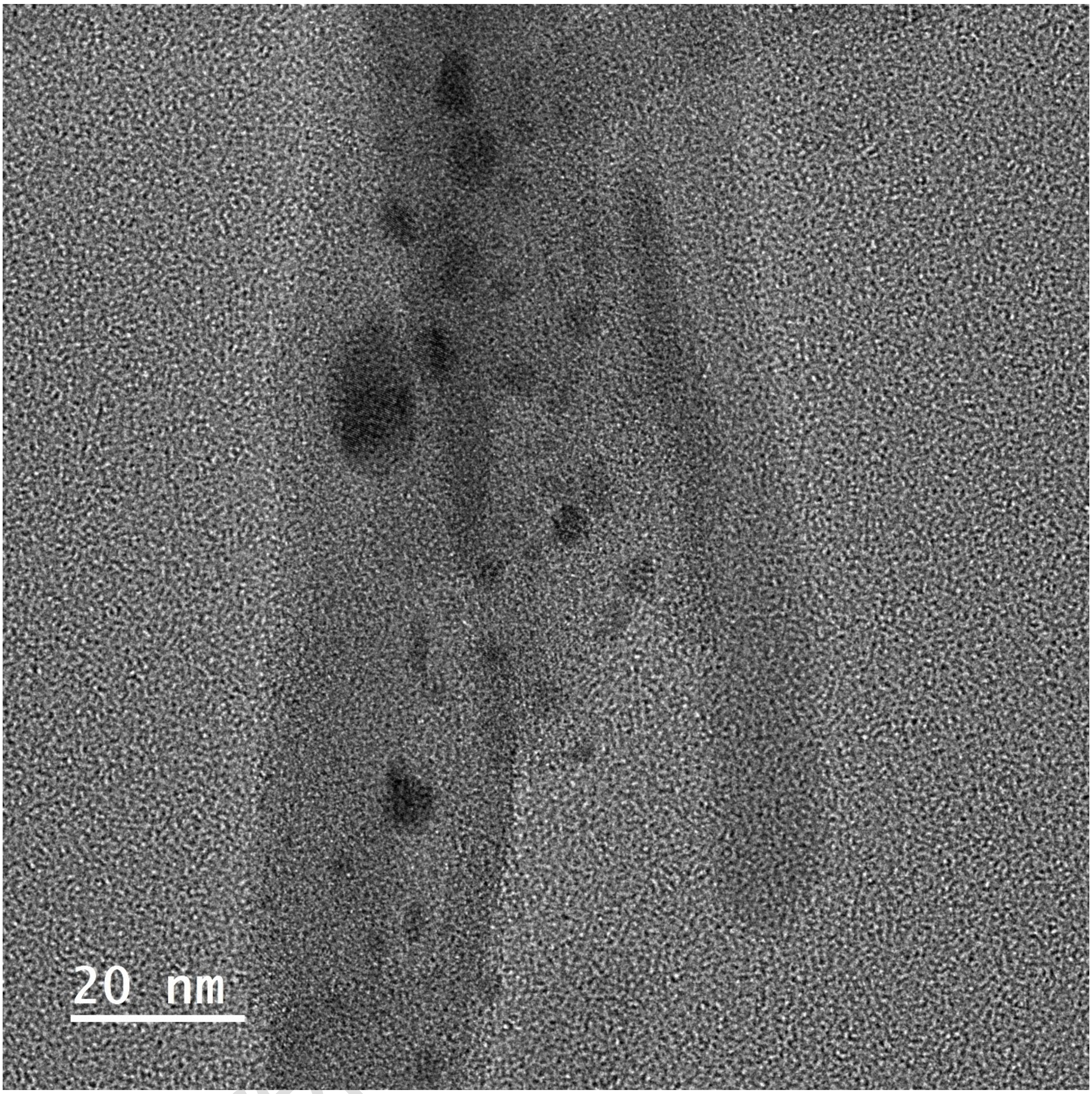


**Fig.3** TEM images of the as-prepared sepiolite/Ag composites.

The crystal structure of the composites was further investigated by XRD analysis as shown in **Fig.4**. The diffractogram of the pure sepiolite exhibits characteristic reflections of the unaltered microfibrous clay. The reflections at $2\theta = 7.2°$, $20.6°$, $26.6°$ and $35.0°$ correspond to the primary diffraction of the (110), (131), (040), and (400) planes of sepiolite (Jiang et al., 2021a), respectively. After modification, the characteristic diffraction peaks of sepiolite can still be observed, indicating the crystal structure of sepiolite has not been destroyed. The characteristic

XRD peaks of ZnO, CuO and Ag nanoparticles are found in the patterns (Ding et al., 2023; Ding et al., 2019). The XRD analysis demonstrates that the approach proposed in this work could be successfully used to prepare sepiolite-based composite. The EDS analysis of the as-prepared composites is shown in **S3-S5**. Ag, Cu and Zn elements can be detected in the composites. The element analysis indicates that the elemental content (>95%) in the as-prepared composite materials is significantly higher than that in the materials prepared using the hydrothermal method, indicating that the solid-phase sintering technology we proposed is more efficient. The reason is that during the solid-phase sintering process, elements such as Ag, Cu, and Zn are essentially not lost.

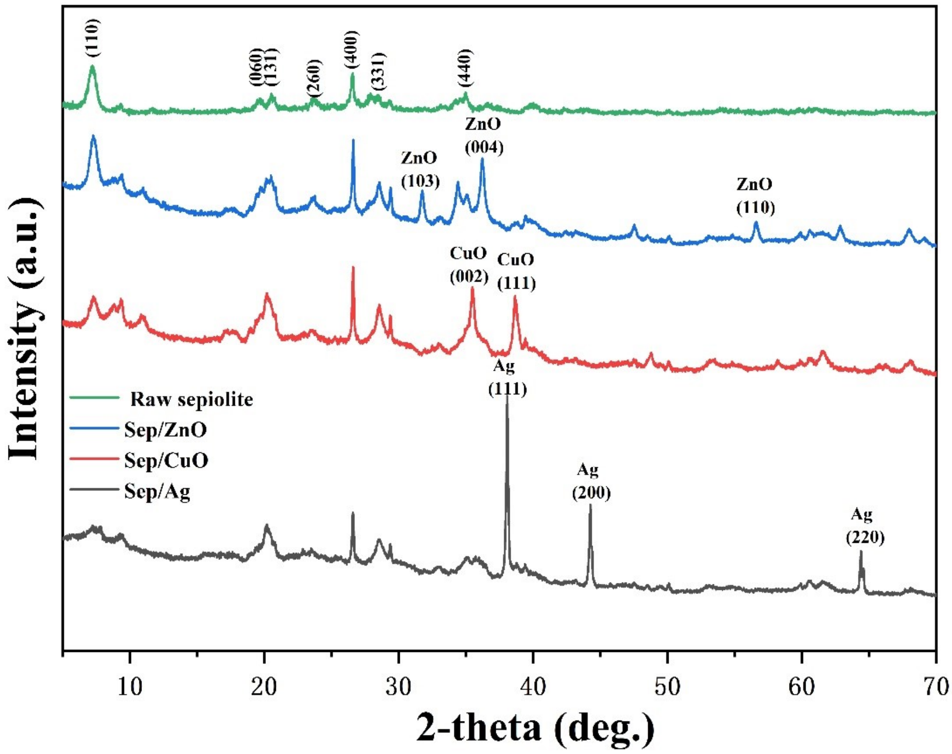


**Fig.4** XRD patterns of the as-prepared sepiolite-based composites

Sepiolite holds significant potential for the development of sustainable antibacterial materials, suitable for applications in food packaging, cosmetics, drug delivery systems, and implantable

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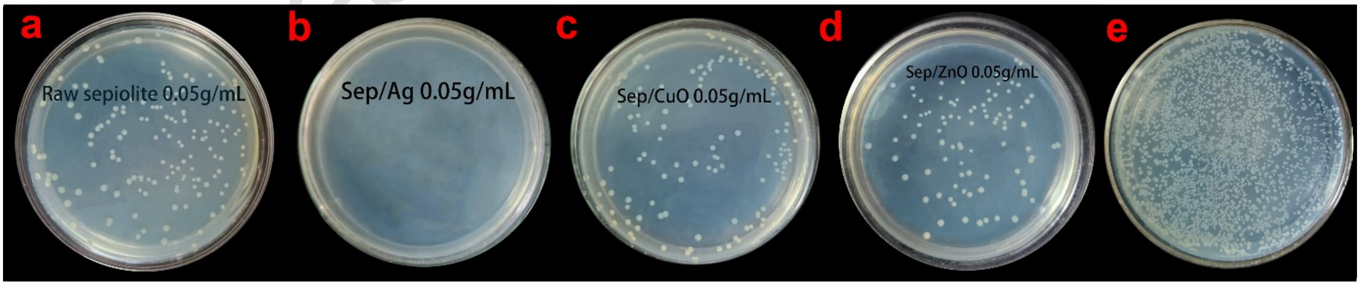
devices (Lisuzzo et al., 2020; Yang & Wang, 2022). However, raw sepiolite materials have been found to be ineffective against bacteria such as E. coli and S. aureus (Benli & Yalın, 2017). A particularly effective strategy is the combination of sepiolite with nanoparticles like Ag and Cu (Benli & Yalın, 2017; Díez et al., 2017; Esteban-Cubillo et al., 2006). The antimicrobial activity of sepiolite and its composites against E. coli (ATCC 25922) is illustrated in **Fig.5a-5e**. The raw sepiolite showed poor antibacterial capability against E. coli when compared to the untreated control group, which is in line with previous findings. Typically, the surface of sepiolite nanofibers carries a negative charge (Dikmen et al., 2012), which is neutralized by counterions and water molecules. From this perspective, there is a mutual exclusivity between sepiolite and bacteria. Therefore, it is hypothesized that surface complexation occurs between the bacteria and the surface hydroxyl groups of sepiolite.Upon modification with nanoparticles, the Ag-modified composites displayed the most potent antibacterial capability, followed by those modified with CuO and ZnO. The calculated antibacterial rates for the composites are depicted in **Fig.5f**. The results indicate that the antibacterial rate of the Sep/Ag composite approaches approximately 100%. Given the low content of Ag, CuO, and ZnO in the composites (estimated at around 5%), the observed antibacterial capability of the prepared samples is remarkable.



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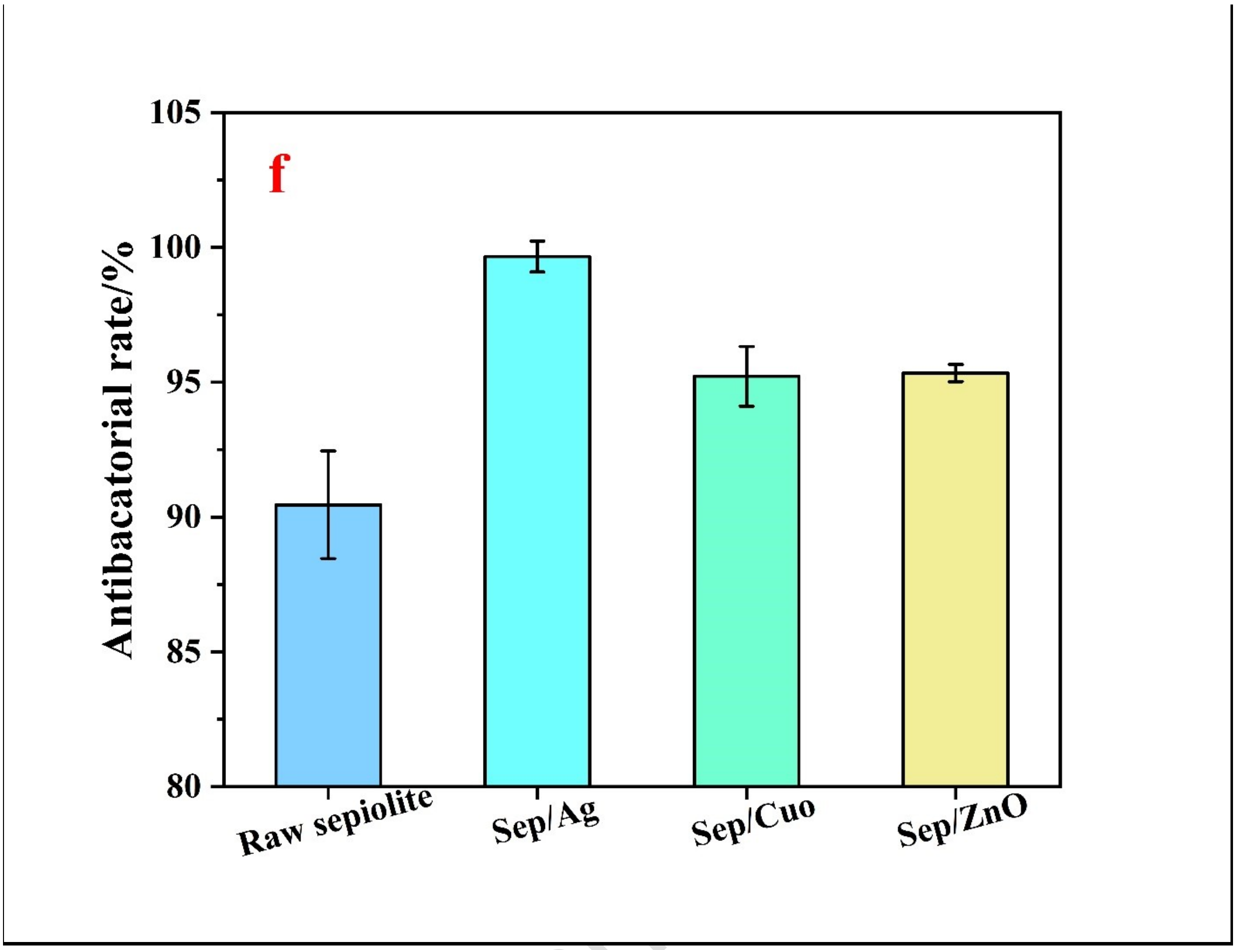


**Fig.5** Antimicrobial activity of sepiolite and its composites towards E. coli. (a) Sep; (b) SEP/Ag; (c) Sep/CuO; (d) Sep/ZnO; (e) Control group; (f) calculated antibacterial rate.



The antimicrobial activity of sepiolite and its composites against S. aureus (ATCC 29213) is shown in **Fig.6**. The composites exhibited similar antimicrobial activity against S. aureus as that against E. coli. Among the four samples, the Ag-modified composites demonstrated the strongest antibacterial capability. It can be observed that untreated sepiolite materials did not show a significant antibacterial effect, indicating selective antibacterial activities of sepiolite. It can be inferred that the antibacterial properties of the composites are attributed to the Ag, CuO, and ZnO components incorporated into the sepiolite nanofibers.

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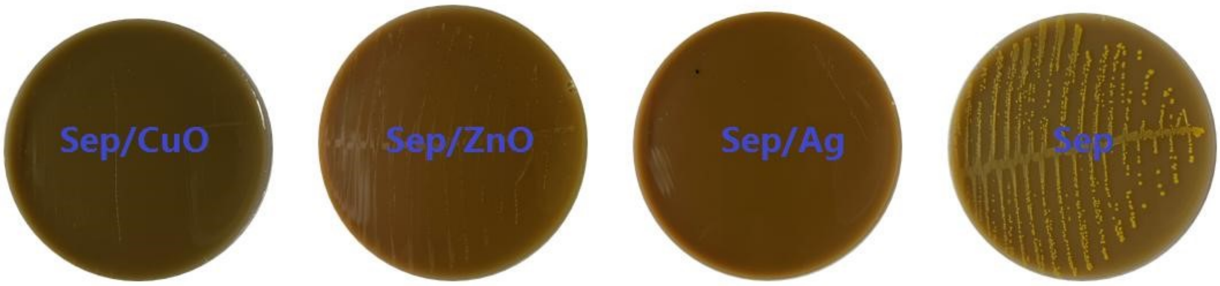


**Fig.6** Antimicrobial activity of sepiolite and its composites towards S. aureus.

The antibacterial mechanism of the sepiolite composites is presented in **Fig.7**. For example, sepiolite/Ag composites release Ag ions in a sustained manner (Abad-Álvaro et al., 2019; Li et al., 2022). Positively charged Ag ions interact with negatively charged cell membranes due to electrostatic attraction (Domínguez et al., 2021). The denaturation of proteins causes the cell membrane to become permeable and further damages the membrane structure. The accumulated ions within the cells tend to bind with DNA, RNA, and other cellular components, hindering genomic replication and ultimately causing bacterial damage (Briffa et al., 2020; Dos Santos et al., 2014). In addition, reactive oxygen species (ROS) induced by the nanoparticles lead to oxidative stress in the bacterial cell, resulting in cellular inactivation (Li et al., 2012). Sepiolite nanofibers play a crucial role in the process mentioned above. Sepiolite improves the dispersion of nanoparticles, and sepiolite nanofibers anchored with nanoparticles can directly react with bacteria. In this way, the presence of nanoparticles enhances the antimicrobial activity of sepiolite.



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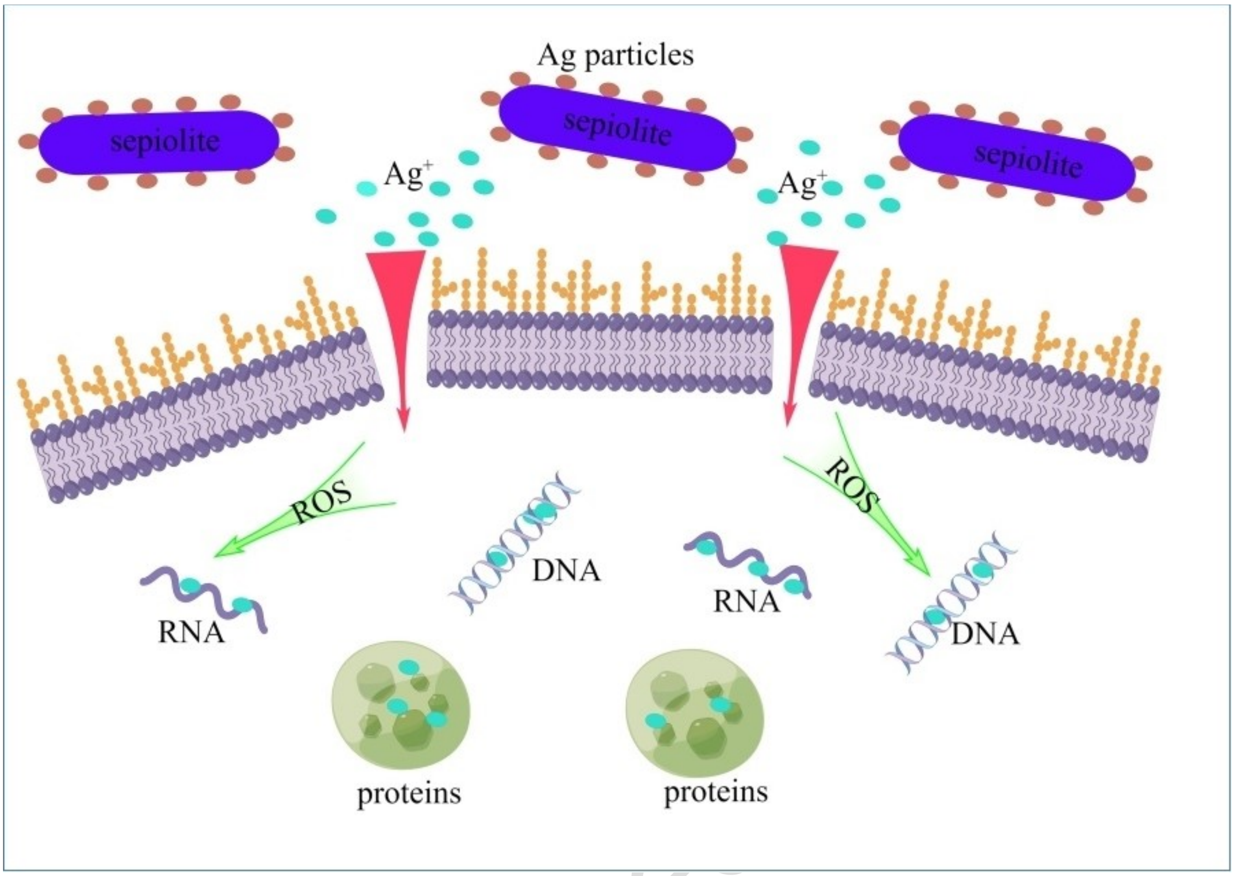


**Fig.7** Antibacterial mechanism of the sepiolite composites



The antimicrobial activity and hydrophilicity of sepiolite composites make them ideal for creating medicated dressings. Workability and water retention are critical for the effectiveness of medicated dressings. Thus, the rheological properties of the mud-like sepiolite composite mixtures were investigated. **Fig.8a** illustrates the relationship between water content and the viscosity of composite mixtures, which are formulated with a fixed proportion of sepiolite and CuO, demonstrating their signature pseudoplastic flow characteristics (Katoueizadeh et al., 2021). The dynamic viscosity of the composites decreased with increasing shear rate, indicating shear-thinning behavior. As water content increased, the viscosity of the composites dropped rapidly. The high water retention capacity of sepiolite ensures that only an optimal water content level maintains the workability of the composites(Jiang et al., 2023). Beyond this point, further increments in water content led to a more gradual decrease in viscosity. The data reveal that the

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Sep/Ag and Sep/ZnO composites exhibit similar rheological properties to pure sepiolite. In contrast, the Sep/CuO composite shows a lower viscosity. This difference may be due to the larger particle size of the components within the Sep/CuO composite (Hu et al., 2020; Pastoriza-Gallego et al., 2011). As shown in **Fig.8c**, with the increase in strain rate, the storage modulus (G′) gradually decreases, while the loss modulus (G″) firstly decreases and then slightly increases. Interestingly, it can be observed that the Sep/CuO composite exhibits rapid recovery of mechanical properties towards a large amplitude oscillatory deformation (**Fig.8d**), known as thixotropy (Jiao et al., 2021; Wang et al., 2010). It indicates that the hydrated Sep/CuO composite exhibits high structural stability. When the strain returns from $\gamma$ =80% to 1%, the sample can recover its high dispersibility within ~25s. During the cycling tests, the G′ and G″ of the hydrated Sep/CuO composite gradually increase due to the accelerated evaporation of the water in the system. However, the materials consistently maintained their thixotropic properties, fully demonstrating the stability of their structural rheological behavior. The workability of the Sep/CuO composite as medicated dressings is shown in **S6**. In the absence of thickeners and water-retaining agents, the hydrated Sep/CuO composite exhibits good adherence to the hydrophilic glass substrates. After 30 min, the mixture did not show a significant flow behavior when the bottles were inverted. As comparison, the mixture exhibits the best workability with a composite/water mass ratio of 1:2.



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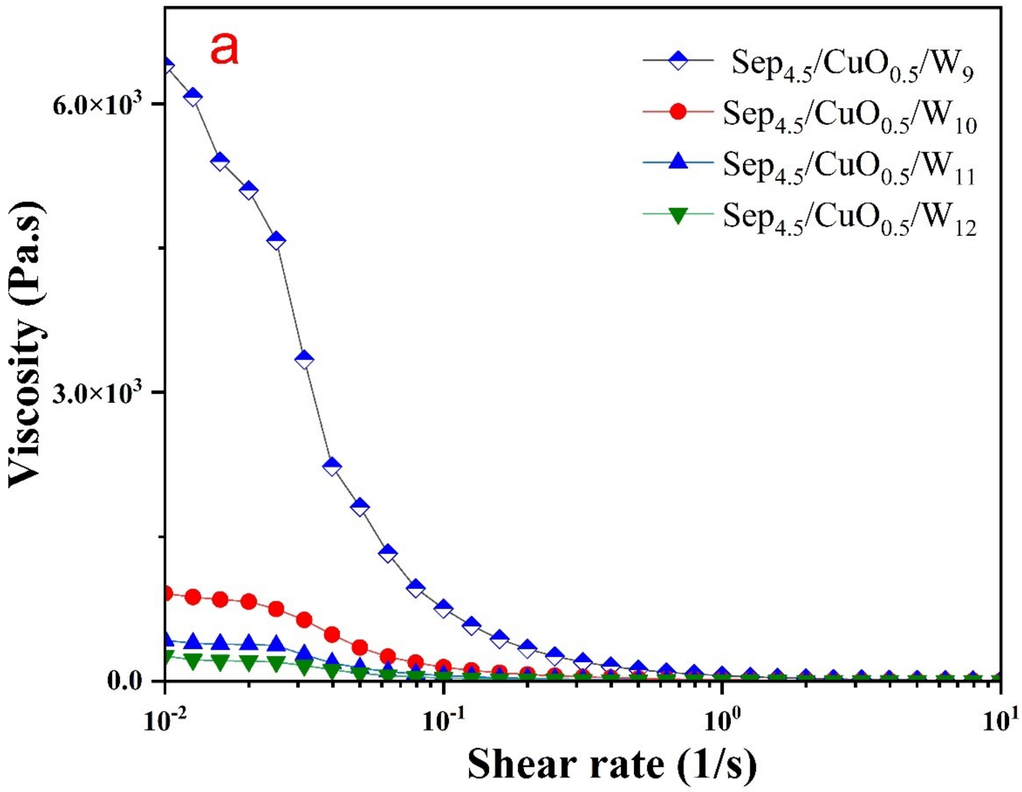




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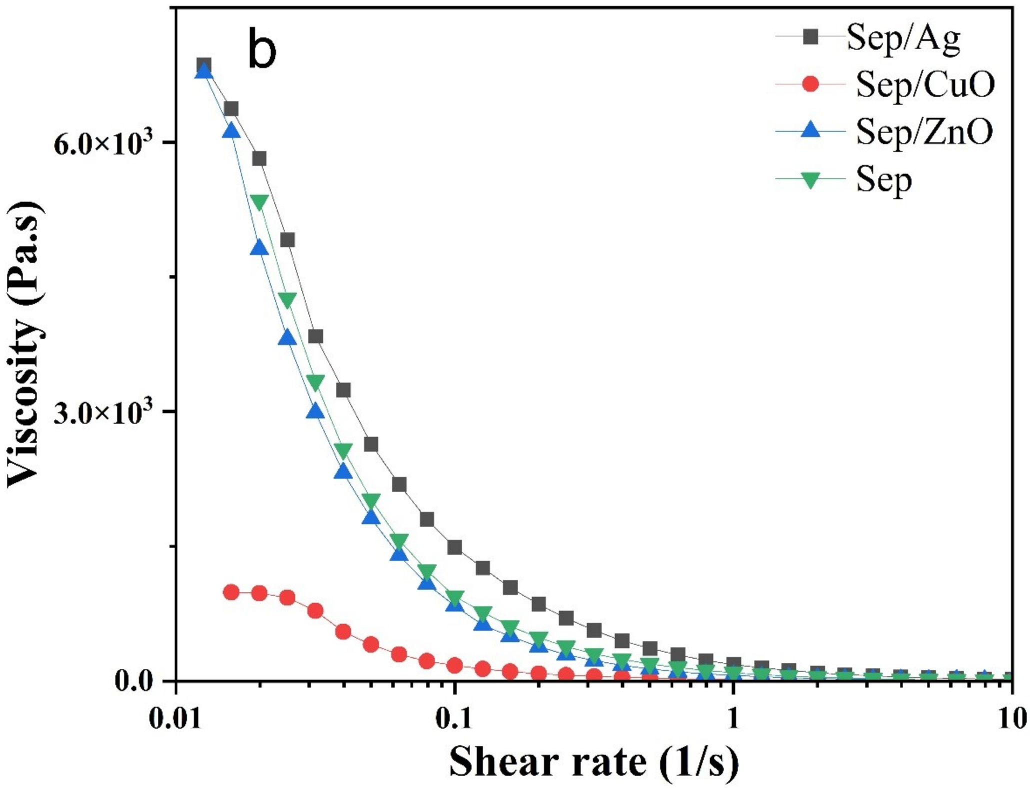




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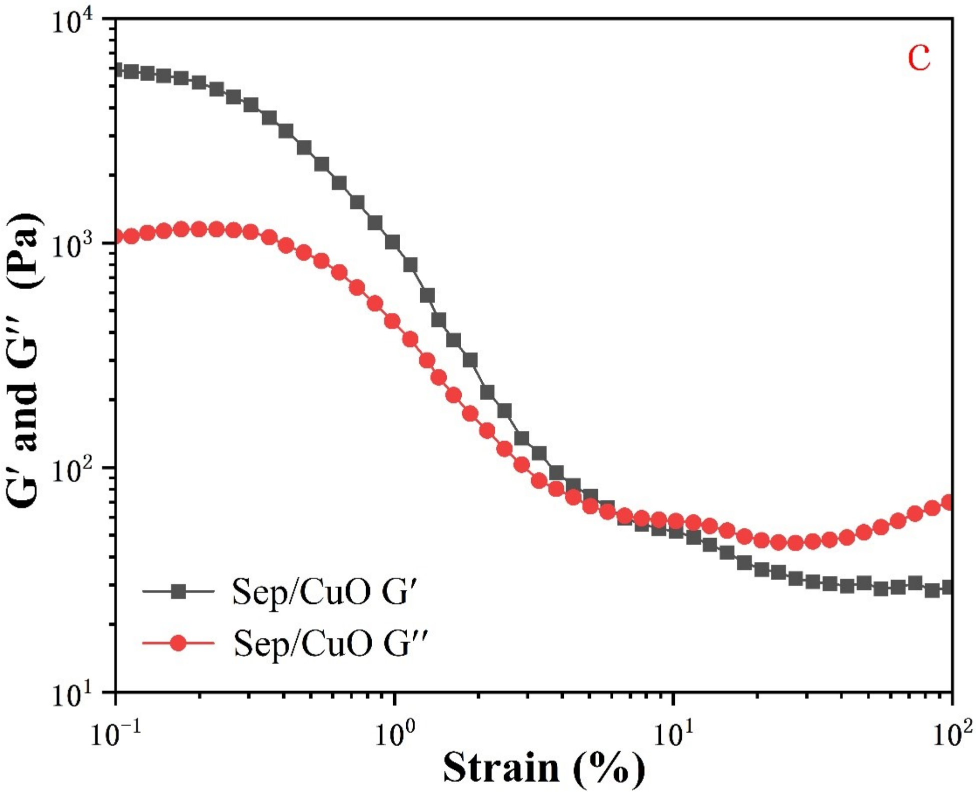




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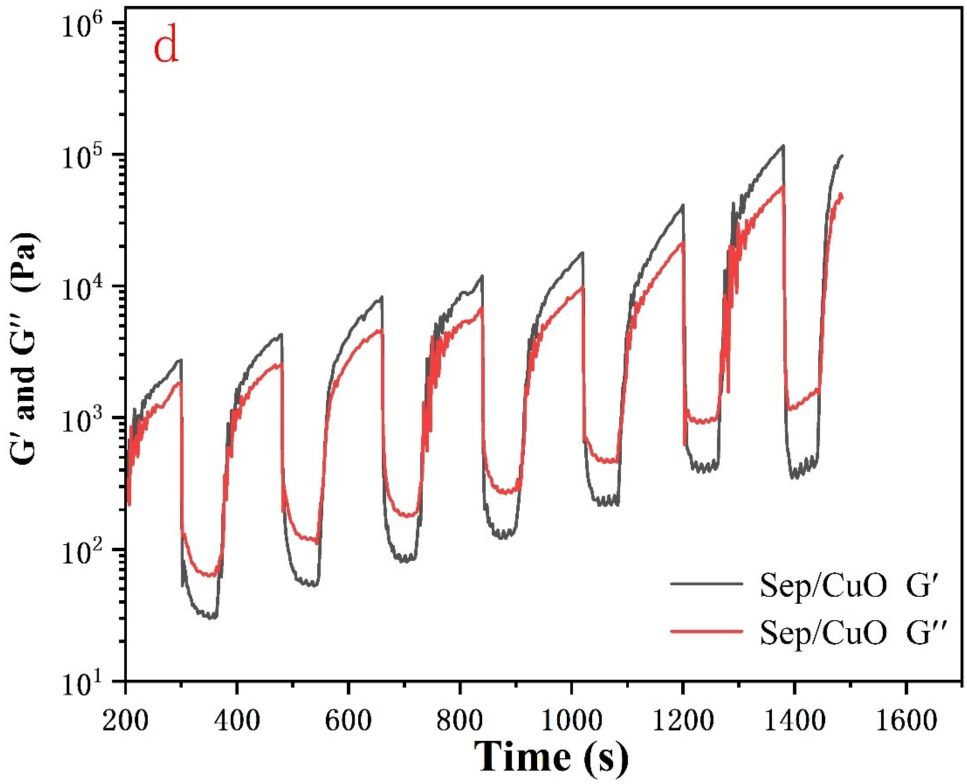


**Fig.8** Rheological properties of the mud-like sepiolite composite mixtures. (a) Viscosity of Sep/CuO composite on different shear rate. (b) Viscosity of composites on different shear rate. (c) G′ and G″of Sep/CuO composite on strain sweep. (d) Dynamic strain amplitude cyclic test ($\gamma$ = 1% for 120 s and $\gamma$ = 80% for 60 s) of Sep/CuO composite.



## 4. Conclusion

In summary, sepiolite-based nanocomposites with improved antibacterial properties have been successfully synthesized using a modified solid-state sintering method. Sep/Ag, Sep/CuO, and Sep/ZnO composites can be synthesized at relatively low temperatures below 500°C. All composites exhibit a fibrous morphology, retaining the characteristic structure of pristine sepiolite. Among them, the sepiolite/Ag composites demonstrate the most potent antibacterial activity, following by CuO and ZnO-modified sepiolite composites. The antibacterial rate of the

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Sep/Ag composite approaches approximately 100%. In the absence of thickeners and water-retaining agents, the hydrated sepiolite-based composites exhibit good rheological properties. The hydrated Sep/CuO composite can firmly adhere to hydrophilic glass surfaces. The high water retention of the composites ensures good skin compatibility, making them suitable for direct application on skin. Compared with conventional clay hydrogels, the sepiolite composites show better antibacterial performance and workability. The results suggest that these composites hold significant potential for clinical use, particularly in the development of wound dressings. This work has promoted the application of clay in the field of biomaterials. Future work needs to further clarify whether clay composites have a promoting effect on wound healing.

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**Authors' contributions**

Y.D and Y.Y designed the project and experiments. Y.J and Z.P prepared the materials and conducted the bio experiments. Y.L, Y.T and J.P analyzed the results and wrote the manuscript and Y.D revised the manuscript.

**Competing interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data Availability**

The datasets used and/or analyzed during the current study are available from the corresponding authors on reasonable request.

**Supplementary information**

Experimental details related to the antibacterial activities of the composites are presented in the Supporting Information (SI) file. In addition, the TEM image and workability of the composite are shown in the SI file.

**Ethical approval**

Not applicable.

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