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Silver oxide decorated urchin-like microporous organic polymer composites as versatile antibacterial organic coating materials

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Microporous organic polymers (MOPs) and metal oxide hybrid composites are considered valuable coating materials because of their versatility derived from the synergistic combination of MOPs' inherent dispersibility and the distinctive properties of metal oxides. In this study, we present the synthesis of sea-urchin-like MOPs hybridised with silver oxide nanoparticles (Ag₂O NPs) to fabricate antibacterial composites suitable for potential antibacterial coating applications. Ag₂O NP-decorated urchin-like MOPs (Ag₂O@UMOPs) were synthesised by employing a combination of two methods: a one-pot Lewis acid-base interaction-mediated self-assembly and a straightforward impregnation process. The as-prepared Ag₂O@UMOPs demonstrated high antibacterial efficacy against both *E. coli* (G⁻) and *S. aureus* (G⁺). The antibacterial mechanism of Ag₂O@UMOPs mainly involved the synergistic effects of Ag₂O@UMOPs accumulation, the release of Ag⁺ ions, and the generation of reactive oxygen species. The exceptional processability and biosafety of Ag₂O@UMOPs make them ideal organic coating materials for convenient application on various substrates. These remarkable features of Ag₂O@UMOPs provide an effective platform for potential antibacterial applications in the biological sciences.

Keywords: Microporous organic polymers, Ag₂O nanoparticles, antibacterial, coating materials

Introduction

Bacterial infections pose a significant threat to public health worldwide as they can lead to severe diseases. Clinically, bacterial infections are typically characterised by chills, high fever, rash, arthralgia, and hepatosplenomegaly.^{1,2} Some patients may present with infectious shock and migratory lesions. Pathogenic microorganisms commonly invade the bloodstream through wounds or infected lesions and cause acute systemic infections. Therefore, there is an urgent need to develop effective antibacterial coating materials to minimise the risk of wound infections.³⁻⁶ These coating materials also facilitate the treatment of bacterial contaminants in various environments.⁷⁻⁹ In recent years, metallic oxide materials (e.g. Ag₂O, ZnO, MgO, CaO, CoO, TiO₂, Cu₂O, TiO₂, and Fe_xO_y) have garnered attention owing to their bacteriostatic and/or bactericidal effect.^{10,11} Metal ions such as Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺, and Co²⁺ play essential roles in various metabolic processes in living bacterial strains and typically become toxic only at higher

concentrations.¹² Interestingly, non-essential metal ions, such as Hg²⁺ and Ag⁺ present much stronger antibacterial activity, even at low concentrations.¹³⁻¹⁵ Because of their detrimental environmental impact, Hg²⁺ ions are not suitable candidates for obtaining antibacterial materials.^{16,17} Consequently, Ag⁺ ions were more suitable for this purpose. Silver oxide nanoparticles (Ag₂O NPs) demonstrate superior antibacterial activity because of the continuous release of Ag⁺ ions. These ions can easily destroy bacterial cell walls by binding to oppositely charged components of the bacterial membrane.^{18,19} On the other hand, Ag₂O NPs can generate reactive oxygen species (ROS) such as hydrogen peroxide (H₂O₂), superoxide (•O₂⁻), and hydroxyl radical (•OH), which can induce oxidative stress and disrupt bacterial membranes.²⁰

Ag₂O NPs are commonly prepared by physical and chemical methods. Physical methods such as microwave, ball milling, laser, and quenching can yield Ag₂O NPs with high purity. However, they often require expensive machinery and involve harsh conditions.^{21,22} Chemical methods involving mixing a silver precursor with ammonia can easily produce Ag₂O NPs.^{23,24} However, the agglomeration of particles caused by their high surface energy significantly hampers their practical applications. It should be mentioned that particle size, shape, and surface properties are crucial factors in determining their antibacterial performance.²⁵⁻²⁷ Polymer stabilisers, surfactants, and solid supports are commonly used to reduce particle agglomeration.²⁸ Although numerous reports are available on the preparation and characterisation of polymer-stabilised

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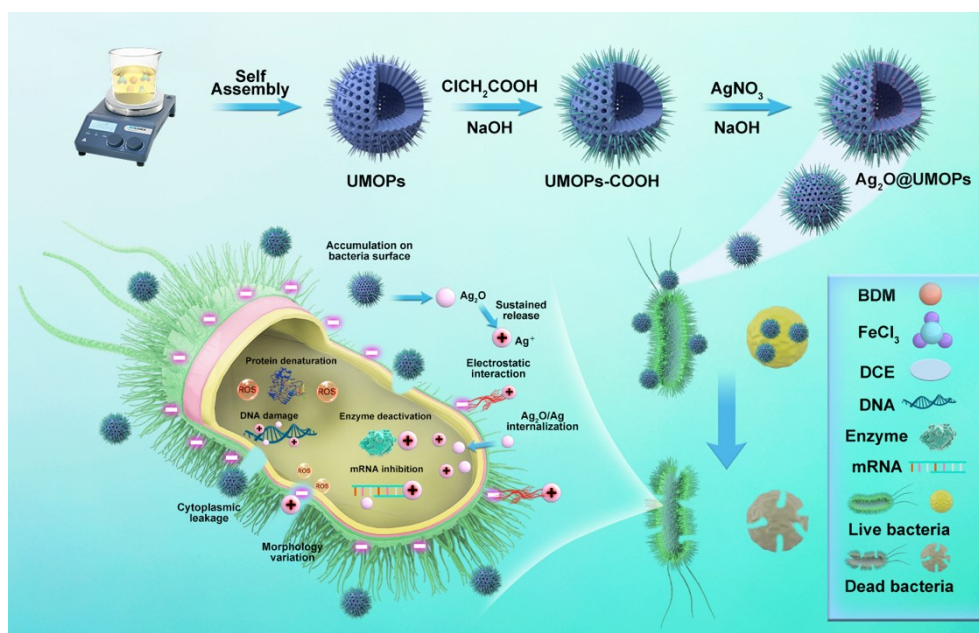
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silver, methods for preparing polymer-stabilised silver oxide are scarce. In addition, Ag_2O NPs have been reported to show low toxicity to soil microorganisms, while displaying high toxicity to pathogenic microorganisms. This property significantly enhances the antibacterial selectivity for specific antibacterial applications. Accordingly, there is a significant demand for the development of stable and effective platforms to address bacterial infections.²⁹⁻³¹

Figure 1. Schematic diagram of the preparation and antibacterial application of $\text{Ag}_2\text{O}@$ UMOPs.

Microporous organic polymers (MOPs) and metal oxide hybrid materials with advanced coating properties have proven valuable for a variety of applications.³²⁻³⁵ Because of their extremely high surface areas, hierarchical pore channels, and versatile surface modification abilities, MOPs have the inherent strength to support Ag_2O NPs.^{36,37} MOPs feature abundant micro-, meso-, and macropores, which can be readily controlled to achieve hierarchical pore size distributions. The cross-linked frameworks, combined with the hierarchical pore sizes, created numerous transportation channels that were well suited for the deposition of Ag_2O NPs. MOPs typically exhibit well-defined and controlled morphologies. With respect to the hollow urchin-like morphologies, Ag_2O NPs have the capability to decorate both surfaces of the frameworks and be anchored inside the holes, thereby significantly reducing the possibility of agglomeration. In addition, MOPs with surface carboxyl functionalities can interact with Ag^+ ions under basic conditions, ensuring successful hybridisation as composites for specific coating applications. Although a number of studies have investigated the antimicrobial effect of MOPs loaded with Ag, few have investigated the antimicrobial effect of Ag_2O on MOPs, and the compound antimicrobial effect and mechanism are urgently needed.

Hyper-crosslinked polymers (HCPs) are useful MOPs materials commonly obtained with high stability and porosity under mild reaction conditions.³⁸⁻⁴¹ Recently, we developed a unique Lewis acid-base interaction-mediated self-assembly method that allowed the in situ formation of hollow spherical HCPs with hydroxyl functionality.^{42,43} Specifically, the one-pot Friedel-Crafts self-crosslinking reaction using 1,4-benzenedimethanol as the monomer and iron chloride as the catalyst enabled the formation of HCPs characterised by inner hollow structures and outer needle-shaped spheres, resembling sea urchins. These sea-urchin-like HCPs spontaneously formed under suitable conditions without the use of templates. We envision that these HCP-based MOPs with defined morphologies and functionalities can serve as ideal supports for Ag_2O NPs.

Herein, we report the synthesis and characterisation of Ag_2O NP-decorated urchin-like MOPs ($\text{Ag}_2\text{O}@$ UMOPs) as versatile antibacterial coatings (Figure 1). Ag_2O NPs were anchored onto sea urchin-like MOPs by applying a combination of Lewis acid-base interaction-mediated self-assembly and a straightforward impregnation process. The UMOPs scaffolds were first synthesised using a one-pot Friedel-Crafts alkylation reaction. UMOPs contain an abundance of carboxyl groups originating from residual hydroxyl groups that undergo carboxylation through a reaction with chloroacetic acid, greatly facilitating the exchange process with Ag^+ ions. Successful anchoring of highly dispersed Ag_2O NPs into UMOPs was achieved via an in-situ reduction process employing NaOH, leading to the formation of $\text{Ag}_2\text{O}@$ UMOPs. The resultant $\text{Ag}_2\text{O}@$ UMOPs exhibited outstanding antibacterial activity against both gram-negative bacteria (*E. coli*) and gram-positive bacteria (*S. aureus*). Specifically, at a concentration of $200 \mu\text{g}\cdot\text{mL}^{-1}$, $\text{Ag}_2\text{O}-3@$ UMOPs achieved antibacterial efficiencies of 99.80% for *E. coli* and 95.30% for *S. aureus*. More importantly, the $\text{Ag}_2\text{O}@$ UMOPs can be easily loaded into polyurethane foam or compressed into a membrane, demonstrating their superior processability. Furthermore, $\text{Ag}_2\text{O}@$ UMOPs also showed good biocompatibility and hemocompatibility. The $\text{Ag}_2\text{O}@$ UMOPs take great advantages of distinctive sea-urchin-like

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morphologies, stable crosslinked structure, high surface area, and abundant micro/mesopores, which may offer sufficient transfer channels for bacteria-containing solutions to contact the active sites on the composites. These features render Ag₂O@UMOPs suitable for coating various substrates to meet various biomedical application requirements.

Experimental

Materials

1,4-benzenedimethanol, chloroacetic acid, 1,2-dichloroethane, acetone, and ethanol were purchased from TCI Chemicals. Anhydrous FeCl₃ (98%), AgNO₃, NaOH, concentrated HCl and ammonia were obtained from Merck. The solvents used for the reactions were dried over CaH₂, fractionally distilled, and then degassed. The ultrapure water (18.2 MΩ cm⁻¹) used in the experiment was obtained from Milli-Q apparatus. Filter paper, nonwoven fabric, and PET foam were obtained from a local market.

Preparation of Ag₂O@UMOPs

Ag₂O@UMOPs were prepared according to the following protocol: UMOPs were synthesised through a one-pot Lewis acid-base interaction-mediated self-assembly process, as extensively documented in our prior study.^{42,43} Briefly, the 1,4-benzenedimethanol (1 mol, 0.65 g) was mixed with FeCl₃ (2 mol, 1.54 g) in the dry 1,2-dichloroethane solutions under the N₂ atmosphere, subsequently, the temperature was set as 80 °C to let the reaction happen. After 18 h, the resultant turbid mixture was filtered and the obtained brown product was sequentially rinsed with acetone, ethanol, and deionised water until the filtrate was clear. The crude solids collected were extracted using ethanol through a Soxhlet process and then dried under vacuum at 80 °C (yield: 112%, based on hypothetical 100% condensation).

The abundant hydroxyl groups present in the UMOPs underwent facile conversion to carboxyl groups through reaction with chloroacetic acid.^{44,45} Briefly, the as-prepared UMOPs (0.30 g) were mixed with 150 mL of deionised water via a process involving both stirring and sonication to yield a well-dispersed solution. Chloroacetic acid (15.00 g) and NaOH (18.00 g) were added to the solution for a comprehensive reaction. The reaction mixture was suspended in a dilute HCl solution. The collected crude solids were thoroughly washed with deionised water and dried to yield carboxyl group-terminated UMOPs (UMOPs-COOH, yield: 58%).

UMOPs-COOH (0.10 g) were dispersed in a 6 mol·L⁻¹ NaOH solution and stirred for 10 h. The salinised carboxyl group-terminated UMOPs and AgNO₃ (0.01 g) were introduced in 50 mL alkaline aqueous solution and allowed to stir at 70 °C for 12 h. The crude solids were separated by centrifugation and washed several times with an excess of deionised water and absolute ethanol to remove physically adsorbed Ag species from the UMOPs. The final products were dried under vacuum at 50 °C for 24 h. By changing the AgNO₃ to UMOPs weight ratio (0.10, 0.20, 0.30), the resulting products, named as Ag₂O-

1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs, were successfully synthesised.

Characterization

Fourier-transform infrared (FT-IR) spectroscopy was performed on a Shimadzu IRPrestige-21 spectrophotometer using the conventional KBr method. The X-ray diffraction (XRD) patterns were observed by a Bruker D8 ADVANCE powder diffractometer using Cu-K_α irradiation (λ = 0.154 nm). The angle-resolved X-ray photoelectron spectroscopy (AR-XPS) analysis was performed on the Theta Probe angle-resolved system by a monochromatic Al-K_α X-ray radiation at 1486.6 eV. A Quantachrome Instruments Nova 3200e operator (USA) was used for N₂ adsorption/desorption isotherm analysis. Under the flowing N₂ atmosphere, the thermogravimetric analysis (TGA, Scinco N-1000) was conducted with a heating rate of 10 °C·min⁻¹ in the temperature range of 30 °C to 800 °C. The differential scanning calorimeter (DSC) analysis was performed on the TA Q200 instrument at a heating rate of 10 °C·min⁻¹ under the N₂ atmosphere. The morphologies of the UMOPs and Ag₂O@UMOPs were characterised using field-emission scanning electron microscopy (SEM, Zeiss Supra 25) and transmission electron microscopy (TEM, H-7600 HITACHI). The fine inner shapes and compositions of the Ag₂O@UMOPs were observed using a high-resolution transmission electron microscope (HR-TEM, TALOS F200X) equipped with a high-angle annular dark-field-scanning transmission electron microscope (HAADF-STEM) and energy-dispersive X-ray (EDX) spectrometer.

Antibacterial analysis

The antibacterial properties of different materials were evaluated using *E. coli* and *S. aureus* as representative bacterial models. To ensure full contact, bacteria suspensions (1 × 10⁶ CFU mL⁻¹) were separately incubated with UMOPs and Ag₂O@UMOPs at concentrations of 25, 50, 100 and 200 μg·mL⁻¹, maintaining the incubation at 37 °C for 12 h. 100 μL of co-culture was subjected to serial dilution in phosphate buffered saline (PBS). 10 μL of the diluted co-cultures was dispersed onto blood agar plates and inoculated at 37 °C for 24 h. Finally, the surviving colonies of bacteria were counted. A positive control group was established using PBS instead of the polymer. The bacterial growth curves of the different materials were measured using the optical density method. Different concentrations of UMOPs and Ag₂O@UMOPs were individually incubated with bacterial suspensions (1 × 10⁶ CFU mL⁻¹) at 37 °C for 12 h. The optical density at 600 nm (OD₆₀₀) was measured for each co-culture at intervals of 2 h. All experiments were conducted in triplicate.

Bacterial membrane integrity test

The integrity of the bacterial cell membrane was assessed using SEM analysis and a Live/Dead BacLight staining assay. A bacterial suspension was cultivated with 200 μg·mL⁻¹ Ag₂O@UMOPs at 37 °C for 12 h. Bacteria suspensions without Ag₂O@UMOPs were used as the control group. To observe the morphologies, the bacteria were subjected to centrifugation and PBS washing,

followed by fixation in a 2.50% solution of glutaraldehyde and paraformaldehyde at 4 °C for 4 h. Afterward, the fixed bacteria were transferred to sliding cards and dehydrated under the gradient concentration of ethanol solution for 15 min. The surface morphology of the dried bacteria was examined using SEM. The LIVE/DEAD[®] BacLight[™] Bacterial Viability and Counting Kit reagents were used to stain the bacteria. Both the control and Ag₂O@UMOPs-treated groups were incubated with propidium iodide (PI) and SYTO9 dyes in a dark environment at 37 °C for 20 min. The resulting suspension was centrifuged and the cells were resuspended in PBS. Fluorescence analysis was performed using a confocal laser fluorescence microscope (CLSM ZEISS 800).

The release behaviour of Ag⁺ ions

Ag₂O@UMOPs were immersed in 20 mL of PBS solution (pH = 7.4) at 37 °C. At different intervals (2, 4, 8, 12, 24, and 48 h), determined volumes of the suspensions were removed and centrifuged. The resulting supernatants were filtered through a 0.22 μm membrane and subsequently analysed to determine the concentrations of Ag⁺ ions using Inductively-coupled plasma mass spectroscopy (ICP-MS, Agilent 7500, Agilent, America).

Intracellular ROS level assay

E. coli and *S. aureus* were stained with ROS-sensitive dye DCFH-DA for 20 min at 37 °C in the dark. The bacterial suspensions were incubated with Ag₂O@UMOPs at concentrations of 25, 50, 100 and 200 μg·mL⁻¹ for 4 h. The resulting bacterial suspensions were collected, centrifuged, and resuspended in PBS. The fluorescence intensity was subsequently measured using a microplate reader at excitation/emission wavelengths of 488/525 nm. H₂O₂ served as the positive control for ROS generation, whereas untreated bacteria served as the negative control.

In vitro cytotoxicity test

To assess the cytotoxicity of the prepared polymers, the MTT assay was performed on mouse embryonic fibroblast cells (NIH-3T3). NIH-3T3 cells were treated with different concentrations of polymers in 96-well microtitre plates and incubated at 37 °C for 24 h. Then, 100 μL of the MTT solution was added into each well and co-cultured for another 4 h. 200 μL of DMSO was added into each well to thoroughly dissolve the purple formazan crystals. Absorbance was recorded using a microplate reader. Untreated bacterial cells served as controls.

Hemolysis assay

The hemolytic activities of the as-prepared polymers were evaluated using fresh mouse blood samples. Briefly, red blood

cells were separated by centrifugation and diluted in PBS. The diluted red blood cells were incubated with different concentrations of polymers at 37 °C for 4 h. Each mixture was subjected to centrifugation, and the absorbance of the resulting supernatant was quantified using a UV-vis spectrophotometre. Deionised water was used as the positive control, whereas PBS was used as the negative control.

Results and Discussion

Synthesis of characterization of Ag₂O@UMOPs

The overall synthesis procedure for Ag₂O@UMOPs is shown in Figure 1. In a precisely controlled experiment, the synthesis of the UMOPs involved a mixture of 1,4-benzenedimethanol and FeCl₃ in a 1, 2-dichloroethane solution. Initially, the hydroxyl groups of 1,4-benzenedimethanol are activated through interactions with a Lewis acid (FeCl₃), resulting in the formation of hydroxyl methyl-substituted intermediates. The reaction exhibited rapid progress, evident as dark brown precipitates forming within just 3 mins at 80 °C. This indicates a near-simultaneous incidence of alkylation, polymerisation, and self-intercrosslinking in the solution state. Subsequently, the reactions were allowed to proceed for an additional 24 h to ensure thorough crosslinking. Following filtration, washing, Soxhlet extraction, and vacuum drying, the resulting materials (denoted as UMOPs) were characterised as fine powders with chrome yellow hues. Our lab has effectively illustrated that imperfect Friedel-Crafts cross-linking reactions can endow HCPs with in situ hydroxyl functionality.⁴² Moreover, our earlier research demonstrated the substantial advantages conferred by hydroxyl groups in enabling the incorporation of a diverse array of chemistries.⁴⁶⁻⁴⁸ Consequently, the carboxylation reaction involving chloroacetic acid under basic conditions successfully transformed the branched hydroxyl groups on the UMOPs surface into carboxyl groups, leading to the production of UMOPs with carboxyl-terminated functionalities (UMOPs-COOH). Then, UMOPs-COOH were subjected to salinisation under basic conditions to facilitate exchange with Ag⁺ ions via electrostatic interaction.^{49,50} Subsequently, the successful anchoring of highly dispersed Ag₂O NPs into the UMOPs was achieved via an in situ reduction process using NaOH, resulting in the formation of Ag₂O@UMOPs.

SEM and TEM were used to observe variations in both the surface and internal morphologies of the UMOPs before and after decoration with Ag₂O NPs. The SEM images reveal the globular morphology of the UMOPs, while simultaneously showing numerous rod-like structures on the surface of the spheres, resembling the spiny sea urchin (Figure 2a1). The TEM images clearly reveal a well-defined boundary at the edge of the sphere, indicating the inherent hollow morphology of the

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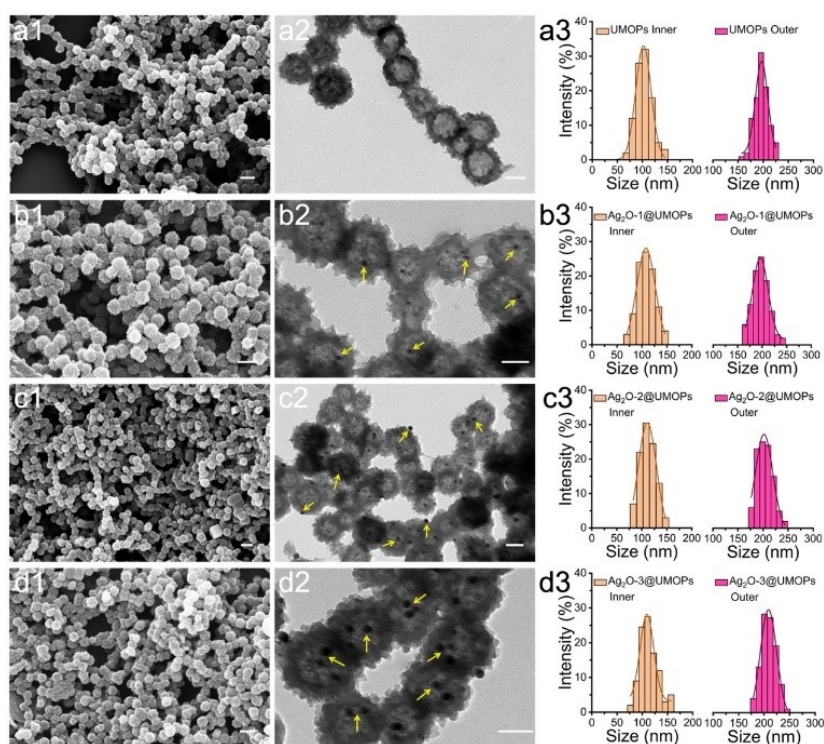


Figure 2. SEM images of (a1) UMOPs, (b1) Ag₂O-1@UMOPs, (c1) Ag₂O-2@UMOPs, and (d1) Ag₂O-3@UMOPs. Scale bars: 300 nm. TEM images of (a2) UMOPs, (b2) Ag₂O-1@UMOPs, (c2) Ag₂O-2@UMOPs, and (d2) Ag₂O-3@UMOPs. Scale bars: 100 nm. Size distribution diagrams of the interior and exterior diameters of (a3) UMOPs, (b3) Ag₂O-1@UMOPs, (c3) Ag₂O-2@UMOPs, and (d3) Ag₂O-3@UMOPs.

UMOPs (Figure 2a2). The particle size distribution exhibited a distinct Gaussian distribution pattern (Figure 2a3). The spheres had an outer diameter of 189 nm, inner diameter of 106 nm, and the rods were between 20 and 29 nm in diameter. Following surface modification with carboxyl groups, sea-urchin-like morphologies were preserved, with only a small portion of the rods displaying slight blunting (Figure S1). After further decoration with Ag₂O NPs, the SEM images of Ag₂O@UMOPs displayed the retained sea-urchin-like morphologies (Figure 2b1, c1, and d1). Furthermore, a smoother surface was observed compared with the initial protruding surface of the UMOPs. The TEM images of the Ag₂O@UMOPs clearly revealed the existence of Ag₂O NPs, both within the interior and on the surface of the UMOPs (Figure 2b2, c2, and d2). Gradually increasing the AgNO₃ to UMOPs weight ratio from 0.10 to 0.30 resulted in a noticeable increase in the average size of the Ag₂O NPs, advancing from 12.41 to 20.50 nm (Figure S2). Additionally, the particle size distributions of the Ag₂O@UMOPs continued to display a Gaussian

pattern, with a slight increase in the outer diameter to approximately 200 nm (Figure 2b3, c3, and d3).

HR-TEM analysis was carried out to characterize the crystalline structure of Ag₂O@UMOPs. Figures 3a1 and a2 clearly revealed the distribution of the crystalline Ag₂O NPs within the amorphous UMOPs matrix. The lattice fringe of 0.27 nm can be indexed to the (111) plane of crystalline Ag₂O (Figure 3a3).^{51, 52} EDX mapping images illustrate the coexistence of Ag with C and O, providing additional evidence of the successful anchoring of Ag₂O NPs within the entire UMOPs framework (Figure 3b1-b5, 3c, and Figure S3). Remarkably, these highly dispersed Ag₂O NPs, whether situated on the surface or embedded within the interior of the UMOPs, provided numerous active sites conducive to engaging with and killing bacteria effectively.

FT-IR spectroscopy and XRD measurements were conducted to further characterise the chemical composition of the Ag₂O@UMOPs. As shown in Figure S4, the cross-linked polymer skeleton of UMOPs exhibits distinct characteristic bands, including the C-H bending vibration around 1436 cm⁻¹, the

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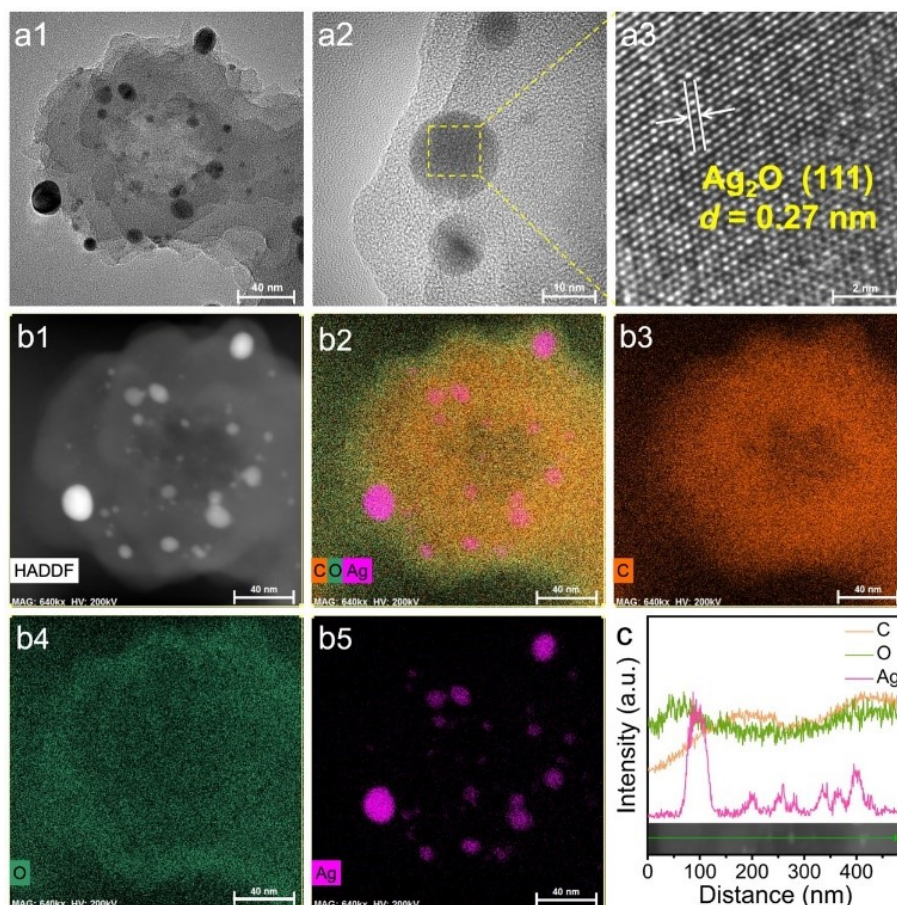


Figure 3. HR-TEM (a1-a3), HAADF-STEM (b1), EDX mapping (b2-b5) images, and energy dispersive spectroscopy line scan of $\text{Ag}_2\text{O}@$ UMOPs. Scale bars: 40 nm in a1 and b1-b5, 10 nm in a2, and 2 nm in a3.

aromatic C=C stretching vibration around 1630 cm^{-1} , C-H stretching vibration around 2850 cm^{-1} , aromatic C-H stretching vibration around 2920 cm^{-1} , O-H stretching vibration around 3440 cm^{-1} . The new bands appeared at approximately 1740 cm^{-1} , 1218 cm^{-1} , and 919 cm^{-1} , are assigned to the C=O, C-O, and O-H stretching vibrations of carboxyl groups, respectively^{53,54}; it suggests that carboxyl groups were successfully conjugated onto the surfaces of UMOPs. However, the characteristic peaks associated with the carboxyl groups nearly vanished upon decoration with Ag_2O NPs. This may be attributed to the decarboxylation of UMOP-COOH under alkaline conditions.^{55,56} In Figure 4a, the wide-angle XRD profile of the UMOPs features a broad diffraction peak, consistent with earlier research findings, indicating the inherent amorphous nature of UMOPs.^{42,43} Upon the formation of $\text{Ag}_2\text{O}@$ UMOPs, the appearance of new diffraction peaks at 2θ values approximately 32.20 , 38.30 , 54.80 , 67.50 , and 77.80

corresponded to (111), (200), (220), (311), and (222) crystal faces of Ag_2O , respectively.⁵⁷⁻⁵⁹ The diffraction peaks of Ag (0) were not observed. By employing the Scherrer equation, the average crystallite sizes of Ag_2O NPs were calculated to be 12.93, 15.74, and 22.31 nm for $\text{Ag}_2\text{O}-1@$ UMOPs, $\text{Ag}_2\text{O}-2@$ UMOPs, and $\text{Ag}_2\text{O}-3@$ UMOPs, respectively. These characteristic peaks collectively offer compelling proof of the crystalline nature of the Ag_2O NPs within the amorphous UMOPs framework, which agrees with the findings from the HR-TEM analysis.

To assess the thermal stability of the as-prepared $\text{Ag}_2\text{O}@$ UMOPs, TGA measurements were carried out under a flowing N_2 atmosphere, covering a temperature range from 25 to $800\text{ }^\circ\text{C}$. As depicted in Figure 4b, the negligible weight loss observed in all samples below $120\text{ }^\circ\text{C}$ can be attributed to the removal of interstitial water and gas molecules. A dramatic

weight decrease occurred in the temperature range of 330–580 °C, which is related to the decomposition of the

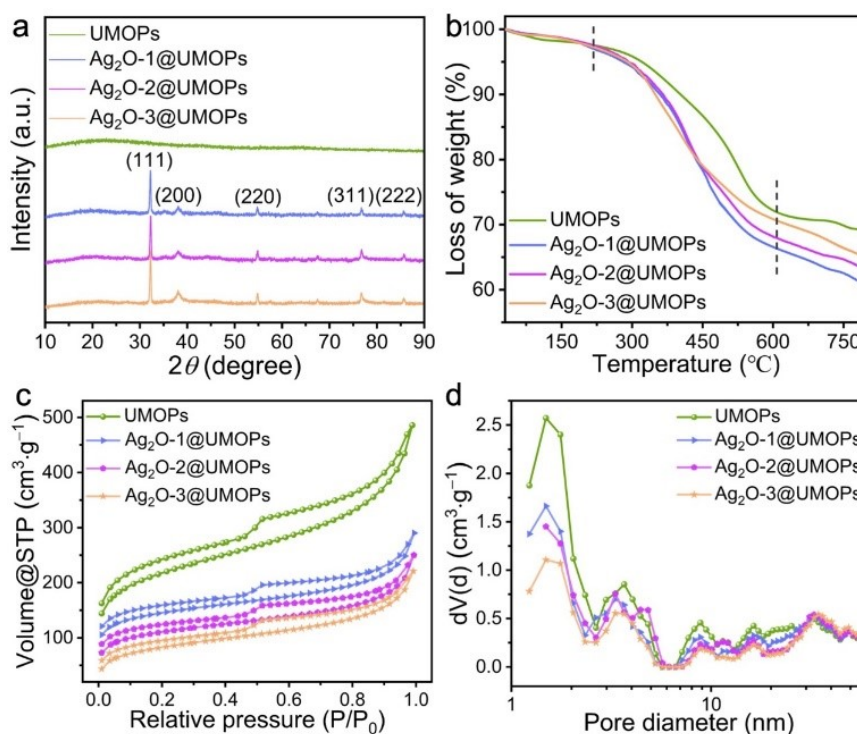


Figure 4. (a) XRD patterns, (b) TGA curves, (c) N₂ adsorption–desorption isotherms, (d) NL-DFT pore–size distribution curves.

polymeric framework. As documented in previous studies, the decomposition of Ag₂O NPs occurs at temperatures above 300 °C.^{60,61} This factor could be responsible for the faster decomposition of Ag₂O@UMOPs than that of the UMOPs. Above 600 °C, the weight loss curve of UMOPs showed a gentle trend, while the weight of Ag₂O@UMOPs continued to decrease because of the progressive liberation of O₂ absorbed by the polymeric framework. Therefore, the residual weight of Ag₂O@UMOPs was lower than that of UMOPs. The residual weights of the UMOPs, Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs were calculated to be 69.15%, 60.64%, 62.97%, and 65.03%, respectively. It can be observed that the weight loss of Ag₂O@UMOPs decreases as the AgNO₃ to UMOPs weight ratio increases from 0.10 to 0.30 because of the increased content of residual Ag after decomposition.⁶² The high thermal stability of the Ag₂O@UMOPs plays a crucial role in their applicability for antibacterial purposes, particularly because many antibacterial polymeric counterparts are limited by their inferior thermal stability.

The unique structures of porous networks endow them with high porosity and a large surface area, thereby offering significant advantages for the effective decoration and transportation of specific guest molecules.^{42,63,64} N₂ adsorption–desorption analysis was conducted to evaluate variations in the porosity and surface area of the Ag₂O@UMOPs. Figure 4c and d

display the corresponding pore-size distributions, as calculated using nonlocal density functional theory (NL-DFT). All samples exhibited typical IV characteristics, confirming the coexistence of hierarchical micro-, meso-, and macropores. As shown in Table 1, the Brunauer-Emmett-Teller (BET) surface areas were calculated as 967.03, 551.26, 486.09, and 413.75 m²/g for UMOPs, Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs, respectively. Significantly, the specific surface areas exhibited a gradual decrease upon doping with Ag₂O NPs, accompanied by corresponding reductions in the pore volume and pore diameter. This can be explained by the abundant embedding of Ag₂O NPs within the UMOPs pores, which causes them to occupy a partial portion of the pore volume, resulting in a decrease in the surface area. Compared to other silver-based scaffolds such as poly(*L*-lactide), cellulose, chitosan, and poly(*N*-isopropyl acrylamide), Ag₂O@UMOPs provide a considerably large surface area and an abundance of hierarchical pore channels.^{65–67} Ag₂O NPs could situate on the surface or embed within the interior of the UMOPs, this provided numerous active sites to engaging with and killing bacteria. These attributes significantly facilitated the adsorption of bacteria-containing solutions, enabling direct and intimate interactions between the bacteria and the active sites of Ag₂O@UMOPs. Moreover, the surface area of Ag₂O@UMOPs surpasses even that of porous polymer-derived silver

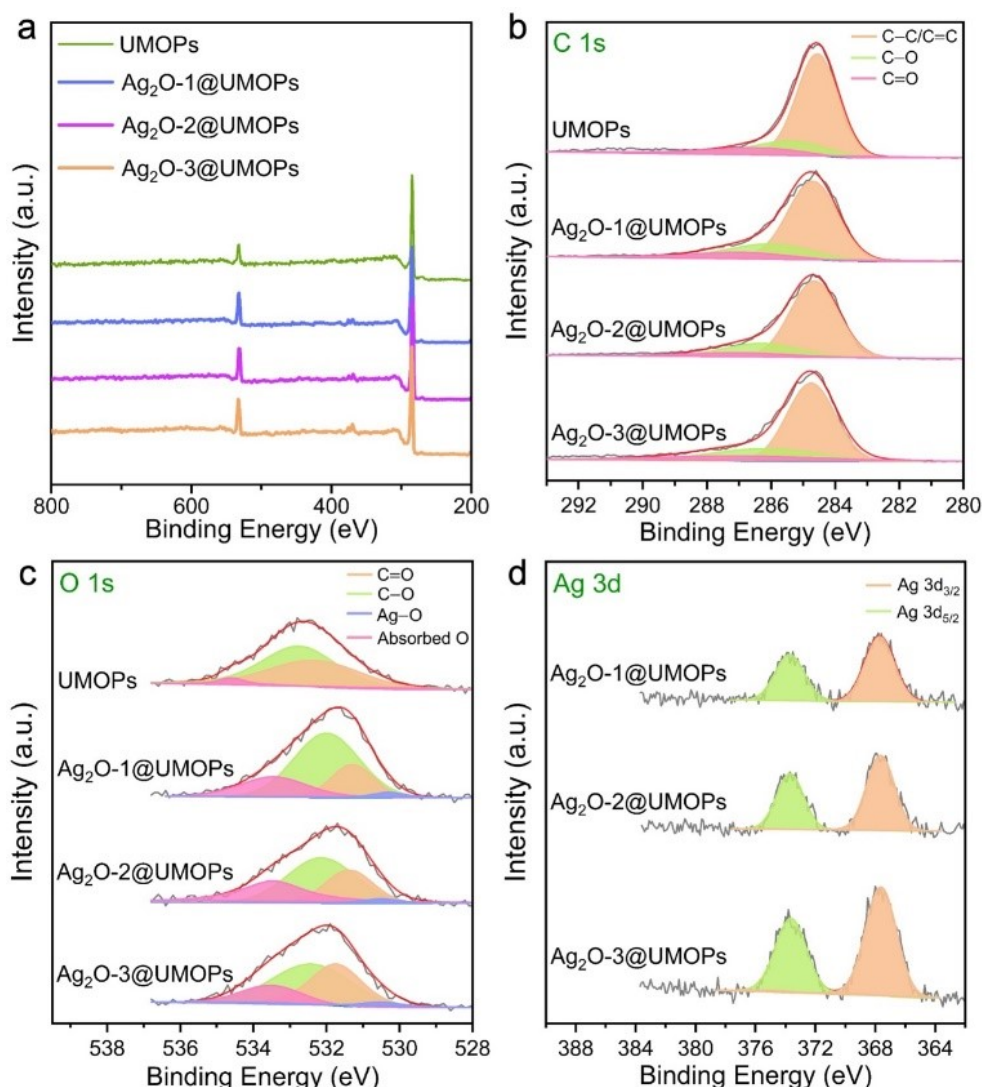


Figure 5. (a) XPS survey profiles, and deconvoluted XPS profiles for (b) C 1s, (c) O 1s, and (d) Ag 3d of UMOPs, Ag₂O-1@UMOPs, Ag₂O-2@UMOPs and Ag₂O-3@UMOPs.

Table 1. Yield and textural properties of UMOPs and Ag₂O@UMOPs.

Entry	Samples	S_{BET}^a (m ² /g)	V_t^b (cc/g)	D_p^c (nm)
1	UMOPs	967.03	0.95	6.24
2	Ag ₂ O-1@UMOPs	551.26	0.77	6.18
3	Ag ₂ O-2@UMOPs	486.09	0.64	6.09
4	Ag ₂ O-3@UMOPs	413.75	0.61	6.03

^aBET surface areas obtained from the N₂ adsorption isotherms. ^bTotal pore volume ($P/P_0 = 0.99$). ^cAverage pore diameter.

nanocomposites, such as metal-organic frameworks, mesoporous silica nanoparticles, and imidazole-based porous organic polymers (Table S1). Collectively, the large surface areas and the abundant hierarchical pores significantly facilitated the adsorption of bacteria-containing solutions, enabling direct and intimate interactions between the bacteria and the active sites of Ag₂O@UMOPs.

XPS analysis provided further insights into the detailed surface components of all the polymers, as well as the exact oxidation states of the elements. The UMOPs exhibit two main peaks at approximately 285 and 532 eV, corresponding to C 1s and O 1s, respectively (Figure 5a, Table S2). As illustrated in Figure 5b, the C 1s deconvoluted peaks at 284.60, 285.50, and

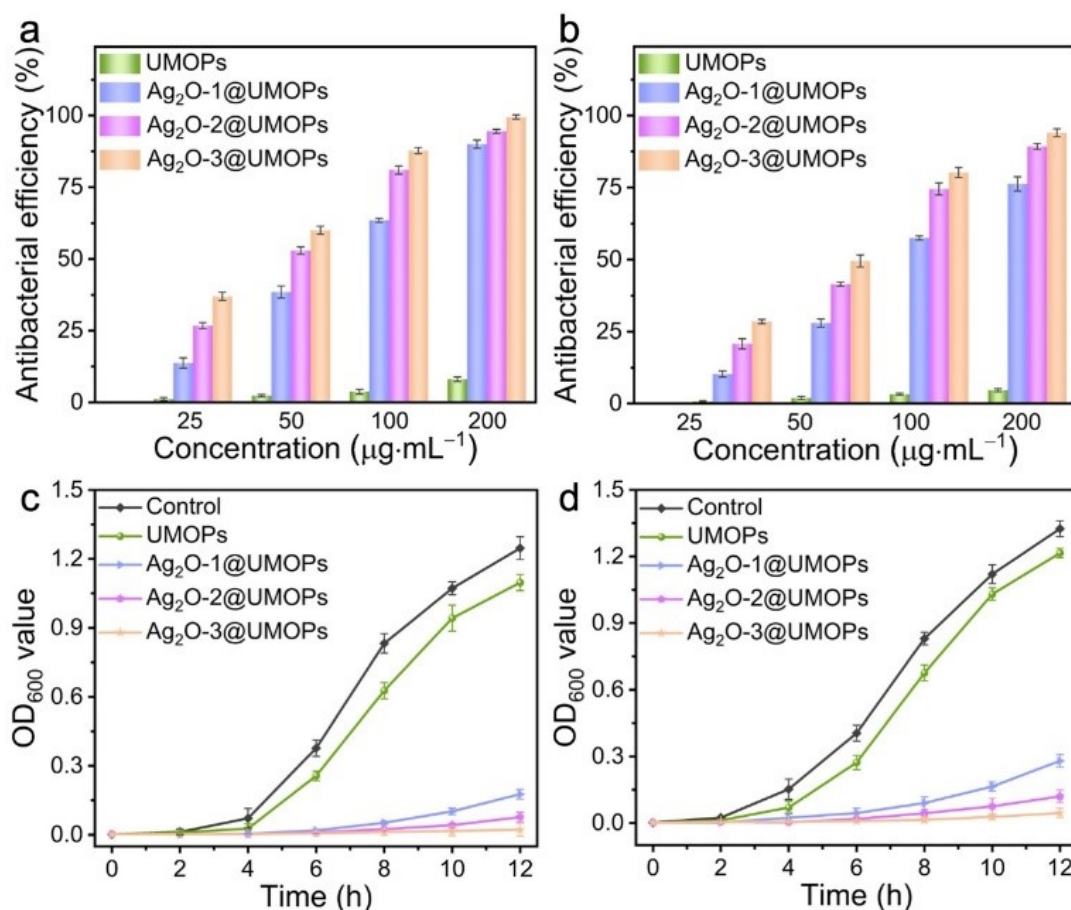


Figure 6. Antimicrobial activity of UMOPs and Ag₂O@UMOPs against (a) *E. coli* and (b) *S. aureus*. Growth curves of (c) *E. coli* and (d) *S. aureus* treated with UMOPs and Ag₂O@UMOPs (200 $\mu\text{g}\cdot\text{mL}^{-1}$), respectively.

289.70 eV corresponded to C–C/C=C, C–O, and C=O bonds, respectively. The deconvoluted O 1s peaks at 532.20, 532.71, and 533.42 eV corresponded to the C=O and C–O bonds, as well as adsorbed O, respectively (Figure 5c). In addition, Ag₂O@UMOPs displayed two additional peaks at 367.71 and 373.80 eV, which can be attributed to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively (Figure 5d). These peaks are in accordance with XPS data previously reported for the Ag⁺ state.^{68,69} Additionally, the deconvoluted O 1s peaks at 530.11 eV, indicative of the O–Ag bond, further confirmed the successful decoration of the Ag₂O NPs (Figure 5c).⁷⁰ These findings are in good agreement with XRD results. The Ag₂O NPs content within Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs was estimated to be 3.83, 6.59, and 7.54%, respectively.

Antibacterial properties of Ag₂O@UMOPs

E. coli (gram-negative bacteria) and *S. aureus* (gram-positive bacteria) were used as representative model bacteria to investigate the antibacterial activity of the synthesised

polymers. As shown in Figures 6a and b, all polymers exhibited concentration-dependent antibacterial ability; the higher the concentration, the better the antibacterial performance. The UMOPs had an almost negligible impact on *E. coli* and *S. aureus* viability, whereas all Ag₂O@UMOPs demonstrated a significant antibacterial effect. This could be attributed to the destructive effects of the Ag₂O NPs embedded in the UMOPs. When *E. coli* were treated with 100 $\mu\text{g}\cdot\text{mL}^{-1}$ of Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs, the antibacterial efficiencies were about 64.53%, 82.40%, and 88.22%, respectively. Furthermore, as the concentration increased to 200 $\mu\text{g}\cdot\text{mL}^{-1}$, the corresponding killing efficiencies of Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs reached 91.62%, 95.57%, and 99.80%, respectively. With regard to *S. aureus*, the killing efficiencies of Ag₂O-1@UMOPs, Ag₂O-2@UMOPs, and Ag₂O-3@UMOPs at a concentration of 100 $\mu\text{g}\cdot\text{mL}^{-1}$ were 58.28%, 75.85%, and 81.50%, respectively. When the concentration was elevated to 200 $\mu\text{g}\cdot\text{mL}^{-1}$, the corresponding antibacterial

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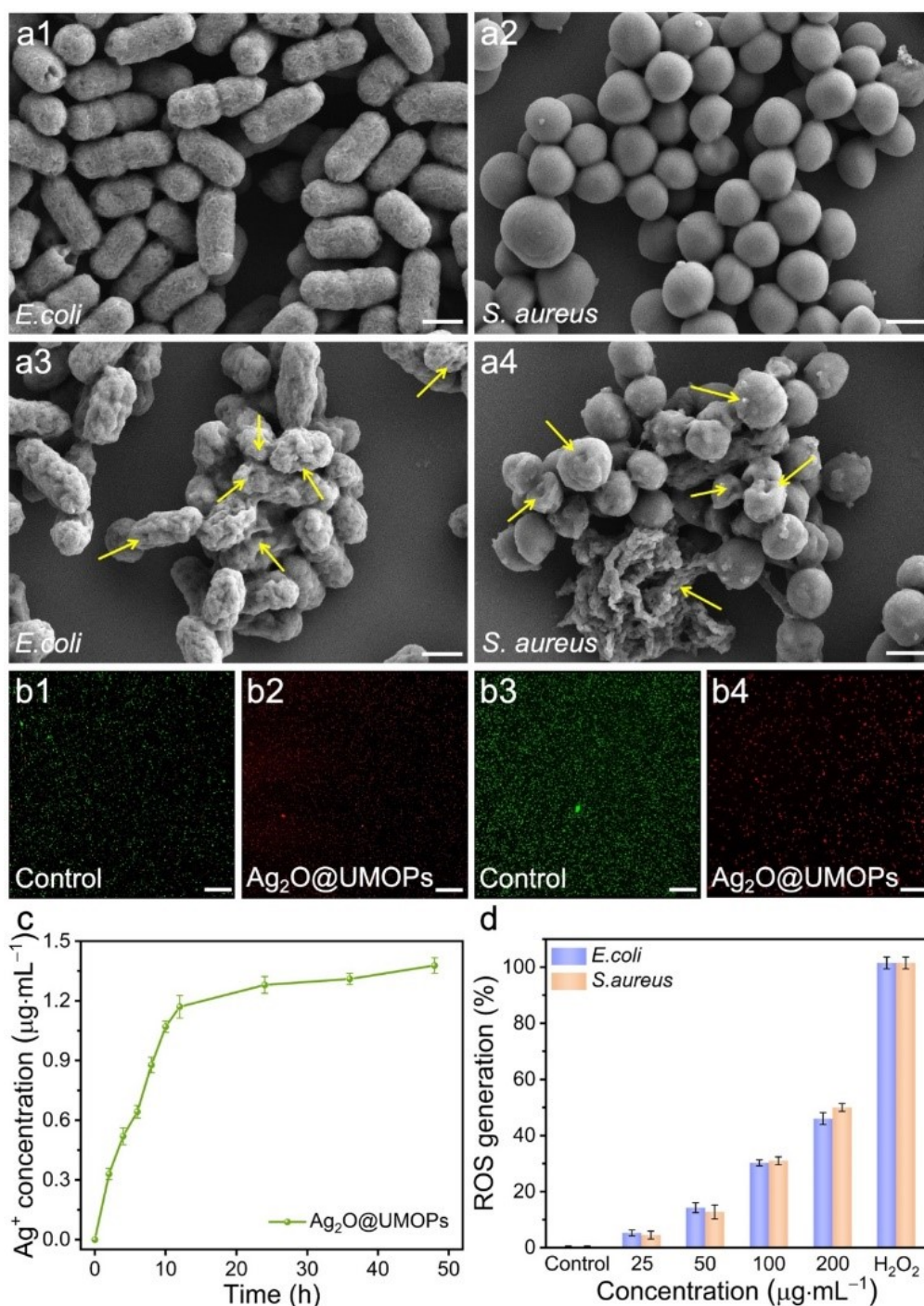


Figure 7. SEM images of control and $\text{Ag}_2\text{O}@\text{UMOPs}$ -treated groups of (a1, a3) *E. coli* and (a2, a4) *S. aureus*. Scale bars: 500 nm. (b) Confocal fluorescence microscopic images of control and $\text{Ag}_2\text{O}@\text{UMOPs}$ -treated groups of (b1, b3) *E. coli* and (b2, b4) *S. aureus*. Scale bars: 200 μm . (c) Cumulative Ag^+ release profile of $\text{Ag}_2\text{O}@\text{UMOPs}$ (200 $\mu\text{g}\cdot\text{mL}^{-1}$) in PBS (pH 7.4). (d) Concentration-dependent ROS generation of *E. coli* and *S. aureus* treated with $\text{Ag}_2\text{O}@\text{UMOPs}$

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efficiencies increased to 78.71%, 90.29%, and 95.30%, respectively. Remarkably, the Ag₂O-3@UMOPs groups demonstrated the best antibacterial performance, probably owing to the highest loading content of Ag₂O NPs.

A bacterial growth kinetic curve assay was performed to further investigate the antibacterial properties of the synthesised polymers. *E. coli* and *S. aureus* were incubated with the UMOPs and Ag₂O@UMOPs solutions at different concentrations. The growth curves of both *E. coli* and *S. aureus* displayed a significant time-dependent trends (Figure 6c, d, S5, and S6). A macroscopic bacterial proliferation phenomenon was observed for UMOPs-treated groups, implying that UMOPs had an almost negligible ability to eradicate bacteria, even at a high concentration of 4 mg·mL⁻¹. As the concentration increased to 8 mg·mL⁻¹, UMOPs presented a certain inhibitory effect on the growth of both *E. coli* and *S. aureus*, probably owing to the membrane stress exerted on bacterial cell walls by the sharp edges and rough surfaces of UMOPs.^{48,71,72} Compared to UMOPs, 200 µg·mL⁻¹ of Ag₂O@UMOPs considerably inhibited the growth of *E. coli* and *S. aureus* within the initial 6 h. Thereafter, OD₆₀₀ values of Ag₂O-1@UMOPs and Ag₂O-2@UMOPs groups gradually increased after incubating for 8 h, suggesting that neither group was able to completely kill bacteria. Nonetheless, the growth curves of the groups treated with 200 µg·mL⁻¹ of Ag₂O-3@UMOPs exhibited an almost flat trend, indicating that the bacteriostatic effect of Ag₂O-3@UMOPs is better than Ag₂O-1@UMOPs and Ag₂O-2@UMOPs. Compared to most reported composites incorporating Ag or Ag₂O NPs, Ag₂O-3@UMOPs achieved outstanding antibacterial performance, even with a low Ag₂O NPs content of only 7.54% (Table S1). Remarkably, the antibacterial efficacy against *E. coli* was notably superior to that against *S. aureus*, likely because of the thicker peptidoglycan layer in the cell walls of *S. aureus*.⁷³ Measurements were conducted to compare the antimicrobial activity of Ag₂O@UMOPs with that of pure Ag₂O NPs. It was noted that the antimicrobial activity of pure Ag₂O NPs reached approximately 100% only at a concentration of 100 µg·mL⁻¹ (Figure S7). However, the Ag₂O NPs content in Ag₂O-3@UMOPs was significantly lower compared to that of pure Ag₂O NPs. This could be attributed to the specific sea urchin-like morphology and the abundance of micro/mesopores in the Ag₂O-3@UMOPs.

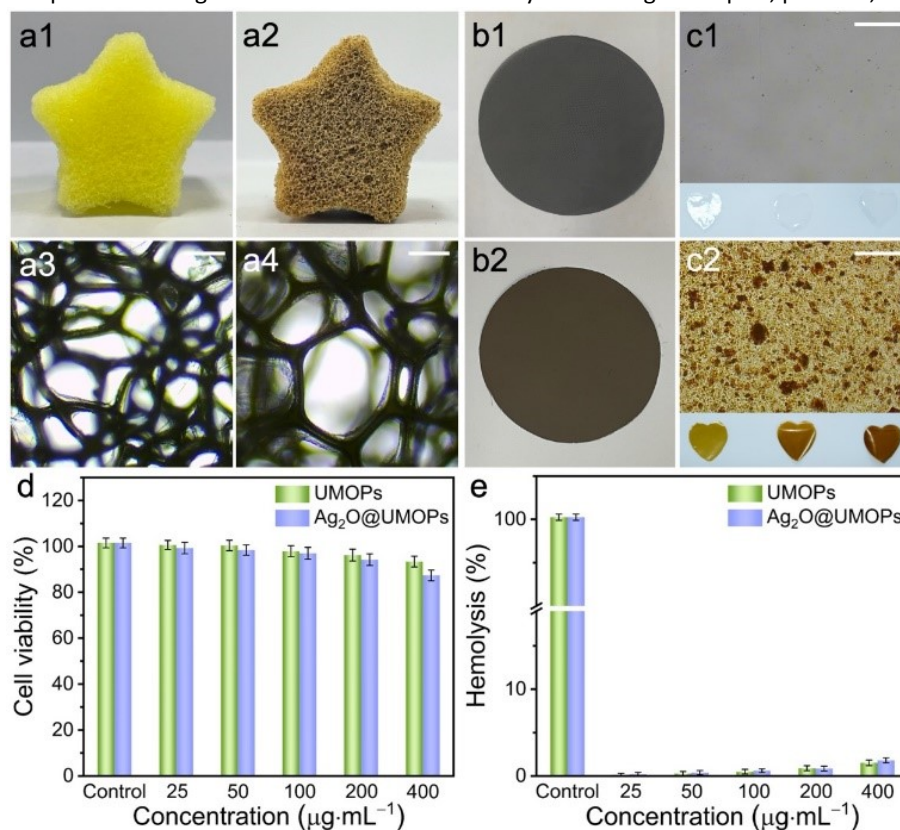
Antibacterial mechanism of Ag₂O@UMOPs

To elucidate the antibacterial mechanism of Ag₂O@UMOPs, SEM analysis was performed to visually assess the integrity of the bacterial cell membranes. As illustrated in Figures 7a1 and a2, the control groups of *E. coli* and *S. aureus* retained smooth surfaces and the original cellular morphologies. In contrast, the

membranes of both *E. coli* and *S. aureus* were severely damaged after treatment with Ag₂O@UMOPs (Figures 7a3 and a4). The bacterial membranes underwent significant distortion and wrinkling with numerous grooves and pits on their surfaces. Some bacteria showed structural collapse and intracellular component leakage, as evidenced by the presence of pores and severely lysed cell membranes (yellow arrowheads). These findings revealed that Ag₂O@UMOPs can effectively disrupt bacterial cell membranes. The Live/Dead BacLight staining assay was further conducted to demonstrate the integrity of the bacterial cell membrane.⁷⁴ SYTO-9 can stain live bacterial cells and generate green fluorescence, whereas PI can only traverse damaged cell membranes, bind DNA, and emit red fluorescence. As shown in Figures 7b1 and b3, the control groups exhibited strong green fluorescence and negligible red fluorescence, suggesting the integrity of the bacterial cell membrane. In contrast, the Ag₂O@UMOPs-treated groups displayed prominent red fluorescence, indicating substantial cell membrane damage in the bacteria (Figures 7b2, b4, and S8). The combined results from the SEM images and staining assays confirmed that Ag₂O@UMOPs disturbed membrane permeability and caused significant morphological changes in bacterial cell membranes. This cascade of effects ultimately leads to the destruction of cell membranes and, consequently, the death of the bacteria. It is well-established that Ag₂O NPs can release Ag⁺ ions and ROS through the dissolution of environmental O₂ or in response to an acidic environment (primarily induced by the metabolic behaviour of bacteria).⁷⁵ Moreover, Ag⁺ ions can interact with sulfur- and phosphorus-containing membrane proteins that are abundant on the surface of bacteria.^{20,21} Hence, we speculate that Ag⁺ ions released from Ag₂O NPs act on the bacterial cell membrane through electrostatic interactions, resulting in enhanced membrane permeability and subsequent membrane disruption. The release of Ag⁺ ions from Ag₂O@UMOPs was monitored at different time intervals. Figure 7c clearly illustrates the initial rapid release of Ag⁺ ions followed by a steady release after immersion for 12 h. Ag₂O anchored into the hierarchical network of UMOPs enabled the sustained release of Ag⁺ ions for more than 50 h, a duration sufficient for effective bacterial elimination. Additionally, the bacterial cell environment may promote the release of Ag⁺ ions owing to the electrostatic interaction between Ag⁺ ions and negatively charged groups on membrane proteins.⁷⁶

Previous studies have demonstrated that metal ions and metal-based NPs can promote the generation of ROS such as

The elevation of ROS levels can perturb intracellular activities by interacting with lipids, proteins, and DNA, ultimately leading



hydrogen peroxide (H_2O_2), superoxide ($\bullet\text{O}_2^-$), and hydroxyl radical ($\bullet\text{OH}$) during the metabolic processes of bacteria.^{77, 78}

Figure 8. Photographs of a star-shaped polyurethane foam and corresponding optical microscopy images of (a1, a3) before and (a2, a4) after loading with $\text{Ag}_2\text{O@UMOPs}$. Scale bars: 200 μm . Photographs of a PTFE membrane (b1) before and (b2) after loading with $\text{Ag}_2\text{O@UMOPs}$. Optical microscopy images of (c1) PS membrane and (c2) PS membrane incorporated with $\text{Ag}_2\text{O@UMOPs}$. Scale bars: 100 μm . (d) Cell viability of NIH-3T3 cells after incubation with UMOPs and $\text{Ag}_2\text{O@UMOPs}$. (e) Hemolysis assay of UMOPs and $\text{Ag}_2\text{O@UMOPs}$.

irreversible oxidative stress. DCFH-DA was selected as the ROS-sensitive probe to evaluate the ROS generation efficiency. DCFH-DA is hydrolysed by intracellular esterases, converting it into non-fluorescent DCFH, which is subsequently oxidised by ROS to produce the green fluorescent product, DCF. Figure 7d illustrates the changes in intracellular ROS levels in both *E. coli* and *S. aureus* when incubated with different concentrations of $\text{Ag}_2\text{O@UMOPs}$. Compared to the control group, higher ROS levels were observed in bacteria incubated with different concentrations of $\text{Ag}_2\text{O@UMOPs}$. Additionally, there was an increase in ROS content corresponding to an increase in the concentration of $\text{Ag}_2\text{O@UMOPs}$. These findings suggest the generation of a substantial amount of ROS in bacteria when $\text{Ag}_2\text{O@UMOPs}$ are present, potentially contributing to combating the bacteria.

To gain a profound understanding of the antibacterial mechanism and nanocomposite size within the intricate milieu of $\text{Ag}_2\text{O@UMOPs}$, we conducted an investigation into the swelling characteristics of UMOPs, $\text{Ag}_2\text{O@UMOPs}$ and Ag_2O NPs in complex media, including PBS and LB broth, the designated mediums for antibacterial activity studies.⁴² As depicted in Figure S9a and b, each category of $\text{Ag}_2\text{O@UMOPs}$ exhibited noticeable swelling after exposure to the solvents for several

hours, particularly notable in the case of PBS. The swelling ability (Q) of $\text{Ag}_2\text{O@UMOPs}$ was quantified by dividing the volume of the swollen polymer by the mass of $\text{Ag}_2\text{O@UMOPs}$. Remarkably, $\text{Ag}_2\text{O@UMOPs}$ demonstrated superior swelling ability, achieving the highest Q value at approximately 40 $\text{mL}\cdot\text{g}^{-1}$ (Figure S9c). Consequently, we postulate that the micro- and mesopore sizes could expand during the swollen state, significantly enhancing the accessible antibacterial sites for interaction with bacteria.^{47, 48} In contrast, pure Ag_2O NPs did not exhibit a pronounced swelling ability, further validating the advantages of employing such a carrier.

Based on the analysis presented above, we speculate that the bactericidal effect of $\text{Ag}_2\text{O@UMOPs}$ may be attributed to the synergistic functions of $\text{Ag}_2\text{O@UMOPs}$ accumulation, release of Ag^+ ions, and generation of ROS. The large surface areas and hierarchical pores create ample channels for bacterial solutions, allowing easy contact and accumulation of $\text{Ag}_2\text{O@UMOPs}$ on the bacterial surface. Moreover, environmental O_2 and acidic environments can trigger the sustained release of Ag^+ ions and ROS from $\text{Ag}_2\text{O@UMOPs}$. The following actions may occur simultaneously: (i) The internalisation of Ag_2O NPs and Ag^+ ions, along with membrane stress induced by the sharp edges and rough surfaces of UMOPs, disrupts the membrane

permeability of bacteria.^{71,72} (ii) The electrostatic interactions between the Ag⁺ ions and the negatively charged groups present in the membrane components further augment the membrane permeability of the bacteria.^{75, 79} This leads to morphological alterations and damage to the bacterial membrane, ultimately resulting in pore formation and cytoplasmic leakage. (iii) Upon entering cells, Ag₂O NPs and Ag⁺ ions perturb bacterial intracellular processes by disrupting DNA structure, impeding mRNA replication and transcription, denaturing proteins, and deactivating enzyme functions.³¹ (iv) Surging ROS levels exacerbate bacterial dysfunction, ultimately leading to bacterial death.⁸⁰ Ag₂O@UMOPs functioned as reservoirs for the gradual release of Ag₂O NPs and Ag⁺ ions into the bacteria. These sequential actions collectively inhibit the repair of damaged membranes, thereby preventing the development of bacterial drug resistance.

Processability, coating properties and biosafety

Processability plays a pivotal role in the commercialisation of MOPs, enabling the expansion of their potential applications and enhancing their overall performance.^{81, 82} Therefore, we tested the potential processability of Ag₂O@UMOPs. As shown in Figures 8a1 and a2, the Ag₂O@UMOPs powders were loaded into the polyurethane foam, utilizing polydimethylsiloxane (PDMS) as adhesive by a simple dipping coating method.^{43, 48, 83} Optical microscopy images demonstrate the continued integrity of the internal structure of the foam, with no noticeable alterations in the pore sizes (Figures 8a3 and a4). The Ag₂O@UMOPs-loaded polyurethane foam excelled at absorbing bacterial solutions, including those found in sewage and medical devices. Simultaneously, the embedded Ag₂O@UMOPs served as potent antimicrobial agents that effectively eradicated bacteria. Moreover, we tested a polytetrafluoroethylene (PTFE) membrane, and the Ag₂O@UMOPs were easily incorporated on the surface of the PTFE membrane (Figures 8b1 and b2). Ag₂O@UMOPs powders, PTFE powders and PDMS adhesive were uniformly mixed and then mechanically compressed into membranes. This allows for a wider range of applications, such as environmental antimicrobials, air pollutant sterilisation, and filtration. In addition to the surfaces of common materials, Ag₂O@UMOPs powders can be easily incorporated into PS and further compressed into membranes. As the quantity of Ag₂O@UMOPs increased, a consistent darkening of the heart-shaped membrane colour was clearly observed (Figures 8c1 and c2). This observation further confirms the exceptional processability of these antibacterial materials. Furthermore, given the impressive antibacterial properties of Ag₂O@UMOPs, PS membranes, with Ag₂O@UMOPs uniformly integrated, have the potential to serve as effective dressing materials for bacterial infections.

The MTT assay was performed on mouse NIH3T3 fibroblasts to evaluate the cytotoxicity of Ag₂O@UMOPs. As depicted in Figure 8d, when treated with Ag₂O@UMOPs at concentrations of 25, 50, 100, 200, and 400 µg·mL⁻¹, the cell survival rates were found to be 97.52%, 96.80%, 95.27%, 92.45%, and 85.79%, respectively. In conjunction with the antibacterial results, Ag₂O@UMOPs, at a concentration of approximately 200 µg·mL⁻¹

¹, exhibited the remarkable capability to eradicate bacteria completely, all while maintaining unaffected cellular activity. A haemolysis assay using fresh mouse blood was conducted to further assess the hemocompatibility of the Ag₂O@UMOPs. Figure 8e shows that no significant haemolytic effect was observed for Ag₂O@UMOPs. These findings indicated the negligible toxicity of Ag₂O@UMOPs at antibacterial concentrations, rendering them an ideal choice for use as organic coating materials on various substrates. These successful attempts also convinced us that these antimicrobial powders can be effectively compounded on the surface or inside a wide range of materials, thus enabling their use in a wider range of applications.

Conclusion

We fabricated a versatile antibacterial coating material based on Ag₂O@UMOPs with a distinctive sea-urchin-like shape. Ag₂O@UMOPs were readily synthesised through a one-pot self-assembly process mediated by Lewis acid-base interactions, followed by carboxylation and anchoring of the Ag₂O NPs. Ag₂O@UMOPs possess a large surface area and high porosity, furnishing a multitude of active sites that are conducive to the effective engagement with and killing of bacteria. The Ag₂O@UMOPs exhibited superior antibacterial activity against both *E. coli* and *S. aureus*. At a concentration of 200 µg·mL⁻¹, Ag₂O-3@UMOPs achieved impressive killing efficiencies of 99.80% for *E. coli* and 95.30% for *S. aureus*, respectively. Interestingly, Ag₂O@UMOPs can be easily loaded onto polyurethane foam or compressed into the membrane. Cytotoxicity and haemolysis assays demonstrated the good cytocompatibility and hemocompatibility of Ag₂O@UMOPs. Consequently, the remarkable thermal stability, processability, and biosafety of the Ag₂O@UMOPs make them suitable for coating a wide range of substrates to meet various biomedical requirements.

Author Contributions

Y.Z., W.S. conceived the idea and designed the experiments. Y.T., Q.L., and Y.Q. performed the experiments. Y.Z. and Y.X. participated in data analyses and discussions. L.Z., D.G.Y., Y.X., X.L., I.K. W.S. Writing – reviewing and editing the manuscript.

Conflicts of interest

There are no conflicts to declare.

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