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Research Article

Functional Surface Coating on Cellulosic Flexible Substrates with Improved Water-Resistant and Antimicrobial Properties by Use of ZnO Nanoparticles

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It is of significant interest to create functional flexible surfaces that simultaneously exhibit high water-resistance and antimicrobial performances for medical or packaging applications. This study reported a synthesis of functional surface coating on flexible cellulose materials (filter papers) with ZnO nanoparticles and binds of renewable soybean oil-based polymers. Self-aggregation of ZnO nanoparticles could form ZnO particles with two regular morphological patterns. Rather than a rod-like morphology, a flower-like ZnO benefited a promotion of surface hydrophobicity. Moreover, surface with the flower-like ZnO showed a 51.6% promotion on antimicrobial activities against Gram-negative bacteria *(E. coli)* than the rod-like ZnO. A low binder/ZnO ratio of 0.2 led to a remarkable improvement on water repelling performances without negative effects on a coating adhesion of ZnO. Under this condition, a hydrophobic surface was achieved with a large static contact angle of 138° when applying ZnO nanoparticles at a dosage of 3 g m^{-2}.

1. Introduction

Introduction of flexible cellulose materials such as microfibrillated cellulose or cellulose nanofibers as functional membrane, supporting component or papers in medicinal and electronic and packaging applications, attracts people's great attentions [1–4]. For a nature of existence of -OH group on cellulose surfaces, the ease of absorbing moisture or directly contacting with water during distribution, storage, and application is of great challenge to mechanical endurances or antidegradability of these cellulose materials. Moreover, additional functional properties such as good antibacterial activity were also usually preferred for preparing functional cellulose materials. Surface modification possessed a great promise for a controlled wettability or hydrophobicity of the functional cellulose materials.

The creation or development of hydrophobic surfaces with (or without) antibacterial function on cellulose materials uses a number of technologies, such as, chemical coating methods using a mixture of 1H,1H,2H,2H-perfluorooctyltriethoxysilane, 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride, and P,P-diphenyl-N-(3-(trimethoxysilyl) propyl) phosphinic amide [5] or fluoroalkyl-functional siloxane [6] through a sol–gel process; laccase-catalyzed hydrophobization with lauryl gallate [7] and grafting with eugenol [8] or ferulic acid [9]; thermochemical fabrication and impregnation of silver nanoparticles with starch [10]; sonochemical cohydrolysis and cocondensation with tetraethyl orthosilicate and alkyltrialkoxysilanes [11]; and physical pad-dry-cure method with MgO/methyl silicate nanocomposites [12].

Other methods such as internal sizing and surface sizing only provide a first barrier for cellulosic substrates against water penetration but often cannot meet the requirements for modern applications [13]. Nowadays, artificial water-resistant surfaces have been fabricated on cellulosic substrate based on selection of appropriate methods to create roughness and/or low surface energy on local surfaces [14]. Fluorinated polymers together with nanoparticles, for example, silica [15] or ZnO [16], were believed to be effective chemicals in building up water-resistant structure on cellulosic surface [17]. However, if an environment concern was taken into consideration, coating with no-fluorinated materials is preferable technology for preparation of highly hydrophobic surface [18].

ZnO is an attractive candidate for surface coating application [19, 20] due to its considerable antibacterial efficiency [21], stability [22], tunable structure [23], and low toxicity [24]. ZnO nanoparticles are promising additives for further improving the hydrophobicity through dedicated surface modification [18] such as stearic-acid modification [25, 26]. On the other hand, preventing undesirable microbial spoilage was also an important property for coating materials [19, 27]. ZnO finds increasing application as an antibacterial material for its promise of withstanding a harsh physical or chemical processing [21], compared to organic antibiotics that were conventionally used [22]. For instance, incorporate ZnO in hygienic coating for sterile packaging use [28].

Because of the promising functional properties, ZnO was introduced in this study for creating functional flexible surfaces that simultaneously exhibit high water-resistance and antimicrobial performances that could be subject to medical or packaging applications. ZnO nanoparticles were applied to build functional layers hierarchically on filter papers as a model of flexible substrate through a surface coating method. Soybean oil-based polymers were used as a green binding reagent for assembling the ZnO particles with cellulosic fibers. With an optimal coating formulation and application dosages, water repelling properties and antibacterial activities of the composite surface were determined for evaluating its feasibility for medical or packaging applications.

2. Materials and Methods

2.1. Materials. Rod-like ZnO were obtained from Aladdin Biochemical Technology, Co. Ltd. (Shanghai, China). Flower-like ZnO were synthesized by a typical hydrothermal method according to the reported method [26]. The average intensity-based hydrodynamic size of ZnO particles was measured using a Zeta Potential analyzer (ZetaPlus, Instruments Corporation, NY, USA). Cellulose filter paper (Whatman #2, 106 g m^{-2}, GE healthcare Life Sciences, Buckinghamshire, UK) was used as the cellulose substrate. Soybean oil-based polymer for binding ZnO nanoparticles on the paper surface was prepared according to the procedure reported in our previous study [29]. The chemicals of acrylated epoxidized soybean oil (AESO), 3-aminopropyltriethoxysilane (APTS), benzoyl peroxide (BPO), and anhydrous acetone were mixed with a weight ratio of 1/0.3/0.004/1. All of the chemicals were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA).

2.2. Methods

2.2.1. Coating ZnO on Paper Surface. Coating slurry was prepared by mixing ZnO particles with binder together. In a typical method, 1 g ZnO particles (dry mass) was dispersed in 5 mL ethanol. All the prepared coating slurry was in an equal volume of 5 mL. The binder was gently added into the slurry at the ratio of 0.2–0.6/1 (binder/ZnO, w/w).

The paper was coated by a rod coater (K303 Multicoater, RK. Print Coat Instruments Ltd., UK) with the coating slurry at a velocity of 3 m min^{-1}. After coating, the paper was immediately transferred for curing at 80°C for 30 min to finalize the bonding of ZnO particles. Coating weight of the ZnO varied from 1.5 g m^{-2} to 4.5 g m^{-2}.

2.2.2. Characterization of Morphologies and Surface Wettability. The aggregation patterns of the commercial and synthesized ZnO particles and distributions of ZnO particles on surface were characterized using a JEOL 6400 scanning electron microscope (JEOL Ltd., Tokyo, Japan). To determine the surface wettability, static contact angles (SCA) of water droplets (3 μL) on the surface coating were measured using an optical tensiometer (Attension Theta, Biolin scientific, Stockholm, Sweden) [30]. Measurement was performed for 10 times on each sample.

2.2.3. Antibacterial Assays. Minimum inhibition concentration (MIC) of ZnO particles against *E. coli* ATCC 11229 was measured by a dilution method [31]. ZnO particles with different concentrations were serially diluted in LB broth. The ZnO dilution and fresh bacterial culture (10^6 CFU mL^{-1}) were equally mixed by volume and incubated at 37°C for 18 h. MIC was determined as the lowest effective concentration of ZnO in inhibiting a visible growth of bacteria.

The antibacterial activity of the ZnO surface coating was quantitatively examined through a cultivation method in shaking flasks. A 0.10 g of paper sample was soaked in a 25 mL flask containing 5 mL culture of *E. coli* (10^5 CFU mL^{-1}). Shaken at 200 rpm, the mixture was incubated at 37°C for 60 min. After cultivation, 0.5 mL culture was successively diluted with 4.5 mL PBS solution to prepare bacterial dilutions. Finally, 0.1 mL of the dilution was coated on LB agar plate. After an incubation at 37°C for 24 h, the number of bacterial colonies formed was counted. Each paper sample was tested in triplicate. Filter paper without surface coating was used as the paper blank.

A reduction rate of bacterial reproduction was calculated to determine the antibacterial efficiency of the surface coatings by

$$\text{Reduction rate } (\%) = 100\% \times \frac{(A - B)}{A}, \quad (1)$$

where A and B were the numbers of bacterial colonies formed from the cultures with paper blank and coated papers, respectively.

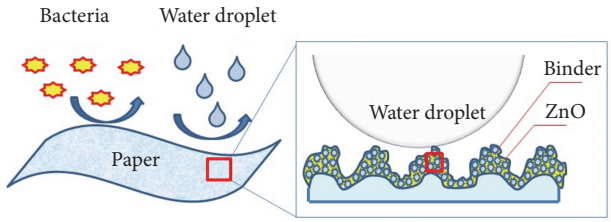


FIGURE 1: Schematic diagram of the surface coating structure.

3. Results and Discussion

3.1. Structure of the Surface Coating. The surface wettability of the surface coating was usually determined by two important factors: surface energy and surface roughness [32]. Natural cellulosic surfaces are hydrophilic or highly affiliative to water. In this work, change in hydrophobicity of cellulosic surface was realized due to the hydrophobic properties of soybean oil-based binder [33]. Low surface energy was achieved after incorporating the hydrophobic binder on cellulosic surfaces. At the mean time, the micro- or nanoscale hierarchical structures of ZnO particles could control the surface roughness (Figure 1).

The use of soybean oil-based polymer in the coating formula as binders relied on its bifunctional roles in the surface coating [34]. On one hand, AESO, the main constituent in the binder, could distribute through chain propagation to form a hydrophobic substance through free-radical reactions. On the other hand, the APTS which attached on AESO through a Michael addition reaction [35] could efficiently provide reactive silanol groups to render covalent bonds between -OH and $\ddot{O}_2^-$ on cellulosic surface and metallic oxide, respectively [33]. The binder was predominantly made up of triglyceride structures and probably possesses a potential degradability [36].

The original pore structure on natrual cellulosic surface and ZnO particles contributed to the increase of water-resistant property of the coated cellulosic surfaces. The interlaced network of cellulose fibers provided basic microstructure of paper surfaces. ZnO nanoparticles coating could lead to three-dimensional structural patterns in micro- and nanoscale to form a hierarchical roughness on cellulosic surface. This specific morphology was believed to be more effective in creating air pockets [37] and increasing the water contact angles of the cellulose materials [38].

3.2. Aggregation of Patterns of ZnO Nanoparticles. In this study, two aggregation patterns of ZnO nanoparticles, that is, rod-like ZnO and flower-like ZnO, were introduced and tested separately (Figure 2). With an average diameter of ~ 2 μm, the 3D structure of the flower-like ZnO was observed by assembing a large number of 15 nm-thick nano-ZnO sheets. The nanosheets intersected with each other to form special porous structures on the flower-like ZnO.

Table 1 demonstrates the average diameters of the ZnO particles with two different aggregation patterns. The hydrodynamic size for both ZnO particles was relatively lower than that estimated by SEM imaging method.

3.3. Factors Affecting the Water Repelling Efficiency of Surface Coating

3.3.1. Patterns of ZnO Particles. Figure 3 shows that the cellulosic surface is superhydrophilic as the SCA is almost 0°. It could be explained by the existing of free hydroxyl groups that had a strong affinity for water. It demonstrated a strong hydrophobicity of the polymer binder was demonstrated as the hydrophilic cellulosic surface became hydrophobic with a SCA of 106° when a 0.3 g m^{-2} binding polymer was applied (Figure 3(b)). With introducing of two ZnO into the coating formula, the SCA of paper was further promoted over 125° (Figures 3(c) and 3(d)). It could be explained by a formation of hydrophobic substance over the cellulosic substrate followed by a decrease of the surface energy with ZnO particles. Additionally, the coverage of hydrophobic ZnO particles introduced micro- and nanoscale roughness, which was able to trap air for forming a solid-air-liquid interface. The multiscale structures, combining micro- and nanometric structuration would provide a remarkable promotion on water-droplet repellency [39]. The use of ZnO particles and polymer binder realized an improved antiwetting property through a surface morphological modification.

Interestingly, differences of the SCA between ZnO particles with distinct morphologies were observed. The flower-like ZnO was more effective in promoting SCA than the rod-like ZnO. As mentioned above, the flower-like ZnO particles tended to form a regular three-dimensional pattern full of micro- and nanostructures (Figure 3(d)) that were believed to be more effective in creating air pockets for an increase of SCA [40]. In contrast, the rod-like ZnO only deposited a flat structure through the surface coating (Figure 3(c)).

3.3.2. Ratio of Polymer Binder and ZnO in the Formula. The dosages of soybean oil-based binder in the coating agent needs to be adjusted to provide sufficient hydrophobicity as well as to ensure a solid affinity of ZnO particles on the cellulosic surface. Figure 4 shows that an increase of binder/ZnO ratio always leads to a decrease of SCA on the surface either with the lower-like ZnO or the rod-like ZnO. Lower ratio benefited a high SCA. The negative effect of an overuse of polymer binder on the SCA could refer to the AESO composition which had caused a loss of surface nanostructures induced by engulfing of ZnO particles and thus a reduction in roughness in the coating layers [15]. In addition, the reduction of the surface roughness was also attributed to the ease of aggregation of ZnO particles.

Even with an increased ratio of binder/ZnO, the flower-like ZnO still showed better performances on improving the water repelling efficiency than the rod-like ZnO did (Figure 4). As all porous structures on the ball-shaped particles could be well filled with the adsorbed binding chemicals, the flower-like ZnO showed an even distribution pattern on the coating surface. The smaller rod-like ZnO tended to gather together with the binding chemicals on the cellulosic surface. Considering a firm adhesion of ZnO particles, a ratio no less than 0.2 should be selected as the optimal level for further application.

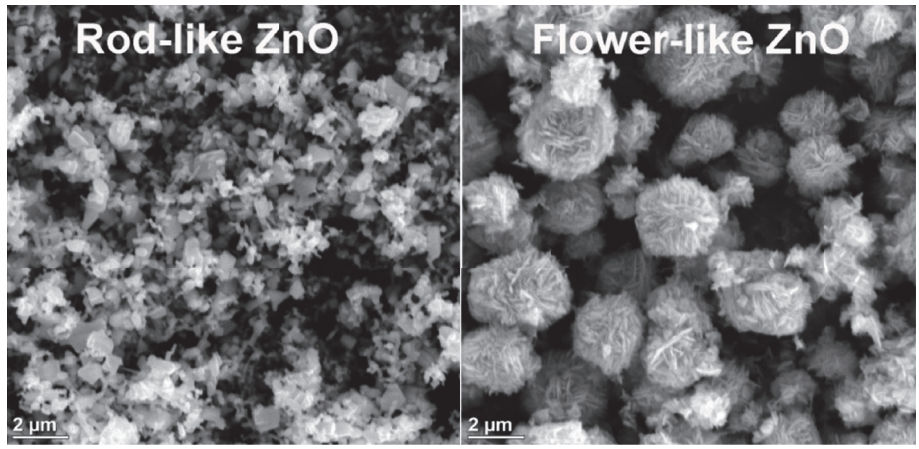


Figure 2: SEM images of the nano-ZnO aggregation.

Table 1: Particle size and polydispersity of the nano-ZnO aggregation.

Aggregation patterns	Hydrodynamic size		SEM observable size	
	Effective diameter (nm)	Polydispersity	Average diameter (nm)	Polydispersity
Rod-like ZnO	124.5	0.13	372.1	0.49
Flower-like ZnO	521.7	0.18	2374.1	0.30

3.3.3. Coating Weight. An increase application of the coating formula from 1.5 to 3 g m^{-2} promotes the SCA with either of the flower-like ZnO or the rod-like ZnO (Figure 5). However, an intensive application of coating weight had a negative effect on the SCA of the cellulosic surfaces. In Figure 6, it is revealed that the coating weight has influenced the surface morphology directly. At a coating weight of 1.5 g m^{-2}, the cellulosic surface was only partially coated by the ZnO particles with binding polymers, leaving the valley area of fiber networks hydrophilic to water. As the increase of the coating weight to 3 g m^{-2}, the cellulosic surface was well covered by the hydrophobic coating with a mixture of micro- or nanostructures exposed on the air-water interface. Upon further increasing the coating weight to 4.5 g m^{-2}, the cellulosic surface is covered by densely packed layers with a significant loss of micro- or nanohierarchical structures (Figure 6). As the fabrication of micro- or nanostructures on the coating surface would reflect the hydrophobicity performances of materials, choosing proper coating weight as well as a premodification of morphologies of the coating substrate would be possible method to adjusting the SCA on the coating surface.

3.4. Antimicrobial Efficiency of the Surface Coating with ZnO Nanoparticles. Besides regulating the surface roughness, the ZnO particles also played a key role in introducing the antimicrobial function to the cellulosic surfaces. Depending on the differences in particle sizes, the bacterial types, and experimental assays, the reported antimicrobial efficiency of ZnO differed with an effective concentrations ranging from 81 to 2835 μg mL^{-1} [41].

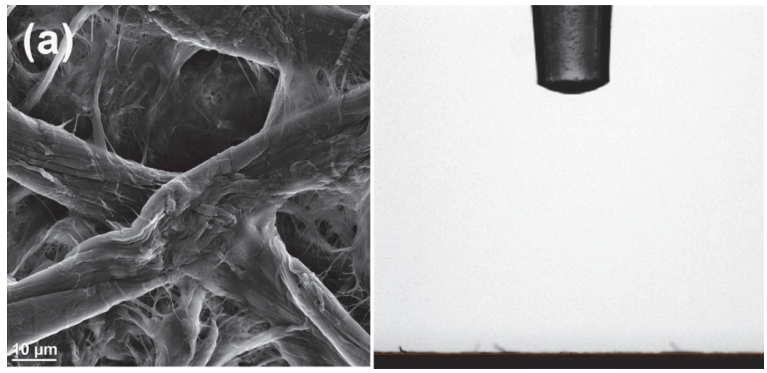
Determination of antibacterial activity of ZnO particles was performed homogenously as it ensured that ZnO particles could be well distributed in the bacterial culture [42]. In this study, we also measured a relative inhibating rate for *E. coli* reproduction (reduction rate) alternatively using the filter papers with immobilized-ZnO-polymer coatings. In this study, the flower-like ZnO-polymer coating shows higher antibacterial activity than that of the rod-like ZnO-polymer coating (Table 2). The result was consistent with the reported literature [43]. Nevertheless we did not find an obvious difference in the MIC between using flower-like and the rod-like ZnO (Table 2).

A coating weight of 3 g m^{-2} led to a 51.6% of reduction rate *E. coli* reproduction by coating with flower-like ZnO particles. The reduction rate was comparable to that with the dispersion of free ZnO particles and the reduced antibacterial efficiencies of the surface coating were mainly from the barrier effects caused by binding polymers [43].

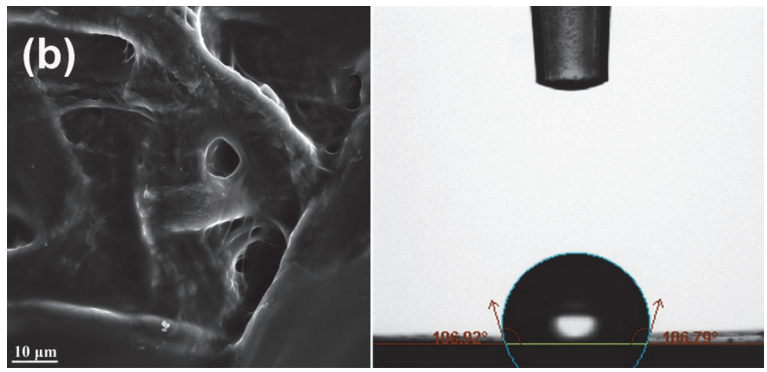
Defect sites could be formed on the flower-like ZnO with a typical structural pattern of 15 nm-thick nanoplates (Figure 2); that was believed to be responsible for the production of reactive oxygen species (ROS) in antibiosis of *E. coli*. In addition, an increase of coating weight resulted in an improvement of antibacterial activities for the coating surfaces. Clearly, a higher availability of ZnO from applying intensive coating weights on cellulosic surfaces corresponded to the promotion on release of ROS [44].

4. Conclusion

Functional flexible cellulosic surfaces with water-resistant and antimicrobial properties were prepared through a coating



(a)



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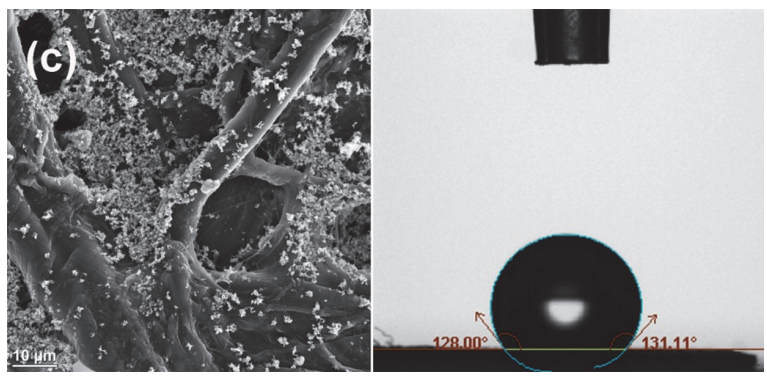
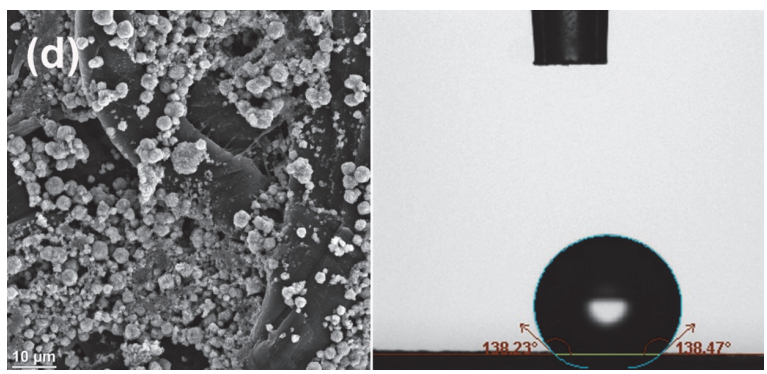


(c)



(d)

Figure 3: SEM images and SCA of (a) cellulosic surface; (b) cellulosic surface + binder; (c) cellulosic surface + binder + rod-like ZnO; and (d) cellulosic surface + binder + flower-like ZnO (with binder/ZnO ratio = 0.2).

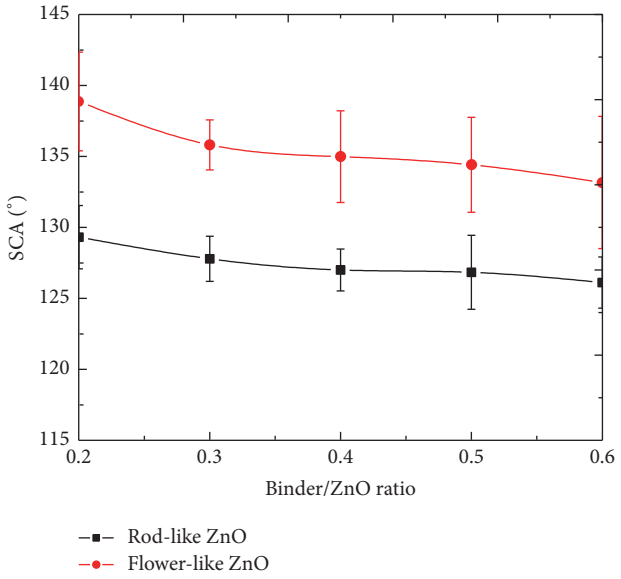


Figure 4: Effect of the binder/ZnO ratio on the SCA of coating surfaces.

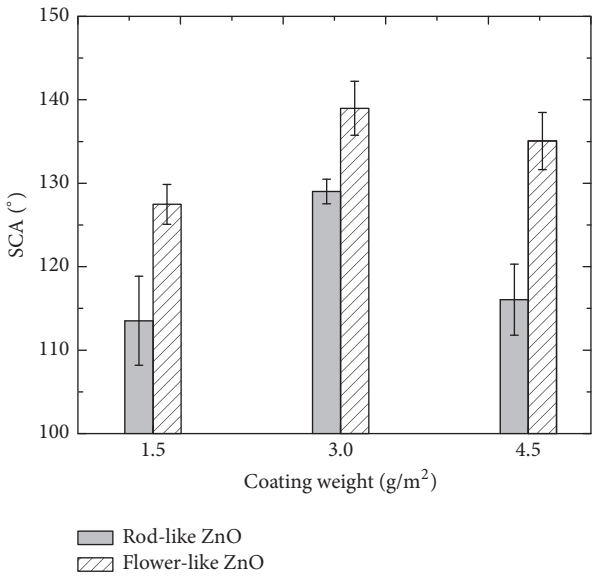


Figure 5: Effect of coating weight on the SCA of coating surfaces (with binder/ZnO ratio = 0.2).

Table 2: Antimicrobial performances of the surface coating with different ZnO aggregations.

	MIC	Reduction of *E. coli* reproduction (%)	
	(μg mL^{-1})	*Coating weight of 1.5 g m^{-2}	*Coating weight of 3 g m^{-2}
Control	0	0	0
Rod-like ZnO	312.5	34.0	45.3
Flower-like ZnO	312.5	44.9	51.6

*Binder/ZnO ratio = 0.2.

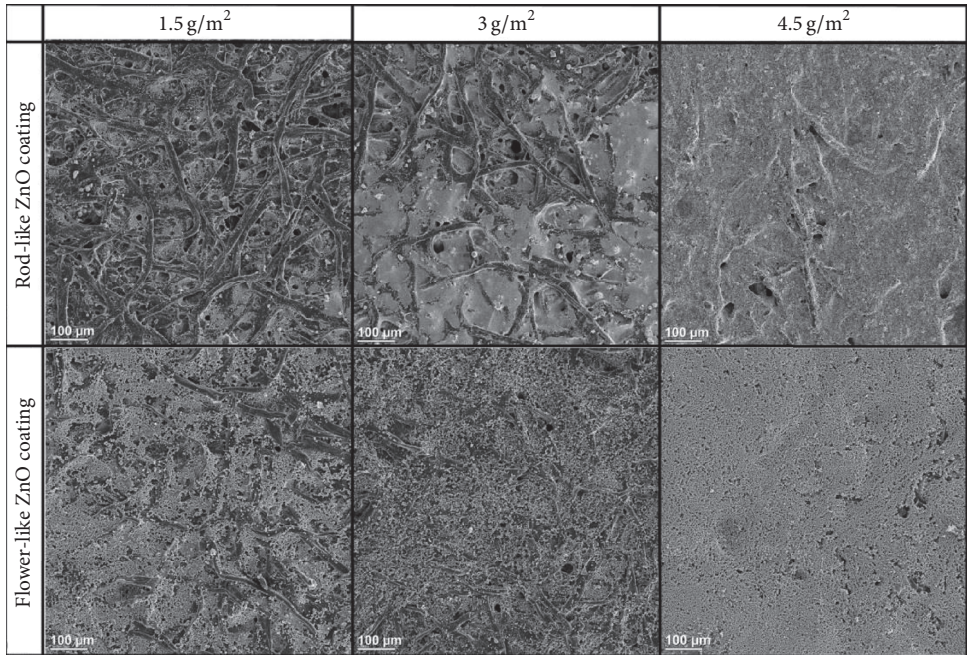


Figure 6: SEM images of the coating surface at different coating weight (with binder/ZnO ratio = 0.2).

method with ZnO nanoparticles and soybean oil-based polymers. The flower-like structural pattern of ZnO effectively promoted the SCA and antimicrobial activities. Under the optimal conditions with a binder/ZnO ratio of 0.2 and coating weight of 3 g m^{-2}, the prepared functional surfaces showed improved hydrophobic and antibacterial advantages with a SCA value of 138° and a 51.6% reduction rate for inhibiting *E. coli* reproduction.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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