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NANOSTRUCTURED ANTIBACTERIAL SILVER DEPOSITED ON POLYPROPYLENE NONWOVENS

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Nanostructured silver films were deposited on polypropylene (PP) nonwovens by RF magnetron sputter coating to obtain the antibacterial properties. Shake flask test was used to evaluate the antibacterial properties of the materials. Atomic force microscope (AFM) was utilized to observe the surface morphology. Energy-dispersive X-ray (EDX) was also employed to analyze the surface elemental compositions. The antibacterial results indicated that the prolonged deposition time led to a significant improvement in antibacterial effect, and sputtering power and argon pressure did not show obvious effect on antibacterial performance. It is believed that the total amount of silver ions released from the silver coating was increased as the deposition time increased. AFM images and quantitative analysis of EDX, respectively revealed that increase in deposition time led to the increased coverage of silver film and the increased silver weight percentage per unit surface, which provided evidences for the increased release rate of silver ions from the coating. Moreover, it was found that the optimum silver coating thickness was about 3 nm, taking antibacterial effect and cost of production into account.

Keywords: Magnetron sputter coating; nanostructured silver films; antibacterial; AFM; EDX.

1. Introduction

Silver has such advantages as broad spectrum antibacterial activity, non-toxicity to human cells and long-lasting effect.[1] Thus, in recent years it has been widely used in medical devices ranging from wound dressings to urinary catheters.[2]

Various techniques have been used to prepare silver films. One conventional approach is chemical silver plating.[3,4] However, this technique generally suffers many demerits, which include low silver pick up onto the substrates and the disadvantages to the environment. Another method of coating silver onto a substrate involves vacuum vapor deposition. This method also has some drawbacks because of the poor adhesion and technological repetitiveness. In this research, magnetron sputter coating was employed to prepare silver films for possessing such advantages as uniform and compact stronger bonding between the film and its substrate and being environmentally friendly.

In this study, nanostructured silver films were deposited on the surfaces of polypropylene (PP) nonwovens by RF magnetron sputter coating. Shake flask test was used to investigate the antibacterial properties of all coated samples. Atomic force microscope (AFM) was employed to observe the surface morphology of nanostructured silver films. Energy dispersive X-ray (EDX) was used to analyze the surface elemental compositions. In addition, the impacts of sputtering parameters such as deposition time, gas

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pressure, and sputtering power on antibacterial properties of the samples were also investigated in this paper.

2. Experimental

2.1. *Materials preparation*

Spun-bonded PP nonwovens with an area mass of $50\,g/m^2$ were used. The samples were first immersed into acetone solution for 30 min to remove the finishes of the textile production, and then were rinsed twice in de-ionized water. The samples were dried at the temperature of 40–45° prior to cutting into 6.5 cm by 5.5 cm for sputtering.

2.2. *Film deposition*

The deposition of the silver films was realized using magnetron sputter coating system with an RF sputter source supplied by Shenyang Juzhi Co. Ltd. The high-purity silver target (diameter: 50 mm; purity: 99.99%) was placed below the substrate at a distance of 170 mm. Prior to the deposition process, the sputter chamber was evacuated to a base pressure of 5×10^{-4} Pa. Argon was used as a sputtering gas. In the experiment, parameters including sputtering power, deposition time, and argon pressure were changed to investigate their effect on the antibacterial properties. During the sputtering, the substrate holder was rotating at a speed of 93 rpm to facilitate the uniform distribution of silver particles on the substrate, and the coating thickness was measured using film thickness monitor (FTM-V) fixed in the sputtering chamber.

2.3. *Antibacterial activity assessment*

The antibacterial effect was investigated using the shake flash test in accordance with GB15979-2002 (Hygienic standard for disposable sanitary products).[5] The test bacteria were *Staphyllococcus aureus* and *Escherichia coli*. In addition to the coated samples, an uncoated corresponding material was tested for comparison. After incubation at $37\pm1°C$ for 36 h, bacteria were counted.

The antibacterial properties of the substrates coated with the silver film were evaluated by calculating the reduction percentage of bacteria by the following formula:

$$Xs = \frac{A-B}{A},$$

where Xs is the reduction percentage of bacteria, %; A is the number of bacterial colonies on the agar plate recovered from bacterial solution at 0 contact time; B is the number of bacterial colonies on the agar plate recovered from the specimen after shaking for 1 h. If the number of bacteria after shaking is larger than the number at 0 contact time, $Xs = 0$.

2.4. *Surface characterization*

A CSPM4000 AFM made by Benyuan Co. Ltd was employed to scan the surface morphology of samples in contact mode. The scanning size was 2500 nm × 2500 nm, and the scanning frequency was set at 1.0 Hz.

2.5. *Elemental analysis*

Silver clusters deposited on the substrate were identified with energy-dispersive X-ray (EDX) provided by OXFORD Co. Ltd.

3. Results and Discussion

3.1. *Antibacterial performance*

3.1.1. *Film thickness effect*

Table 1 shows the antibacterial test results of nonwovens deposited silver films for different deposition times, but with the same gas pressure of 2 Pa and the same sputtering power of 40 W.

All silver-coated PP nonwovens were very effective against both the test bacteria — *Staphyllococcus aureus* and *Escherichia coli*, as shown in Table 1.

Table 1. Relationship between antibacterial performance and film thickness.

Film thickness (nm)	Deposition time (s)	Reduction of bacteria (%)	
		S. aureus	*E. coli*
Uncoated	0	0	0
0.5	71	100	51.44
1	137	100	78.05
2	253	100	98.53
3	424	100	100

The results also showed that the coated samples were more effective against *Staphyllococcus aureus* than Escherichia coli, and the antibacterial performance was significantly improved as the film thickness was increased. In literature,[2,5] it has been reported that the antibacterial effect of silver mainly depended on the total amount of silver released from the coating. It is believed that increasing the coating thickness obviously leads to the release of a larger amount of silver ions, which contributes to the antibacterial performance. Because silver is very expensive and when silver coating thickness exceeds 28 nm it may be toxic to certain human cells.[2] To assure the excellent bacterial properties and to save the cost, the optimal coating thickness was about 3 nm.

3.1.2. *Sputtering power effect*

Table 2 indicates the antibacterial test results of nonwovens deposited silver films under variable sputtering power but with a constant film thickness of 1 nm and argon pressure of 2 Pa.

Results in Table 2 demonstrate that the antibacterial properties did not change significantly as the sputtering power increased.

3.1.3. *Argon pressure effect*

Table 3 gives the antibacterial test results of nonwovens deposited silver films under different argon pressures but with the same film thickness of 1 nm and sputtering power of 40 W.

As argon pressure increased, there was a slight improvement in the antibacterial properties.

These results revealed that the film thickness was the key factor affecting antibacterial properties of the coated materials, and then the effect of coating thickness was further analyzed using AFM and EDX.

Table 2. Relationship between antibacterial performance and sputtering power.

Sputtering power (W)	Deposition time (s)	Reduction of bacteria (%)	
		S. aureus	*E. coli*
40	137	100	78.05
80	42	100	79.39
120	26	100	77.93

Table 3. Relationship between antibacterial performance and argon pressure.

Argon pressure (Pa)	Deposition time (s)	Reduction of bacteria (%)	
		S. aureus	*E. coli*
2	137	100	78.05
5	824	100	77.96
8	2838	100	77.03

3.2. ***AFM analysis***

The AFM image of the uncoated PP surface is presented in Fig. 1(a). The AFM images of PP surfaces deposited with silver films of different thicknesses ranging from 0.5 nm to 3 nm, and with the same pressure of 2 Pa and the same sputtering power of 40 W are given in Figs. 1(b)–1(e).

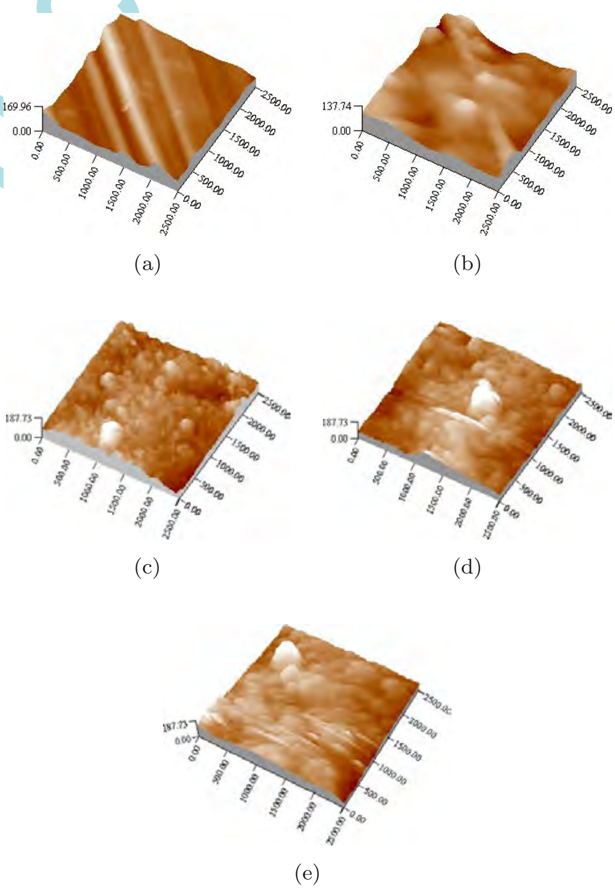

Fig. 1. AFM images of samples coated with silver films of different thicknesses (a) uncoated; (b) 0.5 nm coating; (c) 1 nm coating; (d) 2 nm coating; (e) 3 nm coating.

The uncoated PP surface shows a smooth surface with clear periodic strips on its surface, as shown in Fig. 1(a). The periodic strips were oriented in the fiber axis direction, which was probably induced by the drawing of the fibers. AFM image in Fig. 1(b) indicates that when the film thickness was about 0.5 nm, some small silver particles scattered on the PP is surfaces, and the original structure of PP was still clearly recognized. As the PP is coated with silver film of 1 nm, a mass of small silver particle aggregates with the average grain diameter of 38.4 nm were presented on the PP surface, as illustrated in Fig. 1(c). The image also indicates that the silver thin film covered up the fiber surface; thus the original structure of the PP surface was not visible. Image in Fig. 1(d) reveals that when the film thickness was extended to 2 nm, the layer was composed of silver clusters with the average grain diameter of 49 nm, and the interspaces between particles were slightly decreased. Image in Fig. 1(e) displays the surface structure of the PP fiber coated with silver film of 3 nm; it can be seen that the surface of PP fibers were covered with dense silver particles with the average grain diameter of 71.4 nm.

The AFM images reveal that the increased deposition time led to more aggregates of silver particles and compact film structure. It is believed that as deposition time prolonged, the silver particles on the PP surface became denser, and the rate of collision probability between sputtered particles and the deposited silver particles significantly increased, contributing to larger grain size.

By comprehensive analysis of AFM images and bacterial test results, it can be concluded that as deposition time prolonged, the coverage of silver film increased, leading to the increased release rate of silver ions, which contributed to the improvement in the antibacterial properties.

3.3. *EDX analysis*

Figure 2 shows EDX results for nanostructured silver film with different thicknesses. It can be seen from the results that the uncoated sample shows a single carbon peak, while after sputter coating, silver element was detected. Quantitative analysis of EDX in Table 4 shows that as the film thickness increased, the silver weight percentage per unit surface of the sample gradually increased, which provides evidence for the improved antibacterial properties.

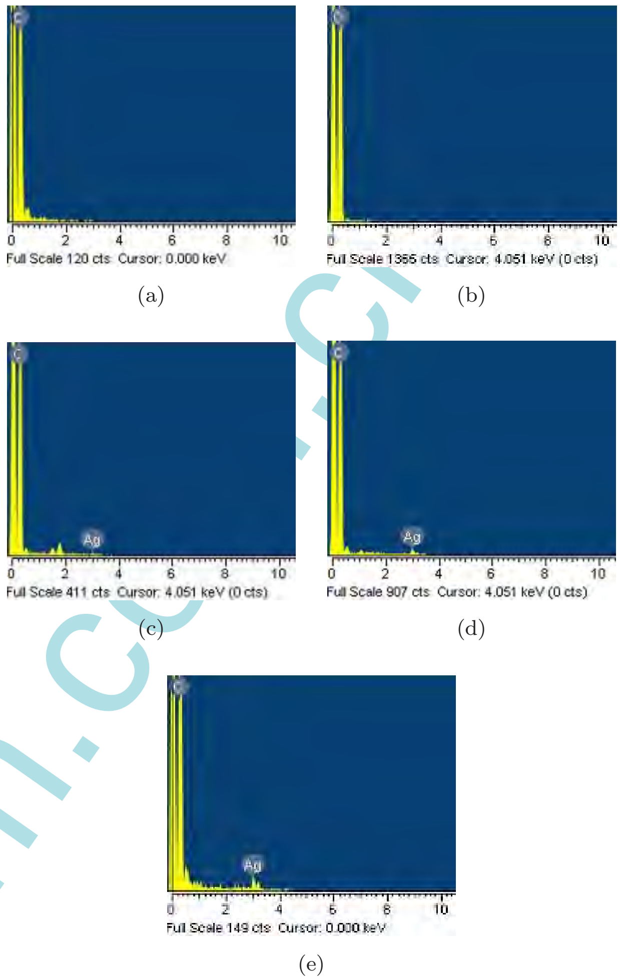

Fig. 2. EDX spectra of nanostructured silver film obtained under sputtering power of 40 W, pressure of 2 Pa, and with the film thickness of (a) uncoated, (b) 0.5 nm, (c) 1 nm, (d) 2 nm, (e) 3 nm.

Table 4. Quantitative analysis of EDX.

Coating thickness (nm)	Weight % (C)	Weight % (Ag)
Uncoated	100.00	0.00
0.5	95.24	4.76
1	78.19	21.81
2	63.30	36.70
3	40.11	59.89

4. Conclusions

In this work, the correlation between the sputtering parameters and antibacterial properties was investigated. Our results show that deposition time affected the antibacterial properties and grain size significantly, while the sputtering power and argon pressure did not show an obvious effect on the antibacterial properties.

The increased deposition time led to the increased coverage of silver film and the increased silver weight percentage per unit surface, leading to an increase in release rate of silver ions from the coating, which resulted in the improved antibacterial properties.

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