# Surface characterization of functional nanostructures sputtered on fiber substrates

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## Abstract

Textile materials consisting of polymer fibers provide an excellent platform for the integration of functional structures to improve the performance of the materials. In this study, the sputter coating of copper was used to deposit functional nanostructures on the surfaces of ordinary polymer fibers, polymer microfibers and polymer nanofibers. The funtionalized surfaces of the fibers were examined using Atomic force microscope (AFM), Environmental Scanning Electron Microscopy (ESEM) and electrical resistance measurement. The observations by AFM revealed the remarkable changes in the surface morphology with different fibers. The ESEM examination showed the introduction of functional Cu nanostructures built on the polymer fiber, microfibers and nanofiber surfaces. It was also found that the electrical resistance of the sputtered copper decreased with the increase in fiber fineness.
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## 1. Introduction

Textile has long been one of the most important materials in the world. With the development of science and technology, textile materials have been specially designed and engineered to meet the demands for a variety of applications ranging from wipes to smart clothes [1]. For these increasing applications it is desirable to produce such textile materials with a well-defined surface properties. Textiles with specific surface properties are also of interest in many technical applications of textiles as the surface features affect adhesion, friction, wettability, biocompatibility, electro-optical properties of the materials. However, the surfaces of polymer fibers are often not ideal for a particular application. The inert nature of many polymer fibers has prevented the expanding applications of textile materials. Various techniques have been developed to modify the surface properties of polymer fibers [2]. In recent years, physical vapor deposition (PVD) [3] has opened up new possibilities in the modification and functionalization of textile materials.

PVD is a process by which a thin film of material is deposited on a substrate. The most promising technique in PVD technology is sputtering[4], which has been widely used to modify various materials in many industries.

The ability to deposit well-controlled coatings on polymer fibers would expand the applications of polymer fibers, based on changes to both the physical and chemical properties of polymer fibers. In this study, textile materials were functionalized using metal sputter coating. The surface morphology and properties of the materials were characterized by Atomic force microscopy (AFM), Environmental Scanning Electron Microscopy (ESEM) and electrical resistance measurement.

## 2. Experimental

### 2.1. Materials

The substrates used in this study were nonwoven textile materials with three difference fiber diameters: nanofibers,

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Table 1
Material specifications

| Sample | A | B | C |
|---|---|---|---|
| Raw material | Polypropylene | Polypropylene | Polyamide 6 |
| Processing | Needlepunch | Meltblown | Electrospinning |
| Mass (g/m$^2$) | 50 | 50 | 50 |
| Fiber diameter | 22 μm | 1–10 μm | 200–800 nm |

microfibers and normal fibers. The details of the materials are listed in Table 1. Before the sputter coatings, the materials were washed with ethanol and distilled water. After washing, the materials were dried in an oven at 40 °C.

A magnetron sputter coating system JZCK-420B was used to deposit a nanolayer on the materials. A high-purity Cu target (99.999%) was mounted on the cathode, and the fiber substrate was placed on the anode with a side facing the target. Argon (99.99%) was used as the bombardment gas. The sputtering pressure was set at 3 Pa. The DC (direct current) power used for Cu sputtering was set at 100 W. The sputtering was performed on one side of the substrate for 10 and 20 min respectively, at room temperature.

## 2.2. Surface characterisation

### 2.2.1. ESEM

ESEM is able to image uncoated and hydrated samples by means of a differential pumping system and a gaseous secondary electron detector [5]. The Philips XL30 ESEM-FEG was used to examine the structural characteristics of the materials. Images were taken at 20 kV and 0.5 Torr.

### 2.2.2. AFM

A Benyuan CSPM 3300 Atomic Force Microscope (AFM) was employed to image the morphology of the fiber surfaces. Scanning was carried out in contact mode AFM [6] with a silicon cantilever. All images were obtained at ambient conditions.

### 2.2.3. EDX

The Philips XL30 ESEM-FEG equipped with a Phoenix energy dispersive X-ray analysis system (EDX) was used to examine the chemical compositions of the sputter coated fibers. EDX is available in all modes in the ESEM and all elements down to boron can be detected, including the light elements, such as carbon, nitrogen and oxygen [7]. In the EDX analysis, an accelerating voltage of 20 kV with accounting time of 100 s was applied.

### 2.2.4. Electrical resistance

The electrical resistance was measured with a digital ohmmeter. The tests were performed three times for each sample and the mean values were recorded and reported.

## 3. Results and discussion

### 3.1. Web structures of materials

The images in Fig. 1 show the web structures of the three different nonwoven substrates. All the images show the
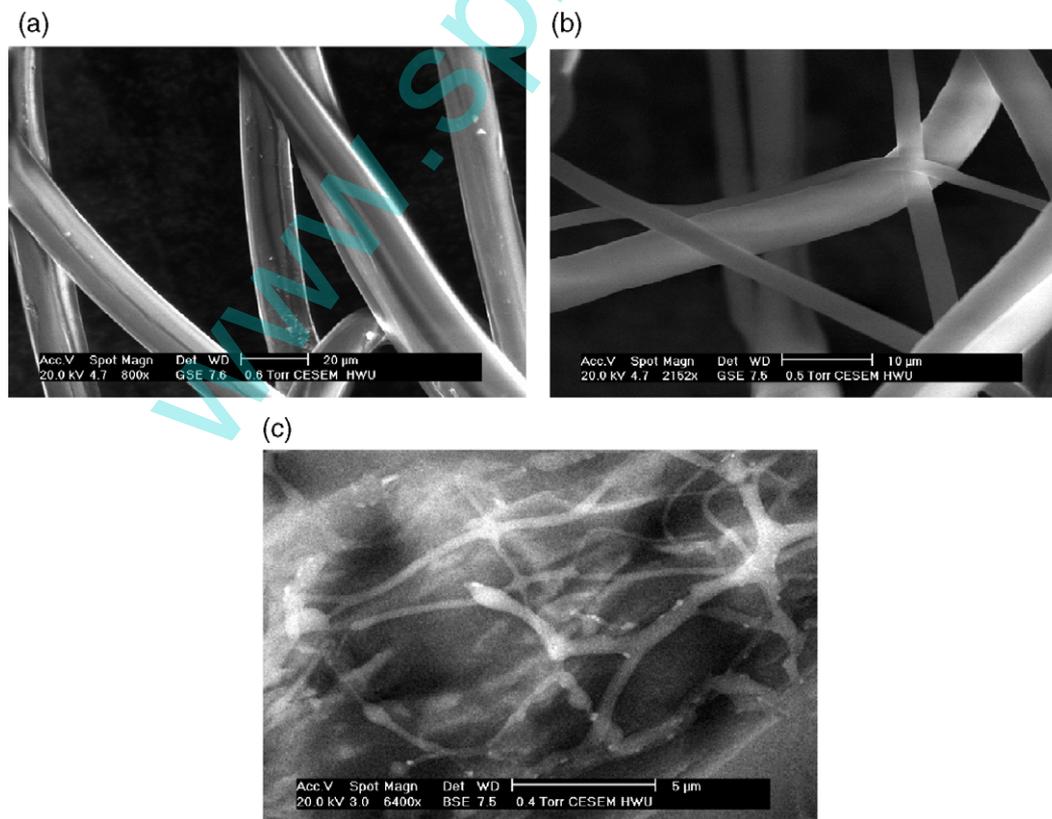


Fig. 1. Fibrous structures in ESEM, (a) sample A, (b) sample B, (c) sample C.
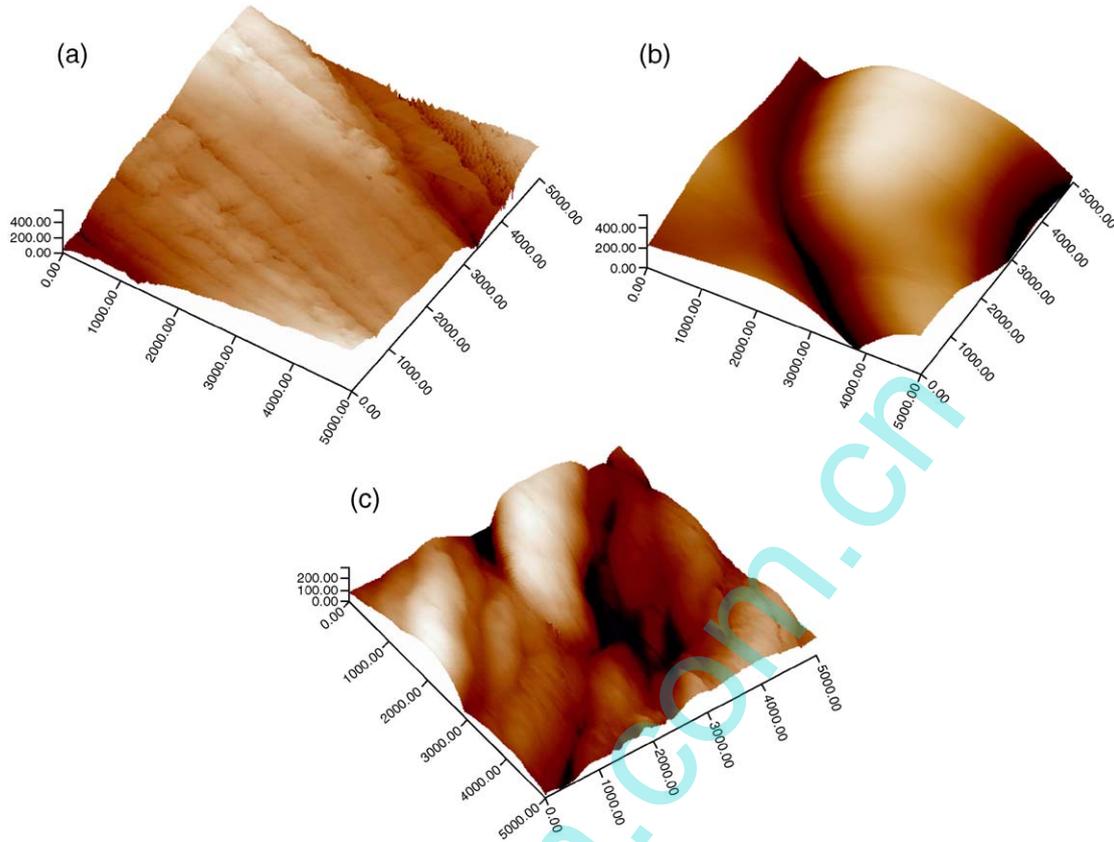
Fig. 2. Surface morphology of the fibers in AFM, (a) sample A, (b) sample B, (c) sample C.

fibrous structures of the substrates, but the images also reveal the difference of the fiber diameters. The needlepunched nonwoven contains coarsest fibers, which have an average diameter of about 22 μm, revealed in Fig. 1a. The fibers in the needlepunched web have similar fineness, but the fibers in meltblown and electrospun webs have variable diameters. The
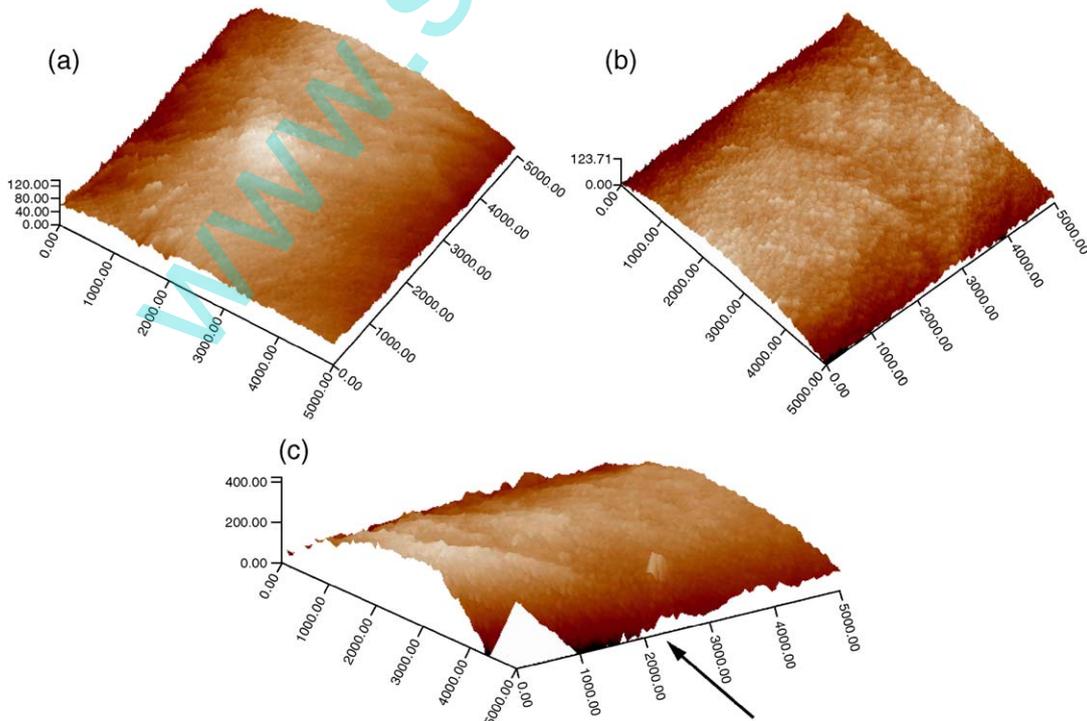


Fig. 3. Surface morphology of the sputter coated PP fiber in AFM, (a) 10 min, (b) 20 min, (c) side of the fiber (arrow direction).
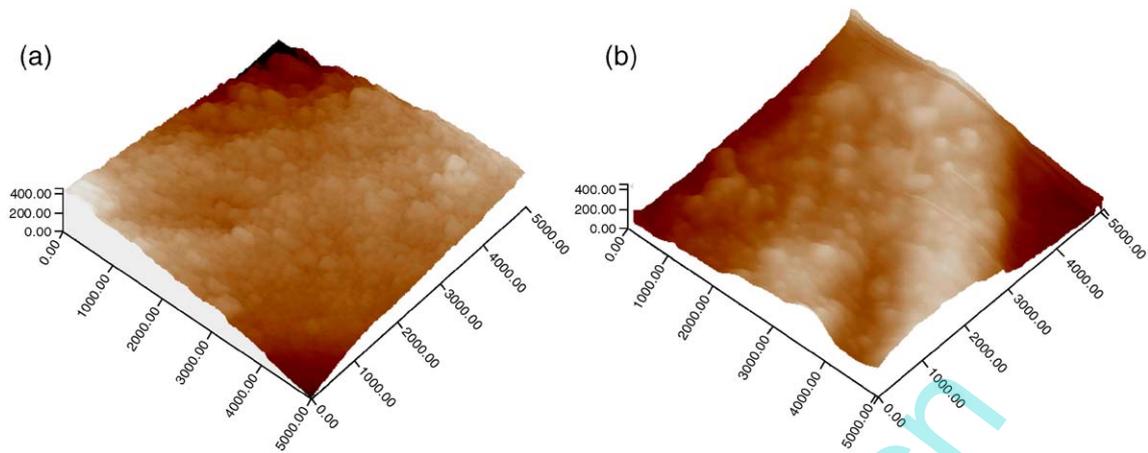
Fig. 4. Surface morphology of the sputter coated PP microfiber in AFM, (a) 10 min, (b) 20 min.

diameters of the microfibers in the polypropylene meltblown web are in the range between 1 to 10 μm, as presented in Fig. 1b. However, the polyamide nanofibers are the finest fibers among all the substrates. The diameters of the nanofibers range from 200 to about 800 nm, as exhibited in Fig. 1c. The increase in fiber fineness contributes the increase in fiber intersections and the decrease in pore size, as illustrated in Fig. 1.

The ESEM images can clearly reveal the fibrous structures of the materials, but at this magnification the surface structure of individual fibers are not very clear. The details of the fiber surfaces can be further analyzed with the AFM.

### 3.2. Surface morphology

The surface morphologies of the uncoated fibers are presented in Fig. 2. The AFM image in Fig. 2a shows the relatively smooth surface with clear fibril structures of the fiber surface. It is attributed to the effect of drawing in the fiber spinning process. As displayed in Fig. 2b, the microfiber in the meltblown substrate also shows a smooth surface without any fibril structures on the surface. The fibers in the meltblown substrate are formed by high velocity attenuation with hot air. Therefore the fibers are not properly crystallized during the process [8]. The nanofibers in Fig. 2c show the rough surface with small groove-like structures, which are formed by the evaporation of the carrier solvent during the electrospinning.

The sputter coating significantly changes the surface characteristics of the polymer fibers. AFM observations clearly reveal the change in surface morphology of fibers sputter coated with metallic layer. Figs. 3a and 3b show the surfaces of the polypropylene fiber sputter coated with copper for 10 to 20 min respectively. The sputtered functional layer covers up the original fibril structures, therefore the fibril structures on the fiber surface are not visible any more. The AFM images also indicate that the sizes of the sputtered Cu clusters are increased as the sputtering time is extended from 10 to 20 min. This is attributed to the growth of the sputtered Cu grains during the coating process. It is also observed that the Cu nanoclusters are firmly distributed on the side of a fiber, as illustrated in Fig. 3c. The arrow in Fig. 3c points the nanocluster on the side of the fiber coated for 20 min. The nanoclusters, however, are not found on the reverse side of the substrate since the coating was performed only on one side of the substrate facing the sputtering target. The AFM
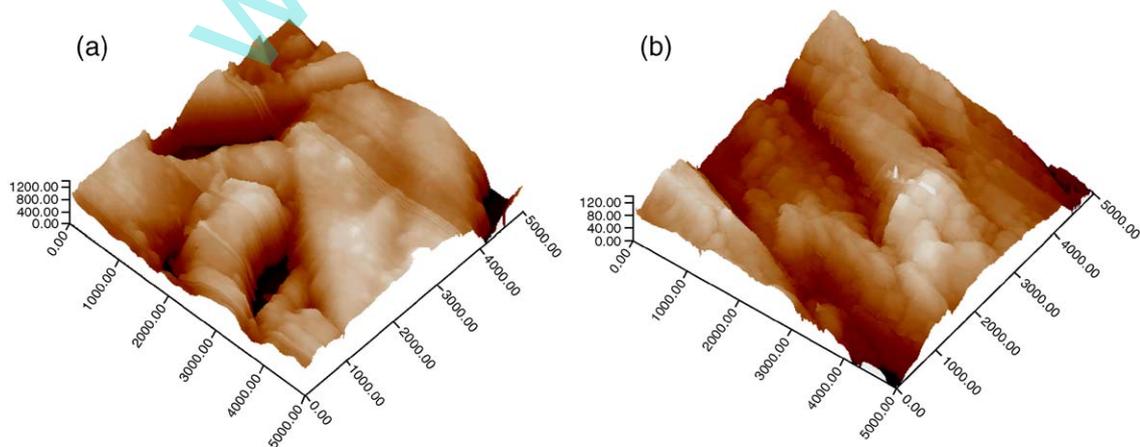


Fig. 5. Surface morphology of the sputter coated nanofiber in AFM, (a) 10 min, (b) 20 min.

Table 2
Average size of the sputtered Cu nanoclusters

| Sample | A | B | C |
|---|---|---|---|
| 10 min coating | 13.6 nm | 17.4 nm | 19.8 nm |
| 20 min coating | 25.7 nm | 30.4 nm | 35.3 nm |

Table 3
Resistance values

| Sample | A | B | C |
|---|---|---|---|
| Original | Out of range (over $10^6$ $\Omega$/cm) | Out of range | Out of range |
| 10 min coating | $2.56 \times 10^2$ $\Omega$/cm | $9.63 \times 10$ $\Omega$/cm | $2.44 \times 10$ $\Omega$/cm |
| 20 min coating | 8.72 $\Omega$/cm | $4.07 \times 10^{-1}$ $\Omega$/cm | $1.6 \times 10^{-2}$ $\Omega$/cm |

observations reveal the thickness variation of the coated layer around the fibers, which is in a range between 15 and 20 nm from top to side.

The similar phenomena are also observed on the polypropylene microfibers, as revealed in Fig. 4. It can be seen that in the initial stage of the deposition, the surface of the microfibers appears to be much rougher than that of the uncoated microfibers. The nanoclusters of copper are clearly recognised on the fiber surface, as exhibited in Fig. 4a. Fig. 4b displays the growth of the nanocluster on the microfiber surface as the deposition is increased to 20 min. It appears that the sizes of the sputtered Cu nanoclusters are also increased as the sputter coating time is increased to 20 min. AFM observations confirm that the existence of the nanoclusters on the side of the microfiber and the thickness variation of the coated layer around the microfibers. The thickness variation, however, is about 10 nm much less than the PP fibers.

The details of the sputtered Cu nanoclusters on the polymer nanofibers can be seen from the AFM images obtained by $5.0 \times 5.0$ $\mu m^2$ scan, as illustrated in Fig. 5. The nanofiber sputtered for 10 min shows the rough surface with clearly recognised Cu nanoaggregates, as displayed in Fig. 5a. The roughness of the nanofiber surface is increased as the sputter coating is expanded to 20 min, as presented in Fig. 5b. This behaviour can be attributed to the nucleation and island formation on the fiber surface as Cu grains are growing. The coating layer of the Cu nanoculsters is also found on the side of the nanofiber by AFM examination. The thickness variation is less than 10 nm for the nanofibers, which is attributed to much smaller radius of the nanofiber.

The sizes of the Cu nanocluster vary from about 10 to over 50 nm as revealed by the AFM analysis. Table 2 presents the average sizes of the Cu nanoclusters sputtered on the fibers with different diameters. It can be concluded that the size of



Fig. 6. EDX spectra of Sample A.

the Cu grain is increased with the sputtering time. It can also be seen that the substrate with finer fibers has larger sizes of the sputtered grains. This phenomenon is attributed to the effect of fiber fineness. The finer fibers may facilitate the aggregation of the sputtered particles.

### 3.3. EDX analysis

The funtionalization of the fiber surfaces by sputter coating is also confirmed by EDX analyses. Fig. 6 shows the EDX spectra of the fibers of Sample A before and after the sputter coating. It can be seen that the fiber dominantly consists of C before the sputter coating. A significant amount of Cu on the fiber surface after sputter coating can be seen in Fig. 6. The amount of Cu is significantly increased as the sputtering time is increased to 20 min. The similar phenomena are also observed on the microfibers and the nanofibers.

### 3.4. Resistance measurement

The results of resistance measurements of the samples are listed in Table 3. The table clearly shows the significant decrease of all the samples in the surface resistance after sputter coating. The surface resistance of all the samples before sputter coating is over $10^6$ $\Omega$/cm, indicating poor electrical conductivity. After the coating for 10 min, the surface resistance of Sample A drops from over $10^6$ to about 250 $\Omega$/cm and Sample B and Sample C show the surface resistance less than 100 $\Omega$/cm. The increase in sputtering time can lower the surface resistance of the substrate, as presented in Table 3. The table also reveals that the fiber fineness has a certain effect on the surface resistance of the materials. The substrate with finer fibers shows a lower resistance. This is attributed to the more fibers and more fiber intersections in the web consisting of finer fibers.

## 4. Conclusion

This study has investigated the functionalization of fibrous substrate using the sputter coating of copper. The surface conductivity of the materials has been significantly improved. The fiber fineness had an obvious effect on the structure of the nanoclusters deposited on its surface. The substrate with finer fibers showed a lower resistance due to the more fiber intersections in the web.

Fibrous materials have been increasingly used in many industries ranging from home decoration to technical applications. Surface properties of the fibers play a very important

role in these increasing applications. The conductive surface is often required for such applications as anti-static, conductive shields, packing and protective materials. Metallic functionalization of fiber materials can be obtained using sputter coating techniques at low temperature. The metallic functionalized fiber materials have great potential for a wide range of applications in many industries.

## Acknowledgement

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