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Research Article

Durable and Washable Antibacterial Copper Nanoparticles Bridged by Surface Grafting Polymer Brushes on Cotton and Polymeric Materials

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To increase the durability of antibacterial coating on cotton and polymeric substrates, surface initiated grafting polymer brushes are introduced onto the substrates surface to bridge copper nanoparticles coatings and substrate. The morphologies of the composites consisting of the copper nanoparticles and polymer brushes were characterized with scanning electron microscopy (SEM). It was found that copper nanoparticles were uniformly and firmly distributed on the surfaces of the substrates by the polymer brushes; meanwhile, the reinforced concrete-like structures were formed in the composite materials. The substrates coated by the copper nanoparticles showed the efficient antibacterial activity against *Staphylococcus aureus (S. aureus)* and *Escherichia coli (E. coli)* even after washing by 30 cycles. The copper nanoparticles were tethered on the substrates by the strong chemical bonds, which led to the excellent washable fitness and durability. The change of the phase structure of the copper was analyzed to investigate the release mechanism of copper ions.

1. Introduction

Bacterial infection, as a major issue, has been arising from bacterial adhesion, growth, and proliferation on surfaces [1–3]. A considerable number of research works have been conducted with the aim of preparing the novel antibacterial materials [4]. The antibacterial properties of gold and silver are well known, and the effectiveness in reducing the growth of several microorganisms has been reported [5–7]. Because of high cost of silver and gold, material chemists have focused their attention on exploring the possibility of using copper as the ultimate antimicrobial agent [8–11].

However, the current techniques, such as spinning and surface coating, for fabricating medical antimicrobial textile using nanoparticles have different limitations. Spinning method works well with the synthetic fiber, but the nature fiber such as cotton is impossible to be melted and spun. Surface coating via physical absorption is the other common technique to obtain the antimicrobial performance. However, the adhesion between the substrate and coating by physical absorption is weak. In composites discipline, Young's modulus of copper is 110~128 GPa, and yet that of the polymeric materials, such as nylon, polypropylene, and polyethylene terephthalate, is around 1~4 GPa. This intrinsic distinction causes that the copper nanoparticles could hardly be coated on the polymer surface to form composites with structural integrity [12]. The most common process of conferring the copper nanoparticles to fabrics materials is utilizing some adhesion and cross-linked agents, such as acrylate and polyurethane, to form a composite coating on the substrate [13, 14]. Consequently, only the exposed copper nanoparticles on the external surface can be released and show antibacterial property subsequently; meanwhile the majority of nanoparticles are blocked in the inner of composites by adhesion agents [15, 16].

Polymer brushes assisted copper electroless deposition methods have been demonstrated to be a powerful tool in preparing copper nanoparticles on polymer

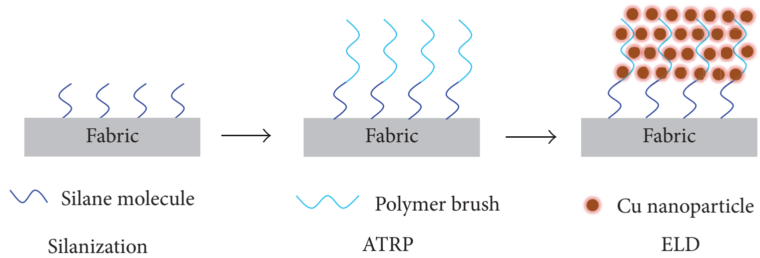


Figure 1: Schematic illustration of the coating-fabricated process linking fabric and free standing nano copper particles by polymer brush.

substrates [17–19]. Heuristically, the free release and reinforced concrete-like antibacterial system were designed by chemical bonds tethered copper nanoparticles on cotton and polyester substrates using atom transfer radical polymerization (ATRP) and electroless deposition (ELD). The cheaper copper nanoparticles with high effectiveness and long durable properties could match the requirement of antibacterial materials for industrial production. In this paper, cotton is chosen as the substrate material because it is used more widely than any other natural fiber, and polyester, as a typical polymeric material, is chosen as another substrate. Meanwhile, two kinds of materials are the major medical materials used in healthcare and medical fields. The antibacterial properties of copper nanoparticles covalently bonded on cotton and polymeric materials by surface grafted polymer brushes were investigated.

2. Experimental

2.1. Materials. All chemicals were purchased from Aldrich. The inhibitor in the monomers, [2-(methacryloyloxy) ethyl]trimethylammonium chloride (METAC), was removed by elution through a neutral alumina plug before use. Cotton yarns and fabric used in the experiments were pretreated by singeing, desizing, scouring, bleaching, and mercerizing. After that, they were cleaned with water, ethanol, and toluene to remove any possible impurities before being used, dried at room temperature, and cured at 105°C for 24 h.

2.2. Fabrication. Cotton or polyester substrates were immersed in an anhydrous toluene solution of 5 mM 3-(trichlorosilyl)propyl 2-bromo-2-methylpropanoate as ATRP initiator in order for the hydroxyl groups of cellulose surface to react with the silane molecules by a condensation reaction. Then the substrates were rinsed for several times with anhydrous toluene and dichloromethane to remove the excess initiator and byproduct and at last dried at 50°C under vacuum for 2 h. The initiator-modified cotton substrates were obtained.

10 mL of 4.5 mol L^{-1} [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METAC) methanol solution was prepared for the polymerization reaction under nitrogen flow at 20°C. 2,2-Dipyridyl (0.48 g), Cu(I)Br (0.12 g), and Cu(II)Br_2 (0.019 g) were mixed into the above solution by stirring under nitrogen flow. The initiator-modified substrates were sealed in Schlenk tubes, degassed by nitrogen, and left at 20°C under nitrogen. Then enough polymerization solution was syringed into each Schlenk tube for submerging each sample completely. The substrates were kept in the solution for polymerization reaction. After polymerization, the samples were removed, cleaned thoroughly by methanol and water, respectively, and then dried under nitrogen flow.

The plating bath for copper electroless deposition was composed of 1 : 1 mixture of freshly prepared solutions A and B. Solution A was composed of 12 g L^{-1} NaOH, 13 g L^{-1} $CuSO_4{\cdot}5H_2O$, and 29 g L^{-1} $KNaC_4H_4O_6{\cdot}4H_2O$. Solution B was 9.5 mL L^{-1} HCHO. Distilled water was used to prepare the plating solution. After electroless deposition, the copper nanoparticle coatings bridged by surface grafted polymer brushes were obtained on the cotton or polyester substrates, expecting the remarkable antibacterial abilities. Figure 1 shows the preparation process of the Cu nanocomposite coating on the fabrics.

2.3. Characterization. The structure of cotton and modified cotton was investigated by Nicolet iS10 FTIR spectrometer. The morphologies of the samples were observed using a field emission scanning electron microscope (FESEM, JEOL JSM-7500). The phase structures of the samples were analyzed on X-ray diffraction (XRD) (Rigaku D/max-2400, Cu K radiation, $\lambda = 0.1541$ nm.). The antimicrobial activity of copper nanoparticles loaded with cotton fabrics against four bacteria, two Gram-positive (*S. aureus* ATCC 25923 and *B. bombysepticus*) and two Gram-negative (*E. coli* ATCC 25922 and *S. maicesceis*), was evaluated by radial diffusion assay [20]. A single colony of each bacterial strain was inoculated into 5 ml of LB at 37°C overnight, and about 50 μl of culture was then added to 5 ml of LB for 3-4 h of incubation until OD_{600} reached 0.4. Approximately 1 ml culture was mixed with 100 ml of sterile LB agar at around 55°C, and the mixture was aliquot in Petri dishes. The entire specimen was cut into 5 mm diameter and incubated overnight at 37°C. The Cu ions release was examined using the standard atomic absorption spectroscopy (AAS) (Z-8000, Hitachi).

3. Result and Discussion

3.1. FTIR Analyses of Cotton and Modified Cotton. Fourier transform infrared spectroscopy (FTIR) was used to demonstrate the structure of unmodified cotton and PMETAC modified cotton in Figure 2. The new peak at 872 cm^{-1} and strengthened peak at 1708 cm^{-1} in PMETAC modified cotton are attributed to quaternary ammoniums groups (QA^+) and the carbonyl groups in PMETAC, confirming the success

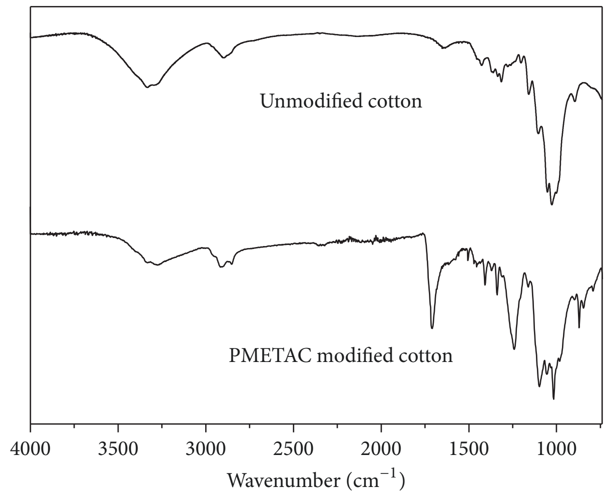
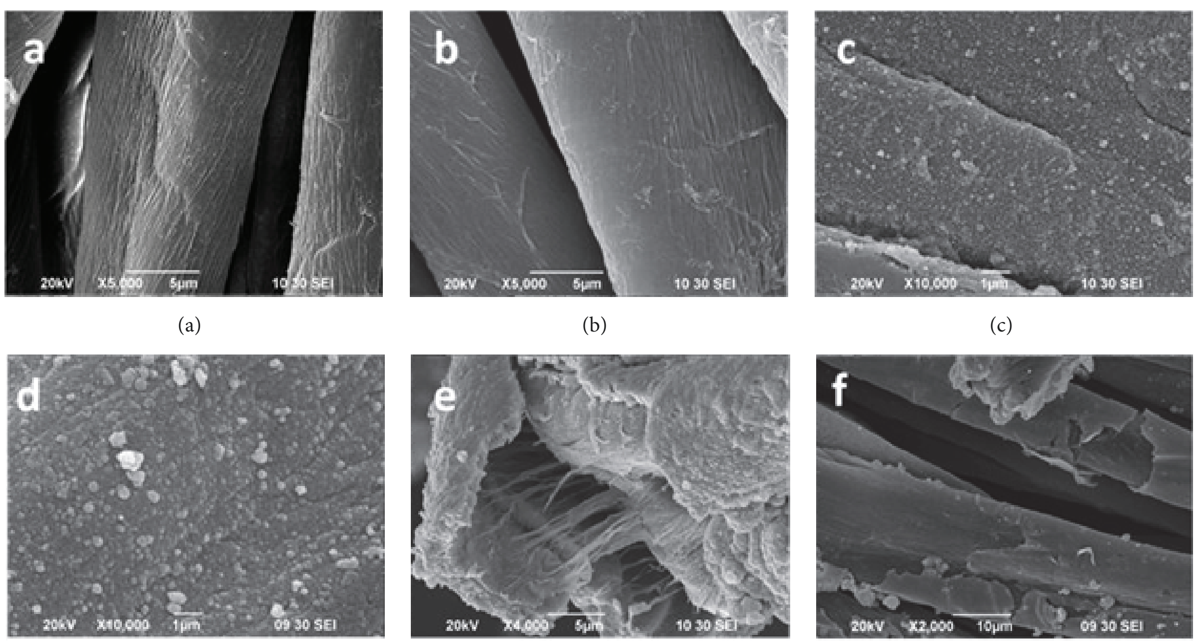


Figure 2: FTIR spectrum of unmodified cotton and PMETAC brushes modified cotton.

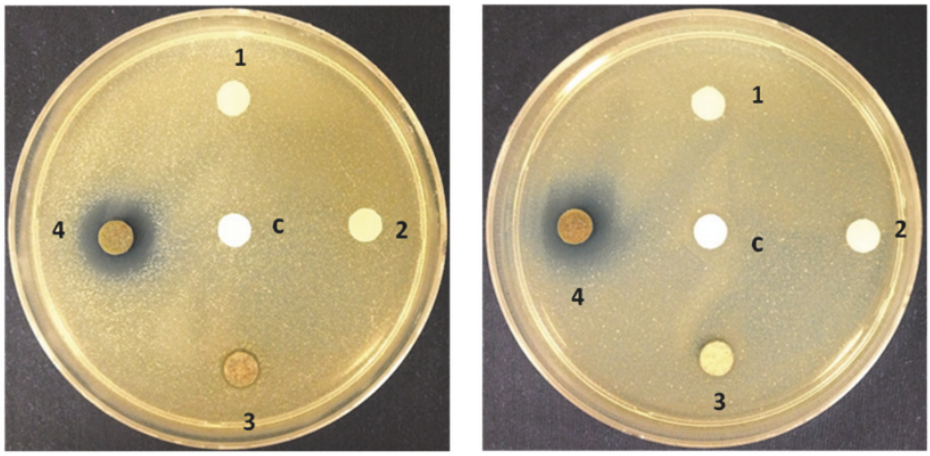


(a) (b) (c) (d) (e) (f)

Figure 3: SEM images of the surface morphologies of raw cotton fibers (a), modified cotton fibers by PMETAC brushes (b), modified cotton fibers by copper nanoparticles (c), modified PET film by copper nanoparticles (d), sectional view of mechanical disruption modified cotton fibers by copper nanoparticles (e), and copper coated cotton fibers by traditional cross-linked polymer (f).

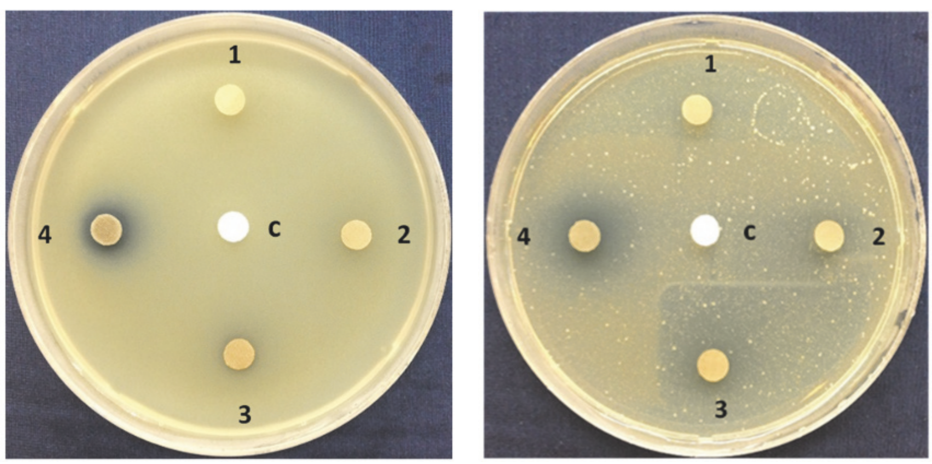
of the grafting process. The peaks of three different C-H stretching vibrations are shown at 2853 cm^{-1}, 2919 cm^{-1}, and 2966 cm^{-1}.

3.2. Surface Morphologies Observation. Figure 3 shows SEM images of the surface morphologies of cotton and polymer fibers at the different treatment period. Compared with raw cotton fibers, the surface morphology of cotton fibers modified by PMETAC brushes has no obvious change (Figures 3(a) and 3(b)). It can be seen that copper particles with diameters of 130 ± 20 nm were continuously and uniformly distributed on the surface of cotton fibers after the treatment process described in Experimental (Figure 3(c)). The repeatable result can be observed when the substrate is changed to polyester (Figure 3(d)). The key feature here is that those reinforced concrete-like antibacterial copper nanoparticles coatings on polymeric materials bridged by polymer brushes offer the unique stability under multiple mechanical bending, stretching, rubbing, and even washing cycles. One piece of coated fabrics was destroyed and the decoyed fiber was observed using SEM. From Figure 3(e), it can be easily discerned that the fiber surfaces are covered by the concrete-like structure composites, which contribute to the extraordinary durability and stability of antibacterial copper nanoparticles coatings



Inhibition on *E. coli* (ATCC 25922) Inhibition on *S. aureus* (ATCC 25923)

Figure 4: Antibacterial *(E. coli and S. aureus)* test of control (c), modified by commercial antibacterial agents 1 (1), modified by commercial antibacterial agents 2 (2), deposited by Ag particles (3), and deposited by Cu nanoparticles (4).



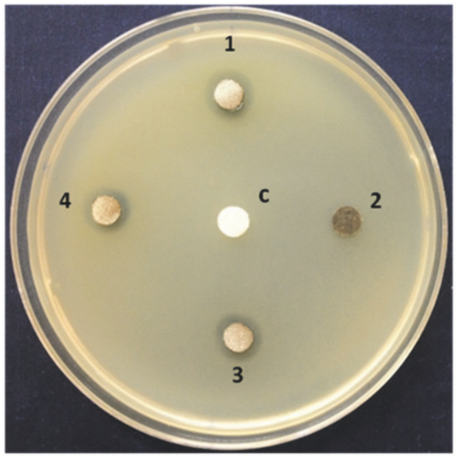
Inhibition on *E. coli* (ATCC 25922) Inhibition on *S. aureus* (ATCC 25923)

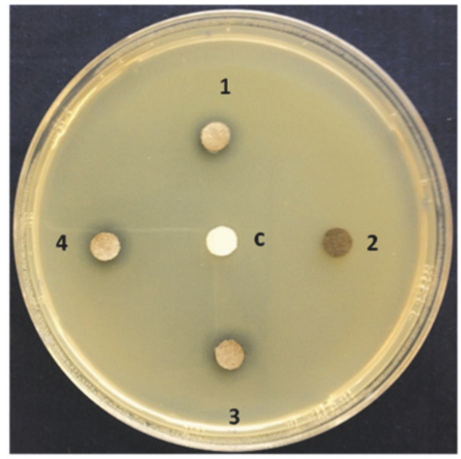
Figure 5: Antibacterial (*E. coli* and *S. aureus*) test of control (c) and the samples with the different deposition time of 5 mins (1), 20 mins (2), 30 mins (3), and 1 h (4).

on polymeric materials. The copper nanoparticle layers and fibers are integrated by interfacial polymer brushes, offering the superior adhesion between Cu nanoparticles and substrate; therefore the polymer brushes function as "concrete iron" in the composite materials. As a comparison, commercial antibacterial cross-linked polymer and copper nanoparticles loaded on cotton fibers also were investigated under SEM and the visible disconnected coating on the fibers can be observed clearly (Figure 3(f)).

3.3. Antibacterial Activity of the Copper Nanoparticle-Modified Cotton Fabrics. In order to investigate the antibacterial activity of the copper nanoparticles-modified cotton fabrics, the control cotton fabrics, commercial antibacterial agents 1, commercial antibacterial agents 2, and silver particles on cotton coated by the binder were chosen as the comparative materials. Among these materials, copper nanoparticles-modified cotton fabrics coated by ATRP and ELD show the most significant antibacterial function to *E. coli* and *S. aureus*, and the silver nanoparticles show antibacterial property, but the antibacterial ring is much smaller than that of copper (Figure 4). No evidence was observed for the two kinds of polyelectrolyte brushes modified fabrics showing antibacterial ring in this test. These results show that the deposited copper nanoparticles present the strong sterilization to the *E. coli* and *S. aureus* due to the free standing of the copper nanoparticles.

Figure 5 presents antibacterial (*E. coli* and *S. aureus*) test of control sample and the prepared coated copper samples at different deposition time. The antibacterial ring method was applied in the antibacterial test. It can be seen that raw cotton fabrics as the control sample showed the dense population of bacterial colonies, while Petri dishes, supplemented with nano-copper coating cotton fabrics at different deposition time, respectively, showed zones of inhibition around the functional specimens. The clearing zone indicates





Inhibition on *E. coli* (ATCC 25922) Inhibition on *S. aureus* (ATCC 25923)

Figure 6: Antibacterial (*E. coli* and *S. aureus*) test of control cotton fabrics without any modification (c) and the sample being unwashed (1) and the sample washed for 10 cycles (3), 30 cycles (4), and PVD-deposited copper on cotton fabrics washed for 5 cycles (2).

the susceptibility of the bacteria to the prepared sample and strong antibacterial activity of nano-copper coating cotton fabrics. What is noteworthy is that the annulus of the inhibition zone increases with the increase of the copper depositing time. In other words, the prepared fibers with more copper nanoparticles show better antibacterial properties, indicating that the copper content influences the antibacterial activity, which is similar to the previous report [21]. The remarkable antibacterial properties of copper nanoparticles-modified fibers could essentially be attributed to the biocidal action of Cu^{2+} ions, which are released from the functional fibers.

3.4. Durable Testing of the Copper Nanoparticle-Modified Cotton Fabrics. In consideration of economic costs, the durability of the antibacterial material is an important factor influencing the practical application. Apparently, the antibacterial properties of functional fabrics, fabricated by electroless deposition by polymer brushes bridged, possessed the excellent washable properties even after 30 cycles of washing, and the antibacterial ring can still be observed (Figure 6). For comparison, copper nanoparticle-coated cotton fabrics by PVD method were tested in the same disk. After even 5 cycles of washing, the PVD functional fabrics showed invisible antibacterial ring, which means that the majority of the functional copper nanoparticles were washed off because of the weak interfacial adhesion strength between copper particles and substrate. The washing testing proves that the polymer brushes-bridged-deposited copper has excellent adhesion and long durable properties, as shown in the schematic diagram of copper ions release and antibacterial performance of the functional fabrics (Figure 7).

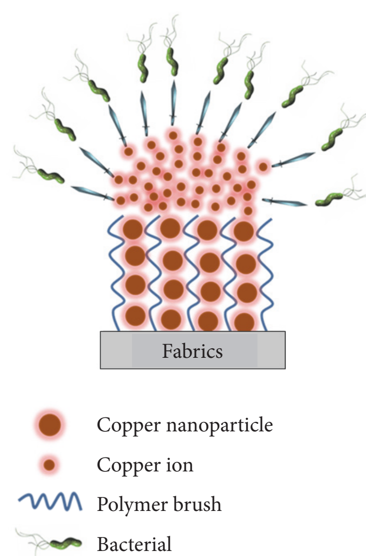


Figure 7: Schematic diagram of copper ions release and antibacterial performance.

3.5. Dynamic Release of Cu(II) from Nanocomposites. Despite the large amount of research works about the antibacterial properties of copper, the antibacterial mechanism is too complicated to reveal completely [9, 10, 22]. Undoubtedly, killing bacteria process of copper started from the Cu ions release. Therefore, understanding the release mechanism of copper ions is considerably important to study the novel copper-polymer antibacterial systems.

The results of Cu^{2+} release experiments carried out with the copper-loaded cotton fibers are shown in Figure 8. To the traditional cross-linked process, the copper nanoparticles are stuck in the cross-linked polymeric matrix, blocking the release of copper ions into the solution, and therefore copper is released in a small quantity. It is shown that the polymer brushes-bridged-deposited copper coatings more easily release the copper ion and have higher release amount. Meanwhile, as the electroless deposition time increases, the copper releases from the free standing coating also increase. This is basically due to the fact that, with the increase of the depositing time, more and more copper nanoparticles are spontaneously assembled onto surface

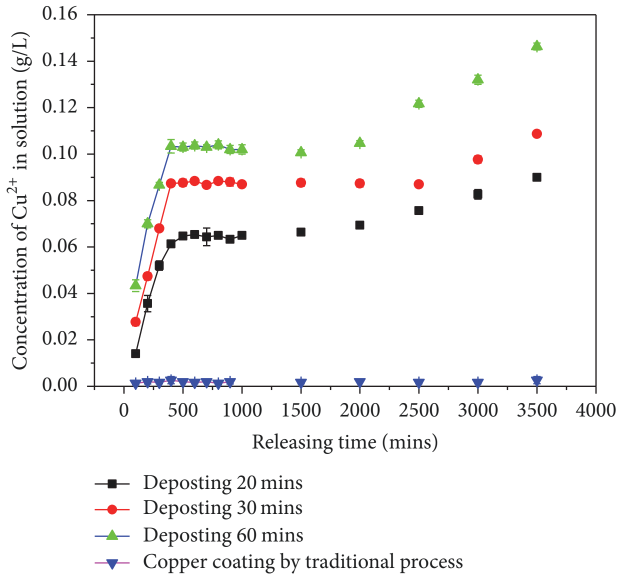


FIGURE 8: Constantly monitoring concentration of Cu^{2+} released from different samples against the releasing time. Reinforced concrete-like antibacterial composites with the different deposition time (20 mins, 30 mins, and 60 mins) and the specimen of copper coating by traditional process.

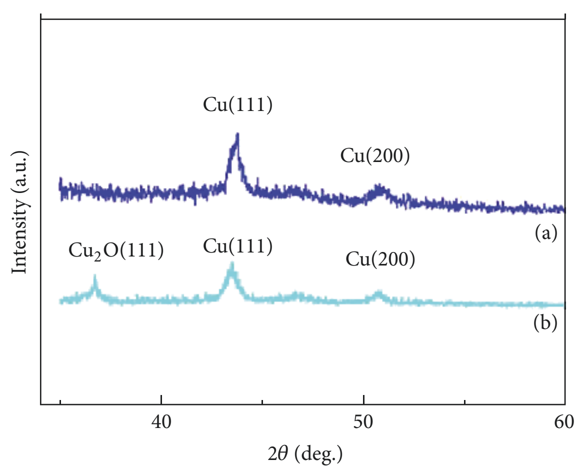


FIGURE 9: X-ray diffraction patterns of the copper coating fabrics before (a) and after (b) antibacterial test.

of polymeric materials and hence antibacterial affection improved accordingly [8, 23]. This is consistent with the antibacterial test as a function of the deposition time in Figure 4. Therefore, by varying the electroless deposition time, copper release and antibacterial property could be regulated.

XRD pattern analysis is utilized to examine the phase structure of Cu. Figure 9 shows the XRD patterns of the fabrics before and after antibacterial testing for 24 h. The functional fabrics before testing present a wide diffraction peak, indicating the formation of Cu nanoparticles. A new peak of Cu_2O emerged on the pattern of the fabrics after the antibacterial testing. It is inferred that a small amount of Cu_2O was formed in ELD process and wrapped in the Cu particles [24], and then antibacterial test made the copper on the outer surface release to copper ions so that the inner Cu_2O was exposed and detected by XRD after test.

4. Conclusion

The reinforced concrete-like antibacterial copper nanoparticles coatings on cotton and polymer substrates were designed and prepared by means of ATRP and electroless deposition. Cu nanoparticles were continuously and uniformly distributed on the fiber surfaces of the substrate. The composite materials present excellent antibacterial *(E. coli and S. aureus)* properties, even after washing by 30 cycles, and durability because of the strong interfacial force between the antibacterial copper coatings and substrates by polymer brushes. Compared with the copper coating by traditional process, the polymer brushes-bridged-deposited copper coating possessed the longer releasing effectiveness and higher releasing concentration attribute to the free-standing copper nanoparticles coatings. The controllable releases of copper ions are expected to be exploited by varying the electroless deposition time. Designed reinforced concrete-like antibacterial composite accomplishes the huge demand on modern medical and healthcare applications, which demonstrate the great potential at polymeric facilities and devices.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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