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Rapid Copper Metallization of Textile Materials: a Controlled Two-Step Route to Achieve User-Defined Patterns under Ambient Conditions

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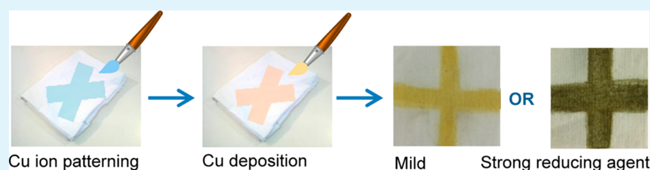
Supporting Information

ABSTRACT: Throughout history earth-abundant copper has been incorporated into textiles and it still caters to various needs in modern society. In this paper, we present a two-step copper metallization strategy to realize sequentially non-diffusive copper(II) patterning and rapid copper deposition on various textile materials, including cotton, polyester, nylon, and their mixtures. A new, cost-effective formulation is designed to minimize the copper pattern migration on textiles and to achieve user-defined copper patterns. The metallized copper is found to be very adhesive and stable against washing and oxidation. Furthermore, the copper-metallized textile exhibits excellent electrical conductivity that is ~3 times better than that of stainless steel and also inhibits the growth of bacteria effectively. This new copper metallization approach holds great promise as a commercially viable method to metallize an insulating textile, opening up research avenues for wearable electronics and functional garments.



KEYWORDS: *textile metallization, chemical plating, autocatalytic plating, electroless copper plating, wearable electronics*

INTRODUCTION

Early in the ancient Egyptian era, earth-abundant copper was mechanically integrated into textile materials as a way to adorn the garments of kings and nobilities. During the period of industrial revolution, new technologies were developed to enable copper metallization of textiles, and many other uses of copper-plated textiles were realized. The incorporation of the conductive copper on the nonconductive textile can introduce many interesting functions/characteristics,[1,2] including high electrical/thermal conductivity[3−5] and good antibacterial/antifungal/antistatic properties.[6] Moreover, strong electromagnetic interference shielding and radar reflectivity[7−10] are also achieved. These novel properties allow the textiles to be used for various intelligent applications, particularly in the emerging area of wearable and flexible electronics.[11−13]

The conventional methods for copper metallization typically involve physical vapor deposition and electrochemical plating.[14] In recent years, cost-effective electroless copper metallization has been developed to deposit a layer of copper structures on a textile. In the current copper plating practice, copper(II) and less reactive reductants are mixed in aqueous solution together with additives, stabilizers, and other necessary chemicals[15,16] to produce a one-pot plating solution. The metallization of textiles is realized by directly immersing the textile into the solution to slowly reduce copper(II) into its metallic state. The one-pot process is usually accompanied by considerable heating of the solution[8,17] and is thus not feasible for textile materials that are sensitive to heat (e.g., thermoplastic materials). Furthermore, as less reactive reductants are used, a lowly adhesive copper film is usually obtained on the surface of the textile. To address this issue, the textile is usually pretreated prior to copper plating by sealing, sandblasting, and etching[17] or by using chemical sensitizers,[18−22] plasma, and supercritical carbon oxide. The surface-treated textile can then have improved adhesion strength through enhanced bonding to copper. However, these pretreatments require special machinery and long processing time, which significantly increase the cost of production.

Furthermore, when the copper(II) solution is applied onto the surface of a textile, it easily diffuses and spreads over the surrounding areas before being metallized on the textile. Consequently, there is a strong demand to develop a nondiffusive ink of copper(II) so as to realize the controlled copper patterning on textiles. Meanwhile, there has been

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continuous progress in the advanced synthesis of copper-related nanostructures,[23−29] which provides deep understanding of the formation of various copper-related nanostructures.[30−35] With the insights gained from these studies, we have found that at a sufficiently high pH value and in the presence of stabilizers, copper(II) can form a nondiffusive, highly viscous copper hydroxide solution that can be painted or printed to produce well-defined patterns on a textile. A separate reducing bath is subsequently applied to realize copper deposition on a textile with well-defined boundaries. In this scenario, the chemical reduction of patterned copper(II) in the form of copper hydroxide on a textile may only lead to heterogeneous nucleation and subsequent growth of copper structures. This differs from the conventional one-pot copper metallization method, where homogeneous nucleation of copper particles occurs, followed by deposition/growth on the textile with low adhesion strength. With our two-step copper metallization approach, we are able to readily produce user-defined copper patterns on textiles that are highly adhesive, conductive, antibacterial, and inert against oxidation. This new copper plating strategy undoubtedly holds tremendous potential as a commercially viable method to metallize an insulating textile without involving an external power source.

EXPERIMENTAL SECTION

Chemicals. Copper(II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, 99.995%), 2,2′-dipyridyl *N,N*′-dioxide (98%), L-ascorbic acid (99%), and polyethylene glycol (average molecule weight 8000) were purchased from Sigma-Aldrich. Sodium borohydride (99.99%) and thiourea (99.0%) were purchased from Acros. Sodium hydroxide (99%) was purchased from Merck. All the chemicals were used without further purification.

Copper Metallization with a Mild Reducing Agent. A copper(II) solution was first prepared by dissolving 224 mg of copper sulfate pentahydrate in 30 mL of water followed by sequentially adding 5 mg of 2,2′-dipyridyl *N,N*′-dioxide and 80 mg of polyethylene glycol. The pH of the resulting solution was adjusted to ∼13 by further adding 120 mg of sodium hydroxide. A reducing solution was also prepared by dissolving 250 mg of ascorbic acid and 5 mg of 2,2′-dipyridyl *N,N*′-dioxide in 20 mL of water. A user-defined copper(II) pattern was first obtained by painting the copper(II) solution onto a cotton textile using a brush 5−10 times. The copper(II)-patterned textile was then immersed in the reducing bath for 1 min at room temperature. A dense deposition of copper was achieved by repeating the copper ion patterning and subsequent copper deposition steps five times. After washing and rinsing to remove residual chemicals, the copper patterns were well-defined and appeared bright yellow in color. A tape-peel test of the copper layer on the textile was performed to reveal its good adhesion property without peeling.

Copper Metallization with a Strong Reducing Agent. A copper(II) solution was first prepared by dissolving 224 mg of copper sulfate pentahydrate in 30 mL of water followed by sequentially adding 5 mg of 2,2′-dipyridyl *N,N*′-dioxide and 40 mg of polyethylene glycol. The pH of the resulting solution was adjusted to ∼13 by further adding 120 mg of sodium hydroxide. A reducing solution was also prepared by dissolving 300 mg of sodium borohydride in 20 mL of water following by adding 3 mg of sodium hydroxide, which can adjust the pH so as to minimize the reaction between sodium borohydride and water. A surfactant solution was further prepared by dissolving 250 mg of thiourea in 20 mL of water. A user-defined copper(II) pattern was first obtained by painting copper(II) solution onto various textiles (e.g., cloths of 100% cotton, 65% polyester with 35% cotton, and 87% polyester with 13% nylon) using a brush 5−10 times. The copper(II)-pattered textile was then immersed in the reducing bath for 30 s at room temperature. A dense deposition of copper was achieved by repeating the copper(II) patterning and subsequent copper deposition steps five times. The textile was then soaked in the surfactant bath for 3−10 min to provide surface protection. After washing and rinsing to remove residual chemicals, the copper patterns were well-defined and appeared dark brown in color. A tape-peel test of the copper layer on the textiles was performed to reveal its good adhesion property without peeling.

Antibacterial Analysis. The bacterial strains used in these studies were *Staphylococcus aureus* ATCC 29213 and *Escherichia coli* ATCC 10536. Experimentally, 1 mL of bacterial suspension at a concentration of 1×10^5 cfu/mL (cfu, colony forming unit) was added onto the control (1 × 1 cm cotton textile), sample 1 (1 × 1 cm copper-metallized cotton textile using sodium borohydride), and sample 2 (1 × 1 cm copper-metallized cotton textile using ascorbic acid), which were placed in a 24-well plate (triplicate tests for each samples). After culturing at 37 °C with shaking at 100 rpm for 1, 3, and 6 h, the bacterial suspension from each well was diluted 10 times and spread on the surface of a Petri dish covered with Luria−Bertani (LB) agar. The agar plates were cultivated for 24 h in a biological thermostat at 37 °C. The grown *S. aureus* and *E. coli* colonies were clearly visible and counted. The antibacterial efficiency (E) was determined according to the following formula, $E\ (\%) = (A - B)/A \times 100\%$. Here A is the number of bacterial colonies grown from the suspension that was in contact with the control, and B is the number of bacterial colonies grown from the suspension that was in contact with the sample 1 or 2.

Characterization. Optical photos were taken by a Canon EOS 40D camera. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) spectra were recorded using a JEOL FESEM JSM6700F SEM. X-ray diffraction (XRD) was performed with a Bruker general area detector diffraction system using Cu Kα radiation (λ = 1.54 Å). The electrical conductivity of copper-metallized textile was measured with a MCP T610 low-resistivity meter from Mitsubishi Chemical Analytech with a standard four-point probe. Five resistance measurements were taken for each sample, and the averaged value was used to calculate the conductivity. The selection of the four-pin probe is to minimize the contact resistance and surface geometry effects.

RESULTS AND DISCUSSION

To produce user-defined copper patterns on textiles under ambient conditions, two consecutive steps were developed, including nondiffusive copper(II) patterning and subsequent reducing-agent-dependent copper deposition on textiles, which are demonstrated and discussed below separately.

Nondiffusive Copper(II) Patterning on a Textile. A copper(II) solution was first prepared by dissolving copper sulfate into 30 mL of water (0.03 mM) together with 2,2′-dipyridyl *N,N*′-dioxide and polyethylene glycol with optimized concentration (see Experimental Section and Figure 1A). After the subsequent addition of sodium hydroxide to adjust the pH to ∼13 (0.10 mM sodium hydroxide), a stable suspension of fine copper(II) hydroxide was formed in the presence of the nitrogen-containing 2,2′-dipyridyl *N,N*′-dioxide and the long chain polyethylene glycol as stabilizers. The resulting solution was then tested as a viscous ink to create user-defined copper(II) patterns on textiles. To do this, the solution was painted on a textile for copper(II) patterning by using a brush. The application of the copper(II) paint solution was repeated a few times. The copper(II) in the form of copper hydroxide is not diffusive, and this is the key to form well-defined copper(II) patterns on textiles. It is noted that there are more than 3 times OH^- used as compared to Cu^{2+} as copper(II) source, which ensured the complete formation of $Cu(OH)_2$. As copper hydroxide is mildly amphoteric, it only dissolves slightly in the concentrated alkali to form $[Cu(OH)_4]^{2-}$.[36]

As shown in the Figure 1B, the freshly produced copper hydroxide solution can be applied to the textile through painting (or printing) to create a pattern of copper(II). The

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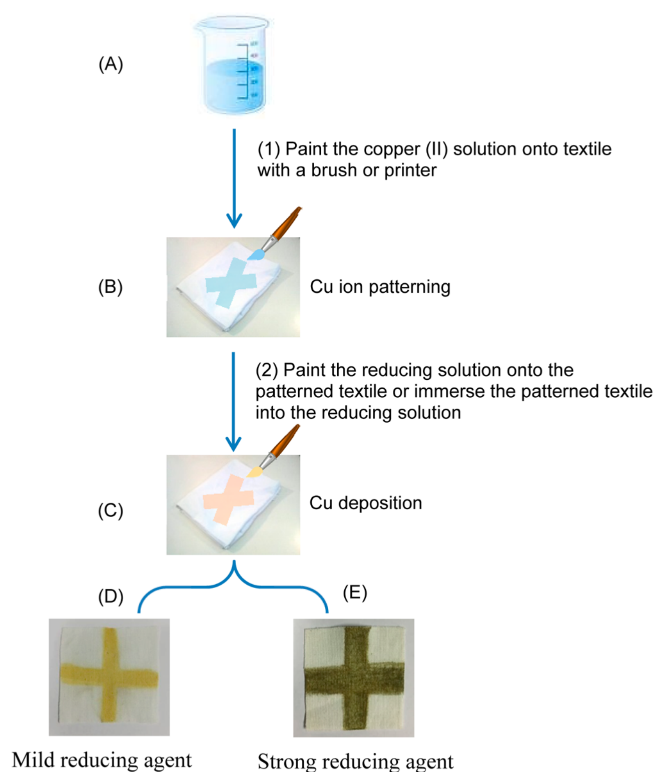

Figure 1. Schematic illustration of rapid copper metallization with user-defined patterns on cotton textile: (A) preparation of copper(II) ion solution, (B) copper(II) ion patterning, (C) copper deposition, and (D, E) copper structures prepared from mild and strong reducing agents, respectively.

portion of the textile painted with copper(II) (i.e., the cross pattern in Figure 1B) exhibits a blue color, which is very distinct from the white nonpatterned areas. As noted above, the nondiffusive copper(II) ink is important in producing well-defined copper(II) patterns. This is because copper(II) can form copper hydroxide in strong alkaline solution to increase viscosity in the presence of stabilizers. When this aqueous-based ink is painted on a textile, although the water is adsorbed quickly into the textile, the insoluble copper hydroxide does not migrate out of the printed patterns, and sharp boundaries are generated. This nondiffusive copper(II) ink can then be transformed into well-defined copper structures through the subsequent copper deposition, which is described in the following section. It is also worth noting that the use of stabilizers is important to create a stable suspension of fine copper hydroxide particles as ink. This can facilitate the rapid formation of fine copper particles via chemical reduction with improved adhesion on the textile. In cases where copper(II) patterning is not required, immersing the textile completely into the copper(II) solution for a few seconds is sufficient for the subsequent copper deposition step [Figure S1, Supporting Information (SI)].

Reducing-Agent-Dependent Deposition of Copper on Textile. After the copper(II) patterning step, the copper deposition on textile is further realized through painting (or printing) a reducing solution (Figure 1C) on the patterned areas where Cu ions were placed earlier in the first step. Alternatively, the textile can also be immersed into the reducing solution. The reducing solution was prepared by dissolving 250 mg of ascorbic acid in 20 mL of water together with 2,2′-dipyridyl *N*,*N*′-dioxide with optimized concentration (see Experimental Section). After painting the reducing solution on the copper(II)-patterned textile (Figure 1B), a light yellow copper pattern was formed through the reduction of copper(II) by ascorbic acid at room temperature (Figure 1D). A dense deposition of copper was achieved by repeating the copper(II) patterning and subsequent copper deposition steps a few more times with intermediate rinsing. A tape-peel test of the copper layer on the textile revealed its good adhesion property, as there is no peeling observed.

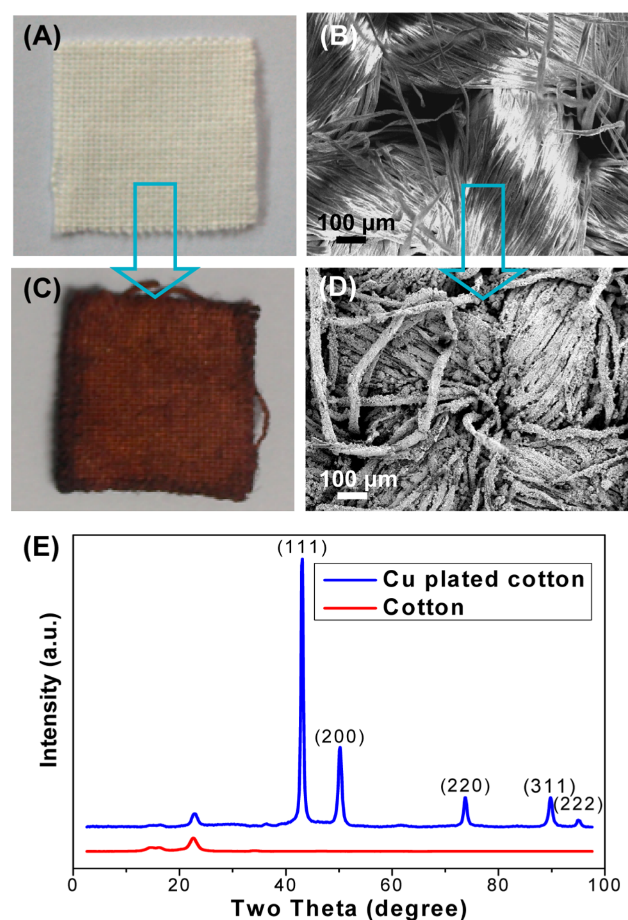

Figure 2. Photos and SEM images of (A, B) untreated cotton and (C, D) copper-metallized cotton produced by using a strong reducing reagent, sodium borohydride. (E) XRD patterns of untreated cotton (red) and copper-metallized cotton (blue).

In addition to the mild reducing agents, such as ascorbic acid, strong reducing agents, such as sodium borohydride, are also used to metalize copper on textiles. It is known that sodium borohydride can drastically reduce copper(II) to metallic Cu and thus is not suitable in one-pot copper metallization. In our method, as the reducing agents are separated from the copper(II) bath, strong reductants can be used even at higher concentration, which enables a fast deposition and better adhesion of copper on the textile. The strong reducing solution was prepared by dissolving 300 mg of sodium borohydride in 20 mL of water following by adding 3 mg of sodium hydroxide, which can adjust the pH so as to minimize the spontaneous reaction between sodium borohydride and water. However, the obtained metallic copper structure tends to be oxidized under ambient conditions, which compromises its performance in the long term. To protect the final copper structures from oxidation

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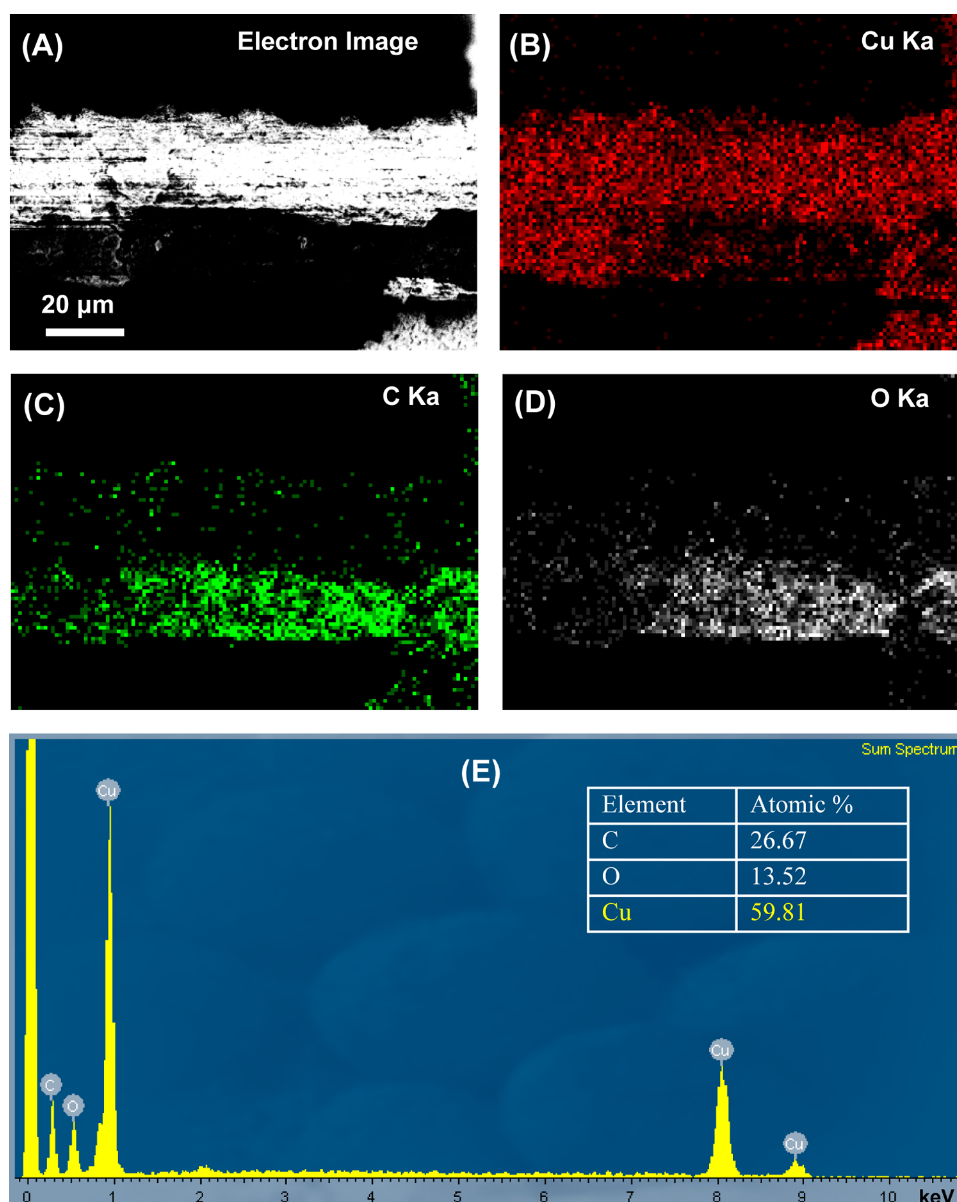

Figure 3. SEM elemental mapping of a cotton fiber from the copper-metallized cotton textile. (A) Electron image, corresponding (B) copper, (C) carbon, and (D) oxygen distribution, and (E) EDX spectrum of the copper-metallized cotton fiber. The scale bars are the same for images A–D.

and corrosion, the textile was further treated in a surfactant solution of thiourea, a sulfur-containing amine that can strongly bind to the copper surface. As in the case of the mild reducing agent, in addition to serving as a reducing agent, ascorbic acid itself can also act as a good binding agent, like thiourea. In general, the strong reducing agent sodium borohydride provides a faster copper deposition than the mild reducing agent ascorbic acid. The copper pattern reduced by ascorbic acid appears in light yellow on the textile (Figure 1D), while the copper pattern reduced by sodium borohydride appears in dark brown on the textile (Figure 1E). A dense copper pattern is produced by repeating the copper(II) patterning and copper depositions several times with intermediate rinsing.

Copper Metallization on Various Textiles. The copper metallization method developed in this research is effective in coating various textile materials that are commonly used in our daily life, such as cotton, polyester, nylon, or their mixtures. For instance, cotton textile appears in white before copper metallization, as shown in the photograph (Figure 2A). The woven fibers of the pristine cotton textile are flat and smooth on their surface, as observed by the SEM image (Figure 2B). After the copper metallization with the strong reducing agent, the textile shows a dark brown color with a metallic luster (Figure 2C). As shown in Figure 2D, small metal grains are coated on the cotton fibers with increased diameters. The copper-metallized cotton textile was exposed to ambient conditions for 1 month to test its stability before XRD characterization. Aside from the diffraction peaks attributed to cotton, the XRD pattern (Figure 2E) also exhibits five peaks at 43.1°, 50.2°, 73.8°, 89.8°, and 95.0°, which match well to the diffractions from (111), (200), (220), (311), and (222) crystalline planes of face-centered cubic (fcc) Cu (JCPDS #03-1018). There are no additional peaks observed from copper oxides, indicating the high chemical purity and stability of the copper-metallized textile.

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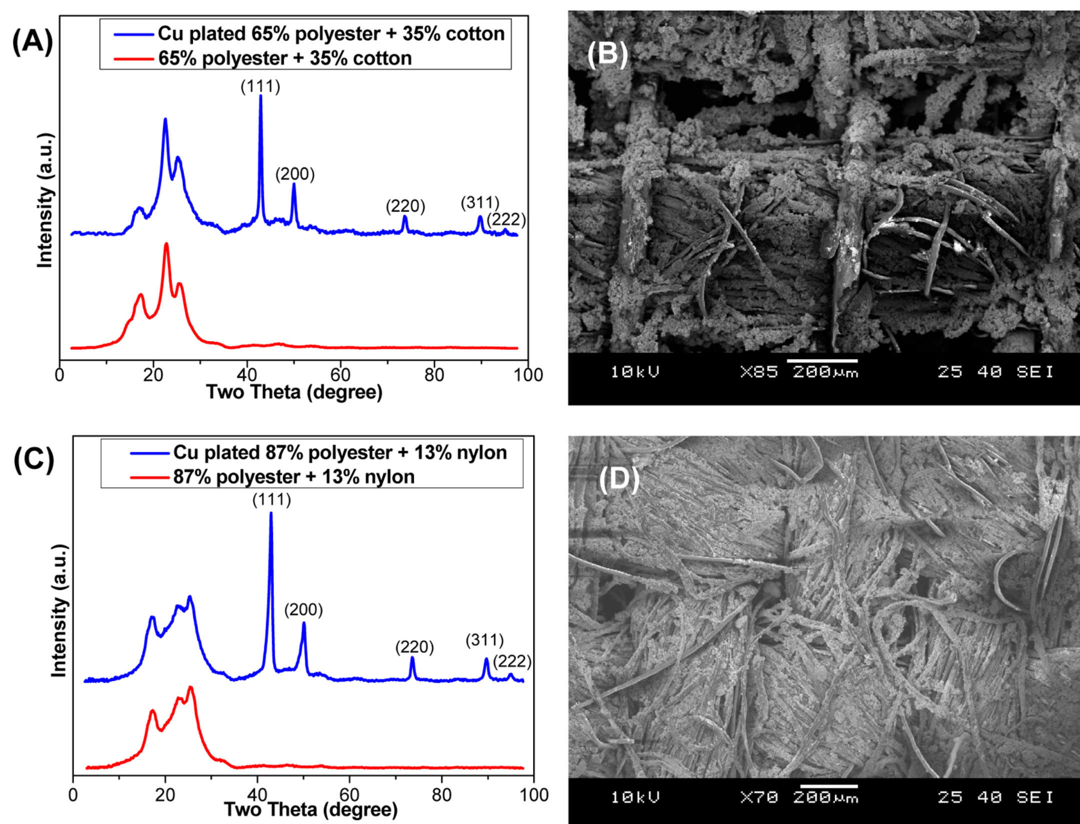

Figure 4. XRD patterns and SEM images of the copper–metallized textiles: (A, B) 65% polyester with 35% cotton, and (C, D) 87% polyester with 13% nylon.

The chemical composition of the copper-metallized textile was further analyzed by using SEM EDX. Typical copper-metallized cotton fibers were selected for inspection under SEM, and the elemental mappings from constituent elements were analyzed under different energy windows (Figure 3). SEM EDX mapping shows that the cotton fibers are entirely coated with copper (Figure 3A–D). Moreover, the quantitative data in Figure 3E shows that more copper was observed than carbon and oxygen, indicating the well-coated copper surfaces around the entire cotton textile.

Composite textiles used in clothing and interior decoration were also utilized to test the effectiveness of our two-step copper metallization method. Both (i) 65% polyester with 35% cotton and (ii) 87% polyester with 13% nylon were coated successfully through this copper metallization approach. Other than the diffraction peaks from the pristine textiles, all the new emerging XRD peaks in Figure 4A,C are indexed to the crystalline planes of fcc Cu (JCPDS #03-1018). Meanwhile, the SEM images after copper metallization in Figure 4B,D reveal the nano- and microsized crystals coating the textile fibers.

Electrical Conductivity. In general, most textile materials are insulating by nature. The copper metallization of a textile can greatly increase its electrical conductivity for use in wearable electronic devices. Here, a square piece of copper-metallized cotton textile with a side length of 1.5 cm was prepared by using strong reducing agent sodium borohydride, and it was subjected to a sheet resistance measurement with a standard four-point probe (Figure S2A, SI). The sheet resistance (R_s) of the copper-metallized textile is 0.17 Ω. The average thickness (t) of the electroless plated copper layer is ~1.5 μm, as measured from the cross-section SEM image of the copper-metallized textile (Figure S2B, SI). The conductivity (σ) of the copper-metallized textile is calculated by $\sigma = 1/R_s t = 3.9 \times 10^6$ S/m, which is about 3 times better than that of bulk stainless steel. In comparison, the untreated cotton cloth was also tested to be a nonconducting material.

Antibacterial Property. Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli* were separately grown in LB medium onto the untreated cotton textile (control) and the copper-metallized cotton textile prepared with the strong reducing agent (sample 1) and the mild reducing agent (sample 2) for 1, 3, and 6 h. The antibacterial efficiency of samples 1 and 2 (normalized to the amount of cells exposed to control) against *S. aureus* and *E. coli* is demonstrated in Figure 5. After 1 h of contact with *S. aureus*, samples 1 and 2 inhibited the growth of bacterial cells by 40% and 68%, respectively. After 3 and 6 h, the antibacterial efficiency of both of the samples increased to more than 90%, indicating that the samples can inhibit the growth of bacterial cells efficiently (Figure 5A). On the other hand, the antibacterial efficiency of samples 1 and 2 against *E. coli* was lower than 30% after 1 and 3 h of contact time. After 6 h, the efficiency was increased to 60% and 76%, respectively (Figure 5B). Figure 5C shows typical photos of LB agar plates where *S. aureus* and *E. coli* bacteria in contact with control, sample 1 and the sample 2 were cultivated for 6 h. These results exhibit that copper metallization is effective in inhibiting the growth of both Gram-positive and -negative bacteria on textiles. As known, copper is one of a small group of metallic elements that are essential to human health. Thus, copper-metallized dressings are desirable to prevent bacterial infection and increase the wound healing rate. Meanwhile, this

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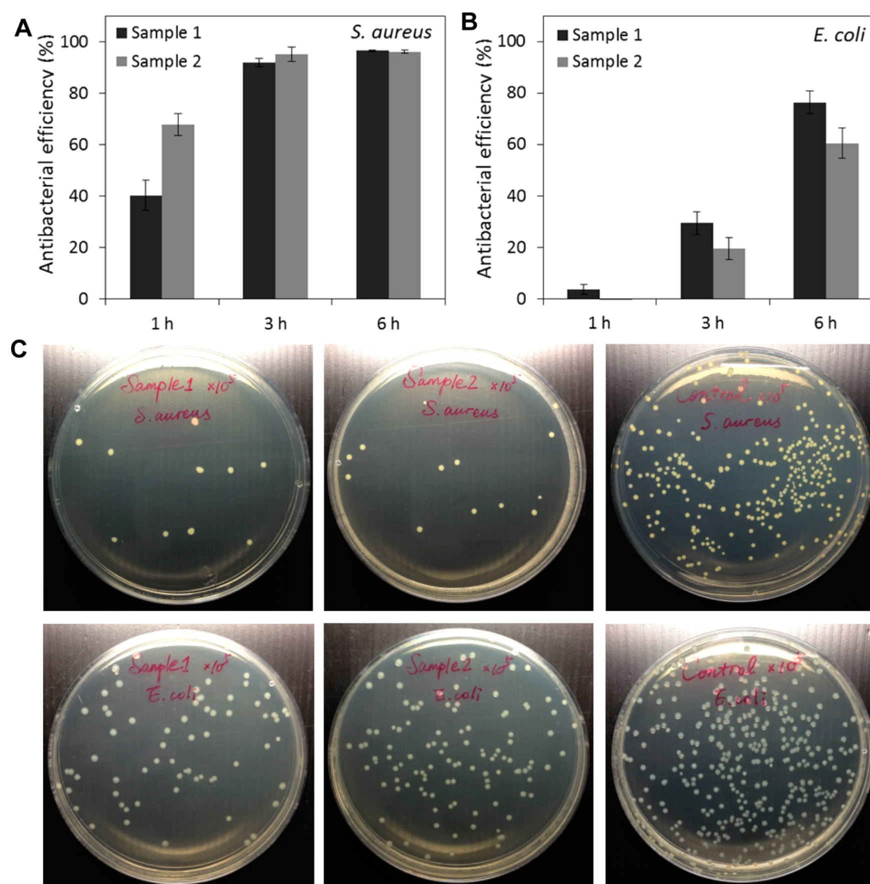

Figure 5. Antibacterial activities of a copper-metallized cotton textiles. Antibacterial efficiency of sample 1 (1 × 1 cm copper-metallized cotton textile using sodium borohydride) and sample 2 (1 × 1 cm copper-metallized cotton textile using ascorbic acid) against (A) *S. aureus* and (B) *E. coli* bacterial cells as a function of the contact time at 1, 3, and 6 h. The bars indicate the standard errors. (C) Photos of *S. aureus* (first row) and *E. coli* (second row) bacteria cultivated on LB agar covered Petri dishes that were in contact with control, sample 1, and sample 2 (from left to right) for 6 h.

approach provides a novel platform to achieve user-defined patterns on textile with enhanced antifouling properties.[37,38]

CONCLUSIONS

In this paper, rapid copper metallization of various textile materials is achieved at ambient temperature. A unique cost-effective formulation is demonstrated to metalize textiles with user-defined patterns for the first time. Experimentally, textile is first subjected to painting with a highly viscous copper(II) bath to create a nondiffusive copper(II) patterning. A separate reducing bath is subsequently applied to realize copper deposition on the textile with well-define boundaries. The two processes were repeated to readily attain a very dense coating of copper, which is encapsulated with surfactants to prevent oxidation and corrosion for enhanced stability and durability. The copper-metallized textile is adhesive, conductive, and antibacterial. With the added advantages of being simple and having low manufacturing cost and high productivity, this two-step method greatly advances the copper metallization technology and brings a new look to textile materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b06807.

Images of copper-metallized cotton cloths without patterning, schematic diagram of the four-probe sheet resistance measurement, and cross-sectional SEM image of a typical copper-metallized cotton fiber (Figures S1 and S2) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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