Polyelectrolyte-Bridged Metal/Cotton Hierarchical Structures for Highly Durable Conductive Yarns

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ABSTRACT A novel, facile, and versatile approach for preparing highly durable, electrically conductive cotton yarns is reported. Polyelectrolyte brushes, a polymer that covalently tethers one end on a surface, are first grown from cotton surfaces by surface-initiated atomic transfer radical polymerization. Subsequent electroless deposition of metal particles onto the brush-modified cotton yarns yields electrically conductive yarns, which have conductivity as high as ~1 S/cm and can be used as electrical wires in wearable, flexible electronic devices. Importantly, the formation of polymer brush-bridged metal/cotton hierarchical structures provides robust mechanical and electrical durability to the yarns under many stretching, bending, rubbing, and washing cycles. With proper selection of metal, the conductivity of the samples remains stable after they are stored in air for a few months. This chemical approach can be extended as a general method for making conductive yarns and fabrics from all kinds of natural fibers.

KEYWORDS: hierarchical structures • conductive yarn • cotton • electroless deposition • polymer brushes • durability • surface-initiated • ATRP

INTRODUCTION

Electrically conductive yarns have attracted considerable attention because of their desirable properties including electrical conductivity, flexibility, electrostatic discharge, electromagnetic interference protection and radio frequency interference protection (1). The development of conductive yarns is also critical for various applications in wearable electronics such as wearable displays, solar cells, actuators, data managing devices, and biomedical sensors (2−6). Conductive yarns directly spun from conductive materials including metals, metal oxides, carbon nanotubes (CNTs), and conducting polymers were first demonstrated as prototype materials for wearable electronics, yet they are expensive and difficult to be produced on a large scale (7−9). A more economic and productive way of making conductive yarns is coating conventional fibers with a layer of metals, CNTs, or conducting polymers, followed by spinning into yarns. This strategy has produced a wide variety of conductive yarns from synthetic fibers with conductivity ranging from 1×10^{-6} to 1×10^{4} S/cm and desirable mechanical properties (10−13). Nevertheless, the production and postdisposal processes of synthetic fibers generate environmental pollution, which is a major challenge to overcome in the next few decades. First, the raw polymers used for spinning into yarns are made through the petrochemical industrial process, from which a large amount of energy is consumed and CO_2 is released. Second, most synthetic fibers are not naturally degradable (14). Such "white pollution" has been a serious environmental concern for decades. Third, the fossil oil resource is not sustainable in the long term (15, 16). Furthermore, garments made of synthetic fibers are not comfortable to wear. As a result, there is an increasing interest in making conductive yarns from natural fibers, which are sustainable, biodegradable, and zero CO_2 emitting in the growth/degradation cycles.

Cotton, cellulose in nature, is the most widely used natural fiber in the world. It is low-cost and clean to produce, and has a wide variety of applications in textile cloth, upholstery, daily care, and medicine (17). Garments made up of cotton are especially popular because of the comfortability to wear. Only a limited number of articles on conductive coating of cotton fibers/yarns have been reported. Most works are focused on the coating of conducting polymers including polypyrrole (PPy) and polyaniline (PANI) by in situ solution or vapor phase polymerization (18−21). Recently, Knittel and Schollmeyer reported the coating of poly(3,4-ethylene dioxythiophene) (PEDOT) (22). The conductivity of such yarns is typically on the order of 1×10^{-6} to 1×10^{-3} S/cm, which limits their applications in some field such as conductive circuits. Besides, the washability of this type of conductive yarns is poor. Because the conductivity of conducting polymers depends greatly on doping, washing in water or detergent will change the doping level dramatically, leading to a rapid drop in conductivity (18). Aging in air is another concern of using conducting polymer coated yarns. A second candidate of conductive coating is
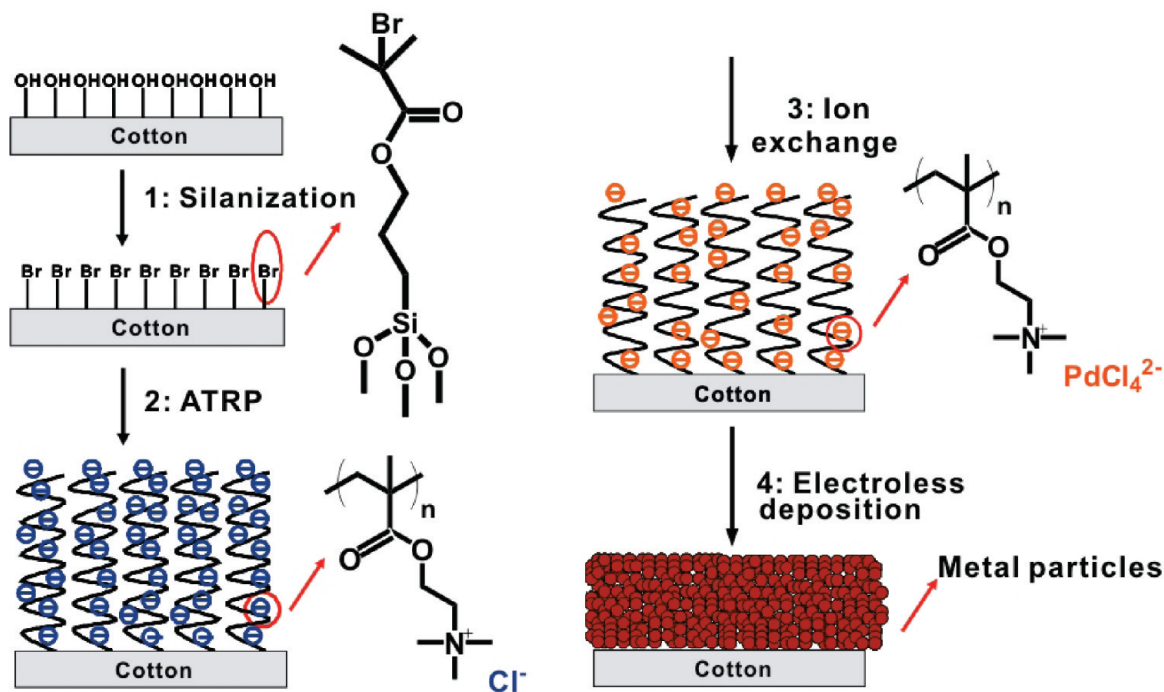
FIGURE 1. Schematic illustration of the process of preparing conductive cotton yarns. The dimension is not drawn to scale.

CNT because of it high conductivity, strength, and stability (23). Shim et al. recently demonstrated the physical padding of mixture of CNTs and polyelectrolyte on cotton yarns (24). The resulting yarns were highly conductive and could be used as protein sensor. However, neither the mechanical durability nor washability of the modified yarns was discussed. On the other hand, metal coating should be an ideal solution to highly conductive yarns. Indeed, metal wire-blended cotton yarns are so far the most adaptable technology. Nevertheless, direct sputtering or inking with metal film/particles on cotton results in flaking off of the metal layer. To date, how to effectively modify the cotton surface with controllable conductivity and high durability remains a great challenge.

To address the challenge, we report here a novel, facile, and versatile approach for preparing highly durable, electrically conductive cotton yarns by electroless deposition (ELD) of metal particles onto cotton yarns modified with polyelectrolyte brushes as adhesion layer. Polyelectrolyte brushes, polymer that covalently tethers one end on a surface, are first grown from cotton surfaces by surface-initiated atomic transfer radical polymerization (ATRP) (25−27). Subsequent ELD of metal particles onto the brush-modified cotton yarns yields electrically conductive yarns. Importantly, the formation of polymer brushes bridged metal/cotton hierarchical structures provides robust mechanical and electrical durability under many stretching, bending, rubbing, and washing cycles. The cotton yarns have conductivity as high as ∼1 S/cm and can be used as electrical wires for powering light-emitting diodes (LEDs). With good selection of metal, the conductivity is stable in air for 2 months until this moment. In principal, this chemical approach can be extended as a general method for

making conductive yarns and fabrics from all kinds of natural fibers.

RESULTS AND DISCUSSION

Synthesis of Polymer Brushes. As a proof-of-concept, we synthesized poly [2-(methacryloyloxy)ethyl-trimethylammonium chloride] (PMETAC) brushes from cotton yarns by water-mediated surface-initiated ATRP, which provides high polymerization speed and good control over brush thickness, uniformity, and density (28). The ATRP method is also recognized as a green chemical approach for polymer synthesis (29, 30). The procedure is schematically illustrated in Figure 1A. In a typical experiment, we first immobilized the ATRP initiator onto cotton surfaces by immersing in the initiator solution for 10 h followed by cleaning (Figure 1A). Subsequently, the initiator immobilized yarns were immersed in a polymerization solution for 10 h at 60 °C, resulting in the growth of PMETAC brushes from cotton surfaces. Finally, the sample was washed with methanol and water several times and dried under N_2. Fourier transform infrared spectroscopy (FTIR) confirmed the success of the grafting process (Figure 2A). The strengthened peak at 1730 cm^{-1} and the new peak at 876 cm^{-1} are attributed to the carbonyl groups and quaternary ammoniums groups (QA$^+$) of PMETAC, respectively. The peaks at 2851, 2918, and 2963 cm^{-1} are attributed to three different C−H stretching states.

Scanning electron microscopy (SEM) shows typical sub-50 nm trench morphology on the surfaces of raw cotton fibers, whereas much smoother morphology is observed on the PMETAC grafted ones (Figure 2B, C). This flattening phenomenon indicates that the thickness of the PMETAC brushes is larger than the half-width of the nanotrenches. We were not able to directly measure the brush
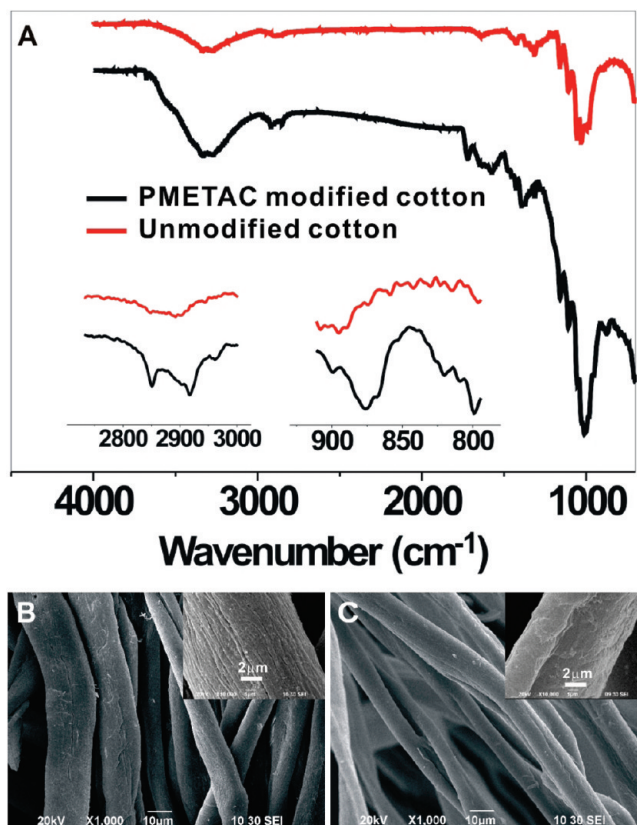
FIGURE 2. (A) FTIR spectrum of PMETAC brushes modified cotton (black) and control cotton (red). SEM images of (B) raw cotton fibers and (C) PMETAC modified cotton fibers in cotton yarns.

thickness from cotton surfaces. From our surface-initiated ATRP comparative experiments on silicon substrates and other literature reports, we estimate that the thickness is ~30 nm (31, 32). The exact grafting density of polyelectrolyte brushes grown via surface-initiated polymerization is difficult to determine experimentally, and depends strongly on nature of the monomer, density of initiator molecules on the surface, and the polymerization conditions (33, 34). For the results described here, the exact grafting density is not important as long as the surface is completely covered (i.e., defect-free) with polymer brushes. Importantly, note that although the entire process was carried out with cotton yarns, the SEM images indicate that initiation and polymerization took place uniformly on every cotton fiber within the yarns.

Electroless Deposition. The PMETAC grafted cotton yarns were immersed into a 5 mM $(NH_4)_2PdCl_4$ aqueous solution (pH ~1) for 15 min, where $PdCl_4^{2-}$ moieties were immobilized onto the brushes by ion exchange because of their high affinity to QA^+ (Figure 1A). The palladium moieties act as effective catalytical sides for ELD of Cu and other metals (35−39). After rinsing with 4 × 200 mL deionized water, the yarns were finally coated with a layer of Cu particles by immersing in a house-made ELD plating bath, followed by water rinsing and blown dry. Typically, longer plating results in heavier yarns, with a saturation plateau occurring at ~60 min (Figure 3A). This can be attributed to the increasing amount of plated metal. We
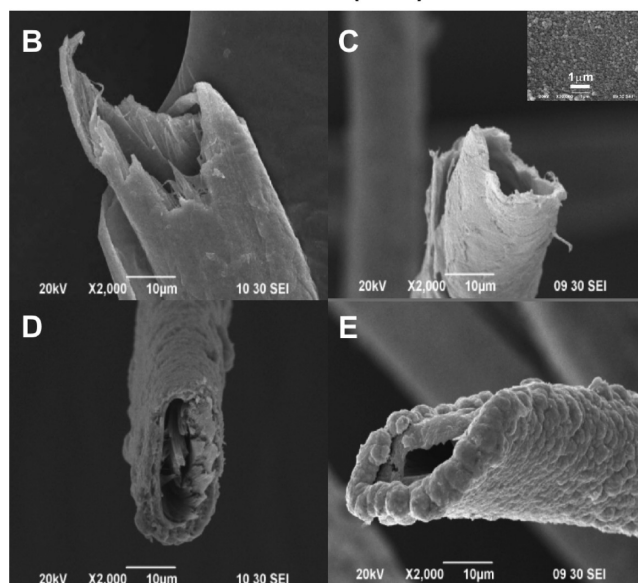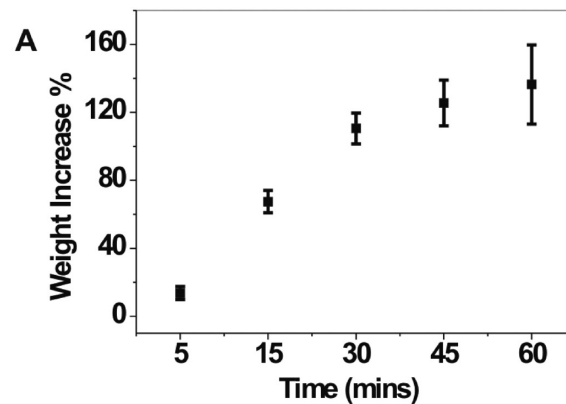

FIGURE 3. (A) Weight increase of cotton yarn at different ELD plating time. SEM images of the cross-section morphologies of PMETAC modified cotton fiber that is immersed in ELD plating bath for (B) 0 s, (C) 1 min, (D) 10 min, and (E) 30 min. The inset in C shows the corresponding surface topographic SEM image, showing that the surface of the cotton fiber is covered by dense Cu particles.

followed the ELD reaction by SEM and energy-dispersive X-ray spectroscopy (EDX). For 5 s immersion, the cotton yarns turned black, from which palladium was detected by EDX (see Figure S1, Supporting Information) and only a trace of copper signal was observed. As time went, the yarns turned brown. Cu particles with diameters of 130 ± 20 nm were observed after immersing for 1 min (Figure 3C). The ratio of Cu to Pd signal in EDX increases dramatically (see Figure S1 in the Supporting Information). No obvious change in size of the particles was observed at increasing deposition time, yet the thickness of the copper layer increased. After 30 min immersion, the thickness of the copper layer grew to more than 1 μm, and the weight of the cotton yarns increased ~2 fold (Figure 3A). No Cu was observed without the immobilization of $PdCl_4^{2-}$.

Conductivity and Mechanical Durability. Bare cotton is well-known to be insulated. In contrast, the as-made Cu-coated cotton yarns are electrically conductive. The conductivity of the yarns increases with increasing ELD time (and thus increasing amount of plated Cu particles), reaching as high as ~1 S/cm at 60 min.

The key feature herein is that PMETAC brushes bridged Cu/cotton hierarchical structures offer unique electrical stability under multiple bending, stretching, rubbing, and even washing cycles. One critical challenge of conductive yarns is the durability under multiple bending and stretching cycles. To investigate that, we first performed electrical conductivity measurement while stretching and relaxing the conductive cotton yarns (30 min plating) in a controlled manner. Interestingly, the conductive yarns exhibit higher conductivity (0.28 S/cm) when straightly stretched (2.2 N), and lower conductivity (0.04 S/cm) when the stress is released. This process is fully reversible after 30 cycles (Figure 4A, showing 10 cycles) and the conductivity of the stretching/relaxing state remains unchanged. When the yarn is bent under stress, e.g., wrapped and stretched around a pen, the conductivity is similar to that of its straightly stretched state. These results can be explained by the fact that the fibers making up the yarn have loose contact while the yarn is relaxed. When the yarn is stretched, the fibers pack more closely and therefore the conductivity of the yarn increases (40). No cracks in the copper layer were found by SEM after this 30-cycle experiment. We further challenged the robustness of the conductive yarns by running through the washing cycles. For proof-of-concept purpose, we used simple hand washing and squeeze-drying (see Movie 1 in the Supporting Information), during which the yarns were also exposed to extensive rubbing. Finally the yarns are fully dried by blowing with N_2 gas. No obvious degradation of the conductivity was observed after 5 washing and drying cycles (Figure 4B). Again, the morphology of the copper coating shows no evidence of cracking under SEM. It should be noted that the development of adhesion between metals and substrates has been a major issue in the industry for decades. Direct coating of cotton fibers/yarns with metals typically resulted in flaking off at bending and rubbing, and cannot withstand washing tests.

We measured the yarn's breaking strength and extension. The breaking strength and extension of the Cu-plated conductive yarns are 6.4 N and 9.1%, respectively, slightly lower than those of the unmodified cotton yarns (7.2 N and 10%, Figure 5). This phenomenon may arise mainly from the initiation procedure, in which HCl is produced. Such acidic moieties are known to degrade cellulose and influence cotton strength. To verify that, we measured the mechanical properties of initiator modified cotton yarns. Indeed, the breaking strength and extension drop by 20%, being 5.8 N and 8.3%, respectively. The polymer brushes bridged copper/cotton hierarchical structures seem to provide extra strength and extensibility to the fiber.

Stability in Air. Currently, slow decrease in conductivity of the Cu-plated yarns can be observed when the sample is placed in air (Figure 6A). The conductivity decreased to 10% (0.08 S/cm) of its original value (0.8 S/cm) after the sample was stored in air for 7 days. X-ray diffraction measurement reveals oxidation of the Cu layer (Figure 6B). The 2θ peaks at 44.3, 51.4, and 75.4 degrees correspond to
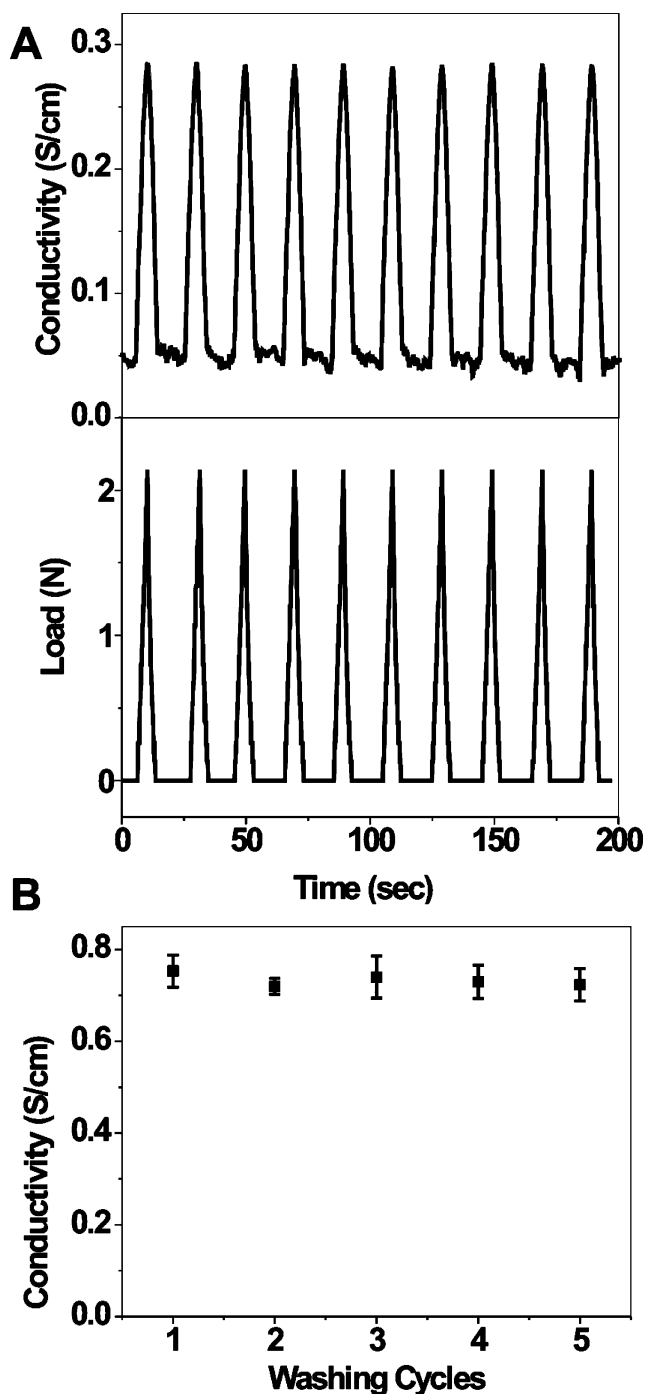

FIGURE 4. (A) Conductivity test of the conductive cotton yarn (30 min plating) under repeatable stretching and relaxing cycles. The upper part shows the conductivity readout, whereas the bottom part shows the loading readout. The conductivity of the conductive cotton yarn increases when the applied load is increase. (B) Washability test of the conductive cotton yarns (60 min plating). The conductivity maintains constant after 5 washing cycles.

the (111), (200), and (220) crystal plane of Cu, respectively. The peaks at 35.2 and 38.9° corresponds to copper oxide and cuprous oxide, respectively. This instability may be solved by capping the metal by self-assembly, electrochemical deposition, or physical encapsulation that has been developed by the electronic industry.

Ni-Plated Conductive Cotton Yarns. An alternative method to increase air stability of conductive yarns is to
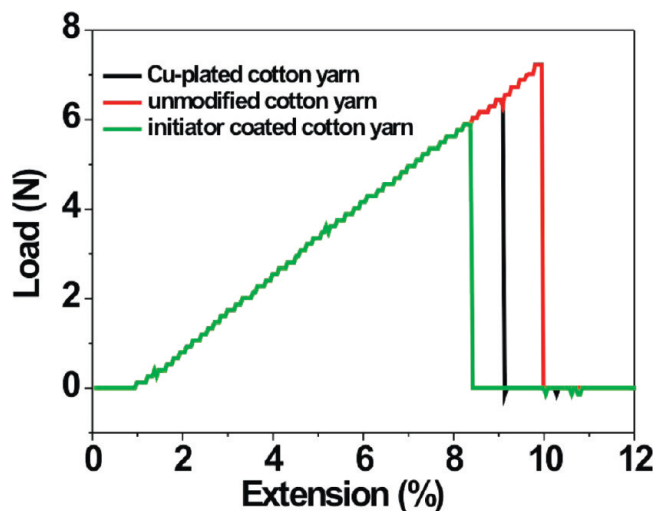
FIGURE 5. Tensile strength measurement of unmodified (red), initiator-coated (green), and Cu-plated (black) cotton yarns.
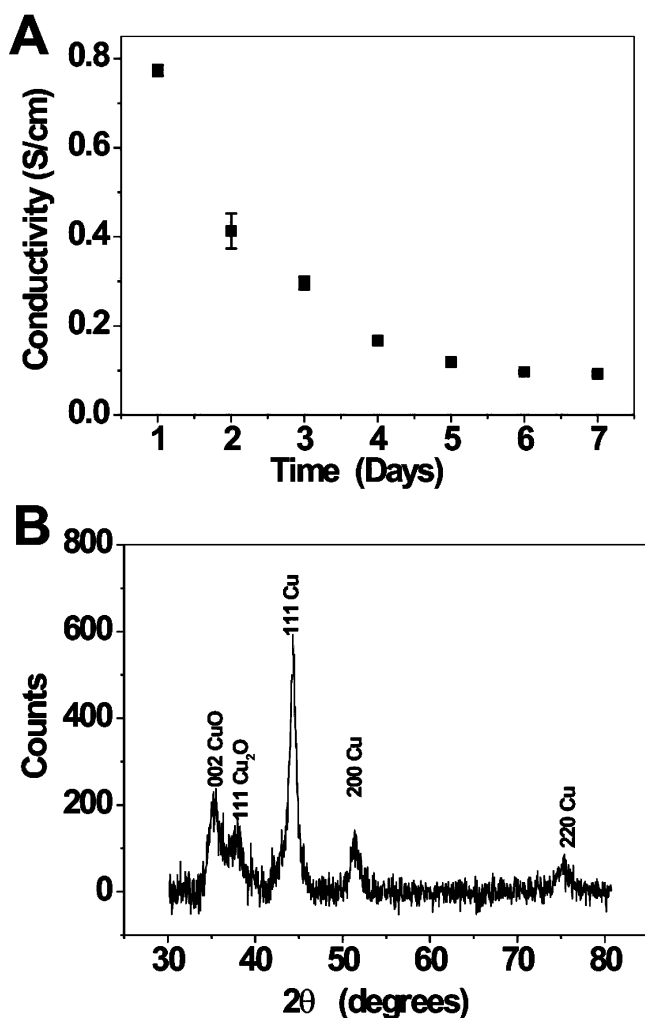

FIGURE 6. (A) Conductivity aging test of Cu-plated cotton yarns. **(B)** XRD spectrum of Cu-plated cotton yarns stored in air for 2 days.

FIGURE 7. (A, B) SEM images of Ni-plated cotton yarns by ELD. The PMETAC brush-modified cotton yarns were placed in a Ni plating bath for 2 h. **(C)** Conductivity test of Ni-plated cotton yarn under repeatable stretching/relaxing cycles.

deposit other air stable conductive metal. As proof-of-concept, we demonstrate here using Ni. Instead of Cu, Ni particles were deposited onto PMETAC brush modified cotton by ELD. SEM images show that the cotton surfaces ar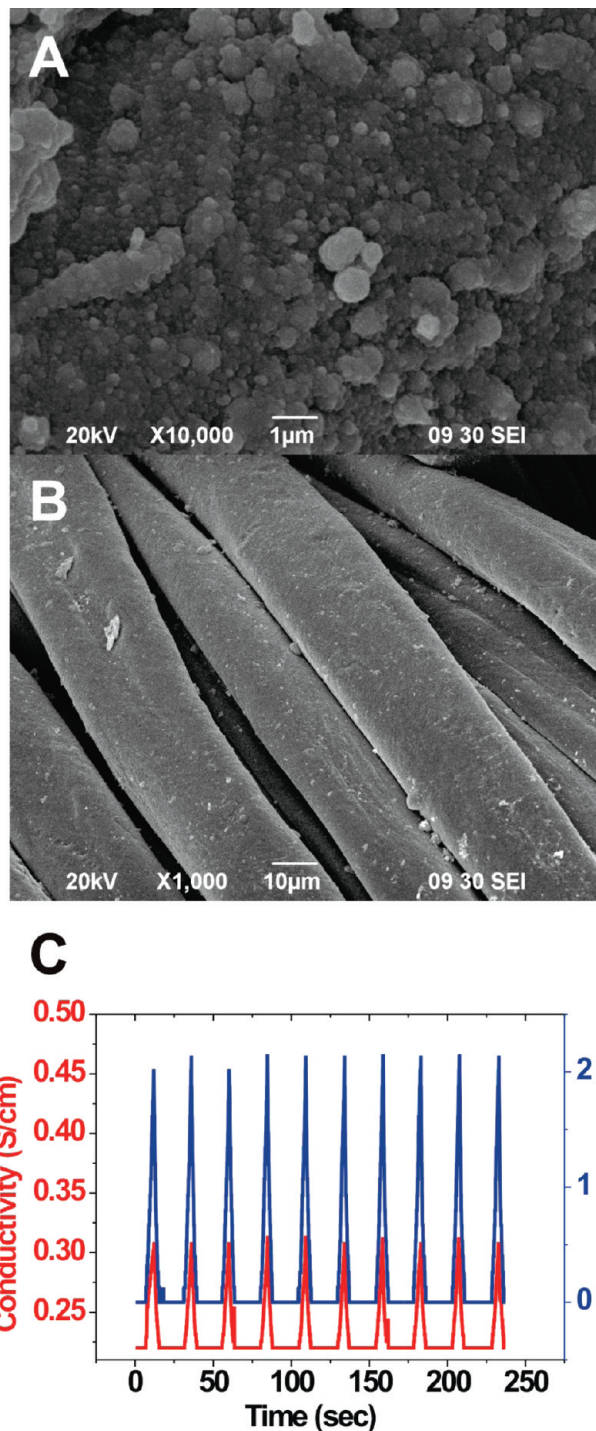e densely covered with aggregates of Ni nanoparticles (Figure 7A, B). The as-made Ni-plated cotton yarns are electrically conductive with good air stability. The measured conductivity was ~0.3 S/cm (freshly made conductive yarn after 2 h ELD plating) and remained constant in air for 2 months until this moment. We performed the same conductivity measurement under mechanical stretching/relaxing cycles to the Ni-plated cotton yarns. Again, the yarns exhibited higher conductivity (0.31 S/cm) at stretching state and lower conductivity (0.22 S/cm) at relaxing state revers-
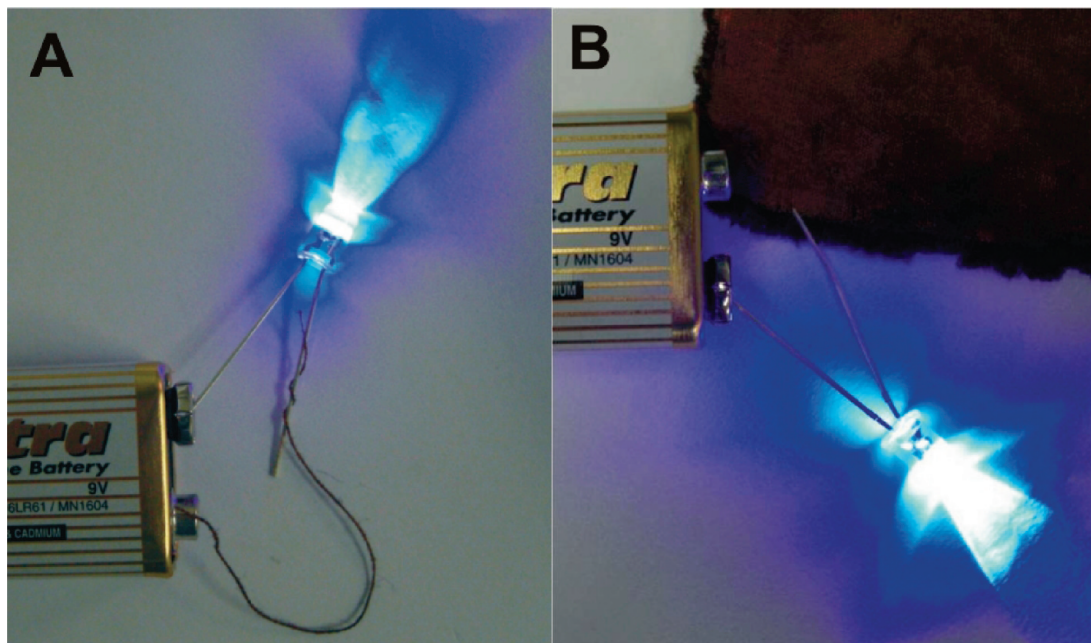
FIGURE 8. Digital images of electronic circuits. (A) Conductive yarn or (B) fabric is used as electrical wire or substrate for powering a blue LED. The yarn or fabric was placed in contact with the battery and LED without using extra conductive glue or paste.

ibly. No apparent decrease in the conductive performance was observed under a simple mechanical or washing test.

Applications. Because of the high conductivity and robustness, the as-made conductive cotton yarns (both Cu- and Ni-plated) can be used as conductive wires in electronic circuits. As a proof-of-concept, we constructed a simple circuit by bridging a 9 V battery and one electrical contact of a blue LED with our conductive yarn (Figure 8A). When the other contact between the LED and the battery was made, the LED turned on immediately and illuminated for more than 5 min until we disconnected the contact. The LED can be repeatedly switched ON and OFF by connecting and disconnecting the contact without loss of fidelity (see Movie 2 in the Supporting Information).

This chemical route can be easily extended to making conductive cotton fabrics. For simple proof-of-concept purpose, we made a piece of Cu-plated cotton fabric following the same chemical procedures shown in Figure 1. The fabric surfaces show similar Cu coating to that of Cu-plated cotton yarns (not shown). As shown in Figure 8B, a LED can be illuminated by using a 9 V battery and this fabric as conductive substrate.

CONCLUSIONS

In conclusion, a novel, facile, and versatile approach for preparing electrically conductive cotton yarns is demonstrated. PMETAC brushes are first grown from cotton surfaces by surface-initiated ATRP. Subsequent ELD of metal particles onto PMETAC-modified cotton forms polymer-bridged metal/cotton hierarchical structures, which result in the formation of conductive cotton yarns. These conductive yarns are highly durable because (1) the polymer brushes served as a strong adhesion layer leading to excellent mechanical and electrical stability under extensive rubbing,

bending, stretching, and washing; and (2) the conductivity can remain stable in air with proper choice of metal. Such conductive cotton yarns can be used as electrical functional wires in electronic circuits of powering a LED. In principle, this approach can be extended to the coating of metals on all natural fibers, yarns, or fabrics. The use of natural fibers for making conductive yarns are more environmentally friendly compared with those made of synthetic fibers. Such conductive articles should find a wide variety of applications in wearable and flexible electronics, radiation and electromagnet protection, energy, and biomedical industries.

EXPERIMETNAL SECTION

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. The initiator for ATRP, 3-(trichlorosilyl)propyl 2-bromo-2-methylpropanoate, was synthesized by our lab. Cotton yarns and fabric used in the experiments were both 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.

Immobilization of ATRP Initiator. Cotton yarns were first immersed in an anhydrous toluene solution containing 5 mM 3-(trichlorosilyl)propyl 2-bromo-2-methylpropanoate (ATRP initiator), allowing the hydroxyl groups of cellulose to react with the silane molecules through a condensation reaction. The cotton yarns were then rinsed several times with fresh anhydrous toluene and dichloromethane to remove the excess physisorbed initiator and byproduct molecules, followed by drying in a vacuum at 50 °C for 2 h.

Surface-Initiated ATRP. For the preparation of the polymerization solution, commercially available 9.2 g of 2-(methacryloyloxy)ethyl-trimethylammonium chloride (METAC) was dissolved in 10 mL of MeOH at 20 °C and degassed by passing a continuous stream of dry N_2 through the solution while being stirred (20 min). 2,2-Dipyridyl (0.48 g), Cu(I)Br

(0.12 g), and Cu(II)Br$_2$ (0.019 g) were added to above solution. The mixture was then further stirred and degassed with a stream of dry N$_2$ (15 min). Initiator-modified substrates were sealed in Schlenk tubes, degassed (4 × high-vacuum pump/ N$_2$ refill cycles), and left at 20 °C under N$_2$. The polymerization solution was then syringed into each Schlenk tube, adding enough solution to submerge each sample completely. The samples remained in the solution for polymerization. After polymerization the samples were removed, washed with methanol and water, and then dried under a stream of N$_2$.

Electroless Deposition. The Cu electroless plating was performed in plating bath containing 1:1 mixture of freshly prepared solutions A and B. Solution A consists of 12 g/L NaOH, 13 g/L CuSO$_4$ · 5H$_2$O, and 29 g/L KNaC$_4$H$_4$O$_6$ · 4H$_2$O. Solution B is 9.5 mL/L HCHO in water. The electroless plating of Ni was performed in the following steps, in the plating bath consisting of 40 g/L nickel sulfate hexahydrate, 20 g/L sodium citrate, 10 g/L lactic acid, and 1 g/L dimethylamine borane (DMAB) in water. A nickel stock solution of all components except the DMAB reductant was prepared in advance. A DMAB aqueous solution was prepared separately. The stock solutions were prepared for a 4:1 volumetric proportion of nickel-to-reductant stocks in the final electroless bath. After mixing, the solution was adjusted with ammonia to pH ∼8.

Conductivity Test. Electrical conductivity of the copper-coated cotton yarns was measured by a two-probe method with a Keithley 2010 Multimeter. The load and deformation were recorded using an Instron mechanical testing system (Model 5566). The distance of the testing probes was 3.5 cm. For cyclic tension, specimens were repeatedly stretched and recovered in 30 cycles with a maximum extension up to the strain of 50%. Each cycle takes about 20 s. At least five specimens from each sample were tested and an average value was taken. All tests were carried out at 20 °C and 65% RH.

Supporting Information Available: EDX spectrum of conductive yarns (PDF); movies showing the hand washing process and electronic circuits using conductive yarns (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

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