Facile Fabrication of Conductive Ultrahigh Molecular Weight Polyethylene Fibers via Mussel-Inspired Deposition

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ABSTRACT: The conductive ultrahigh molecular weight polyethylene fibers are fabricated by electroless silver plating. The extremely inert and smooth surfaces of fibers are first activated by dopamine self-polymerization. Then, metallic silver layers are deposited on the surface via electroless silver plating. The chemical composition, surface topography, and crystal structure of fibers are studied by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, and X-ray diffraction (XRD), respectively. The XPS spectra certify the existence of polydopamine layer on surface. The XPS spectra and the XRD spectra prove that the silver particles deposited on the surface are pure in zero-value state and of high crystallinity. The resistance of the silver-coated fibers is 0.15 Ω/cm per bundle measured by two-point method. These conductive fibers with high conductivity are expected to use as the electrical wires. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Conductive fibers play a significant role in the area of aerospace, microelectronics, medicine, precision vehicle, and automotive industry on account of their electric properties recently.[1,2] The ultrahigh molecular weight polyethylene (UHMWPE) fibers are one of the high-performance materials which can be the ideal materials to fabricate conductive fibers. As the fibers have excellent intrinsic properties of very high tensile strength and module, lower density than any other organic fibers, perfect wear resistance, low friction, and excellent toughness.[3,4] Meanwhile, the comprehensive properties of the UHMWPE fibers are notably better than other high-performance materials, such as amide fibers,[5,6] carbon fibers,[7] and glass fibers.[8] However, there is few report or news about the fabrication of conductive UHMWPE fibers up to now.

There are several conventional routines to obtain conductive fibers, such as doping or coating with conductive materials,[9–11] spinning conductive polymer into yarn,[12,13] and surface metallization. Therein, surface metallization is a facile way to obtain surface-metallized fibers, containing metal vapor deposition,[6,14] and electroless plating.[15–18] Electroless plating is constantly used as one of the preferable techniques to treat fibers owing to its efficiency in metallization of plastic surfaces. It is generally required a multistep pretreatment of cleaning, surface sensitization, or activation before plating because of the infeasibility to directly deposit metals on the inactive surface. Therefore, the pretreatment is the crucial step to prepare conductive fibers. However, the surface of UHMWPE fibers is extremely chemically inert and extra smooth for its low surface energy and high crystallization, respectively.[19,20] As a result, it is tough for UHMWPE fibers to absorb any sensitizing or activating agents on their surfaces and poorly interfacial adhered with metals. Therefore, the key point to prepare conductive UHMWPE fibers is finding an easy and effective way to activate the surfaces.

Mussel-inspired surface chemistry is widely used in surface functionalization owing to mussels' well-known adhesion on any natural or artificial organic/inorganic substrates.[21–24] As one kind of the catecholamine used in the mussel-inspired chemistry, 3,4-dihydroxyphenethylamine (dopamine) is able to self-polymerize into a monolayer strongly attached on the surface of substrate with the assistance of oxygen in alkaline aqueous solution. A possible routine of the self-polymerization is showed in Supporting Information Figure S1.[25–27] The polydopamine monolayer is rich in hydroxyl (—OH) and amide groups (—NH—), which results in effectively chelation with metallic cation.[28,29] Therefore, the pH-induced oxidative self-

Additional Supporting Information may be found in the online version of this article.

polymerization ability of dopamine has led to a versatile method of functionalizing the surface. Particularly, it is suitable for the extreme inert surfaces of polyolefin polymers. It is also expected to substitute the sensitizing and activating agents for the toxic heavy metal ions in the pretreatment step of electroless plating. Liao et al.[30] prepared silvered polyimide film via electroless plating by using dopamine to activate the surface. The silvered polyimide film showed high reflectivity of 95% and good conducive property with a surface resistance of 1.5 Ω. The same preparation applied by Wang et al.[31] was used to metallize the surfaces of silica microspheres with continuous and compacted silver layers.

In this article, we take the advantage of the special property of dopamine to activate the surfaces of UHMWPE fibers. A layer of polydopamine covered on the surface is applied to a kind of efficient and safe agents for sensitizing and activating the inert surface. The method of electroless silver plating is utilized to metallize the surfaces of UHMWPE fibers. Therefore, the conductive UHMWPE fibers with high electric conductivity are fabricated via a mussel-inspired deposition.

EXPERIMENTAL

Materials

UHMWPE fibers (diameter, $\sim$ 22 μm) were fabricated by our own. Dopamine hydrochloride ($C_8H_{11}NO_2 \cdot HCl$, AR) was purchased from Sigma-Aldrich (Shanghai, China) Trading Co., Ltd and used without further purification. Tris(hydroxymethyl)aminomethane ($C_4H_{11}NO_3$, BR), hydrochloric acid (HCl, 36–38%, AR), silver nitrate ($AgNO_3$, AR), potassium sodium tartrate ($C_4H_4O_6KNa \cdot 4H_2O$, AR), and ammonia ($NH_3 \cdot H_2O$, 25%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China) and used as received. Deionized water (0.5–0.8 μS/cm) was produced by our own.

Dopamine Activation

UHMWPE fibers were cut short as 30 cm in length and fastened with paper clips to prevent the separation of the individual fibers. The fibers were ultrasonically rinsed in the acetone solution for 1 h and dried in the air. Dopamine solution (2 g/L) was prepared by dissolving the dopamine hydrochloride in the Tris-HCl buffer solution (10 mM, pH 8.5). The surface activation was performed by mixing these fibers with the dopamine solution under magnetic stirring at room temperature (28°C) for 24 h. Then, these dopamine-activated UHMWPE fibers were washed in the flowing deionized water and dried in the air.

Electroless Silver Plating

Ammoniacal silver nitrate solution was prepared by dripping ammonia solution into $AgNO_3$ solution (40 g/L) until the mixed solution turned into transparent. Besides, extra ammonia solution (10 mL/L) was added. Subsequently, potassium sodium tartrate was dissolved in deionized water to prepare the reducing solution (200 g/L). The plating bath contained the same volume of the ammoniacal silver nitrate solution and the reducing solution. Then, a length of dopamine-activated UHMWPE fibers was placed in a 100-mL breaker, and 50mL of the plating solution was added. The electroless plating was carried out at

room temperature (28°C) for 8 h. The silver-coated UHMWPE fibers were washed in flowing deionized water and dried in air.

Characterization

The weight increment of UHMWPE fibers was monitored by an analytical balance (Mettler Toledo, AL104). The resistance of straightened silver-coated UHMWPE fibers was measured by a digital multimeter (Victor, VC9807A+) using the two-point method. Scanning electron microscopy (SEM) micrographs were obtained from a Hitachi TM1000 (15 kV, Japan). Samples about 2 cm in length were stuck on the specimen stages with double-side conducting adhesive tapes and sputtered with a thin layer of aurum at a current of 15 mA for 80 s prior to SEM analysis. X-ray diffraction (XRD) spectra were recorded from a D8 Advanced (Bruker AXS) using Cu Kα radiation for a 2θ range from 5 to 90° at a resolution of 0.02°. Samples were prepared by tidily sticking on the silica wafer with double-side adhesive tapes prior to XRD analysis. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos AXIS UTLTRADLD multifunctional X-ray Photoelectron Spectrometer (Shimadzu Japan) with a monochromatized Al Kα source (1486.6 eV) under ultrahigh vacuum (10–8 torr) at a reduced power of 120 W and a voltage of 14 kV. Samples about 1 cm in length were directly stuck on the specimen stage with adhesive tapes. The spectra were acquired at a takeoff angle of 90° between the sample surface and the photoemission direction. All binding energies were calibrated by C1s hydrocarbon peak at 284.6 eV.

RESULTS AND DISCUSSION

Appearance and Surface Topography Micrographs of UHMWPE Fibers

The conductive UHMWPE fibers are prepared via electroless silver plating by utilizing dopamine as an activating agent. The UHMWPE fibers are coated with a dark brown layer by comparing with the original fibers [Supporting Information Figure S2(a, b)] after activating in the dopamine buffer solution. In the plating bath, $[Ag(NH_3)_2]^+$ ions absorbed by the polydopamine monolayer are reduced to metallic silver particles by reducing agents. Then silver particles are deposited on the surface of fibers which show a silvery luster [Supporting Information Figure S2(c)].

The surface topography micrographs obtained from SEM are shown in Figure 1. The surface of original fibers is smooth and bright, whereas the surface of dopamine-activated fibers is definitely rough [Figure 1(a, b)]. As shown in Figure 1(b), there are some heterogeneous particles attached on the surface of polydopamine layer. These heterogeneous particles are the clumped polydopamine particles adhering on the surface because of inefficient stirring.[21,25] The silver layer is coated on the surface of dopamine-activated fibers after electroless plating [Figure 1(c)]. There are a mass of silver particles deposited on the surface which form a continuous and stable metallic silver layer. The weight increment between the dopamine-activated fibers and the silver-coated fibers is 95.5% which proves that a large quantity of silver particles have deposited on the surfaces. Figure 1(d) shows the micrograph of silver-coated fiber without dopamine-activated process as a comparison. There is hardly any
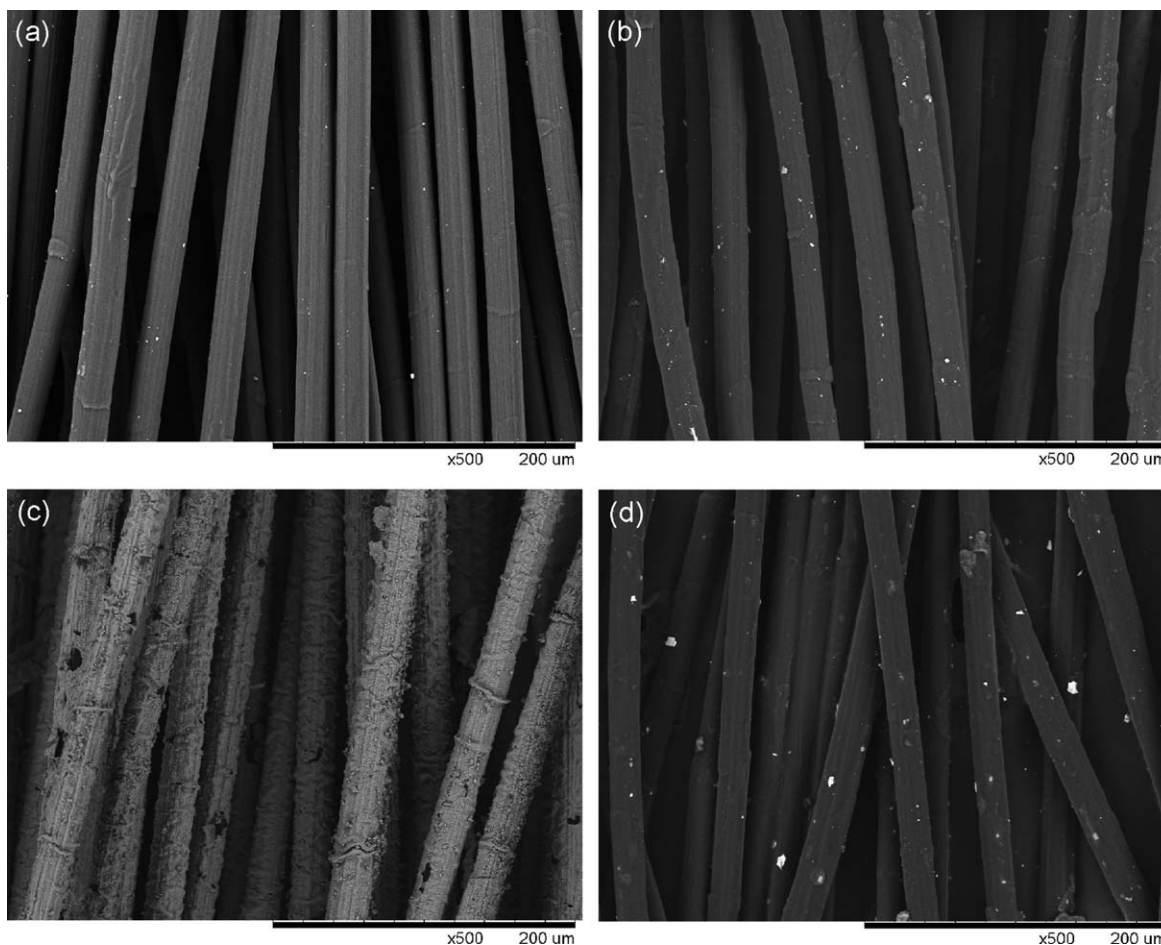
Figure 1. SEM micrographs of (a) original fibers, (b) dopamine-activated fibers, (c) silver-coated fibers, and (d) silver-coated fibers without dopamine activation.

silver particle deposited on the surface owing to the inert surface of original fibers. Thus, it indicates that the dopamine layer with abundant catechol and amino groups contributes to the significant improvement of silver deposition on the inert surface of UHMWPE fibers.

Surface Chemical Composition and Structural Characterization of UHMWPE Fibers

XPS spectra are used to detect the surface chemical states of elements as shown in Figure 2. The survey-scan spectrum of the original fibers contains Si2p (102 eV), C1s (284.6 eV), and O1s (532 eV) peaks [Figure 2(a)]. The C1s core-level spectrum of the original fiber is curve-fitted with three components, C—C/C—H, C—O, and C=O species at binding energy (BE) of 284.6, 286.1, and 287.6 eV, respectively. The unexpected appearance of Si2p and O1s peak is possibly attributed to a small quantity of UHMWPE resin catalyst and alkylphenol antioxidant.[32] The N1s peak in the survey-scan spectrum of dopamine-activated fibers and the C—N species (285.5 eV) in the C1s core-level spectrum [Figure 2(b)] prove that the polydopamine layer has adhered on the surface.

XPS spectra are also used to confirm the chemical state of the silver layer deposited on the surface. Figure 2(c) shows the sur-vey-scan spectrum and the Ag3d core-level spectrum of silver-coated fiber. The powerful signals of silver at the BEs of 370 eV (Ag3d), 571 eV (Ag3p3/2), and 602 eV (Ag3p1/2) demonstrate the existence of silver layer on the surface. There are four peaks at the BEs of 368.2, 371.0, 374.2, and 377.0 eV deduced from the Ag3d core-level spectrum. However, the metallic silver species conventionally has two peaks at BEs of 368.2 and 374.2 eV corresponding to Ag3d5/2 and Ag3d3/2, which can confirm the silver in metallic state. As well known, the peak shifts caused by the charging effect will be conspicuous in the XPS measurements of nonconductive or semi-conductive samples.[33,34] These two additional peaks may be the peak shifts of Ag3d5/2 and Ag3d3/2 owing to the nonconductive part of Ag separately deposited on the extremely nonconductive surface of UHMWPE fibers.

XRD spectra are utilized to detect the crystal structures of silver deposited on the surface as shown in Figure 3. There are several intrinsic characteristic peaks of UHMWPE fibers at the 2θ values of 19.7, 21.9, 24.3, 30.4, 36.6, 41.1, and 44.3° [Figure 3(a)] corresponding to (0 1 0), (1 1 0), (2 0 0), (2 1 0), (0 2 0), (3 1 0), and (2 2 0) planes of polyethylene, respectively (JCPDS card No. 053-1859). The XRD spectrum of dopamine-activated fibers in Figure 3(b) shows no significant difference by comparing
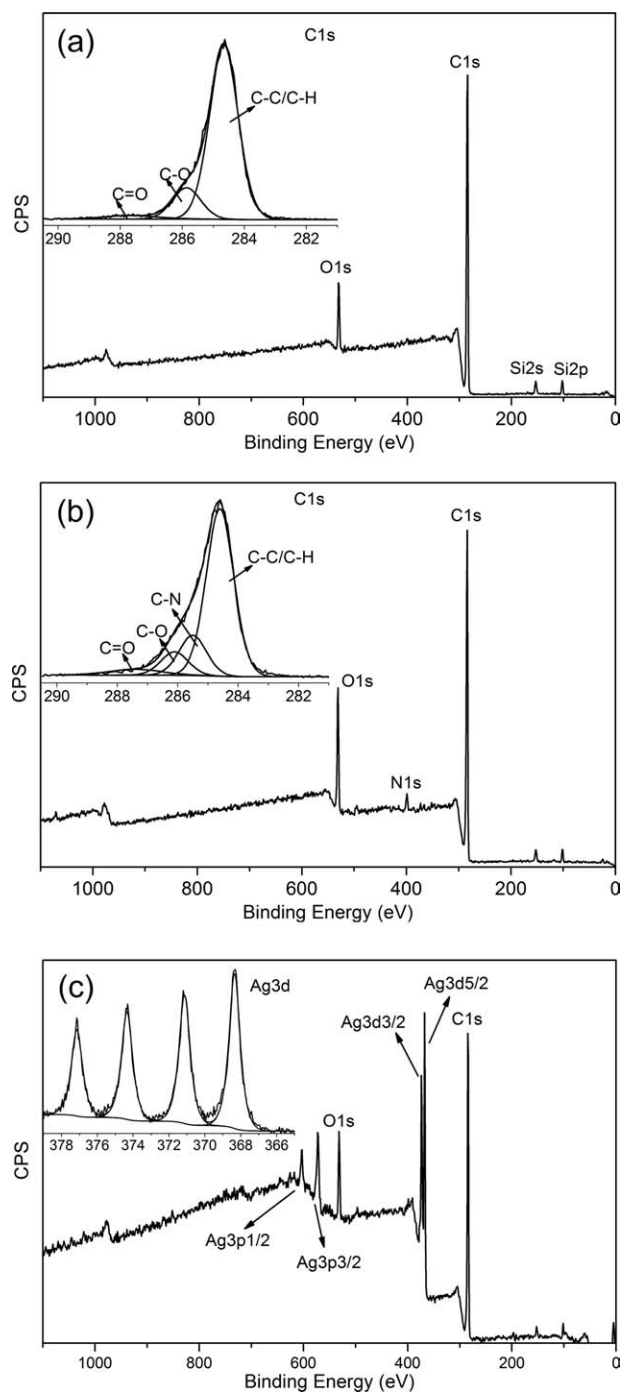
Figure 2. XPS survey spectra of (a) original fibers, (b) dopamine-activated fibers, and (c) silver-coated fibers.

Figure 3. XRD spectra of (a) original fibers, (b) dopamine-activated fibers, and (c) silver-coated fibers.

which demonstrates that the silver particles coated on the surface of UHMWPE fibers are pure with high crystallinity.

Electrical Conductivity of Silver-Coated UHMWPE Fibers
The silver-coated fibers show dramatically electrical conductivity, acting like electrical wires shown in Figure 4. A bundle of silver-coated UHWMPE fibers is installed in series instead of electrical wire. The detailed circuit diagram is shown in the top right corner of Figure 4. The flash lamp gives out bright light as the DC power supply is turned on when the voltage is adjusted to 8.5 V. The resistance of the silver-coated fibers is 0.15 Ω/cm per bundle measured by the two-point method which is lower than the resistance of conductive fibers fabricated by other methods. Furthermore, the substrate of UHMWPE fibers used in this study endows the conductive fibers with high mechanical performance.

The reaction condition of silver electroless plating can influence the weight increment and the resistance of silver-coated fibers.

Figure 4. Conductive UHMWPE fibers (F) install in a simple series circuit with a flash lamp (L), a resistance (R, 100 Ω), and a DC power supply (DC, 8.5 V). As turning on the DC power supply, the flash lamp give out bright light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with the original fibers, illustrating that the polydopamine layer on the surface does not affect the original crystallization structures. The XRD spectrum of silver-coated fiber in Figure 3(c) shows some distinct characteristic peaks at the 2θ values of 38.4, 44.6, 64.7, 77.6, and 81.8° corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of silver, respectively (JCPDS card No. 087-0597), in addition to the XRD peaks of UHMWPE fibers. Furthermore, no peak of impurities is found
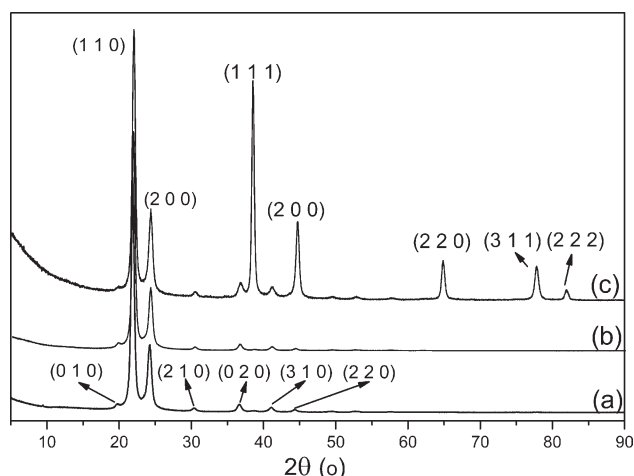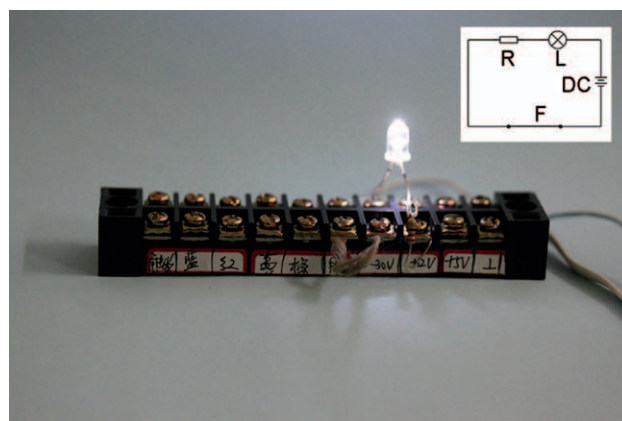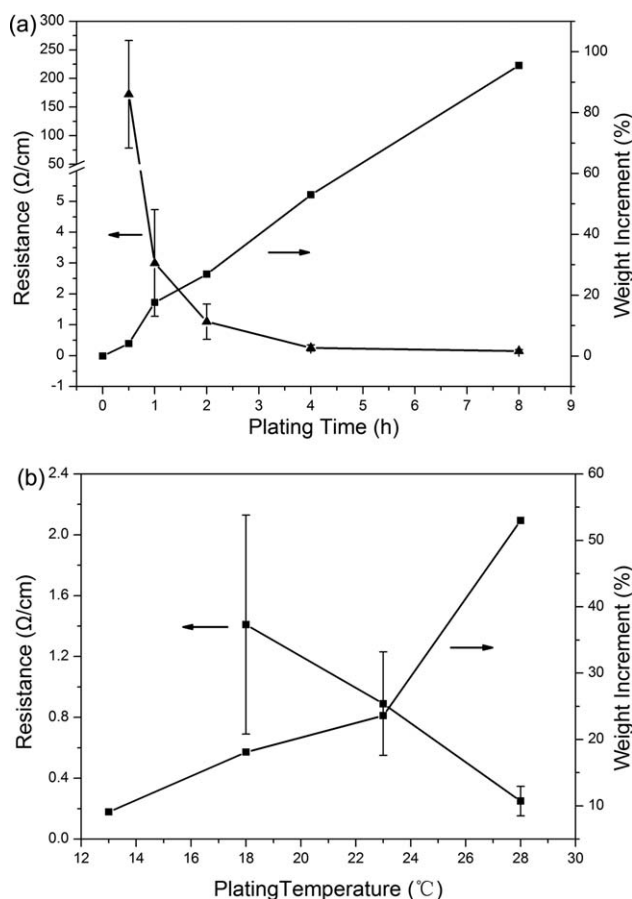
Figure 5. The weight increment and the resistance of silver-coated fibers are varied with (a) plating time and (b) plating temperature.

As known, the plating time controls the quantity of metal particles deposited on the surface, whereas the plating temperature primarily controls the reaction rate of redox and the deposition rate of metal. Figure 5(a, b) shows that the weight increment and the resistance of silver-coated fibers are varied with plating time (a) and plating temperature (b). Figure 5(a) shows that the weight increment appeared to a clear positive correlation with the plating time. However, the resistance decreases sharply at first and then decreases tenderly to a constant value (about 0.1 Ω/cm per bundle), appearing to be a reciprocal resistance and plating time relationship. The variation of the weight increment and the resistance is caused by the variation of the surface silver layer condition which is shown in Supporting Information Figure S3. As the plating time increased, the silver layer on the surface is becoming more stable and thicker which results in fewer layer pieces are peeled off. The low resistance of silver-coated fibers plated for more than 4 h is attributed to the stable and continuous silver layer on the surface [Supporting Information Figure S3(c, d)]. Although the silver layer is stable when the fibers are plated for 0.5 h, the resistance is still very high which is about 172.5 Ω/cm per bundle. It can be explained that there are not enough quantity of silver particles to form a continuous silver layer which is shown in Supporting Information Figure S3(a). A similar variation trend with a nearly linear weight increment and plating temperature relationship is shown

in Figure 5(b). Similarly, the resistance decreases clearly along with the increase of the plating temperature because of the variation of the silver layer condition as shown in Supporting Information Figure S4. The resistance of most parts of silver-coated fibers plated at 13°C is beyond the scope of the analytical balance because of discontinuous silver layer [Supporting Information Figure S4(a)]. In summary, the stable and continuous silver layer on the surface attributes to the excellent conductivity of silver-coated fibers.

CONCLUSIONS

The silver-coated UHMWPE fibers with excellent conductive property are fabricated by the method of electroless silver plating with the assistance of dopamine. The dopamine solution is utilized to effectively activate the inert surface of UHMWPE fibers. The resistance of the silver-coated fibers can be as low as 0.15 Ω/cm per bundle, which might lead to a promising application in the field of conductive polymer fabrics. Furthermore, these conductive fibers are propitious to apply in harsh environment condition attributed to the excellent mechanical and chemical properties of UHMWPE fibers.

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