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Silver-decorated and palladium-coated copper-electroplated fibers derived from electrospun polymer nanofibers

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HIGHLIGHTS

- Silver and palladium fibers were fabricated by the combination method.
- Fiber morphologies and elemental compositions were analyzed by SEM, EDX, and XPS.
- The high electrical performance of the fibers was exhibited with transparency.

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ABSTRACT

Here we introduce novel methods of forming silver (Ag) and palladium (Pd) fibers. The Ag and Pd fibers are fabricated by the combination of electrospinning, electroplating, and ion-exchange techniques. Their properties are characterized by scanning electron microscope with energy dispersive X-ray spectroscopy, sheet resistance meter, UV–Vis spectrophotometer, and X-ray photoelectron spectroscope. These non-woven metal fibers are free-standing and film-shaped with high electrical conductivity, as well as flexibility. Such properties are attractive for future applications of these materials in various electrochemical processes.

1. Introduction

Various studies related to nano- and micro-fiber technologies have considerably contributed to technological advances at numerous fields of engineering [1] including batteries [2–6], solar cells [7,8], cooling high-power electronics [9–23], purification membranes [24], filters [25], drug delivery materials [26–31], self-healing composites [32–43], and so on. The growth of these fiber-related technologies is accordingly expected to increase continuously in the future. Among several fiber fabrication techniques [44–47], electrospun nanofibers have been most widely used for such high-tech engineering industries. Electrospinning is considered as one of the most effective methods of forming uniform nanofibers, which allows one to easily modify fiber diameters [48], to achieve a large surface area [49] and form fabrics of macroscopic sizes [50].

One of the most widely regarded advantages of using electrospun nanofibers is that it is possible to combine in them two or more materials, and/or combine electrospinning with the other fabrication processes. This enables formation of novel functionalized or uniquely structured nanofibers. For example, ceramic silica nanofibers were developed by mixing a polymer with other chemical materials [51], or silica-decorated carbon nanofibers were formed by using both electrospinning and dip coating [52]. More recently, high-performance transparent conducting electrodes (TCEs) were formed by using electrospinning and electroplating methods [53].

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Copper (Cu) and silver (Ag) belong to the group of the most extensively studied metals for electrochemical applications due to their superior electrical conductivity, non-toxicity, and easy availability [54,55]. In particular, they have revealed enhanced performances when fabricated with nano- or micro-sized dimensions such as in Cu- and Ag-nanowires. Palladium (Pd) has been also broadly used as a catalyst in various fields [56,57]. However, the use of these metals in nano-scale objects has been continuously challenged because of complex fabrication processes and scalability problems.

Here, we introduce a novel method of fabrication of Ag-decorated and Pd-coated fibers by combining electrospinning, electroplating, and ion-exchange methods. The Ag-decorated fibers are core-shell structured with Cu, and thus possess not only highly textured surfaces but also superior electrical conductivities. The intact Pd-covered nanofibers are introduced for the first time. These fibers are attractive as a novel catalytic chemical material.

2. Experimental methods

2.1. Materials

Polyacrylonitrile (PAN, M_w = 150 kDa) and *N,N*-dimethylformamide (DMF, 99.8%) for a solute and a solvent, respectively, were purchased from Sigma-Aldrich. The 8 wt% PAN solution was prepared by dissolving PAN powder in DMF and magnetically stirred until becoming homogeneous. Sulfuric acid (H_2SO_4, >97.5%), hydrochloric acid (HCl, >35%), copper (II) sulfate ($CuSO_4$, >99.99%), and formaldehyde (>35%) were also purchased from Sigma-Aldrich and mixed at the fixed ratio for the electroplating solution (Table 1). Silver nitrate ($AgNO_3$, >99.0%) was also purchased from Sigma-Aldrich, and 0.01, 0.03, and 0.06 wt% of $AgNO_3$ powder were dissolved in DI water and magnetically stirred until becoming homogenous to prepare the ion-exchanging solution. Palladium (II) nitrate ($Pd(NO_3)_2$) hydrate was also obtained from Sigma-Aldrich, and 1 wt% $Pd(NO_3)_2$ hydrate powder was dissolved in DI water and stirred similarly to the $AgNO_3$ solution.

2.2. Copper-electroplating of electrospun polyacrylonitrile nanofibers

Silver (Ag) and palladium (Pd) were deposited by ion-exchange onto copper (Cu)-electroplated fibers. The Cu-electroplated fibers were fabricated using a recently introduced method where metals were electroplated onto electrospun polymer nanofibers [10,53]. It should be emphasized that Cu-electroplated fibers could acquire different chemical compositions (either being pure Cu or Cu_xO) with the drying atmosphere being either an inert gas or air, respectively. Fig. 1 illustrates how the fiber morphology and structure change according to the fabrication process used. First, PAN nanofibers were electrospun onto a Cu-frame under the fixed conditions listed in Table 2 and depicted in Fig. 1a. Then, platinum (Pt) was sputtered with a thickness of a few nm (not shown here) to impart a minimum conductivity for the following electroplating process. Next, the Cu-frame with the deposited nanofibers (cathode) was electroplated using a thin Cu-film (anode) at the fixed conditions (Table 3) and then dried in an inert gas atmosphere. Drying in the inert gas prevented oxidation of the Cu-electroplated fibers, thus, pure Cu-fibers were obtained as illustrated in Fig. 1b.

2.3. Silver ion-exchange on copper-electroplated fibers

Prior to the ion-exchange process, the free-standing Cu-electroplated fibers (which were suspended on the Cu-frame, cf. Section 2.2) were transferred onto supporting glass slides, which prevented the Cu-electroplated fibers from being floated in the

Table 1
Electroplating solution. Each 'weight ratio' value is based on the hydrochloric acid weight as 1.

Material	Weight ratio
Sulfuric acid	10
Hydrochloric acid	1
Copper sulfate	32
Formaldehyde	20
DI water	200

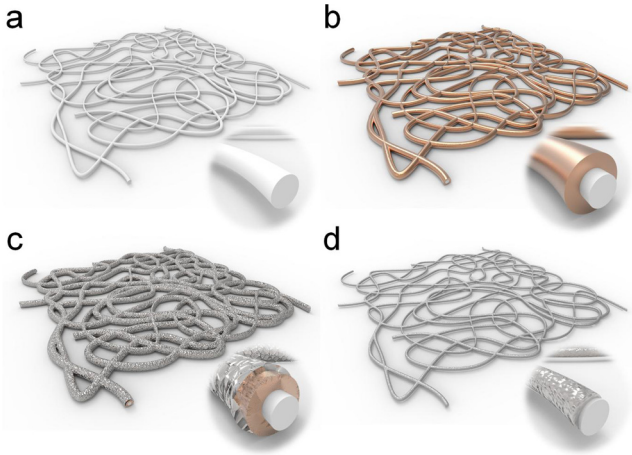

Fig. 1. Schematic of: (a) the electrospun PAN nanofibers, (b) the Cu-electroplated fibers, (c) the Ag-decorated fibers formed by ion-exchange, and (d) the Pd-coated fibers formed by ion-exchange.

Table 2
Experimental conditions for electrospinning PAN nanofibers.

Parameter	Value
Flow rate (μL/h)	200
Applied voltage (V)	8
Needle size	18-gauge
Needle-to-substrate distance (cm)	15
Electrospinning time (s)	90

Table 3
Experimental conditions for electroplating the PAN nanofibers.

Parameter	Value
Applied voltage (V)	3
Electrode size (cm^2)	3.5 × 2.5
Cathode-to-anode distance (cm)	2
Electroplating time (s)	7

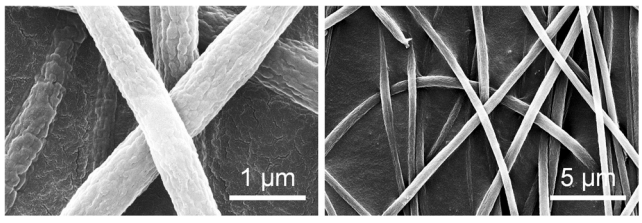

Fig. 2. SEM images of the electrospun PAN nanofibers.