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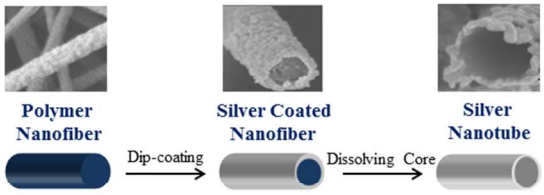

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COMMUNICATION

A Simple Method for Fabricating Silver Nanotubes

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We report an easy and simple approach for making silver nanotubes (NTs) using electrospinning. Silver nanoparticles were first deposited on electrospun polymer nanofibers template by dip-coating in aqueous medium. Subsequently, selective dissolution of the polymer core led to the formation of silver NTs. Average diameter of the NTs was 250 nm and wall thickness was about 50 nm. This method allows synthesis of large quantity of silver NTs with high yield. Wall thickness and porosity of the NTs could be readily tuned by varying the dipping time and concentration of the metal precursor. The approach developed is very general and could be used for fabricating NTs of a variety of noble metals, bi-metals and metal oxides.

Introduction

Metal nanostructures have attracted considerable research interest because of their unique optical and electronic properties. Large number of applications of such nanostructures in sensors, supercapacitors, nanoscale electronic circuits, plasmonic devices and photovoltaics have been reported.[1-6] It is well known that the optical and electronic properties of metal nanomaterials or nanostructures are dependent on their shape, size and organization.[7,8] One-dimensional (rods, tubes, wires) and two-dimensional (lines, arrays, dots) nanostructures offer a myriad of opportunities and are expected to play an important role in nanostructured devices.[9-14] Hence, developing an easy and cost-effective approach for creating nanometer scale structures is important for various technological applications. Though numerous techniques have been developed for fabricating metal dots, arrays and wires, preparing metal nanotubes (NTs) easily and inexpensively is still a challenge.

Since the discovery of carbon NTs, various types of NTs have been synthesized using inorganic and organic materials.[15,16] In past two decades, new methods have also been developed for synthesis of metal and metal oxide NTs.[17-21] most commonly used method for the synthesis of NTs employs template of nanoporous membranes. Recently, Lahav et al. have demonstrated synthesis of gold NTs using silane treated nanoporous alumina template membrane coated with gold nanoparticles.[20] Xia et al. have used the seed growth method to synthesize silver nanorods and NTs.[18] Qu et al. have also used porous alumina membrane as a template to create silver NTs. An aqueous KOH solution (1.0 M) was used to remove the template.[22] However, reported methods of synthesizing metal NTs require either multiple steps or high temperature treatment and are not cost-effective. Therefore, there is need to develop a facile and inexpensive approach for the synthesis of metal NTs for various practical applications. Recently, electrospinning has proven to be a simple and low-cost approach for making nanofibers of organic and inorganic materials.[23] In this letter, we report a widely applicable, simple and inexpensive technique for fabricating silver coated polymer nanofibers and silver NTs using electrospun polymer templates.

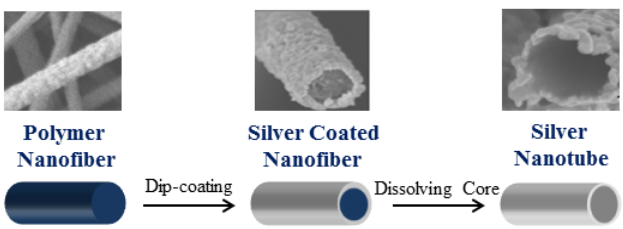

Figure 1. Schematic of the steps involved in the fabrication of silver NTs: Fabricating polymer nanofibers by electrospinning, dip coating silver nanoparticles on the nanofibers and forming silver NTs by washing away the polymeric fiber core.

Results and Discussion

Figure 1 depicts the steps involved in the fabrication of silver NTs. The polymer nanofibers used as the template for silver coating were electrospun on an indium tin oxide (ITO) coated glass substrate. Deposition of silver nanoparticles on the polymer nanofiber core was carried out by dip-coating. Silver is not soluble in most common organic solvents, therefore, selective removal of the polymer core leads to the formation of silver NTs. Poly(acrylonitrile) (9% by weight, Molecular Wt. 150,000) solution first prepared in dimethyl formamide (DMF) wasused to electrospin the nanofibers.[23,24] The polymer solution was filled in a glass pipette with a conducting electrode inserted to impart charge at high voltages. Polymer nanofibers were collected on the grounded ITO substrate at a distance of 15 cm from the pipette under an applied voltage of 15 kV. Deposition of silver was achieved by dipping the nanofibers in an appropriate mixture of silver nitrate, ammonium hydroxide and sodium hydroxide. Dextrose and disodium salt of ethylenediamine tetra-acetic acid were used as reducing and chelating agents for the silver ions and reduced silver.[7,25] This process facilitates deposition of silver nanoparticles on the surfaces

of the electrospun polymeric nanofibers. For the fabrication of silver NTs, continuous coating of silver nanoparticles is essential. However, simply increasing the coating time does not produce continuous silver coating. To achieve continuous silver coating, a wetting solution (mixture of tin and palladium chloride) was employed to wet the surfaces of the polymer nanofibers. Applying wetting solution significantly improved the adhesion of silver nanoparticles on the fiber surfaces and was critical for smooth silver coating. It takes few minutes to deposit a layer of silver nanoparticles (about 50-60 nm thick). Formation of free standing silver NTs was achieved by subsequently dissolving the polymer cores with DMF under sonication. The aggregates of silver nanoparticles and the wall thickness of the NTs can be readily tuned by varying either the deposition time or the concentration in the silver precursor.

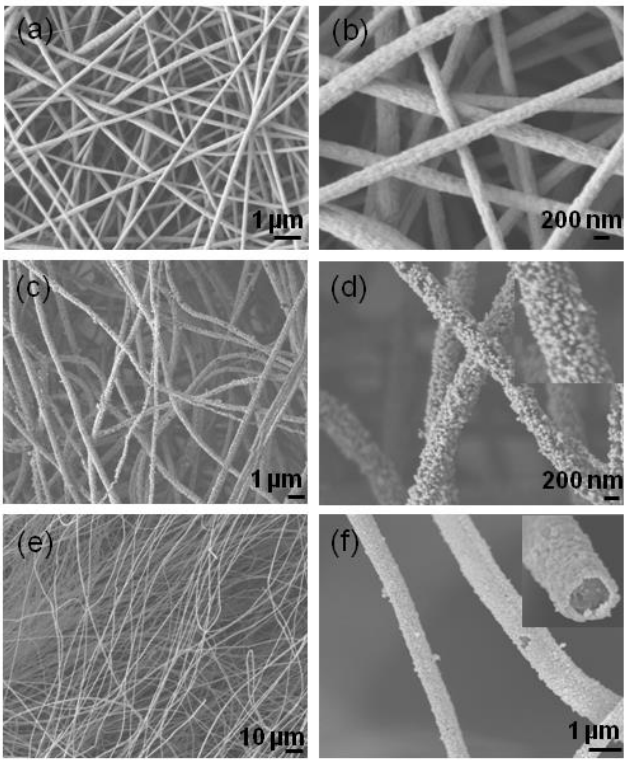

Figure 2. SEM images (a) and (b) of the electrospun polymer nanofibers, (c) and (d) of the polymer nanofibers coated with silver nanoparticles and (e) and (f) uniform silver nanoparticle coating using wetting solution.

Morphologies of the electrospun polymer nanofibers and the silver coated nanofibers were examined by scanning electron microscopy (SEM). Figure 2 shows SEM images of the polymer nanofibers with and without the silver coating. Average diameter of the electrospun polymer nanofibers is about 250 nm as shown in Figure 2 (a) and (b). Nanofibers decorated with silver nanoparticles are depicted in Figure 2 (c) and (d). Inset image in Figure 2 (d) shows the SEM view of a single nanofiber coated with silver at high magnification. SEM images clearly indicate that the silver coating is porous and not densely packed, and the nanoparticle aggregates are separated by tens of nanometers. Dipping the nanofibers in wetting solution prior to silver coating enhanced the continuity dramatically due to increased adhesion of the silver nanoparticles on the surfaces of the polymer nanofibers. Figure 2 (e) and (f) exhibit uniform silver coating on the polymer nanofiber surfaces. The silver coating is dense and smooth. The cross sectional view of a silver coated polymer fiber, as shown in the inset of Figure 2 (f), clearly shows that the silver nanoparticle coating is continuous. Application of wetting solution has led to the continuous and smoother coating of the silver nanoparticles on the surfaces of the polymer nanofibers.

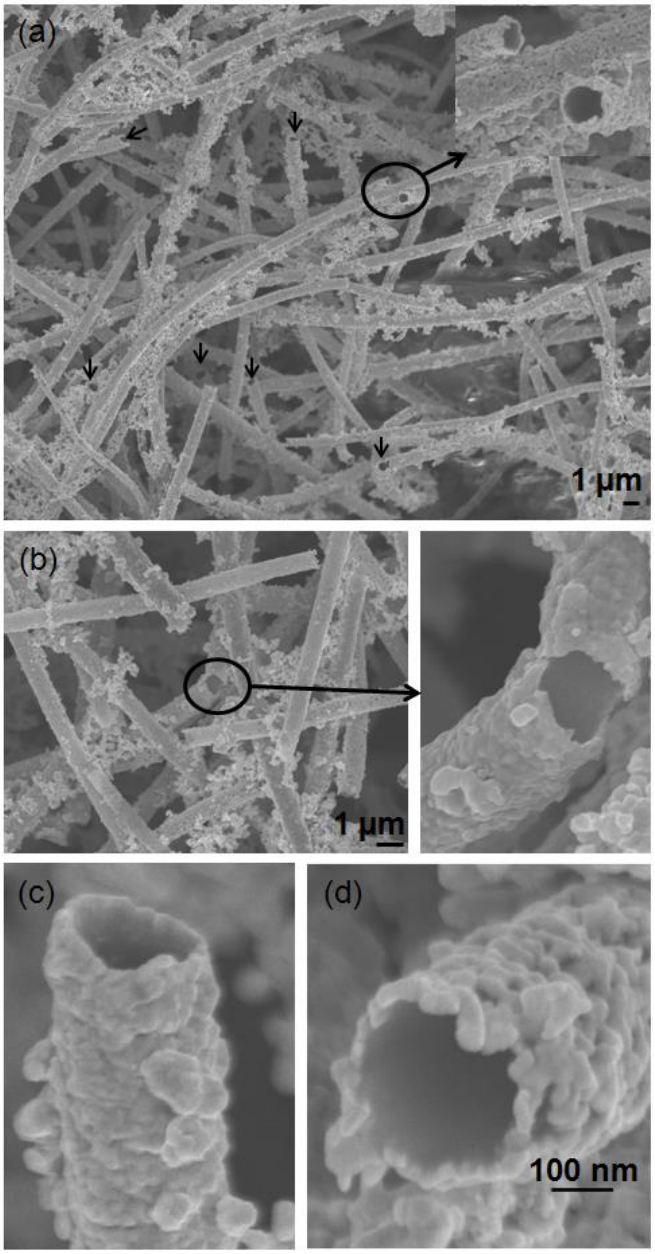

Figure 3. SEM images (a) of synthesized silver NTs, (b) of a broken NT at two different magnifications and (c) and (d) views of two silver NTs at high magnification.

Free standing silver NTs were obtained after selective removal of the polymer nanofiber core by dissolving in DMF for 10 min. Figure 3 shows SEM images of the fabricated silver NTs. These SEM images confirm the formation of free standing silver NTs and removal of the polymer nanofiber core. Figure 3 (a) exhibits the SEM image of silver NTs as pointed by arrows and the open-ends of two tubes as marked in a circle. High magnification image of the silver NTs in the circled area is shown in the inset of Figure 3 (a). Figure 3 (b) shows the SEM image of a silver NT cracked in the

middle. The cracked region (circled) is shown in the inset of Figure 3 (b) at high magnification. This indicates that the polymer fiber core was washed away after sonication in DMF. Figure 3 (c) and (d) show the SEM images of two single silver NTs at high magnification. Typical wall thickness of the hollow tubes is about 50 – 80 nm and the tube diameter varies from 200 nm to 400 nm. These tubes are composed of silver nanoparticles fused together. Inner walls of the tubes are smoother than the outer walls, which can be attributed to the smooth surfaces of the polymer nanofibers.

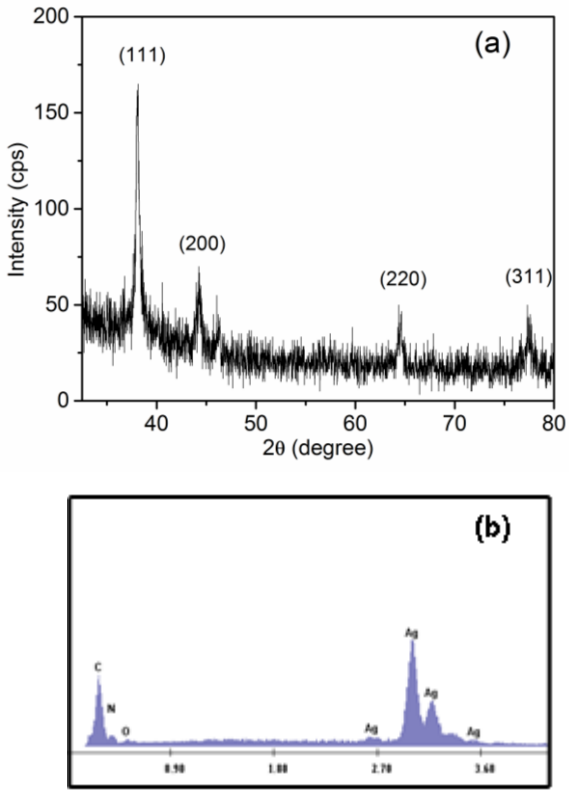

Figure 4. (a) XRD pattern and (b) EDS of the silver NTs.

Structural analysis of the synthesized silver NTs was performed by X-ray diffractometry (XRD). Figure 4 (a) shows the typical powder XRD pattern of the synthesized silver NTs. Four XRD peaks at 38.0°, 44.2°, 64.6° and 77.3° correspond to the reflections from (111), (200), (220) and (311) crystalline planes of the face-centered cubic structure of metallic silver, indicating that the silver nanoparticles are highly crystalline[26]. Energy dispersive spectrometry (EDS) was also carried out on the NTs. The presence of silver is clearly observed in the EDS spectrum as shown in Figure 4 (b). We also want to note that silver can get oxidized at ambient conditions[27]. X-ray photoelectron spectroscopy can be used as a tool to investigate the oxidation state of silver nanoparticles[12].

Conclusions

In summary, a simple method has been demonstrated for fabricating silver NTs employing electrospun polymer nanofibers and dip-coating method. Silver coating has been realized under ambient conditions by solution coating process which is amenable for highly scalable production. The precursor solution consists of a silver source and a reducing agent. Removing the polymer fiber core with a solvent has resulted in the formation of the silver NTs. This simple and versatile method could be easily adapted for synthesis of NTs of other noble metals, bimetals or metal oxides. The ease of electrospinning and the availability of wide variety of polymers for electrospinning could open up great opportunity to fabricate metal and metal oxide NTs for diverse potential applications.

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