

DOI: 10.1002/adma.200600098

Conductive Gold Films Assembled on Electrospun Poly(methyl methacrylate) Fibrous Mats**

By Gaoyi Han,* Bin Guo, Liwei Zhang, and Binsheng Yang

The preparation and design of confinement structures on a sub-micrometer scale have attracted great attention because of the potential for new materials properties and applications in a broad range of areas. Many materials with sub-micrometer dimensions have been fabricated, including inorganic and organic materials.^[1]

Self-assembly of colloidal metal particles has generated great interest as a powerful fabrication method of macroscopic surfaces with well-defined and controllable nanostructures.^[2] Gold is of great interest because of its chemical and electrical properties. Electrical conductivities of assembled materials that are close to that of bulk gold have been achieved by self-assembly of colloidal gold particles using linker molecules between the particles^[3] or by increasing the gold coverage by a reduction process.^[4] The applications of assembled gold films include as surface plasmon resonance (SPR) substrates, substrates for surface-enhanced Raman spectroscopy (SERS), catalytic surfaces, electrodes, and production of patterns in microscale and nanoscale structures.^[5–8] However, most of the prior work has centered around fabrication of films on substrates such as glass or other oxide surfaces, silicon, and polymers.^[9–12]

Electrospinning is a simple and convenient method of generating polymer fibers, inorganic fibers, and hybrid fibers with diameters ranging from tens of nanometers to several micrometers.^[13] The spinning process uses a high static voltage to create a strong electric field and to impart some charge to a viscous polymer solution. Once the field strength has surpassed a threshold to overcome the surface tension of the polymer, fine jets of the polymer solution are ejected from the capillary tip and undergo a whipping process, which leads to the formation of ultrathin fibers as the solvent evaporates. The fibers deposit onto a grounded conductor as a nonwoven mat and can act as a template or substrate for organic and in-

organic materials. For example, poly(*p*-xylylene) and aluminum sub-micrometer tubes have been fabricated using chemical vapor deposition (CVD) to coat electrospun fibers.^[14] Titanium dioxide tubes have been prepared from polymer fibers coated with titanium dioxide by the sol-gel technique,^[15] and continuous thin coatings of titanium dioxide or tin dioxide on electrospun polymer fibers have also been prepared by solution deposition.^[16]

In this communication, we report on using electrospun fibrous mats as substrates for a solution deposition of continuous thin gold coatings on fibers. The procedure used for coating gold consists of three steps. First, poly(methyl methacrylate) (PMMA) fibers containing a gold salt are produced by electrospinning; second, the gold salt is reduced by a dilute solution of NaBH₄ and then washed with water and dilute HCl solution thoroughly; finally, gold is plated on the surface of the fibers by using gold particles embedded on the fiber surface to catalyze reduction of Au³⁺ by hydroxylamine so that the size of the gold particles increases until a continuous coating is formed.

Figure 1A shows two scanning electron microscopy (SEM) images of hybrid PMMA/gold-salt fibers electrospun from a chloroform solution of PMMA and a gold salt. It can be seen that the fibers exhibit random orientation because of the bending instability associated with the spinning jet. The surfaces of the fibers are smooth and the average diameter of the fibers is about 500 nm, suggesting that the gold salt is dispersed in the PMMA fibers uniformly. After the gold salt embedded in fibers is reduced with NaBH₄, the yellow fibrous mat becomes brownish. Its SEM image is shown in Figure 1B. In contrast to a gold colloid assembly on a silane-coated polymer surface^[9] where the spherical gold particles are clearly visible, but in accordance with previous research by Kim et al.^[17] on electrospun poly(ethylene oxide) (PEO)/gold-nanoparticle hybrid fibers, we presume that the gold nanoparticles may be dispersed both on the fibers' surfaces and interiors. A transmission electron microscopy (TEM) image (Fig. 1C) shows that the gold nanoparticles are roughly spherical in shape and separated from each other, each having a diameter of approximately 5–10 nm, although some particles aggregate into clusters. Because the compact polymer network can prevent the gold particles from growing further after nucleation, gold nanoparticles have a small size and roughly uniform dispersion in ultrafine PMMA fibers. Figure 1D shows the UV-vis spectra of the gold salt (spectrum A) and gold nanoparticles (spectrum B) that came from the hybrid fibers dissolved in chloroform. The gold salt has an absorption

[*] Dr. G. Y. Han, B. Guo, Prof. L. W. Zhang, Prof. B. S. Yang
Chemical Biology and Molecular Engineering Laboratory of
the Ministry of Education
Institute of Molecular Science, Shanxi University
Taiyuan 030006 (P.R. China)
E-mail: han_gaoyis@sxu.edu.cn

[**] This work was supported by the National Natural Science Foundation of China (grant no. 20371031), the Natural Science Foundation of Shanxi Province (grant no. 20041102), and the School Foundation of Shanxi University. The authors thank Prof. Xu Bingshe of the Taiyuan University of Technology for performing the SEM measurements. Supporting Information is available online from Wiley InterScience or from the author.

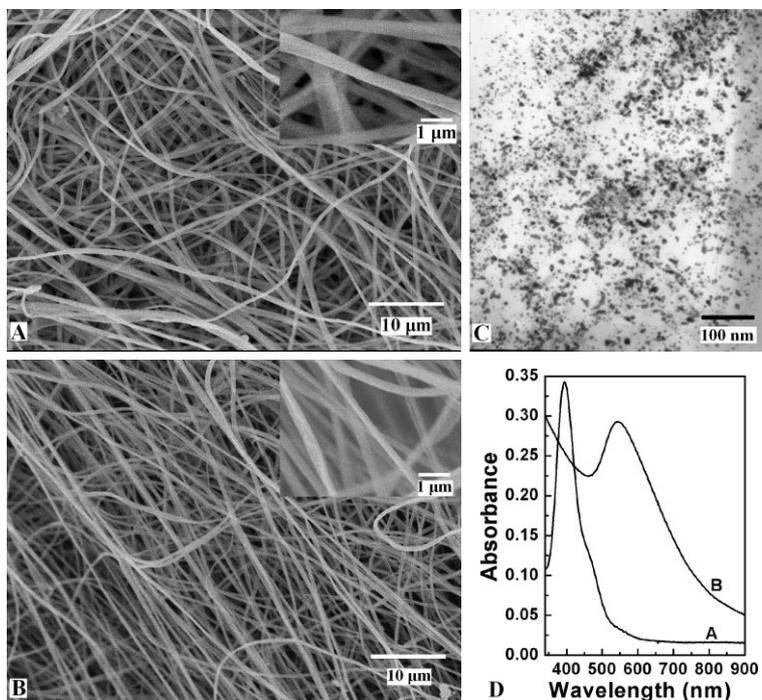


Figure 1. Field-emission SEM (FESEM) images of A) an as-electrospun PMMA/gold-salt hybrid fibrous mat and B) a PMMA/gold-nanoparticle hybrid fibrous mat prepared by reduction of gold salt by NaBH₄. C) Transmission electron microscopy (TEM) image of the gold nanoparticles embedded in the PMMA fibers. D) The UV-vis spectra of the gold salt (spectrum A) and gold nanoparticles (spectrum B) dispersed in PMMA fibers.

peak at about 394 nm, and after it is reduced, the absorption peak moves to 544 nm. According to the literature, the optical spectrum of spherical gold particles with an average size of 3.4 nm or more is generally dominated by the plasmon band centered at around 520 nm, caused by the excitation of surface plasmons.^[10] When gold nanoparticles aggregate, their SPR shifts to longer wavelengths. The absorption peak at 544 nm indicates that there is slight aggregation of gold nanoparticles in the PMMA fibers. This result is consistent with that of TEM.

When the fiber mat is immersed in a solution of HAuCl₄·2H₂O and NH₂OH·HCl for gold plating, we find that

fibers on the inside of the mat cannot be effectively gold plated, while the surfaces of the mats show a gold color. This is because the reduction of Au³⁺ by hydroxylamine is so fast when catalyzed on the surfaces of gold particles^[12] that the reagent cannot diffuse into the mat, and the reduction reaction occurs only on the surfaces of the fibers on the exteriors of the mats. When we filter the plating solution through the mats quickly, we find that the reduction reaction occurs effectively on the surfaces of the fibers both on the inside and outside. Figure 2A shows the SEM image of a mat plated with 200 mL plating solution. It can be seen from this SEM image together with the TEM image that the gold particles have grown from 5–10 nm to about 20–50 nm, and they have begun to form a continuous film on the surface of the fibers although the fibers are not completely covered. When the fibrous mat is treated with 400 mL plating solution, a larger fraction of the surfaces of the fibers are coated with gold particles because the gold particles have grown more (ca. 100 nm). However, the SEM and TEM images show that there are some defects in this sample. The spherical shape of the particles is no longer retained, and the growth leads to irregularly shaped particles. When 600 mL plating solution is used to plate the mat, a densely packed continuous film with few defects is formed by the even larger immobilized gold particles (>100 nm), although some fibers have cracks along their axes.

though some fibers have cracks along their axes.

The conductivity of the gold-coated mats has been measured using the four-point probe method and found to be 2.0×10^3 , 5.2×10^3 , and 9.3×10^3 S cm⁻¹ for samples gold plated with 200, 400, and 600 mL electroless-plating solution, respectively. The final gold-coated fibrous mats (treated with the 600 mL electroless-plating solution) show a typical gold-yellow reflective surface. The mats are also stable mechanically and bending the mat does not delaminate it.

We have also evaluated the effects of thermal treatment on the nanostructure of the gold films on fiber surfaces. When we heat the mat plated with 600 mL electroless-plating solution

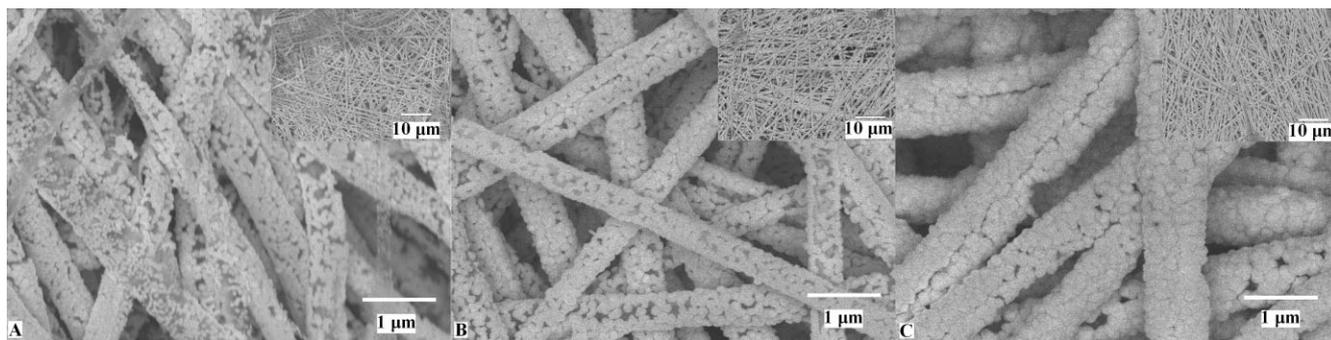


Figure 2. FE-SEM images showing the growth of gold films on PMMA/gold-nanoparticle fibers treated with a) 200 mL, b) 400 mL, and c) 600 mL electroless-plating solution.

at 150 °C in air for 2 h, we find that the gold film structure on the fiber surface collapses (Fig. 3A), due to the burning shrinkage of PMMA, and the shapes of the fibers became irregular, indicating that the surface gold particles have high adhesion to the polymer surface. After being annealed at a higher temperature (300 °C), the fibers become more irregular and the particles are in closer contact (Fig. 3B). Finally, all the gold particles coalesce and the gold fiber surface becomes smooth (Fig. 3C) after annealing at 450 °C. The conductivity of the annealed mats increases distinctly; it has been measured using the four-point probe method and found to be 1.8×10^4 , 2.6×10^4 , and 7.5×10^4 S cm⁻¹ for samples thermally treated at 150, 300, and 450 °C, respectively.

Figure 4 shows the X-ray diffraction (XRD) patterns of samples. The sample of PMMA fibers containing a gold salt shows three broad peaks, indicating the size of the gold salt particles embedded in the PMMA fibers is small. After the gold salt is reduced, there are three broad diffraction peaks, centered at 38.45°, 64.11°, and 78.37°, because of the very small gold particles. After the mat is plated with 400 mL plating solution, the XRD pattern shows clearly the diffraction peak of Au(111) at 38.15°, Au(200) at 44.51°, Au(220) at 64.68°, and Au(311) at 77.66°. In contrast to the result of electroless gold plating on high-index glass,^[18] the peaks of Au(220) and Au(311) do not have very small intensities compared to the Au(111) peak, indicating that gold particles on the surface of ultrafine fibers are less oriented than on the surface of glass.

In conclusion, conductive gold films have been successfully assembled on flexible electrospun PMMA ultrafine fibrous mat substrates containing gold nanoparticles reduced from a gold salt by filtering a HAuCl₄·2H₂O and NH₂OH·HCl solution through the mats. In this procedure, the gold particles already attached to the fiber surface grow through the surface-catalyzed reduction of Au³⁺ by hydroxylamine, and the enlarged gold particles increase the fraction of the surface covered with gold until a shiny continuous gold layer is formed on the fibrous mat with conductivity of about 9.3×10^3 S cm⁻¹. After the mat has been annealed at 450 °C, the conductivity of the mat is as high as 7.5×10^4 S cm⁻¹, and the gold particles coalesce and form ultrafine gold fibers with

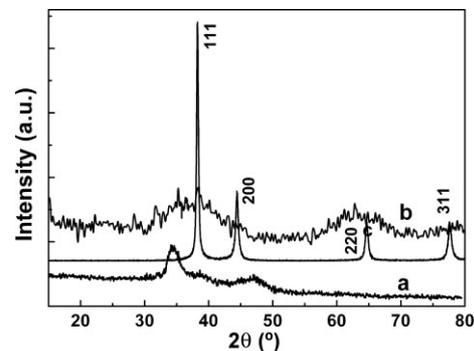


Figure 4. XRD patterns of samples of A) PMMA/gold-salt fibrous mat, B) PMMA/gold-nanoparticle fibrous mat, and C) gold-coated PMMA/gold-nanoparticle fibrous mat.

a smooth surface. The stable and continuous gold-coated fibrous mats may be used as electrodes for electrochemical experiments or for fabrication of electronic devices.

Experimental

Chemicals: HAuCl₄·3H₂O (>99.9 %) and NH₂OH·HCl were purchased from Beijing Chemical Company. PMMA powder was synthesized by emulsion polymerization according to a previously described method [19]. The other chemicals were reagent grade and used directly.

Preparation of the PMMA/Gold-Salt Hybrid Fibers: Chloroauric acid (60 mg) was dissolved into a mixture of deionized water (2 mL) and chloroform (5 mL). Under constant stirring, tetrabutylammonium bromide (100 mg) was added to the mixture. After the aqueous phase became colorless, the organic phase was separated and washed with water thoroughly, then the organic phase was dried over anhydrous MgSO₄ and solvents were removed using a rotary evaporator to give a brown-red powder. After the resulting powder had been dissolved in chloroform (6 mL), PMMA powder (120 mg) was dissolved in the solution for electrospinning.

Fibers were electrospun from chloroform solution of PMMA and the gold salt. The solution was fed at a rate of approximately 1.0 mL h⁻¹ through a stainless-steel syringe pipette needle carrying a potential of +7.5 kV. Fibers were collected on a filter paper placed on a sheet of electrically grounded aluminum foil placed 12 cm below the syringe tip. The resulting fibrous mats were collected and then dried at room temperature for 10 h under vacuum.

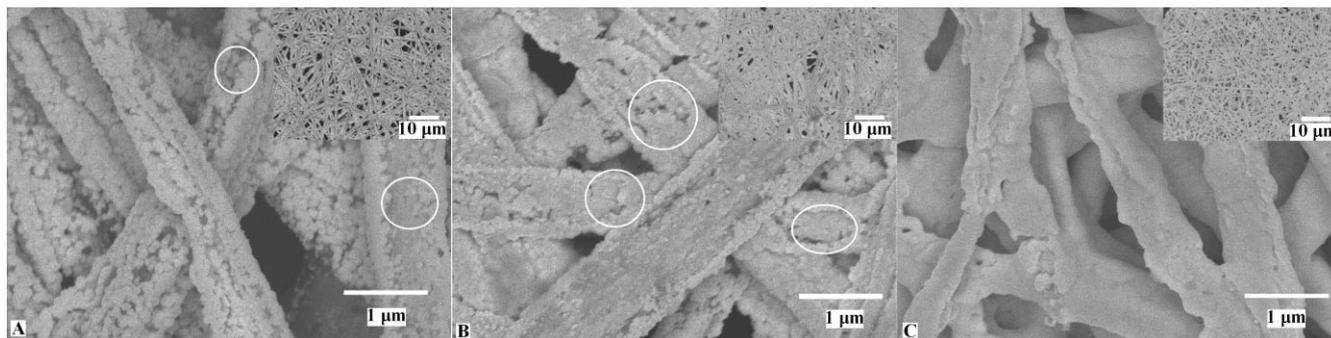


Figure 3. FE-SEM images of gold-coated PMMA/gold-nanoparticle fibrous mats annealed at different temperatures in air for 2 h at A) 150, B) 300, and C) 450 °C.

Preparation of Gold-Coated Fibrous Mats: Prior to the gold coating, all glassware was soaked in a mixture of nitric acid (45 mL) and hydrochloric acid (135 mL) for 1 h, and then thoroughly cleaned with deionized water. The fiber mats together with filter paper were cut into circles of 3.5 cm diameter. The mats were placed in a vacuum funnel, and dilute NaBH₄ solution (1 mM, 200 mL) was filtered through the mat. By this procedure, the gold salt embedded in PMMA fibers was reduced to gold nanoparticles. Subsequently, the mat was washed with water (600 mL) and dilute HCl solution (0.01 M, 400 mL) separately by filtration. The gold particles immobilized on the polymer surface were enlarged by filtering 200, 400, or 600 mL electroless-plating solution containing 0.1 mg mL⁻¹ HAuCl₄·3 H₂O and 0.02 mg mL⁻¹ NH₂OH·HCl until the filtrate became colorless. By this procedure the reduction of Au³⁺ by hydroxylamine was catalyzed by the gold nanoparticles embedded on the surface of the fibers. In order to investigate the effect of annealing, the gold-coated fibrous mats treated with 600 mL electroless-plating solution were heated at 150, 300, or 450 °C in air for 2 h.

Characterization of Fibers and Gold-Particle-Coated Fibers: UV-vis spectra of the gold salt and gold nanoparticles were measured on a Hewlett Packard 8453E single beam diode array recording spectrophotometer by dissolving the samples in chloroform using a quartz cell (10 mm path). Transmission infrared spectra were recorded on a Shimadzu FTIR 8000 series spectrometer. XRD patterns were measured by a Bruker D8 Advance X-ray diffractometer. A piece of mat was placed on the sample holder and was scanned from 10° to 80° (2θ) at a speed of 0.02° s⁻¹. Scanning electron microscopy images were taken using a JEOL-JSM-6700 (Tokyo, Japan) field-emission microscope operated at an accelerating voltage of 10 kV. A piece of PMMA/gold-nanoparticle hybrid fibrous mat was placed on a copper grid for investigation with a transmission electron microscope (JEM 2000FX, JEOL, Tokyo, Japan).

Received: January 16, 2006

Final version: April 6, 2006

Published online: June 8, 2006

- [1] a) G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, 254, 1312. b) G. A. Ozin, *Adv. Mater.* **1992**, 4, 612. c) J. M. Schnur, *Science* **1993**, 262, 166. d) C. R. Martin, *Science* **1994**, 266, 1961. e) F. T. Edelmann, *Angew. Chem. Int. Ed.* **1999**, 38, 1381; *Angew. Chem.* **1999**, 111, 1473.
- [2] a) M. Giersig, P. Mulvaney, *Langmuir* **1993**, 9, 3408. b) S. A. Harfenist, Z. L. Wang, M. M. Alvarez, I. Vezmar, R. L. Whetten, *J. Phys. Chem.* **1996**, 100, 13 904. c) R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, *Science* **1996**, 273, 1690. d) M. J. Feldstein, C. D. Keating, Y.-H. Liao, M. J. Natan, N. F. Sherer, *J. Am. Chem. Soc.* **1997**, 119, 6638. e) K. C. Grabar, P. C. Smith, M. D. Musick, J. A. Davis, D. G. Walter, M. A. Jackson, A. P. Guthrie, M. J. Natan, *J. Am. Chem. Soc.* **1996**, 118, 1148. f) S.-H. Park, J.-H. Im, J.-W. Im, B.-H. Chun, H.-H. Kim, *Microchem. J.* **1999**, 63, 71.
- [3] M. D. Musick, C. D. Keating, M. H. Keefe, M. J. Natan, *Chem. Mater.* **1997**, 9, 1499.
- [4] K. R. Brown, L. A. Lyon, A. P. Fox, B. D. Reiss, M. J. Natan, *Chem. Mater.* **2000**, 12, 314.
- [5] Y. Jin, X. Kang, Y. Song, B. Zhang, G. Cheng, S. Dong, *Anal. Chem.* **2001**, 73, 2843.
- [6] K. C. Grabar, R. G. Freeman, M. B. Hommer, M. J. Natan, *Anal. Chem.* **1995**, 67, 735.
- [7] A. Doron, E. Katz, I. Willner, *Langmuir* **1995**, 11, 1313.
- [8] P. C. Hidber, W. Helbig, E. Kim, G. M. Whitesides, *Langmuir* **1996**, 12, 1375.
- [9] L. Supriya, R. O. Claus, *Langmuir* **2004**, 20, 8870.
- [10] a) S. Hrapovic, Y. L. Liu, G. Enright, F. Bensebaa, J. H. T. Luong, *Langmuir* **2003**, 19, 3958. b) K. R. Brown, M. J. Natan, *Langmuir* **1998**, 14, 726.
- [11] C. A. Goss, D. H. Charych, M. Majda, *Anal. Chem.* **1991**, 63, 85.
- [12] R. G. Freeman, K. C. Grabar, K. J. Allison, R. M. Bright, J. A. Davis, A. P. Guthrie, M. B. Hommer, M. A. Jackson, P. C. Smith, D. G. Walter, M. J. Natan, *Science* **1995**, 267, 1629.
- [13] a) D. Li, Y. N. Xia, *Adv. Mater.* **2004**, 16, 1151. b) D. H. Reneker, I. Chun, *Nanotechnology* **1996**, 7, 216. c) A. Frenot, I. S. Chronakis, *Curr. Opin. Colloid Interface Sci.* **2003**, 8, 64. d) G. Larsen, R. Ve-larde-Ortiz, K. Minchow, A. Barrero, I. G. Loscertales, *J. Am. Chem. Soc.* **2003**, 125, 1154. e) H. Q. Dai, J. Gong, H. Kim, D. Lee, *Nanotechnology* **2002**, 13, 674. f) D. Li, Y. L. Wang, Y. N. Xia, *Nano Lett.* **2003**, 3, 1167. g) W. E. Teo, M. Kotaki, X. M. Mo, S. Ramakrishna, *Nanotechnology* **2005**, 16, 918. h) A. Melaiye, Z. Sun, K. Hindi, A. Milsted, D. Ely, D. H. Reneker, C. A. Tessier, W. J. Youngs, *J. Am. Chem. Soc.* **2005**, 127, 2285.
- [14] M. Bognitzki, H. Q. Hou, M. Ishaque, T. Frese, M. Hellwig, C. Schwarte, A. Schaper, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2000**, 12, 637.
- [15] R. A. Caruso, J. H. Schattka, A. Greiner, *Adv. Mater.* **2001**, 13, 1577.
- [16] C. Drew, X. Liu, D. Ziegler, X. Wang, F. F. Bruno, J. Whitten, L. A. Samuelson, J. Kumar, *Nano Lett.* **2003**, 3, 143.
- [17] G. M. Kim, A. Wutzler, H.-J. Radusch, G. H. Michler, P. Simon, R. A. Sperling, W. J. Parak, *Chem. Mater.* **2005**, 17, 4949.
- [18] Z. Hou, N. L. Abbott, P. Stroeve, *Langmuir* **1998**, 14, 3287.
- [19] J. Pavlinec, M. Lazar, *J. Macromol. Sci., Pure Appl. Chem. A* **1994**, 31, 1469.