Synthesis and Assembly of Metal Nanoparticles on Electrospun Poly(4-vinylpyridine) Fibers and Poly(4-vinylpyridine) Composite Fibers

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Received November 4, 2005
Revised Manuscript Received March 8, 2006

Metal nanoparticles are of continuing interest because of their unusual properties compared to bulk metals and potential applications in novel electrical, optical, magnetic, catalytic, and chemical/biochemical sensing technologies.[1] In some applications, metal nanoparticles are immobilized or synthesized in situ on various supports, such as silica and metal oxide surfaces,[2] polymer micelles,[3] microspheres,[4] carbon,[5] and carbon nanotubes.[6] Microfibers such as natural porous cellulose fibers[7] and modified commercial polyacrylonitrile fibers,[8] which have large specific surface areas, have also been reported to be used as substrates for the adsorption of different metal ions and in situ synthesis of metal nanoparticles.

Electrospinning is a simple electrostatic method for the preparation of polymer nanofibers and composite nanofibers.[9−11] Many applications of electrospun fibers have been proposed to take advantage of their specific characteristics such as large surface area-to-volume ratio and ease of fabrication.[10,11] The diameters of fibers prepared by this method can range from tens of nanometers to several micrometers. The morphology of the electrospun fibers depends on the solvent and the solution properties,[12] as well as other processing variables.[13] Various polymers have been successfully electrospun into ultrafine fibers in recent years, mostly from solutions and some from melts. Electrospinning followed by calcination has also been used to prepare metal oxide fibers such as TiO_2.[14]

The incorporation of metal nanoparticles into polymer nanofibers has recently been reported by electrospinning from a solution mixture of the polymer and a palladium salt, followed by reduction.[15] The application of this material as a catalyst has also been studied. A limiting feature of this preparation method is that some of the metal nanoparticles are embedded within the fibers. Li et al.[16] recently reported the preparation of gold nanoparticles on the surface of electrospun nanofibers of titania by photocatalytic deposition. Here we report immobilization of gold and silver nanoparticles on electrospun polymer fibers by in situ synthesis as well as assembly of colloidal gold on electrospun polymer fibers.

The adsorption of metal ions and metal nanoparticles from aqueous solution to a substrate surface is usually controlled by the properties of the surface. Surface functional groups such as amino, carboxyl, pyridyl, and thiol can be used to facilitate the adsorption of metal ions and metal nanoparticles. Poly(4-vinylpyridine) (P4VP) has been widely used as a surface modifier for the immobilization of nanoparticles on the surface of different substrates because of the strong affinity of the pyridyl group to metals, its ability to undergo hydrogen bonding with polar surfaces, and its electrostatic interaction with anions in its quaternized or protonated form.[17] In this study, fibers of P4VP and fibers of P4VP blended with poly(methyl methacrylate) (PMMA) (w/w, 50:50) were fabricated by electrospinning. Gold and silver nanoparticles were either synthesized on the surface by absorption of metal ions and subsequent reduction or by assembly directly from colloidal gold solution.

Fibers of P4VP and P4VP/PMMA (w/w, 50:50) were electrospun using an apparatus and process described previously.[12] *N*,*N*-Dimethylformamide (DMF) was used as the solvent for the polymer solution because it tends to reduce bead formation and fiber diameter due to its high dielectric constant.[12] A P4VP solution was prepared by dissolving 350 mg/mL P4VP (Aldrich, $M_w = 160\,000$) in DMF. A P4VP/PMMA (w/w, 50:50) solution mixture was prepared by blending 50 mg/mL each of P4VP and PMMA (Aldrich, $M_w = 350\,000$) in DMF at room temperature. A clear P4VP solution was obtained while the P4VP/PMMA solution remained somewhat cloudy. During electrospinning, the applied voltage was held constant at 20 kV, and the distance between the polymer solution and the aluminum foil collection screen was kept at 25 cm. The dry fibers were collected as a fiber mat on the aluminum foil and stored at room temperature. The fibers were examined using a Hitachi S-570 scanning electron microscope (SEM). Prior to SEM observation, the fiber samples were sputter-coated with Au/Pd to minimize sample charging. The morphologies of the

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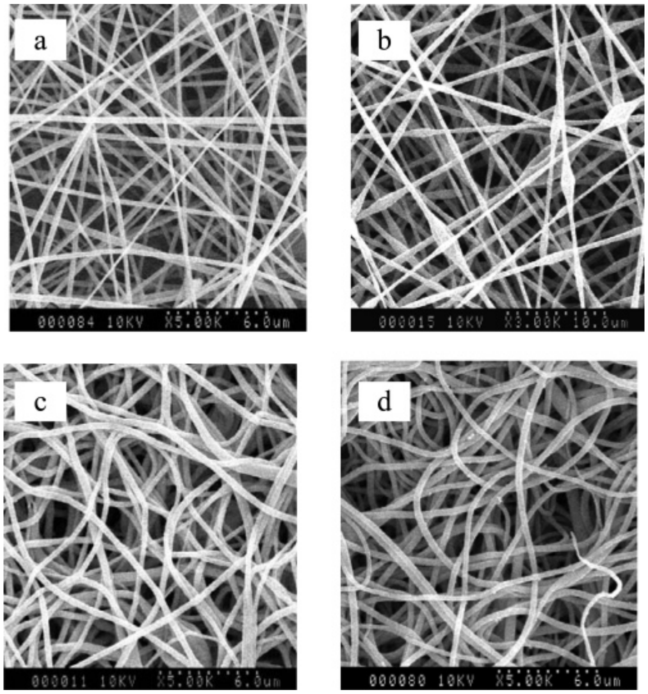

Figure 1. SEM images of (a) P4VP fibers from 350 mg/mL P4VP in DMF solution (×5K), (b) P4VP/PMMA fibers from 50 mg/mL P4VP and 50 mg/mL PMMA in DMF solution (×3K), (c) P4VP fibers with Au nanoparticles (×5K), and (d) P4VP fibers with Ag nanoparticles (×5K).

electrospun P4VP fibers and P4VP/PMMA fibers are shown in Figure 1a,b. The P4VP fibers have a smooth surface morphology with an average diameter of 290 nm. Fibers with a “beads-on-string” morphology were produced from the P4VP/PMMA blend. The average fiber diameter of P4VP/PMMA was 432 nm with 1.01 μm diameter beads.

Adsorption of gold ions on the surface of the P4VP fibers was achieved by immersing the pure polymer fibers into the gold precursor solution at room temperature. $HAuCl_4$, which is often used in the preparation of gold nanoparticles, has been shown to coordinate to the pyridyl groups of P4VP by protonation followed by electrostatic interaction of the quaternary ammonium species with $AuCl_4^-$ anions.[3] However, dissociation of P4VP fibers from the P4VP fiber mat was observed after soaking in 10 mM $HAuCl_4$ solution (pH $\sim$ 2) for 15 min as a result of the partial dissolution of protonated P4VP fibers in acidic media. To overcome this problem, $NaAuCl_4$ was selected as the gold precursor. The complexation of nitrogen in the pyridyl group with $AuCl_4^-$ by replacement of Cl^- in the $AuCl_4^-$ ions[3] can lead to coordination of Au ions on the fiber surface. Au ions were adsorbed on the electrospun P4VP fibers peeled from the aluminum foil by dipping them in a 10 mM aqueous $NaAuCl_4$ solution. After soaking overnight in the yellow $NaAuCl_4$ solution, the white P4VP fibers changed from white into bright yellow consistent with the adsorption of Au ions on the fibers. The fibers were rinsed thoroughly with water to remove excess metal ions that were not anchored. The Au ion loaded fibers were then reduced using a 50 mM $NaBH_4$ solution for 1 min. After reduction, the fiber color changed from yellow to black, indicating conversion of the gold ion into gold metal. After rinsing with water, the fibers were dried at room temperature.

Figure 1c shows SEM image of the P4VP fibers covered with gold nanoparticles. Compared to the P4VP fibers shown in Figure 1a, the morphology of the fibers covered with gold nanoparticles was unchanged, but the fiber diameters increased slightly to 362 nm because of swelling of the P4VP fibers during ion adsorption. Transmission electron microscopy (TEM) images of P4VP fibers covered with metal nanoparticles were collected on a Hitachi H-7000 instrument operating at an acceleration voltage of 100 kV. TEM specimens were prepared by ultrasonic dispersion of the fiber materials in water. A drop of the aqueous solution containing the dispersed fibers was transferred onto a copper grid covered with lacy carbon film and dried. The adsorption of the gold nanoparticles on the fiber surface can be clearly observed in the TEM image (Figure 2a). Large Au nanoparticles are densely packed on the P4VP fibers. It is expected that the high density of pyridyl groups on P4VP fiber surface allows a high loading of gold salt on the fiber surface leading to the growth of large particles after reduction. The UV−visible absorption spectra of the P4VP fibers and nanoparticles on P4VP fibers recorded using a glass slide as support for the fiber mat are shown in Figure 3. An absorption band in the spectrum of the Au nanoparticles on wet P4VP fibers is observed at 556 nm, which is consistent with the surface plasmon resonance of Au nanoparticles[18] indicating Au nanoparticles on the fiber surface. To test the adhesion of gold nanoparticles on the P4VP surface, the fibers were immersed in water in an ultrasonic bath for 30 min. TEM examination showed that the gold nanoparticles remained on the fiber surface after treatment as a result of the strong affinity of the pyridyl groups to metals through the polar covalent bonding interaction.[17]

The ion adsorption strategy was also applied to silver to demonstrate the versatility of this method. In this case, a 20 mM $AgNO_3$ aqueous solution was used as the precursor

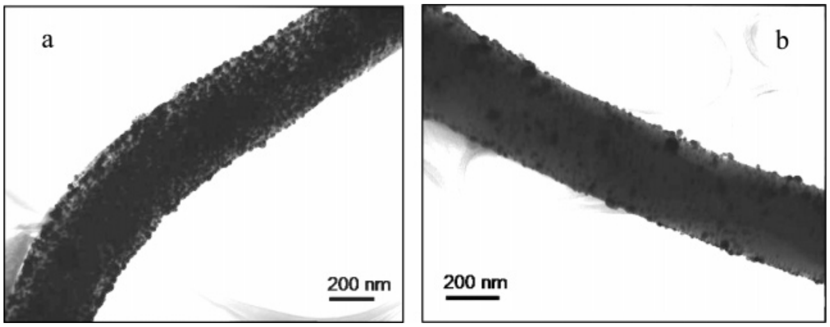

Figure 2. TEM images of (a) Au nanoparticles on a P4VP fiber and (b) Ag nanoparticles on a P4VP fiber.

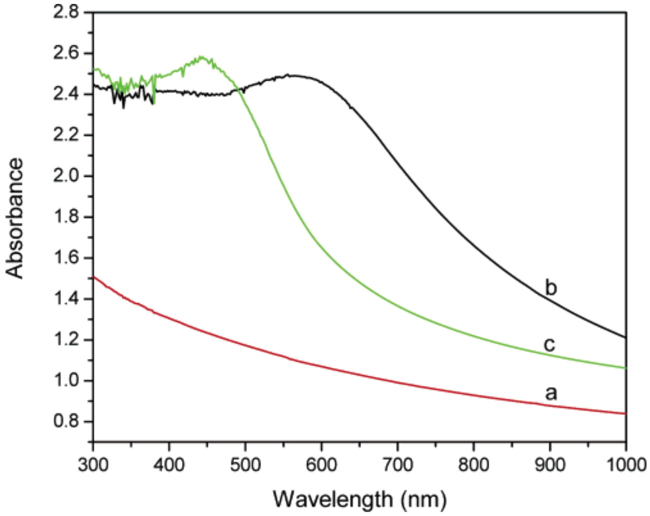

Figure 3. UV−visible absorption spectra of (a) P4VP fibers, (b) Au nanoparticles on wet P4VP fibers, and (c) Ag nanoparticles on wet P4VP fibers.

solution and the same adsorption and reduction procedure was employed for the particle formation. The complexation of silver ions by the pyridine rings leads to the binding of silver ions to the fiber surface. The P4VP fibers were dipped in a 20 mM $AgNO_3$ solution overnight, rinsed by water, and then reduced with 50 mM $NaBH_4$ in an aqueous solution for 3 min. After rinsing and drying, the P4VP fiber mat with Ag particles appeared brown in color, consistent with formation of Ag nanoparticles anchored on the fiber surface. SEM examination, shown in Figure 1d, reveals that the average fiber diameter of P4VP with Ag nanoparticles is 356 nm. The formation of Ag nanoparticles on the fiber surface was also confirmed by the TEM observation in Figure 2b. The density of Ag nanoparticles on the P4VP fiber surface appears to be less than for the Au nanoparticles. As shown in Figure 3c, one UV−visible absorption band is observed at 440 nm, which is attributed to the surface plasmon resonance of Ag nanoparticles[19] in agreement with the formation of Ag nanoparticles on the fiber surface.

Colloidal metal nanoparticles can also be directly assembled on the surface of functional electrospun fibers. As a first example of this procedure, colloidal gold was synthesized by citrate reduction of $HAuCl_4$ in solution, where citrate ions play the role of both reducing agent and protecting group.[20] A 1 mM $HAuCl_4$ solution was prepared from 19.9 mg $HAuCl_4 \cdot 3H_2O$ dissolved in 50 mL of water. The solution was brought to boiling, and a 2% solution of sodium citrate (5 mL) was added with continued boiling for 30 min. This produced a colloidal gold solution with a wine red color and a pH of ∼6. Assembly of preformed gold nanoparticles on fibers was carried out by simply immersing a fiber mat of P4VP or P4VP/PMMA in the colloidal gold solution overnight followed by rinsing with water and air-drying. The gold colloids demonstrated strong affinity toward the fibers of P4VP and P4VP/PMMA, which is likely due to electrostatic interaction between negative citrate ion protected gold nanoparticles and positively charged pyridyl groups at pH ∼ 6. The adsorption of gold colloids on the fiber surface was rapid as indicated by the quick color change of the fibers after immersion of P4VP fibers or P4VP/PMMA fibers into the colloidal solution for only several minutes. Exposure of P4VP fibers to the colloidal gold solution overnight, however, caused severe swelling of individual P4VP fibers and an increase in their diameter while shrinking the whole fiber mat. Exposure of P4VP/PMMA fibers to gold

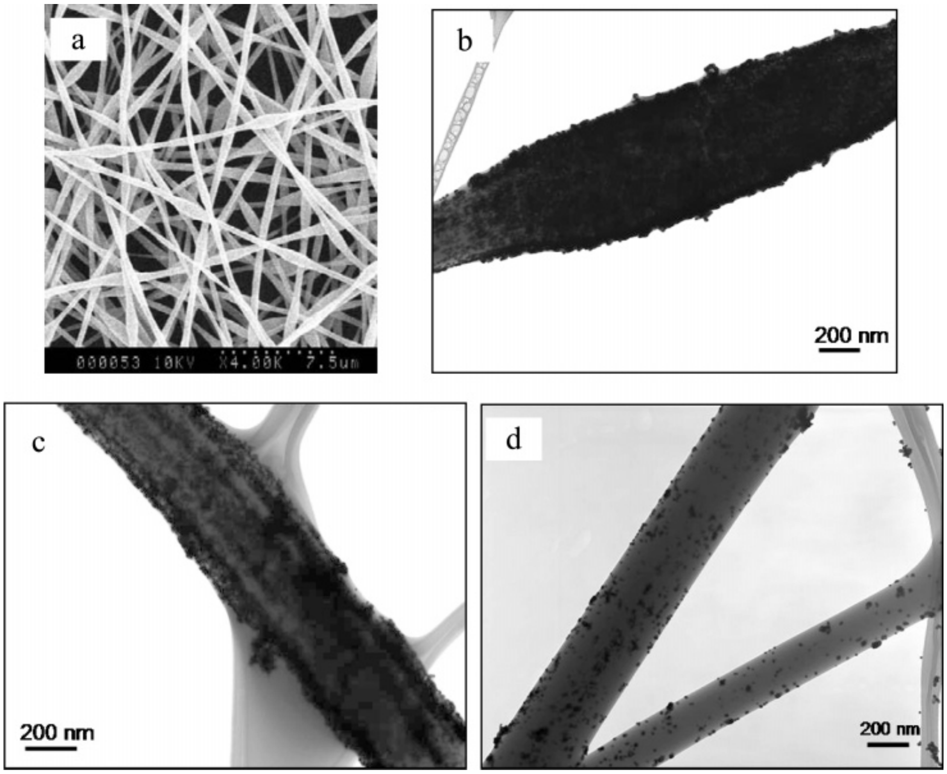

Figure 4. (a) SEM image of colloidal gold nanoparticles on P4VP/PMMA fibers. TEM images of (b) gold nanoparticles on the bead of P4VP/PMMA, (c) gold nanoparticles on the fiber string of P4VP/PMMA, and (d) PMMA fibers after immersing in a colloidal gold solution.

colloidal solution overnight produced fibers with a deep purple color from the adsorbed Au nanoparticles. Figure 4a−c shows SEM and TEM images of P4VP/PMMA fibers after assembly of Au colloids. The fiber shape was maintained, but the distribution of the Au nanoparticles on the fiber surface was uneven. More particles were found closely packed on the beads (Figure 4b) than on the fiber strings (Figure 4c). Along the fiber string, several stripes with packed particles were separated by stripes with few particles (Figure 4c). This result suggests that phase separation of P4VP and PMMA in electrospun P4VP/PMMA fibers has occurred. The co-continuous, phase separated structure along the fiber axis has been observed previously with electrospun fibers of blended polylactide and poly(vinylpyrrolidone) and was ascribed to phase separation during fiber formation by Wendorff et al.[21] This intrinsic fiber phase morphology was used for the preparation of porous fibers by selective removal of one component. In our case, phase structures of P4VP and PMMA as strips along the fiber string were generated by phase separation and preserved by rapid solidification during the electrospinning process. Because the P4VP phase adsorbs colloidal gold very well and the PMMA phase does not, the stripes containing gold nanoparticles appear. Given the high density of nanoparticles on the beads, it is also possible that the beads contain P4VP as a major component. To prove that the PMMA phase has no strong affinity toward the colloidal gold, PMMA fibers were fabricated from 80 mg/mL PMMA in a DMF solution[12] and immersed in a colloidal gold solution according to the same procedure as above. The TEM image, Figure 4d, indicates that only a few gold nanoparticles were sparsely dispensed on the PMMA fiber surface.

In summary, we have demonstrated the synthesis of gold and silver nanoparticles and direct assembly of colloidal gold nanoparticles on the surface of P4VP fibers and P4VP/PMMA composite fibers. These fibers with functional pyridyl groups can be easily fabricated from P4VP solutions and blends of P4VP/PMMA solution by electrospinning. Gold and silver nanoparticles were formed on the fiber surface by in situ synthesis as well as assembly from a colloidal solution. TEM and UV−visible spectra confirm the presence of gold and silver nanoparticles on the fiber surface. This simple approach is versatile and applicable to many other combinations of electrospun functional fibers and suitable metal nanoparticles, where functional groups can be introduced on the fiber surface during fabrication or by subsequent surface modification of the electrospun fibers.

Acknowledgment. We acknowledge Henry Eichelberger in the Department of Biological Sciences at SUNY Binghamton for assistance in SEM and TEM image collection and financial support from Semiconductor Research Corporation (SRC) and the Integrated Electronics and Engineering Center (IEEC). The IEEC receives funding from New York State Science and Technology Foundation, the National Science Foundation, and a consortium of industrial members.

CM052436P

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