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One-Pot Synthesis of Polyaniline−Metal Nanocomposites

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Composite materials consisting of polyaniline nanofibers decorated with noble-metal (Ag or Au) nanoparticles were synthesized with γ radiolysis. Aqueous solutions of aniline, a free-radical oxidant, and/or a metal salt were irradiated with γ rays. Exposure of the solutions to γ rays caused aniline to polymerize as very-thin fibers. Metal particles were also formed during irradiation and decorated the fibers. The shape and size of the metal particles could be changed from nanometer-sized spheres to micron-sized dendrites by varying the ratio of aniline to the metal precursor. Polyaniline-metal composites were characterized using UV−Vis spectroscopy, infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The electrical conductivity of the composites increased with the loading of metal in the nanocomposites and was up to 50 times greater than that of polyaniline fibers alone.

Introduction

Polyaniline has been extensively studied because of its stability and tunable electrical properties,[1] yet a great deal is still not known about how to make structures that take advantage of this polymer's unique properties. For example, polyaniline nanofibers are more responsive than bulk polyaniline to external stimuli because of their large specific surface areas. These nanofibers show promise in sensing and catalytic applications.[2−4] Syntheses of polyaniline nanofibers using electrochemistry or wet chemistry have been reported. In most reports, soft[5−7] or hard[8,9] templates were employed to achieve the nanostructures. Recent reports have shown that polyaniline nanofibers could be produced with templateless methods, such as interfacial polymerization,[10] nanofiber seeding,[11] or radiolysis.[12]

Polyaniline−metal nanoparticle composites reportedly show enhanced sensing and catalytic capabilities, as compared to those of pure polyaniline.[13−16] In the synthesis of polyaniline−metal composites, metal ions are often reduced in the presence of preformed polyaniline. In the resulting composites, metal nanoparticles are often not effectively dispersed into the polymer matrix, because metal ions and nanoparticles interact strongly with the imino groups of the polymer and are reduced at the point of contact.[17] To counteract this problem, Kinyanjui et al. recently developed a procedure where a gold salt acts both as an oxidizing agent to polymerize aniline and as a source of metal atoms.[18] This procedure yields well-dispersed Au nanoparticles in bulk polyaniline. The specific surface areas of the composites prepared with this procedure are probably not large, which might represent a drawback for sensing applications.

In this paper, we report a technique to synthesize composites containing polyaniline nanofibers decorated with metal nanoparticles. Our technique extends our previous work, where we showed that polyaniline nanofibers could be formed by exposing aqueous solutions of aniline and an oxidant to γ irradiation.[12] Addition of a water-soluble metal salt to the parent solution does not alter the morphology of the polyaniline fibers and yields metal nanoparticles that decorate the fibers. Our method has several advantages over existing techniques. Fiber synthesis does not require templates, nor does it require large amounts of organic solvents (as in interfacial polymerization)[10] or preformed nanofiber seeds (as in the nanofiber seeding method).[11] Well-dispersed fiber−metal composites are produced in a single reaction setup, and the morphology of the metal nanoparticles can be controlled by varying the aniline/metal salt ratio.

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Experimental Section

Materials. Silver nitrate ($AgNO_3$) and hydrogen tetrachloroaurate ($HAuCl_4$) were obtained from Alfa Aesar. Aniline, hydrochloric acid (HCl), nitric acid (HNO_3), benzoyl peroxide, and ammonium persulfate (APS) were purchased from Aldrich Chemicals. Aniline was distilled before use, and all other reagents were used as received.

Synthesis. A metal salt; a dopant; and, in some cases, an oxidant were added to aqueous solutions (typically 10 mL) with an aniline concentration of 0.1 M. Ammonium peroxydisulfate or benzoyl peroxide was used as the oxidant, with a concentration of 0.02 M. The metal salts, $AgNO_3$ and $HAuCl_4$, were added at a concentration of up to 0.1 M. The dopant used was either HCl (for the Au composites) or HNO_3 (for the Ag composites). The dopant concentration was 0.3 M in all cases. In experiments where an oxidant was not employed, aniline and $HAuCl_4$ were added to final concentrations of 0.1 and 0.02 M, respectively. All solutions were purged with nitrogen before γ irradiation. After exposure, the polymer suspensions were centrifuged at 5000 rpm for 10 min and filtered, and then the powders were washed with water, methanol, and ether to remove unreacted precursors, oligomers, and other byproducts.

Irradiation. The samples were irradiated with γ rays from the fission products of the University of Missouri-Rolla's nuclear pool reactor. The reactor was operated at 180 kW for a 1−2-h period and then shut down. After about 1 h, the samples were placed in the reactor in front of the core. The samples were irradiated after the reactor was shut down to prevent neutron bombardment and activation of the sample. Because of the decay of the fission products, dose rates decreased exponentially with time. Radiation dose rates varied from an initial value of about 1.5 $kGy\cdot h^{-1}$ to about 0.3 $kGy\cdot h^{-1}$ at the end of the irradiation period. Because polymerization occurs without irradiation at room temperature, samples were placed in front of the core within about 4−5 min after they were prepared. The samples were exposed to γ rays for up to 24 h, after which polymerization was complete. Samples were irradiated with a total dose of 3.5 kGy, at an initial dose rate of 1.5 $kGy\cdot h^{-1}$. Exposure for longer times (and to higher total doses) did not alter the polymer morphology.

Characterization. The morphologies of the polyaniline−Ag and polyaniline−Au nanocomposites were determined with a Philips EM 430T transmission electron microscope (TEM), operated at 300 kV. TEM samples were prepared by placing a few drops of a polyaniline suspension onto a carbon-coated copper grid and drying them in an oven at 50 °C for a few hours. Selected area electron diffraction (SAED) was used to verify the crystal structures. X-ray diffraction (XRD) was measured with a Scintag PadX diffractometer, equipped with a Cu Kα source. Fourier transform infrared (FT-IR) spectra were taken with a Thermo Nicolet Nexus spectrometer. UV−vis spectra of the aqueous dispersions were obtained using a Varian Cary 50 Bio spectrophotometer. Electrical conductivity of the dried composite pellets was measured with a four-point probe method using a Keithley 2001 electrometer.

Results

Irradiation of the parent solutions with γ rays yielded polyaniline fibers containing well-dispersed noble-metal nanoparticles. Typical bright-field micrographs of polyaniline−Ag and polyaniline−Au composites are shown in Figures 1 and 2, respectively. The polyaniline nanofibers have intermediate shading, and the metal nanoparticles are bright in the TEM micrographs. The polyaniline fibers had typical diameters of 50−100 nm and lengths of 1−3 μm. The shapes and sizes of the metal nanoparticles (bright regions) could be varied by changing the aniline/metal ratio. Spherical metal particles with diameters of around 2 nm were formed at low metal concentrations (0.001 M), as shown in

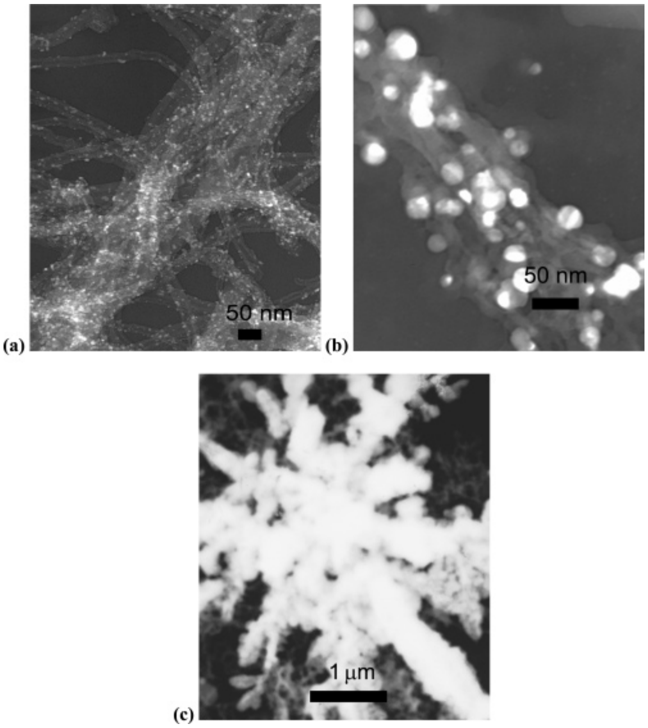

Figure 1. TEM images of polyaniline−Ag nanocomposites obtained by radiolysis of solutions of 0.1 M aniline, 0.02 M APS, and 0.3 M HNO_3. The aniline/$AgNO_3$ mole ratio was (a) 100:1, (b) 10:1, (c) 1:1. For c, the samples were irradiated with a total dose of approximately 3.5 kGy, at an initial dose rate of 1.5 $kGy\cdot h^{-1}$.

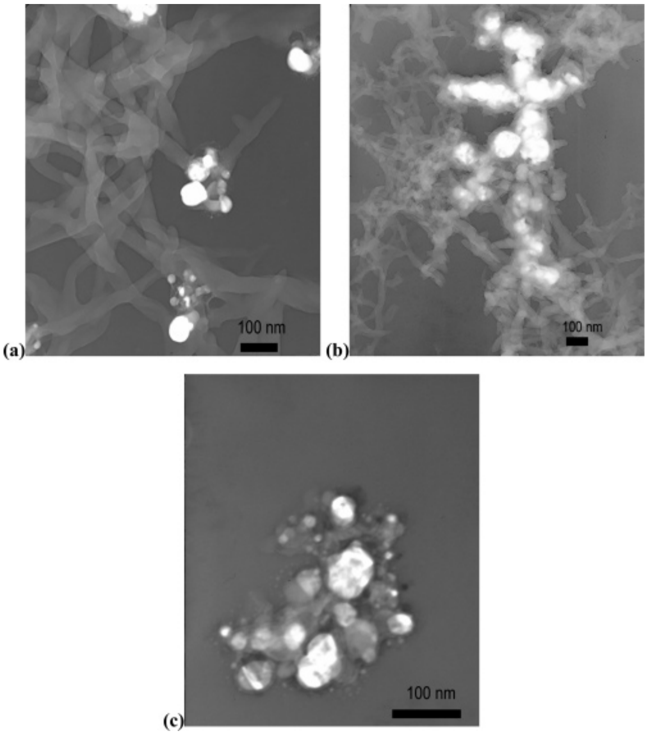

Figure 2. TEM images of polyaniline−Au composites obtained using $HAuCl_4$ as an oxidant. (a, b) Samples exposed to γ rays. (c) Unirradiated sample. The aniline/$HAuCl_4$ mole ratio in the parent solutions was (a) 50:1, (b) 5:1, (c) 5:1. In all cases, the parent solutions had concentrations of aniline and HCl of 0.1 and 0.3 M, respectively. Irradiation doses and dose rates are given in Figure 1.

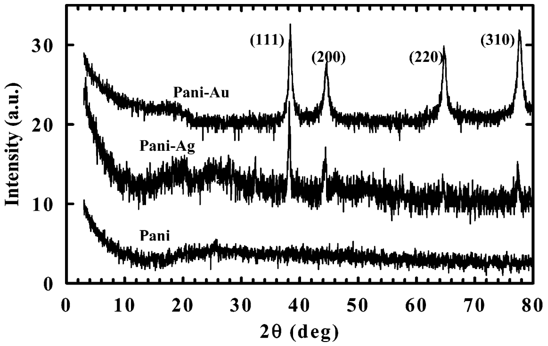

Figure 3. XRD spectra of (bottom) polyaniline (parent solution concentration: 0.1 M aniline, 0.02 M APS, and 0.3 M HCl), (middle) polyaniline−Ag composites (parent solution concentration: 0.1 M aniline, 0.02 M APS, 0.3 M HNO_3, and 0.01 M $AgNO_3$), and (top) polyaniline−Au composites (parent solution concentration: 0.1 M aniline, 0.02 M $HAuCl_4$, and 0.3 M HCl).

Figure 1a. The metal particle size increased to around 25 nm when the metal concentration was increased (0.01 M), as shown in Figure 1b. When aniline-to-metal ratios were close to 1:1, dendritic structures stretching for several micrometers were observed, as shown in Figure 1c. From TEM analysis of samples in different sample regions, the number of metal nanoparticles not bound to fibers was negligible.

Polyaniline nanofibers decorated with well-dispersed gold nanoparticles were obtained by irradiating solutions of aniline and $HAuCl_4$. In this synthesis, $HAuCl_4$ acted both as an oxidant and as a source of metal atoms.[18] The metal nanoparticles decorated the polymer, as shown in Figure 2a,b. The fibers had typical diameters of around 50 nm, and the metal nanoparticle diameters varied between about 10 and 100 nm, depending on the aniline/$HAuCl_4$ ratio. Figure 2c shows, for comparison, the morphology of an unirradiated precursor solution of aniline and $HAuCl_4$. The Au particles had diameters of 5−50 nm, and the polymer had a bulklike morphology.

The chemical identity and structure of the nanoparticles were investigated with selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). All of these techniques showed that the metal nanoparticles were essentially free of contamination, and that they had a structure and lattice parameter close to those of the bulk metals. Representative XRD results are reported in Figure 3. XRD of polyaniline fibers (without metal) exhibited only weak and broad peaks, indicating that the fibers were mostly amorphous. A weak peak at $2\theta = 25°$ was observed in all spectra and was ascribed to the periodicity parallel to the polymer chain.[19] XRD of polyaniline−metal composites exhibited intense peaks corresponding to the (111), (200), (220), and (310) Bragg reflections of Au and Ag. The mean size of the metal nanoparticles was estimated from the XRD spectra using the Williamson−Hall analysis.[20] Ag nanoparticles obtained from solutions with initial $AgNO_3$ concentrations of 0.001 and 0.01 M had diameters of 3 and 25 nm, respectively, in agreement with the TEM results. The diameters of Au nanoparticles obtained from solutions with an initial $HAuCl_4$ concentration of 0.02 M were 16 nm in irradiated samples and 50 nm in unirradiated samples, again in agreement with the TEM results.

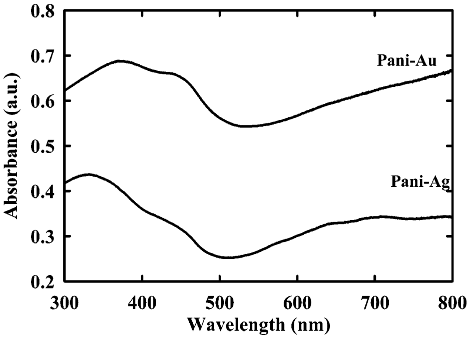

Figure 4. UV−vis spectra of polyaniline−Ag (parent solution concentration: 0.1 M aniline, 0.02 M APS, 0.3 M HCl, and 0.01 M $AgNO_3$) and polyaniline−Au (parent solution concentration: 0.1 M aniline, 0.02 M $HAuCl_4$, and 0.3 M HCl) composites.

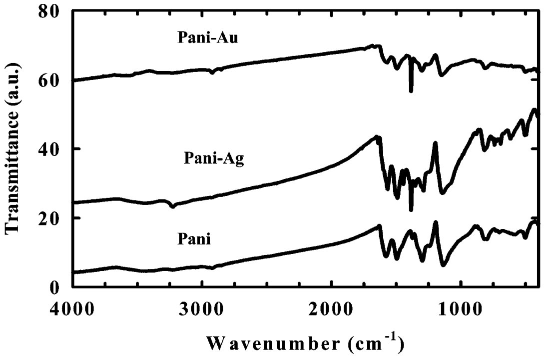

Figure 5. FT-IR spectra of polyaniline, polyaniline−Ag composites (parent solution concentration: 0.1 M aniline, 0.02 M APS, 0.3 M HNO_3, and 0.01 M $AgNO_3$), and polyaniline-Au composites (parent solution concentration: 0.1 M aniline, 0.02 M $HAuCl_4$, and 0.3 M HCl).

The UV−vis spectra of polyaniline−metal composites are shown in Figure 4. In all of the UV spectra, peaks were observed at 350 nm, 420 nm, and between 700 and 800 nm, corresponding to $\pi-\pi^*$ and polaron−π, $\pi-\pi$, and polaron−π^* transitions, respectively.[21] The absorption bands of polyaniline and the surface plasmons of Ag and Au nanoparticles overlap, and because the absorption of polyaniline was very strong, it was difficult to detect nanoparticles using UV−vis spectroscopy. The strongly acidic environment of the solutions might also have reduced the oscillator strength and weakened the surface plasmon absorption.[22,23]

The FT-IR spectra of polyaniline fibers, polyaniline−Ag, and polyaniline−Au nanocomposites are shown in Figure 5. All of the spectra exhibited absorption peaks corresponding to the stretching of quinonoid (1570 cm^{-1}) and benzenoid (1490 cm^{-1}) rings, as well as N−H stretching (3400 cm^{-1}). These results are in good agreement with previous spectroscopic characterizations of polyaniline.[24]

The conductivities of different polyaniline−metal nanocomposites are reported in Table 1. The conductivities increased with increasing metal loading, in accordance with

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Table 1. Electrical Conductivities of Polyaniline (Pani) and Polyaniline−Ag and Polyaniline−Au Nanocomposites[a]

sample (oxidant)	concentration of metal salt in the initial solution (M)	conductivity (S/cm)
Pani (APS)	0	0.02
Pani−Ag (APS)	0.002	0.05
Pani−Ag (APS)	0.02	0.2
Pani−Au ($HAuCl_4$)	0.002	0.1
Pani−Au ($HAuCl_4$)	0.02	1

[a] Parent solutions of all samples had an aniline concentration of 0.1 M and a dopant concentration of 0.3 M. In the synthesis of polyaniline and polyaniline−Ag nanocomposites, 0.02 M APS was used as the oxidant. Polyaniline−Au nanocomposites were synthesized at different oxidant ($HAuCl_4$) concentrations, as shown in Figure 1. The conductivity values are the averages of 3−5 measurements, which were generally within ±10% of each other.

Table 2. Redox Potentials and Concentration Ranges of Species of the Parent and Irradiated Solutions

species (reaction)	E^0 (V vs NHE)	concentration (M)
sodium peroxydisulfate ($S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$)	2.01	0.02
aniline	1.02	0.1
Au ($AuCl_4^- + 3e^- = Au + 4Cl^-$)	0.854	10^{-3}−0.1
Ag ($Ag^- + e^- = Ag$)	0.799	10^{-3}−0.1
Polyaniline (Pani = $Pani^{n-} + ne^-$)	<0.8[17]	
e^-	−2.7[26]	10^{-3} [a]

[a] The solvated electron concentration represents an upper limit and was calculated assuming a generation efficiency of 2.7 electrons per 100 eV of energy deposited by γ radiation and a total dose of 3.5 kGy.[25]

previous reports of polyaniline−metal nanoparticle composites.[22,23]

Discussion

In a previous publication,[12] we showed that polyaniline nanofibers were formed when aqueous solutions of aniline and an oxidant, such as APS, were irradiated with γ rays. The fibers had diameters in the 50−100 nm range and lengths on the order of 1 μm. Some aspects of the mechanism of formation of polyaniline nanofibers during irradiation were previously discussed[12] and are still the subject of continuing research. Our present results show that addition of a metal salt to the initial monomer solution has little effect on the morphology of the polyaniline nanofibers. As shown in Figures 1 and 2, our composites consist of polyaniline fibers decorated with Ag or Au nanoparticles.

The mechanism of metal nanoparticle formation is probably quite complex in polyaniline−Ag nanocomposites, as the solutions contain multiple reducing and oxidizing agents. Reduction potentials and concentration ranges of the components of the parent solutions are reported in Table 2, together with the potentials of two species that are created during the reaction: polyaniline and solvated electrons. From the values in Table 2, we notice that aniline and polyaniline are reducing agents for Ag^+ and $AuCl_4^-$. It is, therefore, not surprising that metal nanoparticles are formed during polymerization. Solvated electrons probably did not play a relevant role in metal reduction, because their concentration was about 2 orders of magnitude lower than the initial aniline concentration. Ammonium persulfate oxidized aniline and probably also scavenged solvated electrons and oxidized metal atoms. Evidently, the oxidant could not prevent formation of metal nanoparticles. This is probably due to the large aniline concentration (about 10 times higher than the oxidant's) and to the decrease in peroxide concentration when aniline is polymerized.

In our focus on oxidants, we found that benzoyl peroxide had several advantages over ammonium persulfate; the most relevant being the purity of the final product. A major issue with ammonium persulfate was the formation of salt adducts (e.g., ammonium chloride or ammonium nitrate) as byproducts during polymerization in both polyaniline and polyaniline−metal nanocomposites. These byproducts were difficult to separate from the end product. In the TEM images of nanocomposites taken after a few cycles of purification, for example, we noticed some crystalline structures whose SAED could not be reconciled with either polyaniline or the bulk metals. These crystals could be removed only after several additional washings. When benzoyl peroxide was used, the byproducts were more easily removed. Polyaniline−gold nanocomposites, obtained by employing $HAuCl_4$ as an oxidant, also contained a small number of byproducts and were easily purified. The polymer−metal interaction could not be investigated in depth, as the polyaniline signal dominated both the UV−vis and FT-IR spectra. We noticed, however, that the metal nanoparticles were fairly strongly attached to the fibers and could only be separated by sonication. Recent reports[27] suggest the presence of oxide states at the interface between metal nanoparticles and polyaniline, and clearly this is an area where future investigation should focus.

Conclusions

We have carried out a one-pot synthesis of metal nanoparticle−polyaniline fiber composites. Our procedure yields high-surface-area nanocomposites in which the sizes of both the polyaniline and the metal are a few nanometers. Fibers can be synthesized with different oxidants (provided the samples are irradiated) and are decorated with metal nanoparticles. The shapes and the sizes of the metal nanoparticles can be varied from nanometer-sized spheres to micron-sized dendrites by increasing the metal-to-aniline ratio. The electrical conductivity of the composites is up to 50 times higher than that of pure polyaniline nanofibers.

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