

High Conductivity of Polyaniline-Silver Synthesized *In Situ* by Additional Reductant

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ABSTRACT: Polyaniline (PANI)-silver complex was obtained from *in situ* reduction of hydrochloric acid-doped PANI by the addition of sodium borohydride. The morphology and structure of the complex were characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, and X-ray diffraction. Four-probe measurements and thermogravimetric analysis were employed to investigate electrical conductivity, thermal stability, and silver content. Conductivity of the PANI-silver composite was up to 535.22 S cm⁻¹ and silver content was 38.48 wt % as determined from the molar ratio of sodium borohydride to silver nitrate of 1.2 used during the synthesis. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 394–398, 2013

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INTRODUCTION

Polyaniline (PANI) exhibits many characteristics that are of interest in materials science; it can be prepared from a wide range of raw materials through simple synthetic methods,¹ and shows good environmental stability^{2,3} and excellent electrical conductivity and electrical activity.⁴ Nano-silver materials are the subject of similar interest due to their high surface energy effect^{5,6} and thermal conductivity performance, as well as excellent antimicrobial and bactericidal activity^{7,8} and catalytic properties.⁹ Materials containing both nano-silver and PANI can display unique combinations of the complementary advantages of each material² and have been widely used in the design of sensors,⁶ secondary batteries, fuel cells,¹⁰ supercapacitors,¹¹ electrochromic devices,⁵ and as electromagnetic shielding military camouflage, and corrosion-resistant paint component.¹² Such PANI-silver composites have been synthesized mainly by *in situ* reduction and *in situ* polymerization methods, with many studies in recent years focusing on *in situ* reduction. For example, Stejskal and coworkers¹² obtained spherical nano-silver particle complexes by reducing silver nitrate with PANI doped with different acids, and reported conductivity and silver content of the hydrochloric acid-doped compound of 22.8 S cm⁻¹ and 27% (compared with a theoretical value of 57%), respectively. Bouazza et al.¹³ showed the impact of the redox state of PANI on the reduction yield of silver nitrate, using a two-step method with auxiliary ultrasound. Sun¹⁴ reacted silver nitrate with sodium dodecyl sulfate-doped PANI at 40°C for 48 h; their conversion rate did not exceed 50% in the absence of external

reductant. PANI-silver composite was obtained by dissolving silver nitrate and PANI in *N,N*-dimethylformamide at 80°C for 4 h, which acts simultaneously as solvent and reductant.⁵ *In situ* reduction can be accomplished using simple equipment and is easily implemented on a large scale. However, the electrical conductivity and content of silver in the resulting complex depend on many factors, including the initial oxidation state and doped state of the PANI, the pH of the solution, and the time and temperature of reaction.^{15,16}

In this article, composite PANI-silver complex was obtained by *in situ* reduction of hydrochloric acid-doped PANI by the addition of sodium borohydride, which can be shorten the reducing time of silver nitrate and increase the content of silver in the complexes, thereby improving their electrical conductivity.

EXPERIMENTAL

Materials

Aniline was distilled twice under vacuum and stored in the dark below -5°C; ammonium peroxydisulfate, acetone, hydrochloric acid, silver nitrate, and sodium borohydride. All chemicals used were of analytical grade. Deionized water was used in all steps.

Synthesis of PANI-Silver Composite

Step I. Synthesis of PANI doped with HCl. In a typical procedure, 4.56 mL of aniline monomer was injected into 250 mL of 2.0M HCl aqueous solution under mechanical stirring. 14.27 g of ammonium peroxydisulfate in 312 mL of 2.0M HCl solution

Table I. Electrical Conductivity of PANI and PANI-Ag

Sample	PANI	PANI1	PANI-Ag1	PANI-Ag2	PANI-Ag3
Conductivity (S cm ⁻¹)	0.7605	0.00093521	33	535.22	498.2

was then slowly added dropwise (30 min) to the above mixture. The polymerization was carried out by mechanical stirring for 8 h and left still for 10 h at room temperature. The resulting

product was obtained by vacuum filtering and washing the reaction mixture, followed with 2.0M HCl solution, deionized water and acetone, and dried under vacuum at 40°C for 12 h.

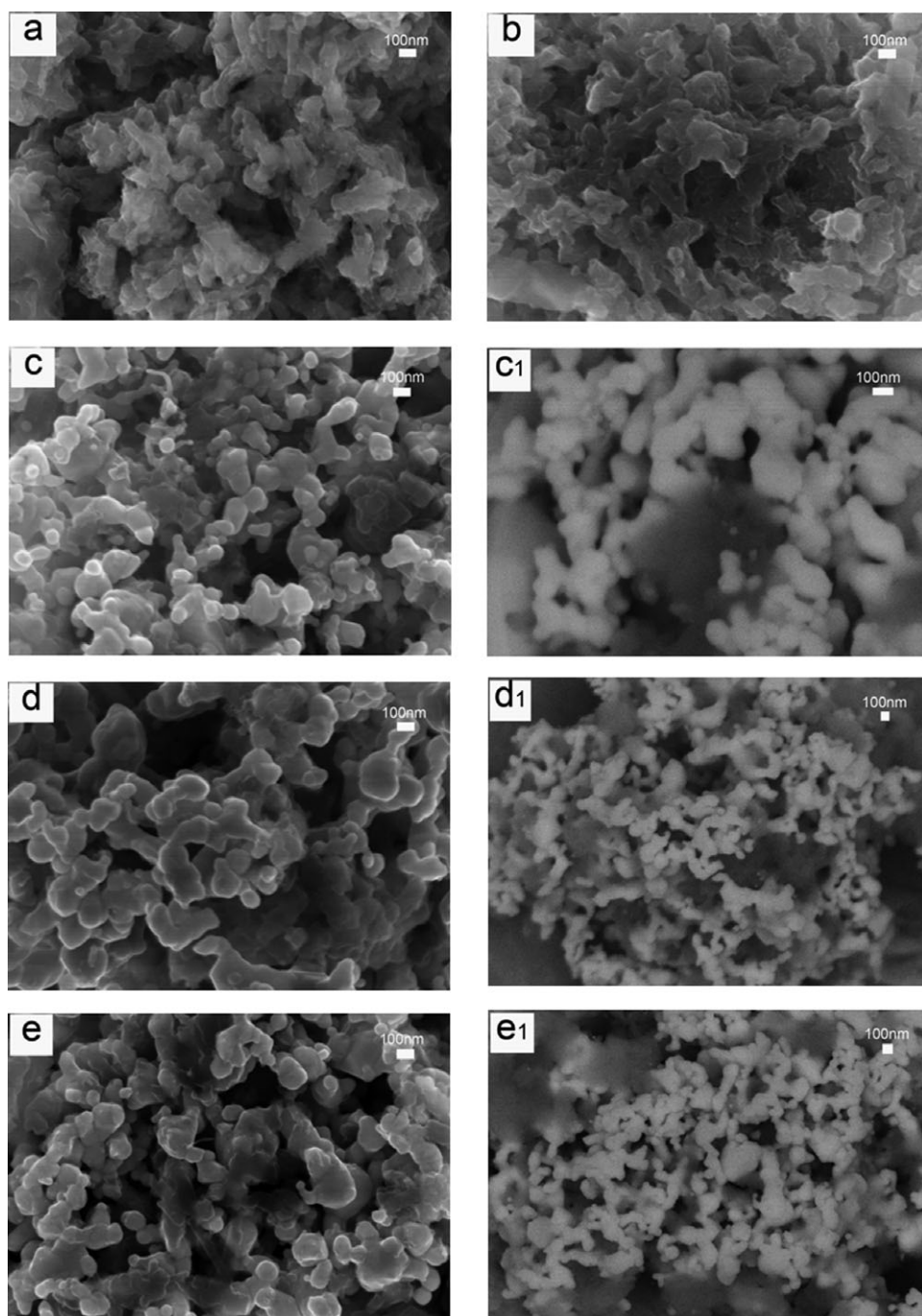


Figure 1. SEM images of (a) PANI, (b) PANI1, (c) PANI-Ag1 nanocomposite, (d) PANI-Ag2 nanocomposite, (e) PANI-Ag3 nanocomposite and back-ground scattering SEM image of (c1) PANI-Ag1 nanocomposite, (d1) PANI-Ag2 nanocomposite, and (e1) PANI-Ag3 nanocomposite.

Step II. Synthesis of PANI-silver (PANI-Ag) composite. PANI-Ag composites were prepared with different molar ratio of sodium borohydride to silver nitrate (1, 1.2, and 1.4, hereinafter called PANI-Ag1, PANI-Ag2, and PANI-Ag3, respectively). The details of the step are as follows. First, 1.4480 g (0.008 mol) of prepared PANI was added into 320 mL of 0.025M silver nitrate solution and the mixture was dispersed by ultrasound accompanied by mechanical stirring for 1 h. A prescribed volume of 0.025M sodium borohydride solution was then added dropwise and the mixture was mechanically stirred for 1.5 h. The resulting product was obtained by vacuum filtration, washed with deionized water, and dried under vacuum at 40°C for 12 h. As a comparative control experiment, PANI was obtained by 1.4480 g of PANI reduced with 448 mL of 0.025M sodium borohydride solution in accordance with the above method in the absence of silver nitrate.

Characterization

Electrical conductivity was measured using the conventional four-probe method on pellets compressed at 20 MPa with a manual hydraulic press at ambient temperature, using the RST-8 four-probe tester. Thermogravimetric analysis (TGA) was performed in air flow ($50 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $10^\circ\text{C min}^{-1}$ with a NETZSCH STA449-C TG analyzer to evaluate the thermal stability of the composite and determine the silver content of the residue. The particle morphology of all the samples was studied on a Hitachi S4800 scanning electron microscopy (SEM). The sample for observation was prepared as follows: a small amount of powder sample was dispersed in ethanol ultrasound for 30 min then dropped on copper to observe the morphology of sample particle. (Before SEM imaging, the samples were not sputtered with thin layers of gold) Infrared spectra were recorded in the $400\text{--}4000 \text{ cm}^{-1}$ range using a fully computerized Thermo Nicolet 6700 Fourier transform infrared spectroscopy (FTIR) Spectrometer. Samples were dispersed in potassium bromide and compressed into pellets. X-ray diffraction (XRD) measurement was performed by the reflection method using a Rigaku 2500 automatic X-ray generator equipped with a goniometer. The X-ray source was graphite-filtered Cu K α radiation ($k = 0.15418 \text{ nm}$) generated at 18 kW.

RESULTS AND DISCUSSION

Electrical Conductivity

Table I summarizes the electrical conductivity of PANI and PANI-Ag composites. As shown, the PANI-Ag composites dramatically differ in their conductivity. When the molar ratio of sodium borohydride to silver nitrate is increased from 1 to 1.2, the composite conductivity increases from 33 to 535.22 S cm^{-1} , decreasing somewhat as the molar ratio was increased to 1.4. The strong influence of the sodium borohydride to silver nitrate molar ratio on electrical conductivity is due to the fact that silver nitrate is reduced by sodium borohydride before PANI is reduced; the conductivity of the composites depends on the oxidation state of PANI and on the silver content. This conclusion is supported by the FTIR and TGA data.

Morphology

Figure 1(a) shows the PANI particles as nanosized and with completely irregular morphology. Analogous morphology was

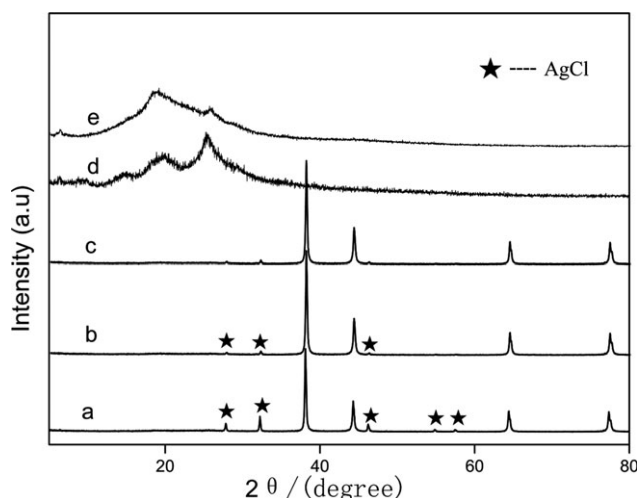


Figure 2. XRD patterns of (a) PANI-Ag1 nanocomposite, (b) PANI-Ag2 nanocomposite, (c) PANI-Ag3 nanocomposite, (d) PANI, and (e) PANI1.

also obtained when PANI was reduced by sodium borohydride in the absence of silver nitrate [Figure 1(b)]. Figure 1(c1–e1) shows the morphology of PANI-Ag1, PANI-Ag2, and PANI-Ag3 particles in back scattering model, we can see PANI particles coat with nano-silver because of different brightness. Figure 1(c–e) shows the morphology of PANI-Ag1, PANI-Ag2, and PANI-Ag3 particles, respectively, formed by PANI particles wrapped with 60–140 nm aspherical nano-silver.

X-Ray Diffraction

Figure 2 shows XRD spectra of PANI and PANI-Ag composites. As shown in Figure 2(d,e), Two broad peaks at $2\theta = 19.6^\circ$ and 25.1° represents the periodicity parallel and perpendicular to the polymer chains of PANI.^{17,18} The X-ray patterns of composite powders following reaction with silver nitrate solutions are in good agreement with standard data of metallic silver. (PDF: 53-0539) All prominent peaks at 2θ values of about 38.3° , 44.5° , 64.6° , and 77.5° coincide with metallic silver provided by our database and correspond, respectively, to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) Bragg's reflection of the silver cubic phase. Additionally, peaks corresponding to silver chloride were observed in Figure 2(a,b); we suspect that silver chloride forms on the surface of PANI due to chloride ions in hydrochloric acid-doped PANI adsorbing silver ions. Therefore, silver particles attached to hydrochloric acid-doped PANI are formed upon reduction of Ag (+) ions to Ag (0) in the presence of excess sodium borohydride.

FTIR Spectra

FTIR spectroscopy is a valuable tool for describing the protonation state of PANI, because this reaction is correlated with changes in the molecular structure of PANI chains. The FTIR spectra of PANI and PANI in PANI-Ag composites (Figure 3) are similar to those reported previously.^{19–21} A broad absorption band above 3463 cm^{-1} is assigned to N–H stretching vibrations; characteristic absorption peaks at around 1585 and 1500 cm^{-1} correspond to C–C stretching vibrations of quinone and benzene, respectively. The peak at 1290 cm^{-1} corresponds to the C–N stretch of a secondary aromatic amine. In-plane

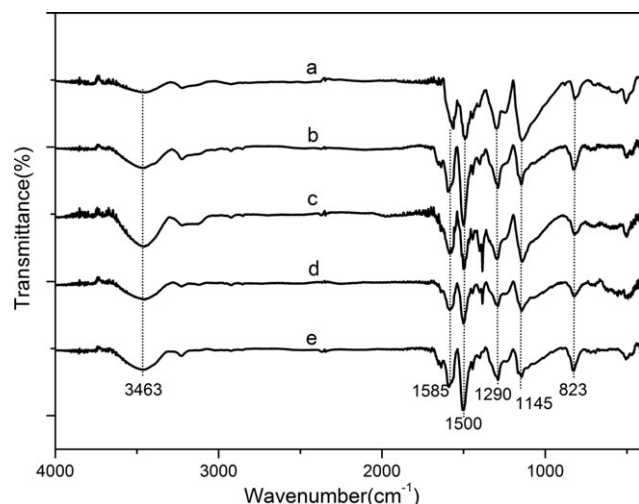


Figure 3. FTIR spectra of (a) PANI, (b) PANI1, (c) PANI-Ag1 nanocomposite, (d) PANI-Ag2 nanocomposite, and (e) PANI-Ag3 nanocomposite.

bending modes of the aromatic C—H are visible at 1145 cm^{-1} , and the peak at 823 cm^{-1} represents out-of-plane deformations of C—H on 1,4-disubstituted rings.

Some minor differences were evident between the IR peak distributions of PANI-Ag prepared with different molar ratios of sodium borohydride to silver nitrate. The small shoulders peak appearing at about 1637 cm^{-1} corresponds to N—H scissoring vibrations of aromatic amines,²¹ and the intensity of peak is gradually increased indicating more benzenoid unit. As well as the intensities of C—C stretching vibrations of the quinonoid and aromatic rings is different. The ratio of the relative intensity of these two peaks can be used to estimate the oxidation state of PANI.^{22–27} The percentage of reduced units (x) versus the percentage of oxidized units (y) was obtained by integration of the FTIR bands (Figure 4):¹⁷

The ratio of x to y (R) for every sample is presented in Table II.

$$R = \frac{x}{y} = \frac{\text{Area}_{\text{reduced}}}{\text{Area}_{\text{oxidized}}} = \frac{\text{Area}_{\nu(1500\text{cm}^{-1})}}{\text{Area}_{\nu(1585\text{cm}^{-1})}} \quad (1)$$

where $\text{Area}_{\text{oxidized}}$ designates the oxidized units area, $\text{Area}_{\text{reduced}}$ designates the reduced units area, $\text{Area}_{\nu(1585\text{ cm}^{-1})}$ is the area of $\nu(1585\text{ cm}^{-1})$, and $\text{Area}_{\nu(1500\text{ cm}^{-1})}$ is the area of $\nu(1500\text{ cm}^{-1})$. As shown in Table II, PANI contained nearly balance of oxidized and reduced units, and R gradually reduced of PANI-Ag1, PANI-Ag2, PANI-Ag3, and PANI1. It is known that a greater or

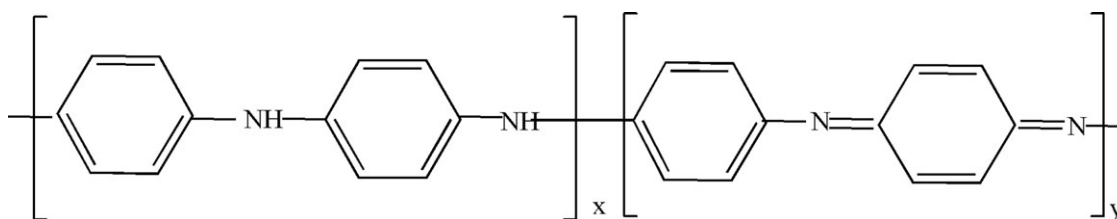


Figure 4. The structure schematic diagram of the PANI.

Table II. R Value of PANI and PANI-Ag Composite

Sample	PANI	PANI1	PANI-Ag1	PANI-Ag2	PANI-Ag3
R	1.230	1.775	1.243	1.280	1.610

lower ratio of oxidized to reduced units decreases the conductivity of PANI, namely, when the oxidized units are equivalent to the reduced units, the conductivity of PANI is best. Thus, the IR data suggest the conductivity of PANI-Ag nanocomposite should decrease slightly at a sodium borohydride to silver nitrate molar ratio of 1.4, in agreement with conductivity data.

Thermogravimetric Analysis

Theoretically, PANI base (8 mmol and 1.4480 g) reduces an equimolar amount of silver nitrate (8 mmol and 1.3590 g) to metallic silver (864 mg); the composite of silver and pernigraniline base produced would therefore contain 37.6 wt % silver.¹² The higher silver content observed may be explained by a decrease in the mass of PANI due to loss of chloride ions from residual emeraldine during treatment with silver nitrate and sodium borohydride, which would make the fraction of silver formally higher. This is in agreement with the results of XRD analysis.

TGA is the preferred method for evaluating the silver content of homogeneous samples; with heterogeneous samples, larger amounts are required for accurate analysis, thus, an ash is used for the determination of silver content.²⁸ TGA allows convenient determination of the silver content of the residue left above 850°C . The TGA curves (Figure 5) provide additional information about PANI and PANI-Ag; for example, the residue of a reference PANI and PANI1 samples without silver was $<1\text{ wt \%}$ above 600°C , which indicates the complete destruction of PANI taking place at $\sim 600^{\circ}\text{C}$; additionally, the silver content of PANI-Ag1, PANI-Ag2, and PANI-Ag3 was observed to be 34.33, 38.48, and 39.64%, respectively.

CONCLUSIONS

In summary, we have synthesized highly conductive PANI-silver nanocomposites using a two-step method with sodium borohydride reduction. Compared with pure PANI, the PANI-silver nanocomposites show enhanced electrical conductivity. Deprotonating and reprotonating of PANI is not required for our method, offering an advantage over other two-step methods for preparing PANI-silver nanocomposite, and thus requiring less time for reducing silver nitrate and increasing the silver content in the complexes. The conductivity of the prepared nanocomposites increased with increasing molar ratio of sodium

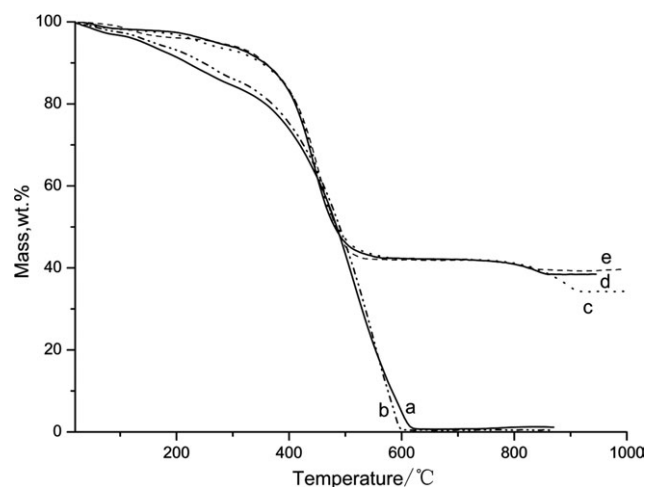


Figure 5. TGA of (a) PANI, (b) PANI1, (c) PANI-Ag1 nanocomposite, (d) PANI-Ag2 nanocomposite, and (e) PANI-Ag3 nanocomposite.

borohydride to silver nitrate, reaching a maximum conductivity of 535.22 S cm^{-1} and 38.48 wt % silver at a molar ratio of 1.2, with conductivity decreasing somewhat at a higher molar ratio. Our results also demonstrate that the conductivity of the composite produced depends on both the oxidation state of PANI and the silver content.

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