Fabrication of Polyaniline/Silver Nanocomposite Under Gamma-ray Irradiation

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Polyaniline (PANI)/silver composite was one-step synthesized under γ-ray irradiation. The structure of the composite was characterized by Fourier transform infrared spectroscopy, UV-Visible, and X-ray diffraction, which indicated that PANI and face-centered-cubic silver were synthesized under γ-ray irradiation. The reaction mechanism were discussed, which revealed that the PANI was formed by the reaction of aniline cation radicals formed by the reaction of aniline cation and ·OH, and Ag was formed by the reaction of Ag+ and e−aq. The morphology of the composite consisted of PANI nanofibers and Ag nanoparticles, and the mechanism of the morphology formation was discussed, which revealed that the rapid mixing like polymerization process might play an important role. It was revealed that the transport behavior of the composite well fitted with the variable-range-hopping model in 80–300 K and deviated from the model below 80 K.

Key words: Polyaniline, Silver composite, Nanofiber, Transport property

I. INTRODUCTION

Recently, fabricating of nanostructured polymer/inorganic hybrid materials has been studied extensively. Polymer doped with a suitable material often exhibits better performance than the pristine polymer in many aspects. Among the polymer/inorganic composites, polymer/metal composites are particular useful as they combine the electrical characteristic of metals and mechanical and processing properties of polymers [1]. The composite of conductive polymer polyaniline (PANI)/silver has attracted much interest because of its environmental stability, conductivity, photonic property, antibacterial property and wide applications in gas sensor, anti-corrosion coating, photonic device, biology device, etc. [2–5].

For the synthesis of PANI/silver composite, many methods have been applied. Generally, these methods can be classified into one-step method and two-step method. In the two-step method, the synthesis of PANI and silver were carried out separately. Besides the direct mixing of PANI and silver together, other methods have also been reported [6]. Shin et al. reported the synthesis of PANI/silver by heating the composite of PANI and organometallic silver compound at 150–230 °C [7]. Choudhury reported the polymerization of aniline in Ag nanoparticle colloid, resulting in PANI/silver composite [8]. Nesher et al. reported synthesis of PANI/silver by the reduction of silver nitrate with N,N-dimethylformamide (DMF) in PANI solution [9]. In the one-step method, Ag+ is reduced by aniline monomer or low oxidized PANI, resulting in PANI and silver simultaneously. However, the reduction of the Ag+ is rather slow, which takes several weeks for the reduction to be completed. So in the two-step method, UV light and ultrasound waves were often applied to accelerate the reaction [10–15]. The composite synthesized by one-step method often exhibit more uniform morphology than that synthesized by the two step methods. In the one-step method Ag was composited by the molecular reaction while in the two-step method Ag was composited by physical mixing, which might be better for the performance of the composite.

γ-ray irradiation is a facile technology in the synthesis of polymer/silver nanocomposite, as shown in our previous work [16–18]. In the synthesis of PANI/silver nanocomposite, the use of γ-ray irradiation had also been reported. Pillalamarri et al. synthesized PANI/silver by the irradiation of the water solution containing AgNO3, aniline and oxidant in one pot, resulting in PANI nanofibers and Ag nanoparticles [19]. Kang et al. synthesized PANI/silver by two steps, they first synthesized the silver colloid by irradiation of AgNO3 with isopropanol as scavenger in ethanol solution, then synthesized PANI in the silver colloid by adding aniline and oxidant [20]. Karim et al. did the similar research in water solution, resulting in silver/PANI core-shell nanostructure [21]. However, there are few report of one-step synthesis of PANI/silver under γ-ray irra-
diation. Moreover, up to now, most research focused on the nanostructure of the PANI/silver composite and less on its transport property.

In this work, we studied the one-step facile synthesis of PANI/silver composite under γ-ray irradiation. The morphology, structure, reaction mechanism as well as the transport property of the composite were investigated.

II. EXPERIMENTS

In a typical synthesis, 6.8 g (40 mmol) AgNO₃ and 1.5 mL (16 mmol) aniline were dissolved in 40 mL HNO₃ solution in a glass vial with stirring in dark. After that, the mixture was aerated with N₂ for 30 min to remove the oxygen solvated in the system and irradiated with a 1.2×10¹⁵ Bq ⁶⁰Co γ-ray source at a dose rate about 30 Gy/min for an adsorbed dose of 8×10³ Gy. After the irradiation, the mixture was collected by centrifugation and washed with deionized water and ethanol for 3 times, respectively. Then the sample was dried under vacuum at room temperature for 48 h.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded with a Nicolet Instrument Co. MAGNA-IR 750 FTIR spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2401PC UV-Vis spectrophotometer. The crystal structures of the samples were characterized by a MAC Science MX-PAHF 18-kW rotating anode X-ray diffractometer with graphite monochromatized Cu Kα (λ=1.54187 Å) radiation in the Bragg-Brentano geometry at room temperature. Scanning electron microscope (SEM) examination of the samples were performed on a JSM 6700F (JEOL) field emission scanning electron microscope. The samples were sputtered with gold for 30 s before examination. Transmission electron microscope (TEM) images were recorded on a Hitachi-800 TEM at an acceleration voltage of 200 kV. The samples were deposited from ethanol suspensions of the products onto thin amorphous carbon films supported by copper grids before examination. The electrical character of the sample was measured by a standard four-probe method.

III. RESULTS AND DISCUSSION

A. Structural analysis

Figure 1 shows the FTIR spectra of the samples prepared at different conditions. In all the spectra of the samples, characterized peaks of PANI at around 1140, 1230, 1300, 1485, and 1575 cm⁻¹ were found, which can be assigned to the C−H in plane bending, C=N stretching, C−N stretching, C=C stretching of benzenoid ring, and C=C stretching of quinoid ring, respectively [6, 22]. These peaks indicated the forming of PANI in all samples. The peak at around 1385 cm⁻¹ was assigned to the nitrate contour-ions, indicating that the PANI in the samples was in emeraldine salt form [10]. The weak peaks at 1440 and 1640 cm⁻¹ were assigned to the phenazine structure of PANI. The peaks at around 3230 and 3500 cm⁻¹ were assigned to the N−H stretching and hydrogen bond interaction in the PANI, respectively [23, 24].

Figure 2 shows the typical UV-Vis spectra of the PANI/silver composite and pristine PANI in emeraldine base form. For the spectra of both PANI/silver composite and pristine PANI, two peaks at around 335 and 630 nm were found, which were characterized peaks of PANI emeraldine base and could be assigned to the π−π* transition and electron transition from benzenoid to quinoind rings [25]. However, in the spectrum of the PANI/silver, another peak at 270 nm was found, which could be assigned to the characteristic absorption of small metallic Agₙ clusters, as discussed in our previous work [17].

Figure 3 shows the XRD patterns of the samples prepared under different conditions. As can be seen, for all the samples five sharp peaks at 38.1°, 44.3°, 64.5°, 77.4°, and 81.6° were found, which could be assigned to the (111), (200), (220), (311), and (222) diffraction peaks of the face-centered-cubic silver (JCPDS No.04-0783) [13]. Meanwhile, the crystal grain sizes of the
silver, which were calculated by Scherrer’s equation using the full width at half maximum (FWHM) of the face (110), were in the range of 20–60 nm, which indicated that the crystal grain sizes of the silver were affected by the synthesis conditions. Two peaks at 19.5° and 25.6° are also found (for some samples, the two peaks are very weak), which corresponds to the distance of crystal planes of 4.6 and 3.5 Å, and could be assigned to the periodical length in the direction parallel and perpendicular to the polymer chain, respectively [26].

B. Reaction mechanism

On the basis of our previous research, we propose here a plausible mechanism for the reaction, as can be seen in Fig.4 [16–18]. The aniline monomer tends to form aniline salt with the H+ of the acid, resulting in aniline cation and acid contour-ion (Fig.4(a)) [27]. Ag+ is known to have high reactivity with e−aq, resulting in Ag (Fig.4(d)). PANI was formed by the reaction of the aniline cation radicals that were formed by the reaction of aniline cation and ·OH (Fig.4 (c) and (e)). We investigated the irradiation of the mixture containing AgNO3, nitric acid, and aniline in the presence of ·OH scavenger, no PANI/silver composite was synthesized during the irradiation, which confirmed the reaction of Fig.4 (c) and (e).

The acid is also an important factor in the synthesis of PANI/silver. We investigated the irradiation without acid and no PANI/silver was synthesized. This indicated that the aniline reacting in the irradiation system was in its cation form. To exclude the effect of contour-ion of the acid, the irradiation in the presence of organic acid camphorsulfonic acid was taken and PANI/silver was obtained, which indicated that the contour-ion of the acid impact little on the synthesis of PANI/silver.

C. Morphology analysis

Figure 5 shows the SEM and TEM images of the samples prepared at different [AgNO3]. As can be seen in

![FIG. 4 Illustration of the reaction mechanism.](image)

![FIG. 5 XRD patterns of the samples prepared at different [AgNO3]. (a) 0.25 mol/L, (b) 0.5 mol/L, (c) 0.75 mol/L, (d) 1.0 mol/L, (e) 1.5 mol/L, while [AgNO3]/[aniline]=2.5.](image)
obtained. Meanwhile, when the [AgNO₃] was increasing, the growth as well as chances of the aggregation would increase, resulting in the changes in diameter and length of the nanofibers and the core-shell nanostructure.

D. Transport property

The transport property is an important aspect of PANI and is investigated by many researchers. However, the charge transport property of PANI is very complex and can be affected by many factors like doping level, crystallinity, proton acid, molecular weight etc. There is not a model or mechanism that can fully describe the transport behaviors of all PANI. Because of the complexity of the transport behavior of PANI, the PANI composite would be more complex in transport behavior. Generally, there are mainly three equations including Arrhenius law (Eq.(1)), variable-range-hopping (VRH) model (Eq.(2)), and thermal activated model (Eq.(3)), those are used to describe the transport behavior in PANI composite [29–34].

$$\sigma = \sigma_e \exp \left( \frac{E_F - E_C}{k_B T} \right)$$ (1)

where $E_F - E_C$ is the energy difference between the Fermi energy and the mobility edge, $\sigma$ is the conductivity at the temperature $T$, $\sigma_e$ is the conductivity at the mobility edge.

$$\sigma = \sigma_0 \exp \left( - \left( \frac{T_0}{T} \right) ^\alpha \right)$$ (2)

$\alpha$ can be 0.25 and 0.5, corresponding to the one-dimensional VRH (1D-VRH) and three-dimensional VRH (3D-VRH) model, respectively. $T_0$ is the Mott’s characteristic temperature and $\sigma_0$ is the conductivity at $T_0$.

$$\sigma = \sigma_0 \exp \left( - \frac{\sqrt{T_0}}{T} \right)$$ (3)

Figure 6(a) shows a typical curve of the variation of conductivity with temperature of the PANI/silver composite. As can be seen, the conductivity decreases with the decrease of the temperature, which indicates a semiconductor transport character. To investigate the charge transport property of the sample, the temperature-conductivity curved line was fitted with both 1D-VRH and 3D-VRH model (Fig.6 (a1), (a2)). In general, it can be seen that the fitted curved line exhibit well linearity at relatively high temperature (>100 K) and poor linearity at relatively low temperature (<100 K). To further investigated the transport property of the PANI/silver composite, we fitted the temperature-conductivity curve with the 1D-VRH and
FIG. 6 Typical temperature-conductivity curves of the composite and its fitted curves by 1D-VRH (1 series) and 3D-VRH model (2 series) at (a) full temperature range, (b) 80–300 K, and (c) below 80 K.

3D-VRH model in the range of 80–300 K and below 80 K, respectively (Fig.6 (b1), (b2), (c1), and (c2)). As can be seen in Fig.6(b1), the curve fitted with 1D-VRH model at 80–300 K exhibits a well linear dependence with a linear factor as high as 0.9996. The curve fitted with 3D-VRH model at 80–300 K also exhibits a well linear dependence with a linear factor (LF) of 0.9970 (Fig.6 (b2)). However, the curves fitted with both 1D-VRH and 3D-VRH model below 80 K exhibit poor linear dependence with their linear factors less than 0.98, indicating that transport behavior of the composite deviates from the VRH model at low temperature.

We also checked the Arrhenius law and activated energy models, but the linearity was not well in the two models. The transport behaviors of other samples prepared at different [AgNO₃] were similar to this one and were not given here.

The highest room temperature conductivity of the samples was about 300 S/cm, which is three orders of magnitude higher than the pure PANI [13]. The room temperature conductivities of other samples prepared at different [AgNO₃] are in the range of 10–100 S/cm.

IV. CONCLUSION

In conclusion, PANI/silver nanocomposite was one-step synthesized under γ-ray irradiation. The structure of the composite was confirmed by FTIR, UV-Vis, and XRD characterization, which indicated that PANI and face-centered-cubic phase silver were synthesized. The investigation of reaction mechanism has revealed that the PANI was formed by the reaction of the aniline cation radicals and Ag was formed by the reaction of Ag⁺ and e⁻. The aniline cation radical was formed by the reaction of aniline cation and ·OH. The morphology of the composite consists of PANI nanofibers and silver nanoparticles. The mechanism of the morphology formation can be described by the rapid mixing like polymerization process in the irradiation system. The transport behavior of the sample is fitted well by the VRH model from 80 K to 300 K and deviates from the VRH model below 80 K, which indicates that there is a change of conducting mechanism around 80 K.

V. ACKNOWLEDGMENTS

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