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A convenient route to polyacrylonitrile/silver nanoparticle composite by simultaneous polymerization–reduction approach

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Abstract

Polyacrylonitrile (PAN)/silver (Ag) nanoparticle composites were in-situ synthesized by ultraviolet irradiation of a mixture of silver nitrate ($AgNO_3$) and acrylonitrile (AN) monomers. The resultant composites were characterized by infrared spectroscopy (IR), X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (TEM). It was found that polymerization of AN monomers and reduction of silver ions occurred simultaneously, thereby leading to the formation of the PAN/Ag composites. TEM image revealed that silver nanoparticles with a diameter ranging from 5 to 10 nm were well dispersed in PAN matrix. It was found from the reaction mechanism that the complex of silver ions with AN monomers provided an excellent precursor for this synthesis, which is responsible for homogeneous dispersion and narrow size distribution of silver nanoparticles. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyacrylonitrile; Silver; Nanoparticles

1. Introduction

Polymer/inorganic nanoparticle composites have been the focus of extensive research efforts through the past decade [1–6]. The introduction of inorganic nanoparticles into the polymer matrix has proved to be an effective and low-cost method to improve the performance of the already existing polymer materials [1–3,6]. Polyacrylonitrile (PAN) is an important engineering polymer material that has been widely used to produce a variety of synthetic fibers. However, strong static electricity makes PAN fibers to absorb dust and microbes easily. It is well known that silver is superior to other nanostructured metal particles for many reasons such as electrical conductivity [7], antimicrobial effects [8], optical properties [9] and oxidative catalysis [10]. Therefore, PAN/Ag nanoparticle composites are expected to provide a possibility to produce functional fibers with anti-electrostatic, fungicidal and ultraviolet-resisting effects.

Many different approaches have been used to prepare polymer/metal nanocomposites. Conventionally, polymerization of monomers and formation of metal nanoparticles were separately performed, and then the polymer and the nanoparticles were mechanically mixed to form composites [11]. However, it is extremely difficult to disperse nanoparticles homogeneously into the polymer matrix, due to the easy agglomeration of nanoparticles and the high viscosity of polymer. In recent years, more attention has been paid to the in-situ synthesis of metal nanoparticles in polymer matrices. This method is based on the reduction of metal ions that are dispersed in polymer matrices. Many polymer thin films, containing noble metal nanoparticles, were prepared by reducing the polymer metal chelate films, such as polyaniline (PANI)/Au, poly(vinyl alcohol) (PVA)/Ag, poly(acrylic acid) (PAA)/Cu [4,12,13]. In addition, PAN/Ag and PVA/Ag composite films were obtained by heat-treatment of silver chelate films [9,14]. Other polymer films containing noble metal nanoparticles were also fabricated using various procedures [15]. More recently, a completely different method was employed to prepare polymer/silver nanoparticle composites, in which the reduction of Ag^+ ions and the polymerization of monomers occurred simultaneously by γ-irradiation [16,17]. Thus, the in-situ nanoparticles were well dispersed homogeneously in polymer matrix. However, the syntheses were mainly carried out in aqueous or alcohol medium since inorganic metal salts, the metal source, only dissolve in these solvents.

Here, we report a convenient procedure for the in-situ preparation of PAN/Ag nanoparticle composite. In the absence of solvent and reducing agent, the polymerization of monomers and reduction of Ag^+ ions occurred simultaneously via ultraviolet irradiation. The reaction mechanism is discussed in detail.

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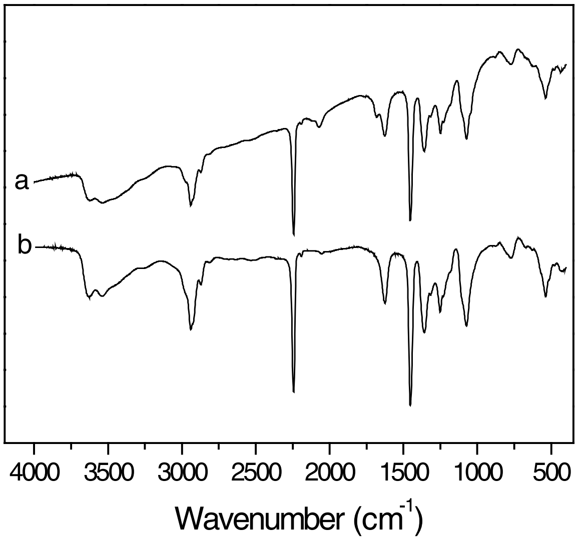


Fig. 1. The FTIR spectra of (a) PAN/Ag nanoparticle composite and (b) pure PAN.

2. Experimental

2.1. Materials

Acrylonitrile (AN) monomer and high purity silver nitrate ($AgNO_3$) were supplied by Shanghai Chemical Reagent Company (China). Benzoin methyl ether was purchased from Tokyo Kasei Kogyo (Japan). Before being used, AN monomer was washed with 5% aqueous NaOH, dried with $CaCl_2$, and then redistilled. Other reagents were used as received.

2.2. Synthesis of PAN/Ag nanoparticle composites

In a typical procedure of PAN/Ag nanoparticle composite, 1.5 g silver nitrate ($AgNO_3$) and 10 mg benzoin methyl ether (as a photoinitiator) were directly dissolved in 30 ml AN monomers at room temperature. The solution was put into a quartz tube, and irradiated with a 125 W mercury lamp for 16 h under N_2 atmosphere. The ultraviolet irradiation caused polymerization of monomers and reduction of Ag^+ ions, simultaneously. The resultant product was carefully washed with distilled water, and further extracted with de-ionized water in Soxhlet extractor so as to remove residual $AgNO_3$. After drying in vacuum oven, the final product was obtained.

The pure PAN was also prepared using the similar procedure as described above.

2.3. Characterization of PAN/Ag nanoparticle composite

The powder samples were pressed into pellet together with KBr for Fourier transform infrared spectroscopy. All infrared spectra were recorded on a Nicolet Model 759 FTIR spectrometer, with the wavenumber ranging from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. The X-ray powder diffraction (XRD) patterns were determined at a scanning rate of 4° min^{-1}, using DXP-18AHF, CuKα diffractometer. The shape, distribution and the crystalline lattice of silver particles were observed by high-resolution transmission electron microscopy (TEM). Before observation, the sample was carefully ground and ultrasonic-dispersed in ethanol. All photographs were taken on JEOL 2010 transmission electron microscope.

3. Results and discussion

3.1. Characterization of PAN/Ag nanoparticle composites

Fig. 1 shows the FTIR spectra of the PAN/Ag nanoparticle composite and pure PAN. It was found that the positions of all peaks were identical in both PAN/Ag composite and pure PAN, which confirms the polymerization of AN monomers and the formation of PAN upon UV-irradiation. Though the ratio of Ag to PAN was increased in production, a shift of the C–N triple bond vibration (at 2244 cm^{-1}) was not detected by IR measurement. This implies that, in the resultant products, there were no chemical linkage or strong interaction between PAN and Ag nanoparticles. The possibility to form a complex between PAN and metal Ag is negligible here. Furthermore, the phase structures of the obtained products were characterized by X-ray powder diffraction (XRD) as shown in Fig. 2. The XRD pattern of pure PAN shows a sharp crystalline peak (17°) and a broad non-crystalline peak (20–30°) in Fig. 2(b). PAN is an unusual polymer in that even an atactic sample can crystallize. The characteristic peak at 17° corresponds to orthorhombic PAN (110) reflection [18]. However, the PAN/Ag composite exhibits a two-phase structure in XRD pattern, as shown in Fig. 2(a). Besides the diffraction peaks of PAN phase mentioned above, the other three peaks

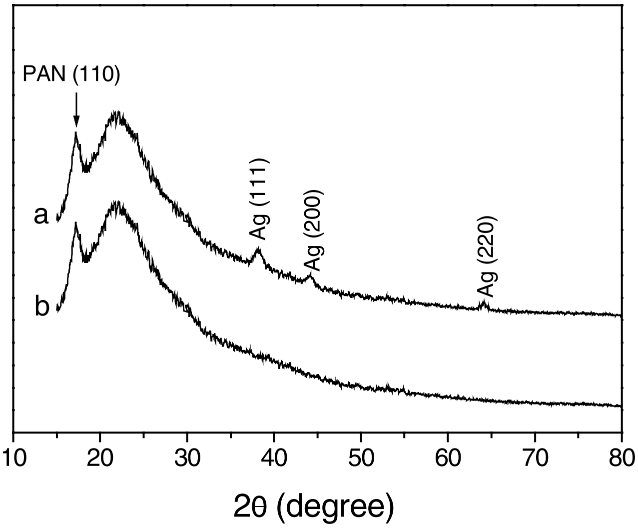


Fig. 2. The XRD patterns of (a) PAN/Ag nanoparticle composite and (b) pure PAN.

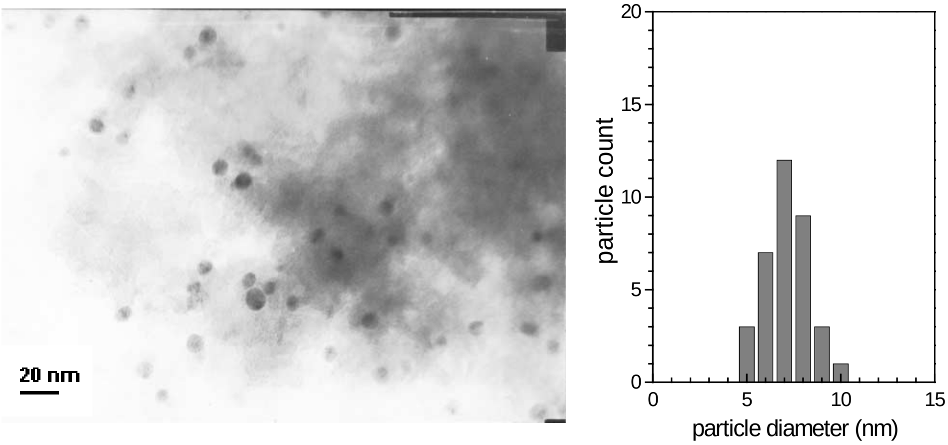


Fig. 3. The transmission electron micrograph and size distribution of nanoparticles for PAN/Ag nanoparticle composite.

correspond to the face center cubic (fcc) silver phase (111, 200, 220) with cell parameter $a = 0.4089$, which is close to the reported data (JCPDS File No. 4-0783). On the other hand, the broadening of these peaks suggests the presence of small silver particles. These results reveal that the product is a composite consisting of a polymer phase and silver nanoparticles.

Fig. 3 presents a TEM image of a typical product. The image shows that nanoparticles are well distributed in PAN network. The observed sizes of particles are about 5–10 nm. Corresponding histograms of nanoparticle size, which are also presented in Fig. 3, reveal a very narrow particle size distribution. The average size diameter is about 7 nm. It was well known that polymers, as protecting agents, are very effective to inhibit the agglomeration of particles. The in-situ occurrence of monomer polymerization and metallic ion reduction should be more beneficial to the formation of well-dispersed and narrow size-distributed nanoparticles.

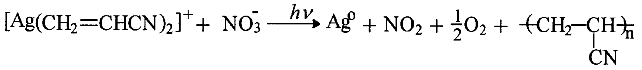
Further, high-resolution electron microscopy (HREM) can provide a deeper insight into the property of the formed particles. Fig. 4 presents HREM image of a single nanoparticle. It can be seen more clearly that the nanoparticle is embedded in polymer matrix. Particularly, the lattice fringes reveal a good crystalline order. The spacing of 0.2352 nm correspond to the (111) plane. The deduced crystalline lattice is equal to 0.409 nm, which is in agreement with the structure of fcc silver. The result further demonstrates that the nanoparticles shown in Fig. 3 are indeed the nanocrystalline of metallic silver.

3.2. Mechanism of synthesis

The in-situ synthesis is based on the finding that silver nitrate ($AgNO_3$) can directly dissolve in AN monomer at room temperature. It has been shown in Refs. [19,20] that silver ions can reversibly react with some olefin molecules to form silver–olefin complexes. Olefin molecules can donate their π-electrons from the occupied 2p orbitals to empty s orbitals of silver ions to form σ-bonds. The back-donation of electron density from occupied d orbitals of silver ions into the empty π^*-2p antibonding orbitals of olefin molecules leads to the formation of π-bonds. The process of silver ions coordinating with AN monomers can be described as follows:

$$Ag^+ + 2CH_2{=}CHCN \rightleftharpoons [Ag(CH_2{=}CHCN)_2]^+ \quad (1)$$

The reversible and specific reaction makes AN monomer an ideal carrier of silver ions, which provides an excellent precursor to synthesize in-situ silver nanoparticles. When the solution was irradiated by ultraviolet, the photoinitiator could induce radical polymerization of AN monomers. At the same time, the coordinating Ag^+ was reduced into metallic silver by photochemical reaction, as described in Eqs. (2) and (3).



$$[Ag(CH_2{=}CHCN)_2]^+ + NO_3^- \xrightarrow{h\nu} Ag^0 + NO_2 + \tfrac{1}{2}O_2 + \left(CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}\right)_n \quad (2)$$

$$nAg^0 \rightarrow (Ag)_n \quad (3)$$

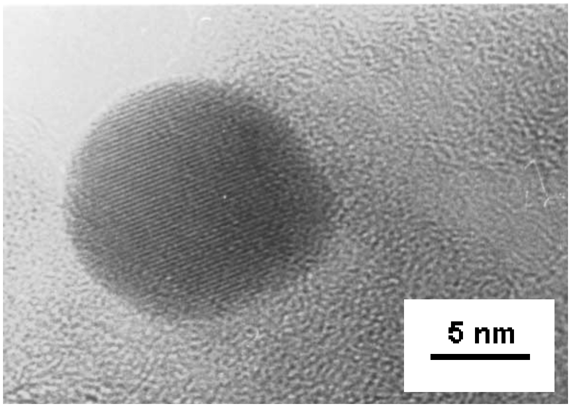


Fig. 4. The high-resolution transmission electron micrograph of Ag nanoparticle in PAN matrix.

Since polymerization and reduction occurred simultaneously, the resulting silver nanoparticles can be spontaneously dispersed in PAN matrix. Further, the narrow particle size distribution may imply that a complex of silver ions with AN monomers plays an important role in particle size distribution.

It was found experimentally that the process of polymerization did not occur in the absence of photoinitiator. Therefore, UV-irradiation cannot directly excite AN monomers to form radicals. Photoinitiator is necessary for the occurrence of polymerization.

In summary, PAN/Ag nanoparticle composite was prepared with simultaneous polymerization–reduction photochemistry route. Silver nanoparticles with narrow size distribution were obtained and were well dispersed in PAN matrix. The synthesis can successfully proceed at room temperature and atmospheric pressure. On the other hand, an important advantage of the in-situ synthesis is that there are no additives (e.g. solvent, surface-active agent and reductant of metallic ions) used. Therefore, the product may be directly used for industrial purpose. Further investigations on anti-electrostatic, anti-microbial and ultraviolet-resisting effects of the composite are currently in progress.

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