

Preparation and optical property of soluble polyimide–silver nanocomposites

Jun-chao Huang, Xue-feng Qian, Ying Ji, Jie Yin, Zi-kang Zhu

School of Chemistry and Chemical Technology,
Shanghai Jiao Tong University, Shanghai 200240, China

1. Introduction

There is intense interest in the synthesis and properties of metal clusters and nanoparticles prepared in both aqueous and organic solutions and prepared in condensed state, for instance, polymers, zeolites and glasses. Clusters, nanoparticles and its-containing materials are potentially useful in a wide range of application, including highly active catalysts ^[1], magnetic materials ^[2], quantum dots and miniaturization of electronic devices ^[3] and nonlinear optical materials ^[4].

We are interested in the ultraviolet irradiation induced reduction of silver ions in polymeric matrices with the concomitant formation of silver nanoparticles, which would ultimately be used for optical application, for it is well known that the third-order optical nonlinearity in the materials doped with metal nanoparticles is strongly enhanced near the surface plasmon resonance frequency. By a sputtering method, ^[5] a wide variety of metal particles can be introduced into the polymer matrices. However, the requirement for the equipment is very high and the metal particles in polymers are not well dispersed using this method. Recently, a γ -irradiation technique has been developed to prepare metal-polymer nanocomposites with homogeneous dispersion of metal nanoparticles in polymer matrices ^[6]. This approach is based on the *in-situ* irradiation reduction of metal ions in the polymer matrix by hydrated electrons produced during the γ -irradiation process. However, the γ -irradiation technique is limited to extend for commercial applications due to the nuclear pollution. In comparison to the γ -irradiation, ultraviolet irradiation has the advantages of easier accessibility, higher safety and can be much more widely used in industry.

In this report, we demonstrate a novel convenient ultraviolet irradiation technique for preparing polyimide(PI)-silver nanocomposites at room temperature. It was found that the silver nanoparticles were homogeneously dispersed in the polyimide matrix and the PI/silver nanocomposites exhibited an ultraviolet-visible (UV-Vis) absorption peak, corresponding to the characteristic surface plasmon resonance of silver particles. In addition, this method may also be extended to prepare other inorganic-polymer nanocomposites.

2. Experimental

0.01 mol MMDA, 0.01 mol OPDA and 2 drops of *iso*-quinoline were dissolved in 40 ml *m*-cresol, consecutively. The mixture was stirred at room temperature for 2 hours and then at 180 °C for 3 hours. The obtained PI solution was precipitated in 200 ml ethanol. The precipitate was immersed in distilled water and ethanol for 2 hours, respectively, and was washed with distilled water and ethanol for several times to remove the residual *m*-cresol. The intrinsic viscosity of this soluble polyimide is 1.3 dl/g and its chemical structure is shown in Fig. 1.

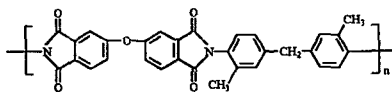


Fig. 1 Chemical structure of the soluble polyimide.

A 250W high-pressure mercury lamp was used as the ultraviolet irradiation source. Two precursors (AgAc , AgNO_3) were introduced as the source of Ag nanoparticles. In one method, 2 g soluble polyimide was dissolved in 14 ml NMP and 1×10^{-3} mol AgAc and 1.2×10^{-3} mol TFA was dissolved in 5 ml NMP. The two solutions were then mixed and irradiated for 12 hours to ensure the complete reduction of AgAc under ultraviolet irradiation at room temperature. Then the product was precipitated quickly to distilled water and washed with distilled water several times. After being dried in vacuum the product was redissolved in chloroform by sonication, and was cast on a glass substrate and dried at 30°C in vacuum for a week. It is worth noting that AgAc is not soluble in NMP. However, if one or more equivalents of TFA are dissolved in NMP followed by the addition of AgAc , AgAc was then dissolved completely with the formation of Ag(I)-TFA complex. When AgNO_3 was used as the source of silver, no addition of TFA was required since AgNO_3 was dissolved in NMP. Apart from the omission of TFA, the procedure of the preparation of PI/silver nanocomposites using AgNO_3 as the source of Ag was identical to that using AgAc .

3. Results and discussion

The FT-IR spectrum of the soluble PI exhibits characteristic absorption peaks of polyimide (Fig. 2). The characteristic absorption bands are observed for C=O unsymmetrical stretching in imide groups (at 1780 cm^{-1}), C=O symmetrical stretching in imide groups (at 1720 cm^{-1}) and C-N stretching in imide groups (at 1380 cm^{-1}). These bands are similar to the literature values [7] and indicate that the soluble PI has been successfully synthesized. In addition, no obvious difference between the infrared spectra of the pure PI and the PI/silver nanocomposites was observed.

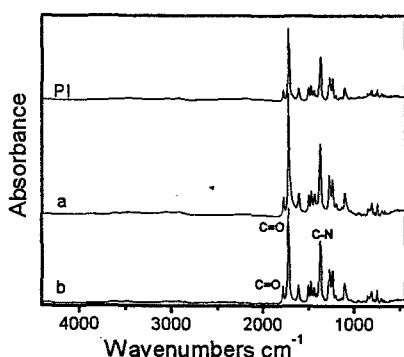


Fig. 2 FT-IR spectra of the soluble polyimide(PI) and the PI/silver nanocomposites prepared by the ultraviolet irradiation technique: PI/silver nanocomposite from the precursor AgAc (a) and AgNO_3 (b).

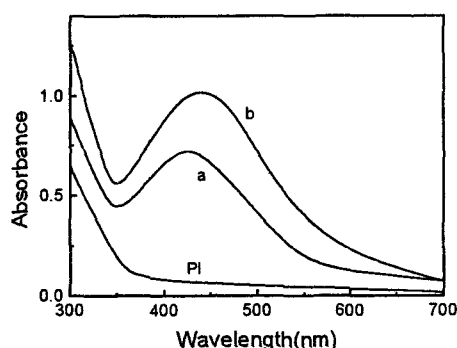


Fig. 3 UV-Visible spectra of the soluble polyimide and the PI/silver nanocomposites prepared by the ultraviolet irradiation technique: PI/silver nanocomposite from the precursor AgAc (a) and AgNO_3 (b).

Fig. 3 shows the UV-Vis absorption spectra of the soluble PI and the PI/silver nanocomposites.

The PI shows no obvious absorption at wavelength above 400 nm. The PI/silver nanocomposites (a, b), however, show two broadened peaks at ~ 420 and ~ 430 nm, respectively. The presence of the two peaks is consistent with the characteristic surface plasmon resonance of silver nanoparticles which are formed upon reduction^[8]. The observed blue shift of the surface plasmon resonance peak from ~ 430 nm in sample (b) to ~ 420 nm in sample (a) may be related to the interband transition of silver and the increase of the average silver particle size which are proved by the XRD results.

Fig. 4 shows that the X-ray diffraction (XRD) patterns of the soluble PI/silver nanocomposite samples obtained by the two methods. The broadened peak at about 20° is corresponding to the phase of polyimide. The four diffraction peaks in the XRD patterns of samples (a) and (b) widen greatly, indicating the formation of the nanometer scale silver particles in the PI/silver nanocomposites. The four peaks can be indexed as 111, 200, 220, 311 planes of the face-centered cubic silver phase with cell parameter $a=0.4087$ nm in sample (a) and $a=0.4088$ nm in sample (b), which are close to the reported data in the JCPDS file No. 4-783. The average size of the nanometer Ag particle is about 8.9 nm in sample (a) and about 8.0 nm in sample (b), calculated from the half-peak width using the Scherrer formula.

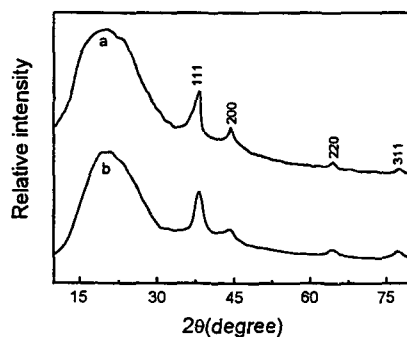


Fig. 4 XRD patterns of the PI/silver nanocomposites prepared by the ultraviolet irradiation technique: PI/silver nanocomposite from the precursor AgAc (a) and AgNO₃ (b).

Direct evidence of the morphology of the PI/silver nanocomposites, the particles size and size distribution was illustrated by TEM (Figs. 5 and 6). The TEM micrographs of the PI/silver nanocomposites (Fig. 5(a,b)) show that the silver nanoparticles were homogeneously dispersed in the two nanocomposites prepared by two approaches. Each approach gave two types of silver nanoparticles with different diameters of 6-10 nm and 15-20 nm, respectively. The size of the smaller particles (6-10 nm) is well corresponding to the values calculated by the XRD linewidth technique. The larger silver particles (15-20 nm) may be due to the aggregation of the smaller ones, resulted from the dissolution and precipitation processes or the heating produced by the bombing of the electron beam to the sample during the TEM measurement. In addition, it was observed from Fig. 6 that the adoption of the two different precursor (AgNO₃ and AgAc) only had an effect upon the size distribution of the silver nanoparticles.

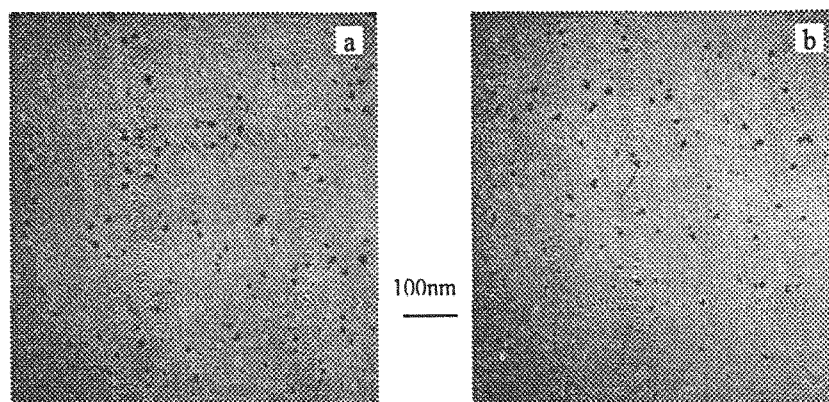


Fig. 5 TEM micrographs of the soluble PI/silver nanocomposites prepared by the ultraviolet irradiation technique: PI/silver nanocomposite from the precursor AgAc (a) and AgNO₃ (b).

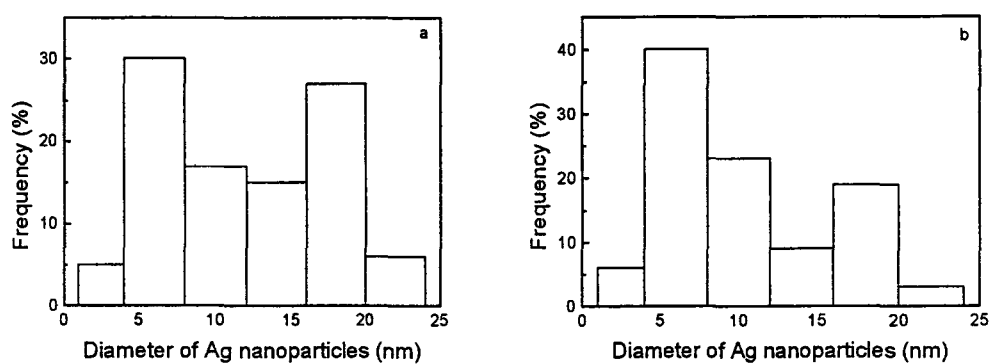


Fig. 6 Silver particle size distribution determined by TEM analysis of the PI/silver nanocomposites: PI/silver nanocomposite from the precursor AgAc (a) and AgNO₃ (b).

4. Conclusions

A convenient method for preparing soluble PI–silver nanocomposites by using ultraviolet irradiation is presented. Two precursors of the silver particles (AgAc, AgNO₃) were used. From the TEM and XRD investigations, the silver nanoparticles homogeneously dispersed in the PI matrix could be divided into two types. The average size of the one type is 6–10 nm, and that of the other type is 15–20 nm, probably from the aggregation of the first one. In the UV-Vis absorption spectra of the PI/silver nanocomposites, the absorption peak due to the surface plasmon resonance of silver particles was observed at 420–430 nm.

References

- [1] L.N. Lewis, Chem. Rev. 93 (1993) 2693.
- [2] N. Roost, L. Ackermann, G. Pacchioni, Chem. Phys. Lett. 93 (1992) 94.
- [3] W.P. Halperin, Rev. Mod. Phys. 58 (1986) 533.
- [4] F. Hache, D. Ricard, C. Flytzanis, J. Opt. Soc. Am. B 3 (1986) 1847.
- [5] A.W. Olsen, Z.H. Kafari, J. Am. Chem. Soc. 113 (1991) 7758.
- [6] Y.D. Ying, X.L. Xu, C.J. Xia, X.W. Ge, Z.C. Zhang, J. Chem. Soc. Chem. Commun. (1998) 941.
- [7] A. Morikawa, Y. Iyoku, M. Kakimoto, Y. Imai, Polym. J. 24 (1992) 107.
- [8] Y. Plyuto, J. Berquier, C. Jacquiod, C. Ricolleau, Chem. Commun. (1999) 1653.