Fabrication of Polymer Crystals/Ag Nanocomposite by Intercalation

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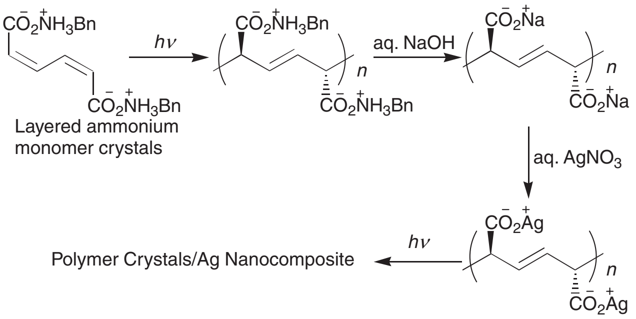
The intercalation of alkali metals into the polymer crystals of benzylammonium muconate is achieved by immersion in the corresponding alkaline aqueous solution at room temperature, followed by an ion-exchange reaction to the silver salt and subsequent photoreduction of the polymer, leading to the fabrication of a new type of nanocomposite consisting of organic polymer crystals and Ag nanoparticles.

In recent years, the control of structure and specific properties has attracted great interest for organic/inorganic nanocomposites, because nanomaterial has several features different from those of isolated molecules or atoms and also of bulk materials. The hybridization of organic materials with nanometals and inorganic nanoparticles has been extensively investigated for various composites including nanowires, nanocrystals, membranes, catalysts, composites, and other supramolecular architectures.[1,2] We have recently reported a new system of organic intercalation, which consists of organic polymer crystals as the host and organic guest molecules.[3,4] In this system, guest amine molecules are intercalated into the interlayer space between the polymer sheets of the host, and the intercalated countercations are regularly arranged at a stacking distance of 5 Å along the polymer chains. It is also expected that metal ions are introduced into the polymer crystals and the subsequent reduction results in the fabrication of composites consisting of layered polymer crystals and the metal. We now report the synthesis of a new type of nanocomposite of layered polymer crystals and Ag nanoparticles (Scheme 1).

Polymer crystals as the host with a layered structure were obtained by the topochemical polymerization of needle crystals of benzylammonium (Z,Z)-muconate.[5] The benzylammonium monomer crystals have an alternately stacked layer structure consisting of the diene carboxylate anion and benzylammonium cation layers, which are supported by two-dimensional hydrogen bond networks and CH–π interactions. This layer structure is maintained during topochemical polymerization to provide a similar layered polymer crystal (Figure 1a). The countercations of the polymers were quantitatively exchanged with the alkali metal ions by the intercalation using a concentrated solution of the corresponding metal hydroxides. For example, when the benzylammonium polymer crystals were dispersed in a concentrated solution of NaOH or LiOH over 2 M in water or an aqueous methanol at room temperature for 1 h, the countercations were quantitatively exchanged with the maintenance of the crystalline structure, as shown in the powder X-ray diffraction profiles[6] (Figure 1b). A characteristic diffraction at $2\theta = 5.2°$ ($d = 17.0$ Å) due to the layer structure of the benzylammonium polymer crystals disappeared during the intercalation of alkali metal ions. The intercalation with KOH also proceeded, but the layered structure could not be maintained owing to the large ionic radius of potassium (Figure 1c).

The use of a dilute aqueous solution resulted in the dissolution of the crystals during the intercalation because of a high ionic strength in the crystals and the penetration of water into the crystals due to the osmotic pressures during the exchange reaction. Table 1 summarizes the solubility of sodium, benzylammo-



Scheme 1.

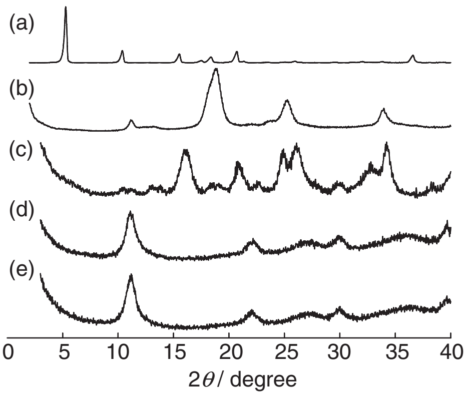


Figure 1. Powder X-ray diffractions of polymer crystals during intercalation (Cu Kα). (a) poly(benzylammonium muconate) ($2\theta = 5.2°$, 17.0 Å, assigned as the 001 plane), (b) poly(sodium muconate) ($2\theta = 18.9°$, 4.7 Å), (c) poly(potassium muconate), (d) poly(silver muconate) before photoirradiation, and (e) after photoirradiation.

Table 1. Solubility of polymer crystals in aq NaOH

[NaOH] /M	Poly(benzylammonium muconate)	Poly(sodium muconate)	Poly(muconic acid)
10	insoluble	insoluble	soluble
2	insoluble	insoluble	soluble
1	partly soluble	insoluble	soluble
0.5	soluble	insoluble	soluble
0.25	soluble	insoluble	soluble
0.10	soluble	soluble	soluble
0 (H_2O)	insoluble	soluble	insoluble

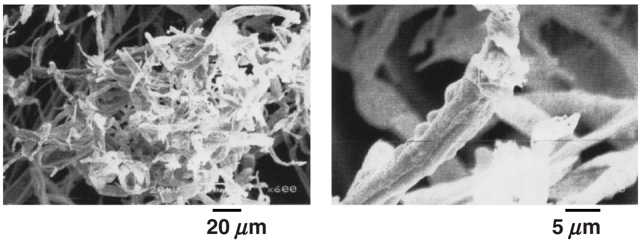


Figure 2. SEM photographs of polymer/Ag nanocomposite obtained by photoreduction of poly(silver muconate) with a high-pressure mercury lamp at room temperature for 1 h. With excess $AgNO_3$ to the carboxylate of the polymer. See also Figure 3.

nium, and acid polymers at various concentrations of NaOH aqueous solutions. The isolated sodium polymer was insoluble in a 0.25 M aqueous NaOH, while poly(muconic acid) was soluble in NaOH solution irrespective of its concentration. These results support the role of the ionic strength inside the crystals. Subsequently, the exchange from the sodium to the silver ion was performed by immersion of poly(sodium muconate) into aqueous $AgNO_3$.[7] X-ray photoelectron analysis and diffraction experiments confirmed the quantitative exchange reaction in the solid state. During the successive reactions from the ammonium to sodium and then to silver ions, macroscopic shape of the needle crystals had no change, but the layered structure of the polymer sheets collapsed by the introduction of silver ions (Figure 1d).

The UV irradiation was carried out using a high-pressure mercury lamp to form Ag particles in the polymer crystals by photoreduction in the solid state. During the irradiation, the polymer crystals became dark brown according to the irradiation time and the fraction of the introduced Ag ions, supporting the formation of Ag particles. The X-ray powder diffraction profile of poly(silver muconate) had no change during the subsequent photoirradiation for the reduction of Ag ions (Figure 1e). The needle shape of the crystals was maintained even after the photoreduction, as shown in Figure 2. A broad absorption was observed at 480 nm in the diffuse reflectance electronic spectrum and their intensity increased during the irradiation. TEM photographs in Figure 3 clearly show that Ag particles with a size less than several nanometers are present throughout the fibrous polymers. The primary particles of Ag further aggregated and grew into larger particles when excess $AgNO_3$ was used as 1 M solution. When the introduction degree of the Ag ions into the polymers is limited during the intercalation using a small amount of diluted $AgNO_3$ solution, it has been revealed that nanoparticles with a regulated particle size are formed without aggregation. For example, the use of 5% Ag cations against the carboxylic acid of the precursor polymer resulted in the fabrication of a composite containing well-controlled Ag particles (Figure 3c), although the amount of the loaded Ag ions was not determined. It had an absorption less than 400 nm in the UV–vis spectrum as expected.

In conclusion, we have succeeded in the fabrication of a new type of polymer/Ag nanocomposite by the intercalation using layered polymer crystals, which were prepared by the topochemical polymerization of ammonium muconate monomer crystals. In the composites obtained in this study, the Ag nanoparticles are homogeneously dispersed in their fibrous polymers. Further characterization of the polymer/Ag nanocomposites is now under investigation.

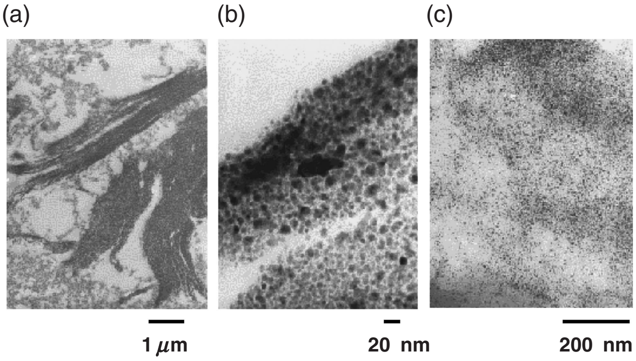


Figure 3. TEM photographs of polymer/Ag nanocomposite obtained from the reactions of poly(sodium muconate) (a) and (b) with excess $AgNO_3$ and (c) with 5% $AgNO_3$ to the carboxylate, and the subsequent photoreduction.

References and Notes

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6 A typical reaction procedure: The crystals of poly(benzylammonium muconate) (0.2 g) were dispersed in an aqueous NaOH (1 M, 20 mL) or in a mixture of methanol and water (50 vol %) of NaOH (1 M, 20 mL) with stirring for 1 h at room temperature. The reaction proceeded heterogeneously. The polymers were filtered, washed with fresh methanol (10 mL), and then dried in vacuo.

7 For an exchange reaction from the sodium to the silver ion, poly(sodium muconate) (0.05 g) was immersed into an excess $AgNO_3$ aqueous solution (1 M, 10 mL) in dark for 1 h at room temperature, and the resulting poly(silver muconate) was filtered, washed with methanol (5 mL), and then dried in vacuo.

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