γ-Radiation synthesis and characterization of polyacrylamide–silver nanocomposites

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Polyacrylamide–silver nanocomposites with a silver particle size distribution ranging from 2 to 20 nm in a polyacrylamide matrix are synthesized by γ-irradiation at room temperature.

Most research has concentrated on the preparation and characterization of single phase materials. More recently the field of interest has broadened to include nanocomposite materials, because of their interesting electrical and optical properties,[1] their possible commercial exploitation and their importance in providing models for understanding the physics of ultrafine particles. Among these materials, organic–inorganic nanocomposites have recently aroused much interest and attention.[2,3] This class of totally innovative materials synergize properties of both components, leading to many applications.[4]

Only a few methods have been used to prepare polymer–metal nanocomposites. Watkins and McCarthy[5] prepared nanocomposites of platinum and poly(4-methylpent-1-ene) **I** by exposing **I** to a solution of dimethyl(cyclooctadiene)platinum in supercritical fluid CO_2 for 4 h and subsequent reduction of platinum. Bronstein *et al*.[6] reported a method for the preparation of polymer–cobalt nanocomposites by mixing $Co_2(CO)_8$ with a polyacrylonitrile copolymer or an aromatic polyamide in dimethylformamide (dmf). $Co_2(CO)_8$ interacts with dmf giving the complex $[Co(dmf)_6]^{2+}[Co(CO)_4]_2^-$, which is converted to nanodispersed Co particles by thermolysis.

In these methods, polymerization of organic monomer and formation of nanocrystalline metal particles are performed separately, and the polymer matrix and metal nanoparticles are hybridized physically to form polymer–metal nanocomposites. Thus, metal nanoparticles are not well dispersed homogeneously in the polymer matrix. Furthermore, thermal treatment or pressure is necessary in these methods. To date, little work has been published regarding the room-temperature preparation of polymer–metal nanocomposites. Recently, we have developed the γ-radiation method to prepare ceramic–metal nanocomposites at room temperature.[7,8] Here, we report a new method for the preparation of polymer–metal nanocomposites by γ-irradiation at room temperature and atmospheric pressure. In this method, the metal salt and organic monomer are mixed homogeneously at the molecular level in the solution, and the formation of nanocrystalline metal particles and polymerization of monomer are simultaneous in solution, leading to a homogeneous dispersion of nanocrystalline metal particles in the polymer matrix.

Solutions were prepared by dissolving analytically pure $AgNO_3$ in distilled water and adding acrylamide as the monomer. Solutions were irradiated in the field of a 2.59×10^{15} Bq ^{60}Co γ-ray source. After γ-irradiation, brown–red, transparent, gelatinous products were obtained. The product was dried in air, and ground to powder which was washed with distilled water and then dried. The concentration of metallic silver in the polyacrylamide matrix was determined by precipitation titration. The sample was dissolved in acetic acid–ethylene glycol (3 : 1, v/v) and nitric acid, adding $NH_4Fe(SO_4)_2$ as a precipitimetric indicator, then titrated using KSCN as a precipitant.

X-Ray powder diffraction (XRD) patterns were recorded using a D_{max} γ_A X-ray diffractometer (Japan) with graphite-monochromated Cu-Kα radiation (λ = 0.541 78 nm). TEM images were taken with a Hitachi Model H-800 transmission electron microscope.

The radiation reduction of Ag^+ ions by hydrated electrons produced during γ-irradiation in solution leads to the formation of metallic silver nanoparticles.[9] This process can be written in terms of eqns. (1) and (2).

$$Ag^+ + e_{eq}^- \rightarrow Ag^0 \text{ (reduction)} \quad (1)$$

$$nAg^0 \rightarrow Ag_n \text{ (aggregation)} \quad (2)$$

At the same time, polymerization of acrylamide monomer occurs in solution upon γ-irradiation.[10] Because reduction and polymerization occur simultaneously in the solution, the silver nanoparticles are dispersed homogeneously within the polyacrylamide network, which effectively prevents further growth of silver nanoparticles.

Fig. 1 shows the XRD pattern of a typical sample of a polyacrylamide–silver nanocomposite prepared by γ-irradiation of a solution containing 0.05 M $AgNO_3$ and 3.52 M acrylamide with a radiation dose of 2.7×10^4 Gy. This shows that the sample consisted of two phases, *i.e*. metallic silver, as indicated by diffraction peaks (111), (200), (220), (311), and non-crystalline polyacrylamide. The average particle size of silver is 11 nm, as estimated by the Scherrer formula. The amount of silver present as metallic species in the nanocomposite is 2.09%, as measured by precipitation titration.

A TEM micrograph of the sample prepared under the same experimental conditions as in Fig. 1 is shown in Fig. 2, from which one can see that the nanocomposite contained fine quasi-spherical metallic silver particles homogeneously dispersed and well separated in the polyacrylamide matrix. A histogram of the silver nanoparticles (Fig. 3) shows a distribution of particle sizes ranging from 2 to 20 nm. The average particle size calculated by the reported method[11] was 10.8 nm, with a standard deviation of 2.3.

In summary, γ-irradiation has been used for the first time to prepare, at room temperature, polyacrylamide–silver nanocomposites with a homogeneous dispersion of silver nanopar-

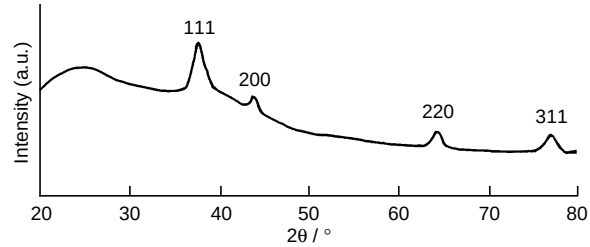

Fig. 1 XRD pattern of the sample prepared by γ-radiation. Solution: 0.05 M $AgNO_3$–3.52 M acrylamide; radiation dose: 2.7×10^4 Gy.

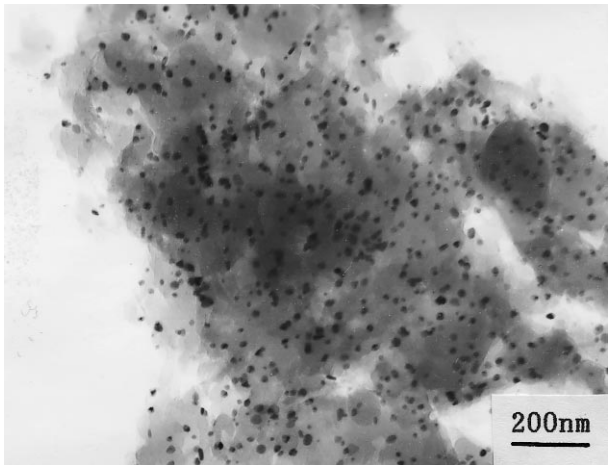

Fig. 2 TEM micrograph of the same sample as in Fig. 1

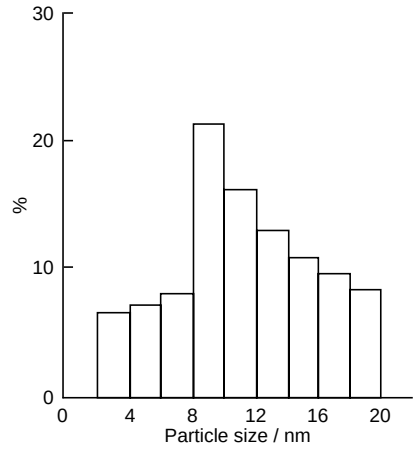

Fig. 3 Histogram of silver particle size in the sample of Fig. 1

ticles in the polyacrylamide matrix. The radiation induced reduction of metal ions and polymerization of organic monomer occurs simultaneously in solution during γ-irradiation, leading to the formation of polymer–metal nanocomposites in a single step. By appropriate control of the experimental parameters, we predict that the γ-radiation method may be extended to the preparation of a variety of polymer–metal nanocomposites as well as polymer–inorganic compound (*e.g*. polymer–metal oxide, polymer–metal sulfide, *etc*.) nanocomposites.

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Footnote

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