Fabrication of Nano-rod Copper-polymer Composites by γ-Irradiation Route in a Heterogeneous System

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Nano-rod copper-polymer composites were synthesized by γ-irradiation in a heterogeneous solution system under atmospheric pressure at room temperature. The product was characterized by XRD, TEM and IR spectrum, respectively. The investigation showed that a rather low dose rate of irradiation was necessary in the formation of nano-rod composites.

Over the past decade, nano-structural materials have been receiving remarkable interest because of their unique characteristics resulting from quantum size effects[1,2] and very promising applications in the field of catalysis, sensor technologies, magnetic recording media and so on.[3–6] Among the variety of metal nano-particles, the coinage metal group, Cu, Ag and Au, is probably studied most extensively. In comparison with Ag and Au, copper particles are highly unstable for oxidation. Conventionally, copper nano-crystal is prepared by many techniques such as pulsed laser ablation,[7] laser irradiation,[8] sono-chemical procedure,[9,10] chemical reduction[11] and electrochemical route.[12] In these methods, however, only spherical copper nano-particles were obtained. Few reports on the preparation of copper nano-rods were found in literatures.

In recent years, research on metal-polymer nanocomposites and their properties has attracted considerable attention due to their potential application in catalysis, electronics and nonlinear optics.[13,14] A wide variety of physical and chemical synthetic approaches have been applied to the preparation of nano-composites. Among them, γ-ray irradiation technique is a novel method compared with other methods for synthesis of nano-composites, which can proceed under atmospheric pressure at room temperature and has successfully been used to prepare polymer–metal nano-composites in a homogeneous solution system.[15–17]

In this report, we extend the above method to the fabrication of nano-rod copper–poly(vinyl acetate) (PVAc) composites in a heterogeneous solution system. $CuSO_4·5H_2O$ and vinyl acetate (VAc) are selected as raw materials. The starting metal salt was dissolved into distilled water. Then vinyl acetate monomer was added. Because the mutual solubility between monomer and water is only about 2%,[18] and the density of VAc monomer is smaller than that of water, the heterogeneous system includes two regions: the upper organic region and the lower water region. After the system was irradiated by γ-ray, the polymerization of monomer and the reduction of metal ions were completed in turn through controlling the dose rate of irradiation. The research showed the formation of copper nano-rods was influenced by the dose rate of irradiation.

In a typical experiment, all used compounds were analytically pure and were used without further purification. To prepare nano-rod copper–polymer composites successfully, appropriate amounts of $CuSO_4·5H_2O$ was dissolved into distilled water to get a 0.025 kmol/m^3 aqueous solution of Cu^{2+} ions. EDTA was added as a coordinating agent at the mole ratio of $CuSO_4$:EDTA = 1:1. Meanwhile, isopropyl alcohol, a scavenger of the oxidative radicals such as OH·, was also needed. After VAc monomer was introduced in the system, the mixed solutions were deaerated by bubbling with nitrogen for about 40 min to remove oxygen solvated in them. Finally, the system was irradiated in the field of a 2.22×10^{15} Bq ^{60}Co γ-ray source at the dose rate of 18 Gy/min for 20 h. After irradiation, a gel-like and viscous product was obtained. The product was repeatedly washed with distilled water to remove impurities, then dried at room temperature.

The product was identified by X-ray powder diffraction (XRD) patterns, using a Japanese Rigaku D/max γ_A X-ray diffractometer equipped with graphite mono-chromatized Cu Kα radiation (λ = 0.154178 nm). The morphology and size of nano-meter metal particles in polymer were determined by Transmission Electron Microscopy (TEM), which was taken on a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. IR spectrum was recorded on a Bruker Vector-22 FT-IR spectrometer scanning from 4000cm^{-1} to 400 cm^{-1} at room temperature, using a KBr wafer.

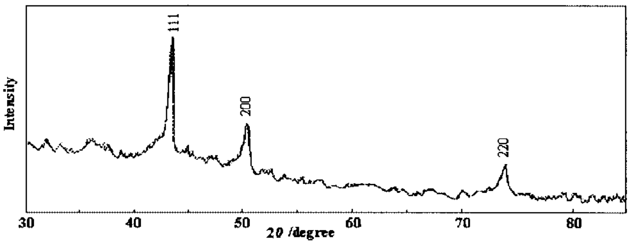

Figure 1. The XRD pattern of the sample prepared by γ-irradiation at the dose rate of 18 Gy/min for 20 h.

Figure 1 is the XRD pattern of the sample prepared by γ-irradiation. Three peaks at 2θ = 43.0, 50.1 and 73.9°can be clearly seen. By comparison with the JCPDS file no.4-0836, these peaks correspond to the three crystalline faces (111), (200) and (220) of cubic metallic copper, respectively, with a lattice parameter a = 3.62 Å.

Figure 2 shows the IR spectrum of the sample, which is similar to the standard infrared spectrum of PVAc and obviously different from that of the vinyl acetate monomer.[19] The strongest peak at 1738.4 cm^{-1} ($\nu_{C=O}$), the characteristic peaks at 1243.0 cm^{-1} and 1023.0 cm^{-1} ($\nu_{C–O}$), and 1373.8 cm^{-1} (δ_{CH_3}) of PVAc confirm that VAc monomer has successfully polymerized under γ-irradiation.

The TEM image of the sample shown in Figure 1 is depicted in Figure 3(a). From the Figure 3(a), one can clearly see that the product consists of a long rod with the size of 150 × 1000 nm and many needle-like rods with the biggest breadth of about

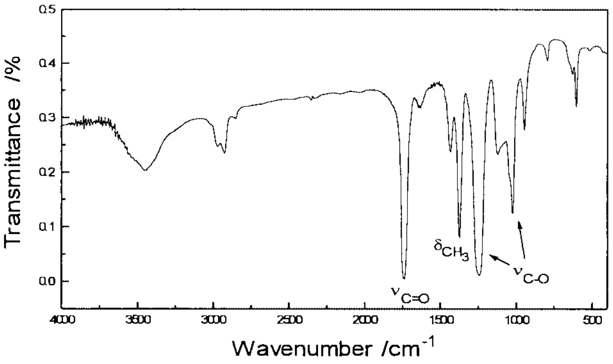

Figure 2. The IR spectrum of the sample shown in Fig.1.

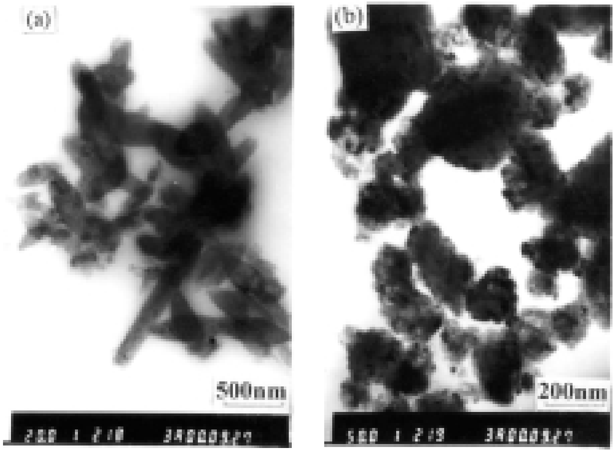

Figure 3. TEM images: (a) the sample prepared by γ-irradiation at the dose rate of 18 Gy/min for 20 h and (b) the sample prepared by γ-irradiation at the dose rate of 50 Gy/min for 20 h.

200 nm and length of about 600 nm. Because of the different color between metal and polymer, the presence of the polymer can be also observed clearly in Figure 3(a).

In addition, it was found that the formation of nano-rod copper–polymer composites was influenced by some factors such as the dose rate of irradiation, reductive atmosphere, inert gas protection and coordination. In our experiment, it was a key that the heterogeneous system was irradiated at a rather low dose rate (18 Gy/min) for a relatively long time. If a rather high dose rate was employed, only nano-particle composites were obtained (Figure 3(b)). Another key factor was to maintain the reductive atmosphere of the system. The experiments showed no copper metal was obtained when the reductive atmosphere of the system could not be maintained. Because water irradiated by γ-ray can generate many active products[20]:

$$H_2O \rightsquigarrow e_{aq}^-, H\cdot, \cdot OH, \text{etc.}$$

Among these products, ·OH is strong oxidative reagent. It can oxidize Cu(0) reduced by e_{aq}^- and H· to Cu(II). So it must be scavenged. In the experiment, isopropyl alcohol was used because it could react with ·OH to produce a kind of reductive radical:

$$(CH_3)_2(OH)CH + \cdot OH \rightarrow H_2O + (CH_3)_2(OH)C\cdot$$

Of course, since isopropyl alcohol was also a chain-transfer reagent, its content was needed to be controlled. Similarly, no nano-rods were prepared when any of other factors was not considered.

In conclusion, nano-rod copper–PVAc composites have been successfully fabricated by γ-irradiation in a heterogeneous system with an upper layer of vinyl acetate monomer and a lower layer of aqueous solution of copper sulfate and EDTA under ambient pressure at room temperature. The investigation shows that the experiment will not succeed until four conditions are realized: reductive atmosphere, inert gas protection, coordinating agent (coordination) and rather low dose rate of irradiation. The possible formation mechanism of copper nanorods in polymer matrix will be further studied.

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