A Convenient Ultraviolet Irradiation Technique for Fabrication of Silver-polymer Nanocomposites

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Silver-polyacrylamide(Ag/PAM) nanocomposites and silver-polymethylmethacrylate(Ag/PMMA) nanocomposites with well homogeneously dispersed silver nanoparticles in polymer matrices were prepared by a novel ultraviolet irradiation technique at room temperature.

Synthesis and characterization of nanometer noble metal particle/organic polymer composites have received much intensive research,[1-5] owing to their optical, electrical, catalytic, and mechanical properties,[6-8] and potential applications in microelectronics.[9,10] Many methods have been exploited to prepare the metal-organic nanocomposites. There have been recent reports on promising attempts in self-organized nanostructuring for gold particles by polymeric and colloidochemical processes.[11] Conventionally, polymerization of organic monomers and formation of metal nanocrystallines were synthesized separately, by which the metal nanocrystallines were not well homogeneously dispersed in polymer matrices, resulting in the uneven distribution of the properties in the nanocomposites.[12, 13] The synthesis of noble metalsols in a polymerizing nonconducting system such as poly(methyl methacrylate) was reported by Nakao and coworkers.[14] Thio-derivatised nanoparticles of Au, Pd, and Ag forming superstructures were recently prepared by the acid-facilitated transfer of well characterized particles in hydrosol to a toluene layer containing the thio.[15] Recently, S. Tamil Selvan[16] reported novel nanostructures of gold-polypyrrole composites by using PY(pyrrole) treating a micellar solution of PS-P2VP[polystyrene-block-poly(2-vinylpyridine)] which had been treated with tetrachloroauric acid. A γ-irradiation technique has been developed to prepare silver-polymer nanocomposites with well homogeneous dispersion of Ag nanoparticles in polymer matrices.[17,18] This approach is based on the simultaneous formation of the irradiation reduction of Ag^+ ions by hydrated electrons produced during the γ-irradiation process and the polymerization of organic monomers. However, the γ-irradiation technique is limited to extend for a range of commercial applications due to the nuclear pollution from the ^{60}Co γ-ray source.

In this communication, we report a novel ultraviolet irradiation technique for preparing silver-polymer nanocomposites in aqueous and nonaqeous systems at room temperature. Compared with the previous γ-irradiation method, the present ultraviolet irradiation technique is more convenient and environmental. It was found that the silver nanoparticles were well homogeneously dispersed in the polymer matrices. The results show that the presence of Ag^+ ions is favorable for the polymerization of organic monomers. This method may also be extended to prepare other inorganic-polymer hybrid nanocomposites.

A 30 W column-like low-pressure mercury lamp (λ = 253.7 nm) was used as an ultraviolet irradiation source. The silver-polyacrylamide (Ag/PAM) nanocomposite was prepared in aqueous system. A solution containing 0.03 mol/L $AgNO_3$ and 3.0 mol/L acrylamide was irradiated for 48 h to ensure the complete reduction of the $AgNO_3$ under the present ultraviolet irradiation at room temperature. The product obtained was washed with distilled water, dried at room temperature and ground into powders for characterization. The silver-polymethylmethacrylate (Ag/PMMA) nanocomposite was prepared by dissolving $AgNO_3$ into methylmethacrylate, in which the methylmethacrylate was used not only as the solvent for $AgNO_3$, but also as the monomer of polymerization. In a typical procedure, 0.1 g analytical grade $AgNO_3$ was added into 10 ml methylmethacrylate. The ultrasonator was used to accelerate the dissolution of $AgNO_3$ in methylmethacrylate. Then, the solution was irradiated for 48 h under the ultraviolet irradiation at room temperature. The prepared Ag/PMMA nanocomposite was treated as Ag/PAM nanocomposite done for characterization. The irradiated solutions were cooled by cold water due to the great exothermic during the irradiation.

The X-ray powder diffraction (XRD) patterns for the samples were determined at a scanning rate of 0.02^0s^{-1} in 2θ ranging from 5° - 70°, using a Japanese Rigakn Dmax γ_A-ray diffractometer with high-intensity CuKα irradiation (λ =0.151478 nm) and a graphite monochromater was set at the diffracted irradiation. TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

Figure 1 shows the XRD patterns of the Ag/PAM nanocomposite sample and Ag/PMMA nanocomposite sample obtained by the present ultraviolet irradiation technique for 48h.

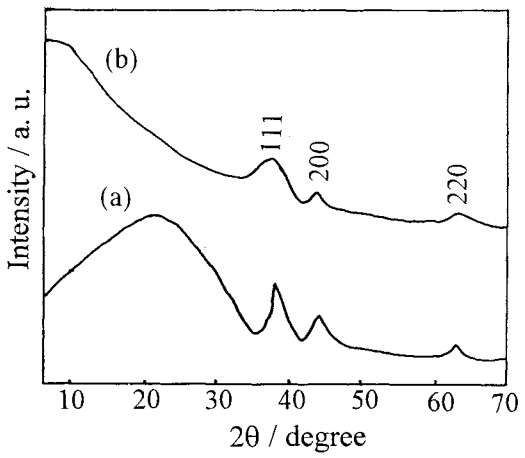


Figure 1. The XRD patterns of the Ag-polymer nanocomposites prepared by the present ultraviolet irradiation technique for 48 h: (a) the Ag/PAM nanocomposite; (b) the Ag/PMMA nanocomposite.

The broadened peak at about 23° in (a) is corresponding with the phase of PAM, and at the diffraction degree less than 20° in (b) corresponding with the phase of PMMA. All other peaks in XRD patterns in (a) and (b) can be indexed as face center cubic(f.c.c.) Ag phase with cell parameter a = 0.4089 nm in Ag/PAM nanocomposite and a = 0.4087 nm in Ag/PMMA nanocomposite, which are close to the reported data (JCPDS File No. 4-0783). The average size of Ag particles in the Ag/PAM nanocomposite is about 15 nm, and about 8 nm in Ag/PMMA nanocomposite, calculated by Scherrer formula.

Figure 2 presents the TEM images of the Ag/PAM powders and the Ag/PMMA powders. The images show that silver nanoparticles were well homogeneously dispersed in both PAM and PMMA. The observed sizes of silver particles are about 10-20 nm in the Ag/PAM nanocomposite, and 5-10 nm in the Ag/PMMA nanocomposite, respectively, which are well corresponding with the values calculated by the XRD linewidth technique. Some large Ag particles were seen in the Ag/PAM nanocomposite, which is due to the aggregation of small Ag particles, resulting from the heating produced by the bombing of the electron beam to the sample during the measurement of TEM.

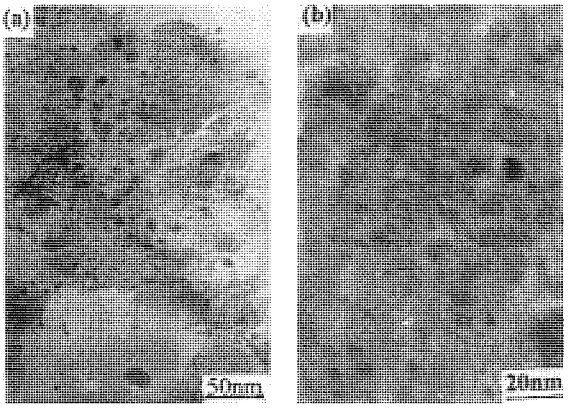
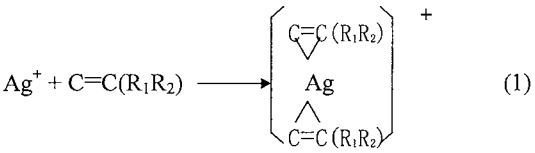


Figure 2. The TEM images of the Ag-polymer nanocomposites prepared by the present ultraviolet irradiation technique for 48 h: (a) the Ag/PAM nanocomposite; (b) the Ag/PMMA nanocomposite.

When pure methylmethacrylate(MMA) or acrylamide(AM) in the absence of $AgNO_3$ was irradiated for 48 h by the present ultraviolet source, the process of polymerization did not occur. We believe that the Ag^+ ions are favorable for the process of polymerization. It is well known that MMA has a particular absorption band at 220 nm. The C=C bond in the MMA monomer absorbs the energy corresponding with the band at 220 nm to form excited state monomer M^*, and to decompose to radicals, leading to the occurrence of the polymerization. The present ultraviolet source can not provide high enough energy to excite the MMA monomer to form M^* and radicals. When $AgNO_3$ was added into MMA, Ag^+ ions may coordinate with the MMA. This process can be written in terms of Eq. (1):



(1)

$R_1 = -CH_3$, $R_2 = -COOCH_3$

This coordination reaction will decrease the electron density of C=C bonds of the MMA, which facilitates the formation of the M^* and radicals by the ultraviolet irradiation, and promotes the process of polymerization. Meanwhile, the Ag^+ ions are reduced into silver nanoparticles, well homogeneously dispersed in the PMMA. It was also studied that whether the producing silver nanoparticles during the ultraviolet irradiation have played a role in promoting the process of the polymerization or not. 0.06 g Ag nanoparticles with average about 10 nm in particle size prepared by the present ultraviolet irradiation were well dispersed in 10 ml MMA. The obtained suspension was irradiated for 48 h by the same ultraviolet source. The result demonstrated that the polymerization did not occur indeed. The influence mechanism of the Ag^+ ions on the process of polymerization will be further investigated.

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