Hybridization of Surface-modified Semiconductor Nanoparticles and a Resin

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A mercapto-terminated linear polymer, which was prepared by a reversible addition-fragmentation chain transfer (RAFT) technique, was used to modify semiconductor nanoparticle surfaces. This modification resulted in an easier dispersion of the nanoparticles in the resins by a simple mixing process, as confirmed by transmission electron microscopy.

Research on nanoparticle synthesis has remarkably developed in recent years, and nanoparticles of various materials in various sizes and size distributions have become available.[1] Semiconductor nanoparticles such as cadmium selenide (CdSe) have been extensively studied in past years both by chemists and physicists, because of its controllable luminescence characteristic as a function of the synthesis conditions (i.e., the quality of the crystal) and the crystal size (i.e., the quantum confinement effect). Very recently, organically capped CdSe nanoparticles were successfully produced using a continuous flow reactor.[2]

It is useful to disperse semiconductor nanoparticles in a resin when making devices such as semiconductor-base light emitting diodes (LEDs). However, the challenging problem is how to disperse nanoparticles in a polymer matrix because it is usually difficult to disperse nanoparticles in a polymer matrix without agglomeration. A well-known approach, i.e., mechanical mixing of nanoparticles and a polymer, results in aggregated structures. Therefore, seeking some effective methods for embedding nanoparticles in a polymer matrix, in which the nanoparticles are somehow present as isolated entities, is quite important.

The nanoparticles may be reaggregated when the resin has melted. Although some studies have already reported that stably dispersing nanoparticles in organic solvents by previously modifying the particle surface with a polymer,[3–7] there are only a few examples of studies on compounding nanoparticles with a polymer.

This paper reports a method that can well-disperse semiconductor nanoparticles in a resin without using a mechanical dispersion technique. The key point is modification of the nanoparticle surfaces with a polymer having the same composition as the resin before adding these particles into the resin. This newly developed method could be applied to the combinations of various kinds of resins and nanoparticles.

Surface modification agents, which may become foreign substances in the composite, were not used in this method. We expect to obtain a resin composite consisting only of nanoparticles and the resin with no other impurities. Consequently, because property deterioration would be attributed to the presence of a large quantity of modification agents, all of the characteristics of the raw materials of the resin and nanoparticles can be utilized without impairment. These composites would be very advantageous for industrial applications.

A thiol-terminated polymer polymerized by living radical polymerization was used to modify the nanoparticle surface. Although a few methods of modification of the nanoparticle surfaces and metal films with a thiol-terminated polymer have been reported,[8] very complicated steps must be followed to obtain the final results. In this study, the RAFT method was used to synthesize the polymer for particle surface modification.[9] Because various thiol-terminated polymers can be polymerized in which the molecular weight was controlled, the application range of this method can be extended.

In this experiment, poly(methyl methacrylate) (PMMA) (weight-average molecular weight is approximately 120000. source: Sigma-Aldrich Co.) was used as the matrix resin without any pretreatment. The CdSe nanoparticles were made using the hot-soap method according to a previous reference,[2] and used in chloroform by capping trioctylphosphine oxide (TOPO). The number-average particle size measured by TEM photography is about 4 nm.

The polymer used for modification of the particle surface was polymerized by controlling the terminal group and molecular weight in accordance with the RAFT method.[9] A linear PMMA polymer was polymerized in a toluene solvent using AIBN as the initiator and thiocarbonyl-thio compound as the chain transfer agent under a nitrogen gas stream, and the remaining thiocarbonyl-thio end group of the polymer was reduced by *n*-butylamine. The obtained thiol-terminated linear PMMA polymer (PMMA-SH) was then dissolved in toluene solution in a nitrogen atmosphere, followed by repeated purification by reprecipitation in methanol to remove the impurities and finally dried under vacuum. Gel permeation chromatography (GPC) provided the number-average molecular weight and the polydispersity index ($M_n = 19000$ and $M_w/M_n = 1.16$). The sulfur content of the PMMA-SH measured by an oxygen flask combustion method was 0.13 wt %.

Because the polymers contain a thiol group at their terminal, they have the possibility of strongly combining with the surface of the semiconductor nanoparticles. This attraction has a strong binding power with the nanoparticle surface compared to the ligands in common particle surface modifications using amine and phosphine oxides. In the last approach, nanoparticles surface-modified with the polymer could be obtained by exchanging their surface ligand with the polymer after the nanoparticles were dispersed in the organic solvent with a common low molecular weight dispersing agent.

The particle surface modification by a polymer was conduct-

Table 1. Weight ratio of capping species and nanoparticles in resin films

Run	Capping Species	CdSe Nanoparticles
a)	TOPO/little	0.2 wt %
b)	SH-PMMA/50 wt %	0.2 wt %
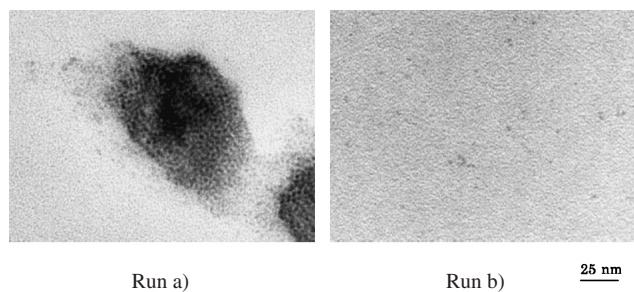
**Figure 1.** TEM micrographs of PMMA/CdSe composite films.

ed by the following method. After the thiol-terminated polymer and the commercial resin matrix were dissolved in chloroform, nanoparticles that were also dispersed in chloroform were added. The modification of the nanoparticle surface with the thiol-terminated polymer took place when the mixture was irradiated with an ultrasonic wave for 15 h at room temperature. The final mixture, i.e., the polymer containing nanoparticles, was placed in a petri dish and the solvent slowly evaporated to obtain a cast film of nanoparticle-dispersed resin of approximately 60-μm thickness. The weight ratio of capping species and nanoparticles in resin films are shown in Table 1.

TEM observations were performed for the ultra-thin sections of the composite films by a JEM1200EX TEM (Japan Electron Optics Laboratory Co.) using an acceleration voltage of 80 kV. The photoluminescence (PL) spectra were taken using an LS55 photoluminescence spectrometer (Perkin-Elmer Japan Co.) For the PL measurement, the excitation wavelength was fixed at 299 nm.

The CdSe nanoparticles capped by TOPO are stably dispersed without aggregation in the organic solvent. However, when they were mixed with resin and the solvent was removed by evaporation, the capped nanoparticles did not evenly disperse in the resin, but gradually aggregated during evaporation of the solvent and finally formed a heavy aggregate of particles. This transformation was due to the large polarity difference between the main chain of the phosphine oxide and the PMMA polymer (Figure 1a). On the other hand, when the nanoparticle surface was capped by the PMMA-SH polymer, the CdSe nanoparticles are well dispersed in the PMMA resin. The most stable condition for dispersing nanoparticles in the resin is obtained when their surfaces are modified by a material, which is similar to the resin component, because the polarities of the particle surface and the resin are exactly the same (Figure 1b).

Figure 2 and Table 2 show the PL spectra of PMMA films containing CdSe nanoparticles. For Run b), because the CdSe nanoparticles were well dispersed in the matrix resin, the PL spectra of the resin film is almost the same as that of nanoparticles dispersed in the toluene solvent.

In conclusion, we achieved the complete dispersion of metal nanoparticles by polymerizing a thiol-terminated polymer using the RAFT method and modifying the nanoparticle surface with this polymer. With this method, hybrid resin composites in which nanoparticles are completely dispersed can, in principle, be easily obtained by any combination, if the combination of metal nanoparticles and resins is one that can be radically
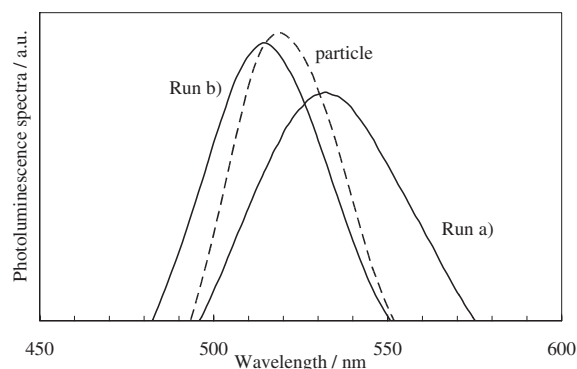
Figure 2. PL spectra of nanoparticles and composite films.

Table 2. PL spectra of nanoparticle and composite films

Run	Capping Species	Maxima/nm	FWHM/nm
CdSe	(in toluene)	519	48
a)	TOPO	532	70
b)	SH-PMMA	515	55

polymerized. Consequently, it is industrially very valuable to make use of these resin composites without impairing the unique quantum size effect of the nanoparticles.

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