

Synthesis and Characterization of Polystyrene-Supported FePt Nanoparticles and CdS Quantum Dots

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We present a general method of supporting nanoparticles by using polymers. As a demonstration, a polystyrene was employed to rigidly support the superparamagnetic FePt nanoparticles and CdS QDs. We successfully fabricated the FePt nanoparticles and CdS QDs rigidly supported in a polystyrene matrix by directly blending the FePt nanoparticles and CdS QDs with the polystyrene at melt state of polystyrene. We characterized them with TEM, XRD, and PL spectrometer.

Keywords: FePt Nanoparticles, CdS QDs, Rigid Nanoparticle Support, Polystyrene.

1. INTRODUCTION

Nanoparticles possess many advantages over bulk materials due to their distinct properties and small size.¹ In order to utilize their properties for a variety of *state-of-the-art* devices, however, nanoparticles occasionally need to be rigidly supported in two-dimensional or three-dimensional arrays prior to application. In this work, we report a simple method of rigidly supporting nanoparticles by using polymers.

Nanopores, such as anodic aluminum oxide (AAO) templates,² can be used to rigidly support nanoparticles. Polymers, however, may be better materials for this purpose because polymers can make fabrication much simpler than nanopores. Also, mass production and fabrication in any shape are all feasible. In this research, we present a simple fabrication method, which is a direct-blending of nanoparticles with a polymer. This method allows nanoparticles to be combined with any polymer. By using this method, we successfully fabricated the superparamagnetic FePt nanoparticles and CdS QDs rigidly supported in a polystyrene matrix. We expect that nanoparticles or QDs rigidly supported in a polymer matrix can be, in general, applied to a variety of areas by using electric, magnetic, and optical properties of nanoparticles.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Superparamagnetic FePt Nanoparticles and CdS QDs

FePt nanoparticles were produced by using the method similar to that previously reported.³ All chemicals were purchased from Aldrich and used as received. Briefly, 197 mg of Pt(acac)₂ (acac = acetylacetonate), 390 mg of 1,2-hexadecanediol, 20 ml of dioctylether were mixed in a reaction vessel and simultaneously magnetically stirred under N₂ flow. After temperature reached 100 °C, 0.17 ml of oleylamine, 0.16 ml of oleic acid, and 0.13 ml of Fe(CO)₅ were added to the reaction mixture. The mixture was refluxed for 30 minutes at 297 °C and then, cooled to room temperature. 40 ml of ethanol was added to the solution to precipitate the FePt nanoparticles. CdS QDs were synthesized by using the method similar to that previously reported.⁴ Briefly, 10 mg of sulfur, 100 mg of Cd(acac)₂ (acac = acetylacetonate), 240 mg of tri-octylphosphineoxide (TOPO), and 210 mg of hexadecane-1,2-diol were added to 10 ml of octyl ether. The mixture was reacted at 280 °C for one hour under N₂ flow and then, cooled to room temperature. After being cooled to room temperature, 20 ml of ethanol and 10 ml of *n*-hexane were added to the solution. Both FePt nanoparticles and CdS QDs were separated from the solution by centrifugation.

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Fig. 1. Schematic diagram of the synthesis of polystyrene.

2.2. Fabrication of Superparamagnetic FePt Nanoparticles and CdS QDs Rigidly Supported in a Polystyrene Matrix (Samples 1 and 2)

As a representative, a polystyrene ($M_w = 4,000\text{--}200,000$, $M_p = 60\text{--}90^\circ\text{C}$) was used to support both FePt nanoparticles and CdS QDs. Both FePt nanoparticles and CdS QDs were blended with 1 g of the polystyrene (see the blending scheme in Fig. 1) at the melting point of the polystyrene of 120°C or so, respectively. 14 mg of the FePt nanoparticles (sample 1) and 33 mg of CdS QDs (sample 2) were used. Mixtures were mechanically stirred at a speed of 100–200 rpm under N_2 flow for a few days to maximize a complete mixing. After blending, the mixtures were cooled to room temperature.

In order to prove whether or not both FePt nanoparticles and CdS QDs are rigidly supported in a polystyrene matrix, both samples in ethanol solvent were sonicated for several hours. However, no FePt nanoparticles and no CdS QDs were liberated from the samples, respectively, indicating that both FePt nanoparticles and CdS QDs are rigidly supported in a polystyrene matrix.

2.3. Characterization

Both FePt nanoparticles and CdS QDs were characterized with a high resolution transmission electron microscope (HRTEM) (Philips, CM 200, acceleration voltages of 200 kV), an X-ray diffractometer (XRD) (Philips, X-PERT, $\text{CuK}\alpha = 1.54184 \text{ \AA}$). FePt nanoparticles were further analyzed with a squid magnetometer (Quantum Design, MPMS 7). CdS QDs were also further analyzed with UV-visible absorption (Beckman, DU 7500) and photoluminescence (PL) spectrometers (home-made).

Both FePt nanoparticles and CdS QDs supported in a polystyrene matrix (samples 1 and 2) were characterized with an XRD and an TEM (Hitachi, H-7600, acceleration voltages of 100–120 kV). For TEM measurement, the samples were cut into slices by an ultramicrotome (RMC, MT-X). Sample 2 was further characterized with a PL spectrometer.

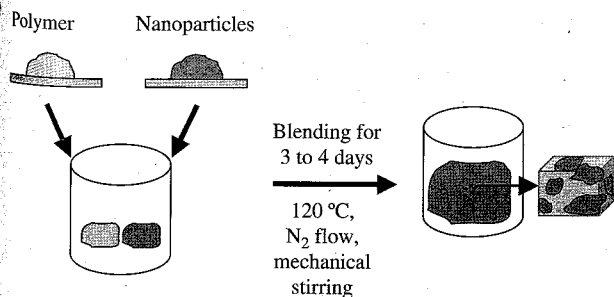


Fig. 1. Scheme for blending of nanoparticles or QDs with a polystyrene.

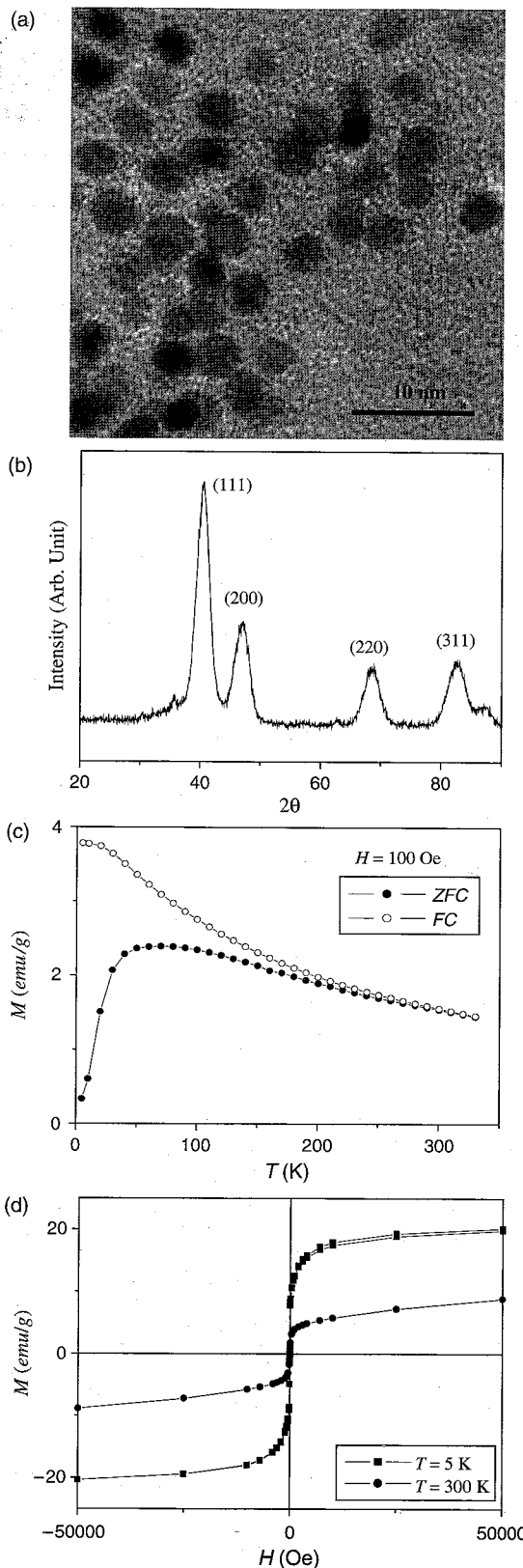


Fig. 2. Summary of characterization of FePt nanoparticles. (a) The HRTEM micrograph. (b) The XRD pattern; the assignments are the Miller indices (hkl). (c) The field cooled (FC) and zero-field cooled (ZFC) magnetization curves with an applied field of $H = 100 \text{ Oe}$. (d) The hysteresis loops at 5 and 300 K.

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3. RESULTS AND DISCUSSION

3.1. Superparamagnetic FePt Nanoparticles and CdS QDs

Figure 2 represents summarized results of characterization of FePt nanoparticles. The particle diameter was measured to be 3.5 ± 0.5 nm with an HRTEM micrograph (Fig. 2(a)). The crystal structure was determined to be face-centered cubic ($a = 3.87$ Å) with an XRD pattern (Fig. 2(b)), which is consistent with the reported data.⁵ Using the full widths at half maximum of the peaks and the Scherrer's formula,⁶ we obtained an average particle diameter of 4.7 nm, which

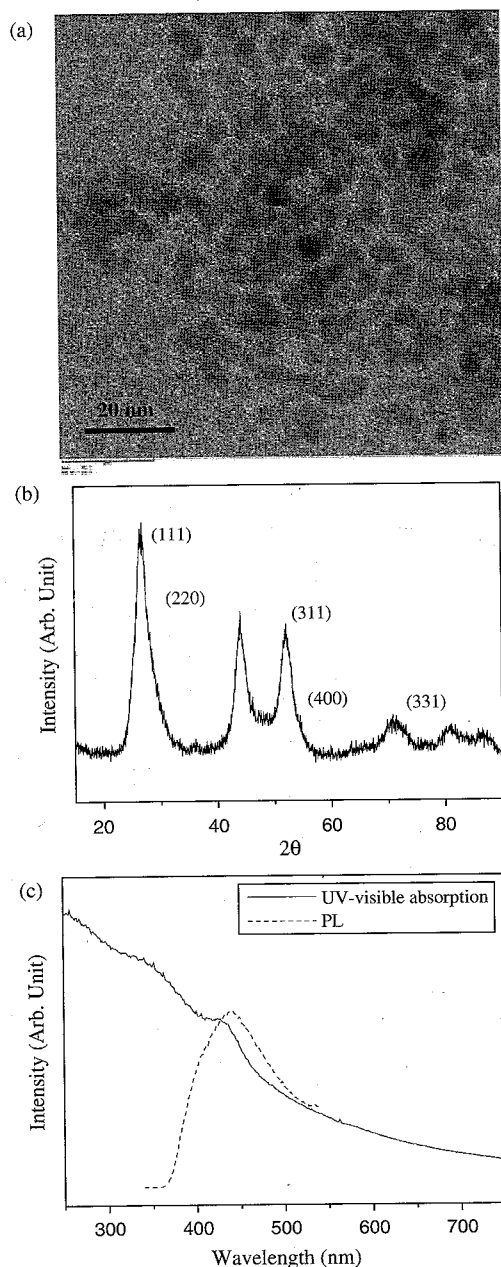


Fig. 3. Summary of characterization of CdS QDs. (a) The HRTEM micrograph. (b) The XRD pattern; the assignments are the Miller indices (hkl). (c) The UV-visible absorption and PL spectra.

is consistent with that observed in the HRTEM micrograph. Magnetic properties were characterized with a squid magnetometer by recording both magnetization curves versus temperature ($M-T$ curves) (Fig. 2(c)) and hysteresis loops ($M-H$ curves) at 5 and 300 K (Fig. 2(d)). These magnetic data show that the FePt nanoparticles have a blocking temperature of 70 K and are superparamagnetic at room temperature.

Figure 3 represents summarized results of characterization of CdS QDs. The average particle diameter (d) of CdS QDs was estimated to be 4.5 nm with an HRTEM micrograph (Fig. 3(a)). The crystal structure was determined to be zinc blende ($a = 5.83$ Å) with an XRD pattern (Fig. 3(b)), which is consistent with the reported data.⁷ Optical properties of the CdS QDs in *n*-hexane were characterized with UV-visible absorption and PL spectra (Fig. 3(c)). The wavelength of the absorption band edge occurring at 450 ± 20 nm is shorter than that of bulk CdS ($=512$ nm),⁸ which is explained by the quantum confinement effect.⁹⁻¹¹ The PL spectrum is slightly red-shifted from the absorption spectrum, as expected because emission occurs after the excited levels are relaxed down to the bottom of a conduction band.

3.2. Superparamagnetic FePt Nanoparticles and CdS QDs Supported in a Polystyrene Matrix (Samples 1 and 2)

Figures 4(a) and (b) show XRD patterns of samples 1 and 2, respectively. As can be seen in Figures 4(a)

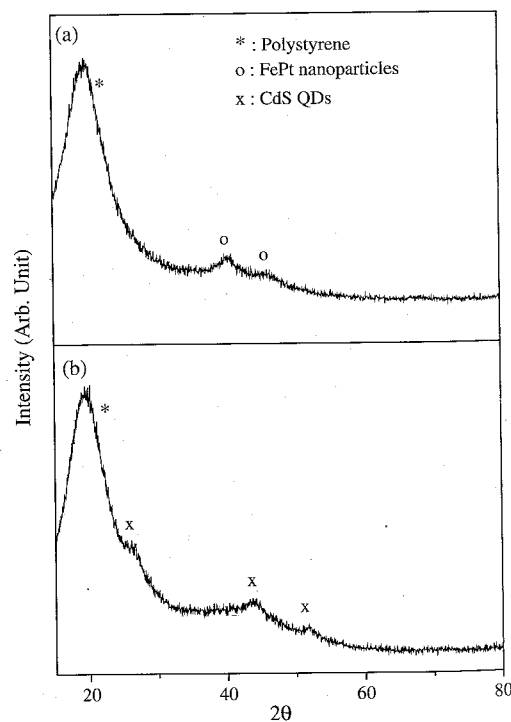


Fig. 4. The XRD patterns of (a) FePt nanoparticles and (b) CdS QDs rigidly supported in a polystyrene matrix.

and (b), weak peak intensities of FePt nanoparticles and CdS QDs were observed, respectively, because their amounts with respect to that of polystyrene are minor.

Figures 5(a) and (b) show TEM micrographs of samples 1 and 2, respectively. As can be seen in Figure 5, both FePt nanoparticles and CdS QDs are not homogeneously dispersed in a polystyrene matrix. Instead, they are locally grouped together like islands and then, somewhat randomly dispersed in each island in the polystyrene matrix. The CdS QDs supported in a polystyrene matrix (sample 2) are further characterized with a PL spectrum as shown in Figure 6. As shown in Figure 6, it is interesting to note that the full width at half maximum of the CdS QDs supported in a polystyrene is narrower than that of free CdS QDs observed in *n*-hexane solution (as previously shown in Fig. 3(c)). This is primarily because

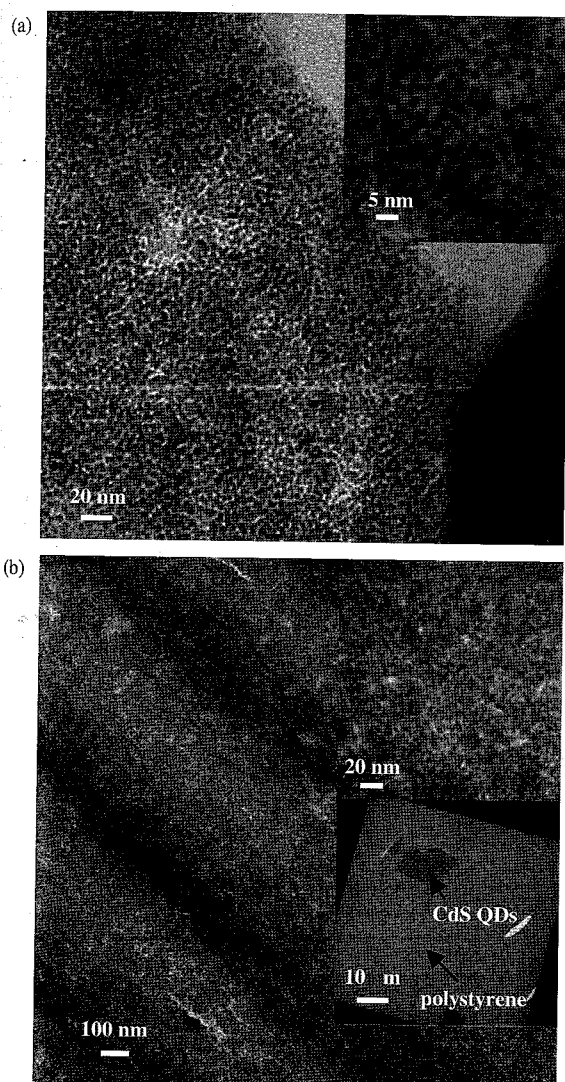


Fig. 5. The TEM micrographs of (a) FePt nanoparticles and (b) CdS QDs rigidly supported in a polystyrene matrix.

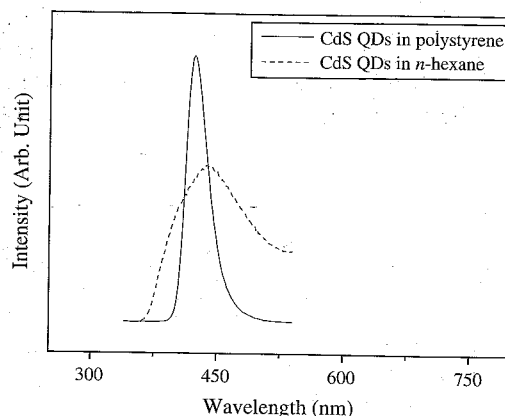


Fig. 6. The PL spectra of CdS QDs rigidly supported in a polystyrene matrix (solid line) and free CdS QDs in *n*-hexane solution (dotted line).

the CdS QDs fixed in a polystyrene matrix are free from Doppler effect.

As discussed above, nanoparticles or QDs can be easily supported by polymers. Polymer supported nanoparticles or QDs will be useful for application. For instance, ferromagnetic nanoparticles can be applied to a high density magnetic recording.^{12,13} Fluorescence QDs can be applied to optical devices.¹⁴⁻¹⁸ Thus, the present fabrication method will be extremely useful for these applications.

4. CONCLUSION

In this research, we demonstrated that polymers can be generally used to rigidly support nanoparticles or QDs. By using a polystyrene and two kinds of nanoparticles, i.e., superparamagnetic FePt nanoparticles and CdS QDs, we successfully fabricated the FePt nanoparticles and CdS QDs which are rigidly supported in a polystyrene matrix. This direct-blending method may be used in fabricating a variety of polymer-supported nanoparticles or QDs. Such nanoparticles or QDs rigidly supported in a polymer matrix, will be extremely useful for a variety of applications such as a high density magnetic recording, sensors, optical devices, and so on by using electric, magnetic, and optical properties of nanoparticles or QDs. Thus, a further application research on polymer-supported nanoparticles or QDs is desired.

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1. INTRODUCTION

Poly(3,4-*e*), commercialized in the 1980s. It has high stability and good film formation. Recently, it has been used as a device by itself, and also useful in various applications such as diodes (LEDs), solar cells, and windows.⁴

Various studies have been reported on the synthesis of polymers with changed functions using different methods. A change of the PSS thin film properties by ion and covalent modification. Atomic layer deposition (ALD) is used to fabricate thin films by means of alternating self-limiting reactions. The functionalization is achieved between an organic and an inorganic semiconductor. The size of the particles

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