A Facile Size-control Method of CdS Nanoparticles In-situ Synthesized in Polymer Matrix by Adjusting Ratio of Acidic Acid with Metallic Complex in Acrylate Photoresist Resin

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A facile method with efficient control of nanoparticles size in polymer matrix by combination of in situ synthesis and photopolymerization is proposed and investigated. The photoluminescence of the CdS–polymer nanocomposites was easily tuned by adjusting the molar ratio of acrylic acid to cadmium acrylate in designed photoresist resins.

Over the past decade, semiconductor nanoparticles showed promising applications in electronic and optical devices and so on.[1] The particle diameter is comparable to or less than the diameter of the bulk semiconductor exciton. In the quantum-confined regime, the control of particle sizes allows the bandgap to be tuned to give the desired electronic and optical properties. For cadmium sulfide (CdS) particles diameter below ca. 60 Å, the absorption spectrum is blue shifted from the bulk.[2] The control of semiconductor nanoparticle sizes has been achieved in a wide range of colloidal and solid-state media, including reverse micelles, surfactant vesicles, zeolites, and several types of ion-containing polymers.[3] Ion-containing homopolymers, random ionomers, and ion-complexing block copolymers have all been used to synthesize various composite materials consisting of nanoparticles dispersed in a polymer matrix. Such composites have been shown a wide range of interesting optical, electronic, and photocatalytic properties.[3]

Photopolymerisable resins, photoresists, are commonly used in two- and three-dimensional (2D & 3D) patterning which have been expected to be used in many advanced fields such as microelectronics and microelectromechanical systems (MEMS).[4] Supplying various functions, such as conductivity, luminescence, and magnetism, to the patterned polymers is of importance for developing polymeric functional MEMS. Design functional polymeric nanocomposites, which are suitable for pattering process by using photocured resins, should open a way for pattering functional MEMS.

In situ synthesis of nanoparticles in polymer matrix is a simple route to obtain nanocomposites. Although the size control of nanoparticles will be a key factor for obtaining the desired properties, however, the size control of nanoparticles is difficult in solid polymer matrix. Therefore, a facile method is expected to control nanoparticle sizes in polymer matrix. In this letter, we report a method of synthesizing CdS nanoparticles in polymer matrix prepared by acrylate photoresist resin in which the size control of CdS nanoparticles was performed by adjusting the molar ratio of acrylic acid with metallic complex in photoresist. The CdS–polymer nanocomposites were characterized by transmission electron microscope (TEM), UV–vis absorption spectrometry as well as fluorescence (FL) spectrometry.

In general, a photoresist resin consists of monomer, oligomer, photoinitiator, and photosensitizer. To synthesize CdS–polymer nanocomposites by using in situ synthesis method, three steps were performed: i) introducing precursors of CdS nanoparticles into photopolymerisable resin, i.e. photoresist; ii) forming and fixing the cores of precursors with nanoscale meter into polymer matrix by photopolymerization; iii) generating CdS nanoparticles via a suitable post-processing in solid polymer matrix. The photoresist resin containing cadmium ion (Cd^{2+}) was designed and synthesized by mixing cadmium methacrylate ($Cd(MA)_2$), methacrylic acid (MA), dipentaerythritol hexaacrylate (DEP-6A) as well as 1 wt % of benzyl and 2-benzyl-2-(dimethylamino)-4′-morpholinobutyrophenone as photoinitiator and photosensitizer, respectively. Here, the complex, $Cd(MA)_2$, is acted as the precursor of CdS nanoparticles in in situ synthesis procedure, MA as monomer, DEP-6A as cross-linker. The cadmium ionic cores are formed in liquid photoresist resins due to the microphase separation arose from ionic interactions in discrete regions of photoresist resin. The liquid photoresist resins containing Cd^{2+} ions are transparent since the cadmium ionic cores are separated in resins with much smaller sizes than light wavelength. These resins were spin-coated on glass slides, then the films were polymerized under the irradiation of a high voltage mercuric lamp (Power: 32.5 mW/cm^2; Wavelength: 365 nm) for 3 min. The polymer film was obtained in which the cadmium ionic cores were fixed in polymer chain networks after photopolymerization of the liquid photoresist resins by UV irradiation. Then, the films with thickness of 2 μm were treated with H_2S gas about 48 h to form nanocomposites.

A series of photoresist resins were designed with almost the same component of cross-linker, DEP-6A, as shown in Table 1, to investigate the effect of size control of CdS nanoparticles in the nanocomposites synthesized by in situ procedure. The CdS–polymer nanocomposites were firstly studied by UV–vis spectrometry. Figure 1a shows the absorption spectra of these CdS–polymer nanocomposites. The data of absorption edges

Table 1. Component of photoresist resin, diameters of CdS nanoparticles, data of absorption, and photoluminescence of CdS–polymer nanocomposites

Resin	DEP-6A /wt %	MA /wt %	$Cd(MA)_2$ /wt %	MA/$Cd(MA)_2$ mol ratio	λ_{edge} /nm	$2R_{abs}$[a] /nm	λ_{FL}[b] /nm
1	22.9	49.1	26.0	6.0	412	2.70	521
2	23.0	53.0	22.0	7.9	371	2.14	513
3	23.1	58.9	16.0	12.0	367	2.09	499
4	23.3	63.3	11.4	18.2	360	2.02	492
5	23.0	69.8	5.2	44.0	345	1.89	474

[a]$2R_{abs}$ were calculated by using following equation: $2R_{abs} = 1/(0.1338–0.0002345\ \lambda_{onset})$.[3e] [b]Excitation wavelength is 355 nm.

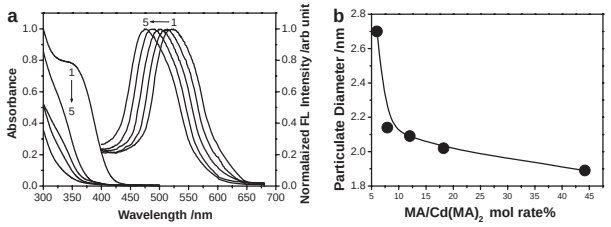

Figure 1. a) UV–vis absorption and fluorescence spectra of CdS–polymer nanocomposites samples 1–5. b) Relationship between $2R_{abs}$ and molar ratio of MA to $Cd(MA)_2$.

(λ_{edge}) were listed in Table 1. Comparison of these spectra shows that the wavelength of the λ_{edge} decreases with the increase of the molar ratio of MA to $Cd(MA)_2$.

For all spectra obtained in this study, the λ_{edge} was converted into an associated CdS particle size, using Henglein's empirical curve which relates the wavelength of the absorption threshold to the diameter of the CdS clusters.[3e] Figure 1b shows the CdS particle diameters plotted vs the molar ratio of MA to $Cd(MA)_2$. The plot indicates that the CdS particle diameters decrease linearly with the increase of the molar ratio of MA to $Cd(MA)_2$ when the ratio is larger than 8.

Remarkable emission tuning of CdS nanoparticles in polymer matrix was obtained by in situ synthesis with careful size controlling in polymer networks. Figure 1a also shows the fluorescence spectra of the CdS–polymer nanocomposites with different molar ratio of MA to $Cd(MA)_2$. The full-width at half maximum (FWHM) in the emission spectra of all CdS–polymer nanocomposites were kept about 100 nm, indicating the similar size distribution of CdS nanoparticles in polymer matrix without the molar ratio change of MA to $Cd(MA)_2$. The maximum wavelengths (λ_{FL}) of main emission bands of CdS nanocomposites were blue-shifted from 521 to 474 nm as the data shown in Table 1, when the molar ratio of MA to $Cd(MA)_2$ was increased from 6 to 44. The emission band is clearly attributed to the near band edge emission of CdS nanoparticles, and the blue shift of emission peaks occurs due to the size effect of CdS nanoparticles.[5]

The diameter of CdS particle in polymer nanocomposites synthesized from the photoresist resins is basically determined by the size of Cd^{2+} ionic cores formed in polymer matrix, which act as the procedures of CdS nanoparticles, since the mobility of metal ions in this kind of solid polymer matrix with network is very poor. However, the size of Cd^{2+} ionic cores fixed in polymer matrix should be influenced by the condition of liquid photoresist resin, because the microphase separation occurs firstly in the liquid photoresist resins. Consequently, tuning the molar ratio of MA to $Cd(MA)_2$ is an easy and efficient method to modulate the size of CdS nanoparticles in polymer matrix when CdS–polymer nanocomposites were in situ synthesized via photopolymerization of photoresist resin.

The CdS–polymer nanocomposites were characterized by TEM as shown in Figure 2a. From the electron diffraction pattern shown in the inset of Figure 2a, the CdS nanoparticles in situ synthesized in polymer matrix were characterized to remain with orthorhombic structure. The size distribution of CdS nanoparticles obtained from the TEM image was shown in Figure 2b, which shows an average diameter of 3.3 nm. The CdS nanoparticles were well separated to the polymer matrix almost without

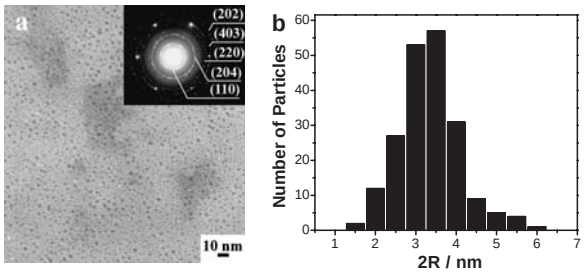

Figure 2. a) TEM image of CdS–polymer nanocomposites synthesized by in situ method in polymer matrix obtained via polymerization of photoresist resin **1**. Inset is the electron diffraction pattern of CdS–polymer nanocomposites. b) The corresponding histogram of CdS particle size; $2R_{TEM} = 3.3$ nm.

aggregations. This fine separation could be contributed to the effect of polymer network formed by the cross-linker and ionic cores at the time of photopolymerization.

In summary, we successfully synthesized CdS–polymer nanocomposites with size-controlling of CdS by an in situ synthesis procedure based on photopolymerization as well as suitable post reaction process via design of photoresist resins. The photoluminescence can be easily tuned from 521 to 474 nm only by adjusting the molar ratio of acrylic acid to cadmium acrylate. This facile method with efficient control of nanoparticle size in polymer matrix should be useful in application of patterning functional polymer composites for fabrication of micromachines and micro-devices.

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