Purification and Optical Properties of Functionalized CdS Nanoparticles

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Abstract

The amino group functionalized CdS nanoparticles have been synthesized by a one-step process. We have developed an easily purification method, by changing the polarity of solvent, to purified CdS nanoparticles with narrow size distribution. Thus, they were useful for biolabeling with multi-colors at the same time.

***Keywords*:** CdS, Nanoparticles, Amino group, Purification

Introduction

To synthesize nanocrystals is the most fundamental part of modern nanotechnology. Many scientists have done a lot of works to produce monodispersed nanoparticles. There are some different physical and chemical characteristics between nanoparticles and bulk materials. When the size of the nanoparticles are smaller than the critical size, the energy level which is near the Fermi level will become discontinuous.[1] The energy gap of semiconductor nanoparticles will be larger than that of the bulk materials.[2,3] Therefore, optical properties have played a key role in the study of semiconductor nanoparticles. The quantum confinement effect is clearly evidenced by the blue shift of the absorption edge energy with decreasing size.[2] Theoretically, if we could control the different uniform size of nanoparticles, we could control over their specially optical properties.

Colloidal nanoparticles have attracted much attention for their uniform size distribution. Many experiments showed the "one-step" reaction to control the uniform size distribution.[4] The process to fabricate monodispersed nanoparticles is inexpensive and facile to industrial application. However, for biotechnological usages, ligand exchange reactions were necessary to give functionalized nanoparticles. Thus, in this report, we discuss the purification of functionalized CdS nanoparticles by modifying the polarity of mixed solvents.

Experimental

Cadmium acetate dihydrate ($CdCH_3COO \cdot 2H_2O$) with purity of 98 % was purchased from Fluka Chemical Co. Sodium sulfide hydrate ($Na_2S \cdot xH_2O$, x was assumed to be 8) was purchased from Merck Chemical Co. 2-Aminoethylthiol was purchased from Tokyo Chemicals Inc. Acetone was purchased from J. T. Baker Chemical Co. All chemicals were used without pretreatment.

The UV-VIS spectra were measured in aqueous solutions with JASCO UV/VIS V-530 Spectrophotometer. The fluorescent spectra were measured in aqueous solutions with HITACHI F-4500 FL Spectrophotometer. For the TEM imaging, nanoparticles were deposited onto the carbon coated copper grids and observed with JEOL 100CX TEM.

Synthesis of cadmium sulfide nanoparticles

Water dissolvable CdS nanoparticles were synthesized by modifying the method used by Pietro et al.[6] Cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$, 0.80 g, 3.0 mmole) was dissolved in deionized water 10 ml. Another solution containing disodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$, 0.24 g, 1.0 mmole) and 2-aminoethylthiol (0.31 g, 4.0 mmole) dissolved in deionized water 5 ml was added into the vigorously stirred cadmium acetate solution. The whole system was stirred for 18 hours without light illumination at room temperature. Then a clear solution became turbid after adding 30 ml of acetone. After centrifuging and washing with acetone for several times, we obtained 0.56 g of a yellow powder assumed to be (0.56g) CdS nanoparticles capped by aminoethyl groups. The schematic depiction of this reaction is shown in Scheme 1.

For purifying the nanoparticles and to gain a uniform size distribution a acetone precipitation method was employed. The CdS nanoparticle powder was dissolved in deionized water. Acetone was then added step wise to precipitate the nanoparticles. The CdS nanoparticle fraction was collected individually from different volume ratios of water to acetone. The nanoparticles were finally dried under vacuum before storage.

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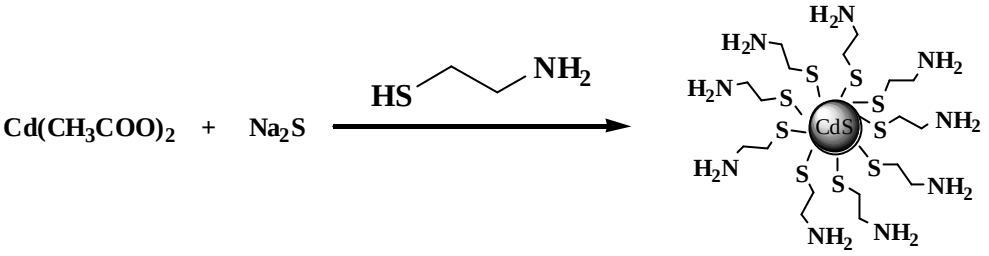

Scheme 1. Schematic depiction of the synthesis of amino groups functionalized CdS nanoparticles

Results and Discussion

By our synthesis, the functional groups in the outer shell of the CdS nanoparticles were amino groups. The purposes were to provide functionalized CdS nanoparticles for bio-usages. The disadvantage of this synthesis method was the large size distribution of the nanoparticles. The Zeta potentials of the nanoparticles were different depending on the amount of amino groups on their surfaces, and this in turn depending on the particle size. Consequently, the polarity of the solvent could be used to separate different sized nanoparticles from solution. By this way, we could purify uniform size distribution of CdS nanoparticles by different ratios of water to acetone.

In this report, two solvent conditions were used as described in Table 1 to precipitate the CdS nanoparticles. First, the solvent of Sample A was prepared to precipitate the first-CdS nanoparticles. After separating the solid precipitated by centrifugation, the solvent system was then adjusted to the condition required for of Sample B and the second precipitate was collected. Both of the two precipitates were dried under vacuum.

Figure 1 shows the UV-VIS spectra of purified CdS nanoparticles. It was easy to distinguish the different band edge of Sample A and Sample B. The CdS nanoparticles that were purified from Sample A absorbed lower energy at peak wavelength of 361 nm as compared with Sample B which the peak appeared at 296 nm. In other words, the CdS nanoparticles of Sample A were larger than that of Sample B.

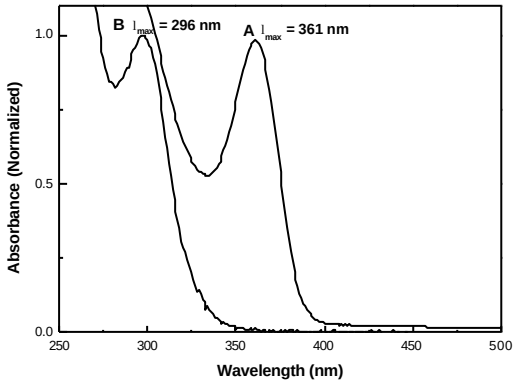

Figure 1. UV-VIS spectra of CdS nanoparticles Sample A (line A) and Sample B (line B).

Table 1. Purifying conditions of precipitating CdS nanoparticles

	Water : Acetone
Sample A	1 : 4.3
Sample B	1 : 20

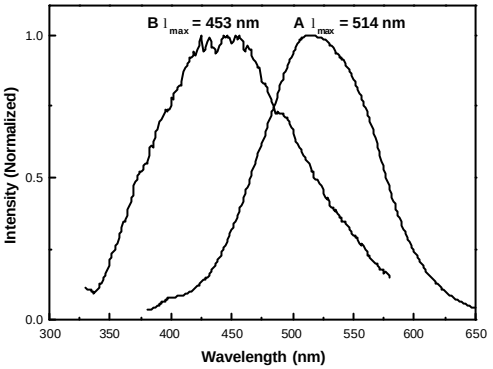

Figure 2. Fluorescent spectra of CdS nanoparticles Sample A (line A) and Sample B (line B).

CdS is a II-VI semiconductor with a direct band gap of about 2.49 eV at room temperature (about 498 nm with the excitation of a exciton).[5] The exciton Bohr diameter of CdS is about 8 nm and quantum effects are expected to appear for small particle sizes.[6] Thus, the energy of exciton is expected to undergo a blue shift if the particle size is as a few nanometers. The theoretical prediction of the ground state energy ($1S_e - 1S_h$ energy) of the quantum dot was given by Kayanuma.[7] It reveals the blue shift from bulk material with the correlation of the diameter of quantum dots as shown in the following equation.

$$E(d) = \frac{2\hbar^2 p^2}{d^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] - \frac{3.572e^2}{ed} - \frac{0.124e^4}{\hbar^2 e^2}\left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right]^{-1}$$

Where m_e^* and m_h^* are the effective masses of electron and hole, and d and e are the diameter and the dielectric constant of the semiconductor. The first term is the kinetic energy of both electron and hole. The second term is their Coulomb attraction. The last term corresponds to the orbital correlation between two particles. In this equation, the second and third terms are dimensional independent. Thus the first term is the difference between the gap of small crystallites and of bulk semiconductors.

According to the previous discussion, the CdS particles

with band edge energies smaller than 2.49 eV had smaller size than that of bulk materials. That is, their band edge wavelengths showed a blue shift from 498 nm. In the spectra of Figure 1, both of Sample A and Sample B had the band edge energies larger than 2.49 eV. This phenomenon revealed that we have synthesized CdS particles in the nano scale. Furthermore, we could purify CdS nanoparticles with two different sizes from the synthesized product.

Figure 3 shows the fluorescent spectra of the Sample A and Sample B. Obviously, larger particles (Sample A) emitted longer wavelength. The Sample A emitted at maximum wavelength of 514 nm and Sample B emitted at 453 nm. This fluorescent phenomenon confirmed the observation in the UV-VIS spectra. That is, the band gap energy was increased with decreasing particle size.

In our result, the CdS nanoparticles could be readily purified with different sizes distribution. These nanoparticles had amino groups coated on the surface. Thus, they were useful for biolabeling as multi-colors at the same time. Here, we have provided an easy way to synthesize functionalized CdS nanoparticles with a one-step synthesis method.

Conclusion

The amino group modified CdS nanoparticles were synthesized by a one-step process. By this method, the size distribution of CdS nanoparticles varied large. However, mondispers fractions could be easily obtained by the fractional precipitation method. Changing the polarity of solvent would allow the selective precipitation of a given size distribution. It provides an easy way to purify CdS nanoparticles using different ratio of aceton and H_2O.

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