

Size-controlled Preparation of Poly(allylamine)-stabilized CdS Nanoparticles by Solution pH

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CdS nanoparticles (CdS NPs) were prepared in an aqueous solution with poly(allylamine hydrochloride) (PAH) as a stabilizer. It was found that the size of CdS NPs was easily controllable with solution pH with good reproducibility. By comparing the pH dependence of CdS NPs stabilized with poly(acrylic acid) (PAA) having an opposite charge to PAH, the electrostatic interaction amongst the polyelectrolyte was believed to have a great influence on the size determination.

The preparation and characterization of semiconductor nanoparticles have been intensively investigated owing to their unique physical and chemical properties when their size is smaller than the exciton diameters of the bulk material. Controlling the size and shape of nanoparticles is an important issue in nanomaterials chemistry. Significant progress has been achieved in controlling the size of nanoparticles by the selection of the experimental conditions, such as stabilizer species,¹ the ratio of reagent concentrations,²⁻⁴ solution pH,^{1,2,5,6} reaction time,^{6,7} and reaction temperature.⁸

Nanoparticle preparation directly in aqueous solution is very favorable for many biological applications. Most investigations on nanoparticle preparation in aqueous solution have been conducted using monomer molecules with thiol groups which are capable of effectively adsorbing on the nanoparticles surface.⁹ Since each polymer chain provides multiple adsorption sites, polymers are capable of effectively encapsulating the surface of nanoparticles in comparison with monomer molecules. In particular the ionization degrees of weak polyelectrolytes such as poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) can be altered with adjustment of solution pH,^{10,11} thereby making it possible to precisely control the structure at the molecular level, the electric field strength formed around at the polymer surface, and the aggregation states of the polymers. Therefore, weak polyelectrolytes as a stabilizer would effectively control the size and the optical properties of CdS nanoparticles (CdS NPs) by adjusting the solution pH. In addition, polyelectrolyte-coated NPs would have free functional groups on the surface available for further functionalization.

We report here that CdS nanoparticle size can be easily and reproducibly controlled by changing pH of the solution containing PAH as a stabilizer. The effect of size control through pH variation was also investigated through the comparison of the pH dependence of PAA with an opposite charge to PAH. To the best of our knowledge, this is the first report in the literature investigating the size control of CdS NPs stabilized with PAH by solution pH.

Twelve mg of PAH was dissolved in 6 mL of a buffer solution and adjusted to appropriate pH with 10 mM sodium acetate (pH 3–6), 10 mM Tris-HCl (pH 7–9), and 10 mM sodium hydrogen carbonate (pH 10–11). In a typical CdS NP preparation, 0.45 mL of 9 mM CdCl₂·2.5H₂O was added to 4.1 mL of

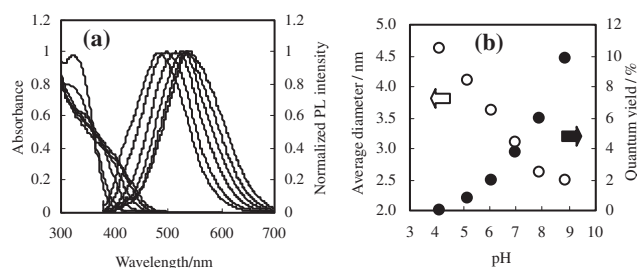


Figure 1. a) Fluorescence and absorption spectra of PAH-CdS NPs prepared in 1.6 mg mL⁻¹ of PAH solution with pH values of 4.6, 5.6, 6.3, 7.0, 8.0, and 9.7 from the right to the left. The excitation wavelength is 370 nm. b) Average diameters (○) and quantum yields (QYs) (●) of PAH-CdS NPs as a function of pH. The diameter (*D*) was calculated using the following equation: $D = 0.1 / (0.1338 - 0.0002345\lambda)$.¹² Quantum yields were calculated against a quinine sulfate reference (QY = 0.55). The excitation wavelength was 370 nm.

2 mg mL⁻¹ PAH solution, and 0.45 mL of 9 mM Na₂S was added dropwise to the mixed solution. The reaction mixture was stirred continuously at room temperature for about an hour. The pH of the solution was almost constant before and after the preparation of CdS NPs.

Figure 1a shows the normalized PL spectra and the absorption spectra of CdS NPs made in a pH range from 4.6 to 9.7. The PL of CdS NPs was scarcely observed around pH 4 and below. The absorption threshold and the PL peak wavelength were blue-shifted with increasing solution pH, indicating that the size of CdS NPs decreased with an increased reaction pH. The average diameter of PAH-CdS NPs estimated from their absorption threshold wavelengths varied from 4.7 to 2.3 nm as the pH was increased from 4.6 to 9.7. The PL intensity also increased with increasing solution pH. Figure 1b shows the dependences of the average diameters and the quantum yields (QYs) on solution pH. The size of PAH-CdS NPs decreased from 4.7 to 2.5 nm and the quantum yield increased from 0.6 to 10% as the pH value was increased from 4.1 to 8.9. The increase of QYs with increasing pH could result from the increase of fluorescence efficiency with decreasing size of CdS NPs. The amount of charge density of PAH polymers changes with solution pH, so that the conformational changes of PAH would be considered to have a great influence on the size determination.

To investigate the effect of charge density of polyelectrolytes on size control, CdS NPs were prepared with PAA, having an opposite charge to PAH, with various solution pH. Figure 2a shows the absorption spectra of PAA-CdS NPs. The absorption threshold wavelength was red-shifted when pH of the solution was increased, indicating that the particle size decreased with the increase of solution pH. It is well known that the emission band gap depends on the size of the CdS NPs and that the blue shift of emission peaks occurs with decreasing

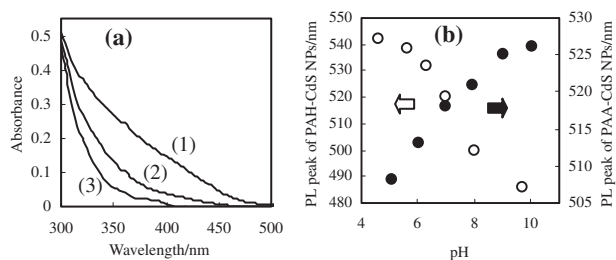


Figure 2. a) Absorption spectra for PAA-CdS NPs prepared at (1) pH 11.8, (2) pH 8.2, and (3) pH 4.1. $[Cd^{2+}] = [S^{2-}] = 0.8$ mM, $[PAH] = 1.6$ mg mL $^{-1}$. b) Dependence of PL peak wavelength for PAH- (○) and PAA-CdS NPs (●) on pH values at the NP formation. $[PAH] = [PAA] = 1.6$ mg mL $^{-1}$, $[Cd^{2+}] = [S^{2-}] = 0.8$ mM. The excitation wavelength is 370 nm.

the size of the NPs.¹³ Figure 2b shows the pH dependence of the PL peak wavelengths of PAH- and PAA-CdS NPs. Although the shifted amount of the PL peak of PAA-CdS NPs was smaller than that of PAH-CdS NPs, the PL peak wavelength of PAA-CdS NPs was obviously red-shifted with an increase of pH, showing the size increase of the PAA-CdS NPs as the pH increased. The PL intensity of PAA-CdS NPs was decreased with the increase of solution pH. The pH dependence of PAH-CdS NPs on the size and the PL intensity showed an opposite behavior to that of PAA-CdS NPs; therefore, it can be concluded that the size of CdS NPs decreases and the PL intensity increase as the ionization degree of both PAH and PAA decrease.¹⁴

The coordinative ability between Cd^{2+} and the functional groups and the surface coverage efficiency of polyelectrolytes on the CdS NPs surface would be important factors in determining the size of CdS NPs. In the case of PAH, the coordinative ability would increase with increasing pH since the positive charge of the amino groups is reduced. The amino groups of PAH would also have a stronger binding ability with Cd on the nanoparticle surface at higher pH. In addition, less protonation of amino groups of PAH at higher pH results in a decrease of the electrostatic repulsion amongst the polymers, resulting in an effective surface coverage with PAH polymers on the CdS NPs. Consequently, these effects would contribute to the decrease in size as the pH of the solution increases. In the case of PAA, the electrostatic repulsion amongst the PAA chains decreased with decreasing pH due to more protonation of carboxyl groups of the polymer chain. Consequently, PAA chains would effectively cover the surface of CdS NPs. However, the coordinative ability of PAA with Cd^{2+} would decrease as the pH decreases, and then the surface binding ability would also decrease owing to the protonated carboxyl groups at low pH. These opposite effects on the size may cause the small PL peak shift of PAA-CdS NPs (ca. 20 nm), compared with that of PAH-CdS NPs (ca. 60 nm). The TEM image and the histogram for PAH-CdS NPs prepared at pH 7.0 are shown in Figure 3. The average diameter obtained from TEM was almost the same as that from the absorption threshold wavelength ($\lambda_{thres} = 435$ nm, $D = 3.2$ nm).

In summary, it was found that controlling the size of PAH-stabilized CdS NPs is easily accomplished by adjusting the pH of

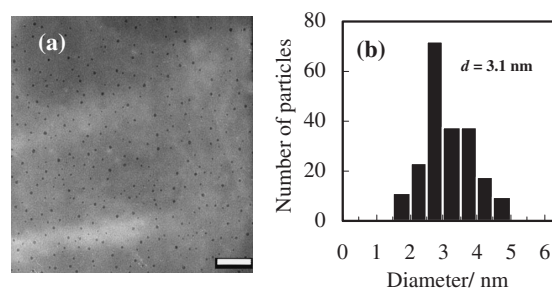


Figure 3. a) TEM image of PAH-CdS NPs prepared at pH 7.0. b) The corresponding histogram of the size of the CdS NPs. The average diameter is 3.1 nm. The scale bar in the image is 50 nm.

the reaction medium with good reproducibility. PAA and PAH seems to give more stable nanoparticles compared with a monomer stabilizer such as thiol. Once PAH- and PAA-CdS NPs were made with a given pH, their sizes were almost constant in a pH range of 5 to 10, indicating that these polyelectrolytes combined with the surface of CdS NPs strongly enough to prevent particle growth in spite of the charge density change of the polyelectrolyte by pH. We will report on the reversible changes of PL intensity of CdS NPs stabilized with polyelectrolytes without change of size.

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