

Poly(vinyl amine) Stabilized Colloidal CdS Quantum Dots of Color-Tunable Photoluminescence: Syntheses and Optical Properties

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ABSTRACT

In this research, poly(vinylamine) (PVAm) was synthesized and employed as a soft template in the preparation of colloidal CdS QDs. The colloidal CdS QD solutions were prepared with PVAm as the stabilizing polymer in a mixed solvent composed of methanol and water. The emitting colors of the prepared CdS QD colloids are tunable by varying the ratio of methanol/water and pH of the solvents. The CdS QD colloids are colorless under UV light at extremely low pH and the low ratio of methanol to water. The emitting color of the CdS QD colloids turn to yellow and orange as increasing methanol content and pH of the solvent. At high pH or when the cosolvent is dominant in methanol the CdS QD colloids show bright to deep blue emission. The optical properties of the CdS colloids have been systematically studied in terms of UV-vis and fluorescence spectrometry.

Keywords: Poly(vinyl amine), CdS, Quantum dot

1 INTRODUCTION

Nanocrystalline semiconductor have been recognized as materials with potential in a wide range of technological applications.[1-3] Typically for the 1-20 nm range most semiconducting materials such as the II/VI semiconductors show optical, magnetic, electronic, and mechanical properties greatly different from those of the corresponding bulk materials.[4] To date, a variety of methods including reverse micelles,[5] organometallic chemistry,[6] and polymers.[7] has been studied extensively to prepare CdS nanocrystallites,

Colloidal semiconducting nanoclusters, or quantum dots (QDs), have attracted much attention in the past decade [1-3] due to their size-dependent optoelectronic properties, which arise from the quantum confinement of electrons and surface effects. For future applications of colloidal QDs in devices of three-dimensional structures and thin films, immobilization of QDs in a condensed phase is required. Various technologies have been developed for anchoring nanoparticles onto inorganic surfaces or trapping them within inorganic porous solids.[8] To attain this target, colloidal QDs are often prepared from organometallic precursors using high-temperature solution chemistry routes.[9] As made, QDs are surface-capped by strong coordinating organic ligands. Exchange of these ligands

permits tailoring the solubility of the QDs in various solvents with preservation of the optical properties. Recently, several groups have explored the synthesis of colloidal CdS QDs using amine-containing polymers and dendrimers as a soft template.[10-12] By means of the remarkable reactivity of amine functionalities, the QD colloids stabilized by amine groups can be subsequently loaded into substrates or onto the surface of nanoparticles, either inorganic or organic.

In this work, poly(vinylamine) (PVAm) was synthesized and employed as the template and stabilizer in the subsequent synthesis of colloidal CdS QDs. PVAm is a new kind of water-soluble polymer, and has not been widely used and studied until the purification of its precursor monomer *N*-vinylformamide (NVF) was settled recently. PVAm has repeat units with a simple molecular structure $-(CH_2-CHNH_2)-$; it could be treated as poly(ethylene) with $-NH_2$ groups on its side chain. The density and sign of charges of PVAm can be easily varied by the degree of hydrolysis and the pH value of the solution.

2 EXPERIMENTAL

Materials. *N*-vinylformamide (NVF, Aldrich 98%) was distilled under reduced pressure at 65°C prior to use. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich 98%), sorbitan monostearate (Span 60, Fluka), sodium sulfide ($Na_2S \cdot 9H_2O$, Aldrich 98%), cadmium chloride ($CdCl_2 \cdot 2.5H_2O$, Showa 98%), NaOH, HCl, and solvents were used as received.

Preparation of Poly(vinylamine)·HCl (PVAm·HCl). Poly(*N*-vinylformamide) (PNVF) was synthesized by the precipitation polymerization of NVF at 65°C, and AIBN was used as the initiator. M_n of PNVF = 76,000 and PDI = 2.61, which were determined by SEC. The hydrolysis of PNVF was carried out in a 2 M NaOH solution at 70°C for 24 hours. The hydrolyzed polymer was acidified with concentrated HCl to pH 2, and then was precipitated into methanol. The resulting polymer, PVAm·HCl, dried at 60°C under vacuum for days. The completeness of hydrolysis was verified by 1H -NMR.

Preparation of CdS colloids. In a typical procedure, the polymer stock solution was prepared by dissolved 17 mg of PVAm·HCl in 6 mL of deionized water. PVAm·HCl stock solution of 3.55×10^{-3} M was prepared by diluting 1 mL concentration solution into 10 mL with water and methanol. The 1.6×10^{-2} M stock solutions of $CdCl_2$ and

Na₂S were prepared by diluting 1 mL solution of each concentrated solution that was prepared by dissolving 92 mg CdCl₂·2.5H₂O in 5 mL water and by dissolving 98 mg Na₂S·9H₂O in 5 mL pure water respectively to 5 mL. The pH value of the solution and the co-solvent composition were adjusted as desired. A 9 mL solution containing 3.6×10⁻³ M PVAm-HCl was mixed with a 0.5 mL 1.6×10⁻² M CdCl₂ solution in a 20 mL vial at 20°C for 5 minutes. A 0.5 ml 1.6×10⁻² M Na₂S solution was injected into the vial by a 500 μL syringe slowly with vigorously stirring for 10 minutes. The final concentration of PVAm-HCl was 3.2×10⁻³ M and 8×10⁻⁴ M for both CdCl₂ and Na₂S.

Characterization. UV-Vis absorbance spectra of colloidal CdS QDs were recorded on a spectrophotometer (UV-160A, SHIMADZU, Japan) with a Deuterium lamp source. The PL spectra were acquired by a fluorescence spectrometer (F2500, HITACHI, Japan) with a xenon lamp source. The excitation wavelength was 320 nm, and the excitation and emission slit widths were both set at 10 nm. All UV-Vis and PL spectra were obtained from 1 mL of aliquot colloidal CdS QDs dispersed in 4 mL solvent in the standard quartz cuvette. The images of colloidal CdS QDs under light or UV irradiation were taken with a digital camera (DX6340, Kodak, USA). The excited wavelengths of UV irradiation were 365 nm by a UV lamp (UVLS-28, Uvp Upland, USA). The size of CdS clusters was directly observed by transmission electron microscopy (H-7500, HITACHI, Japan).

3 RESULT AND DISCUSSION

3.1 Synthesis of PVAm Stabilized QDs

The influence of the composition and pH of solutions on the optical properties of PVAm-stabilized CdS QD colloids have been systematically studied. Figure 1(a) and (b) present the photos of prepared colloidal CdS QD solutions under ambient light and UV (360 nm) irradiation, respectively. The syntheses consisted in mixing PVAm-HCl (0.25 mg/mL) with CdCl₂ (8×10⁻⁴ M) followed by the addition of Na₂S (8×10⁻⁴ M) in 10 mL of solvents, which had various compositions and pH values. The samples prepared in the study are denoted as like CdS-5-0.8, the first value is the initial pH of the solvent and the second the volume fraction of methanol in the solvent. Because PVAm-HCl could not dissolve in neat methanol as pH lower than 7, the corresponding CdS colloids could only be prepared in neat methanol with pH = 7, 9, and 11.

Under ambient light (see Figure 1(a)), the CdS colloids prepared at pH = 2 and 3 (except for CdS-3-0.8), regardless of the cosolvent composition, were turbid yellow. The samples prepared in neat methanol also showed yellow color. These colloids shown yellow color under ambient light were unstable and precipitated after settling for several hours. In addition, the diameter (*d*) of CdS QDs in the yellow colloids is from 3.0 to 7.8 nm, which is calculated by Brus' effective mass model.[13] As the pH of solvents

increased higher than 3, all colloids were colorless and transparent under ambient light. This indicates that extremely small size of the colloidal particles formed (*d* = 3~4.4 nm). These colorless CdS colloids were relatively stable, and no precipitation formed even stored at room temperature for several weeks.

As shown in Figure 1(b) the emitting color of the CdS QD colloid varies with the different volume fraction of methanol and pH of solvents. The general feature of this color map, from upper-left to lower-right corner, is that the prepared CdS QD colloids are colorless (black under the UV lamp) at extremely low pH and methanol content. The luminescence color of the CdS QD colloids turn to yellow and orange as increasing methanol content and pH. At higher pH or when the cosolvent is dominated by methanol the CdS QD colloids show bright to deep blue emission. The results indicate that the emitting color can be easily tuned by varying pH and composition of the cosolvents.

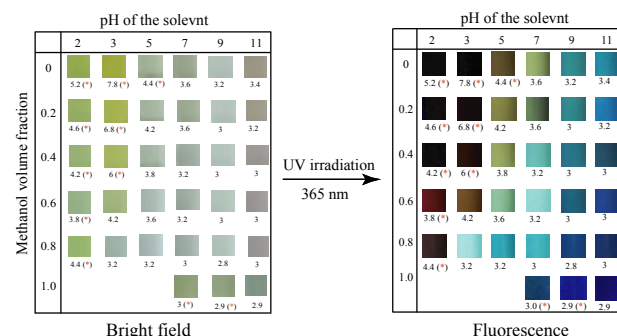


Figure 1. The color map of the prepared colloidal CdS QD solutions at various pHs and compositions of the solvents. The bright filed (left) and corresponding fluorescent (right) images of the solutions in glass vials were taken under ambient light and a 365 nm UV lamp, respectively. The images shown here have been cropped to display the middle part of the vials. The number under each image represents the diameter of QDs. The red star denotes the sample which was unstable and precipitated after settling.

3.2 Effect of Polymer Conformation on the Size of CdS QDs

Figure 2 shows dependence of the size of prepared colloidal QDs on the composition and pH of the solution. At fixed methanol content, the diameter of QDs decreases with increasing pH of the solution. We know that the conformation of polyelectrolyte in the solution is strongly affected by solubility of the polymer and the charge density on the polymer chain.[14] have reported that in aqueous solution at low pH, the polymer chain of PVAm is fully extended; however, at high pH PVAm shows the conformation of compact globule. Therefore, the interior of globular polymer chains can be regarded as “nanoreactors”, in which Cd²⁺ ions react with S²⁻ to give CdS QDs and then stabilized by the amino groups. At low pH and low methanol content, the protonated polymer chains are fully

extended; thus, under this condition the growth of QD particles cannot be controlled and stabilized. This is why the size of prepared colloidal QDs at low pH and low methanol content were larger, and precipitated significantly after settling.

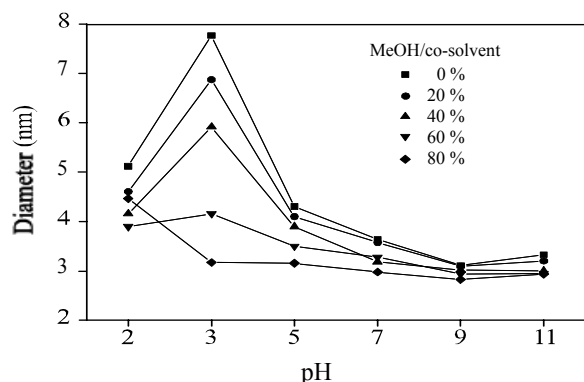


Figure 1. The dependence of the size of prepared colloidal QDs on the composition and pH of the solution.

3.3 Optical Properties of Colloidal QDs

From the UV-Vis absorption spectrum of CdS QDs, first excitonic transition can be determined and thus the particle size is available. Moreover, the sharply rising of absorption onset and appearance of a peak indicates a tight size distribution and good crystal quality. Figure 3(A) to (D) shows the comparison of UV-Vis spectra of the CdS QD colloids prepared at various pHs of the solvents with methanol volume fraction (f_M) of 0, 0.2, 0.4, 0.6, 0.8 and 1. It can be seen that the higher the pH of the solvent the sharper the first absorption peak obtained. At pH = 3 and 5, the distinct first absorption peak only can be observed at $f_M = 0.8$. The plausible interpretation of the observations is that because methanol is a poor solvent for PVAm, addition of more methanol polymer chains shrink and aggregate to form “nanoreactors”. The QDs formed in the “nanoreactors” have a small size and a tight size distribution.

It is well known that the PL properties of CdS QDs can be tuned by changing the particle size; however, in solutions the main factor that affects the PL properties is the chemical composition of the solution. In the present study the factors includes pH of the solution and the cosolvent composition. Figure 4(A) to (D) shows the PL spectra for prepared colloidal CdS QDs at various solutions, which correspond to Figure 3(A) to (D). The photoluminescence of colloidal CdS QDs varies with the change of cosolvent compositions. At pH = 3 (Figure 4(A)), the CdS QDs prepared in the solution with high methanol content ($f_M = 0.8$) exhibits extremely high intensity of emission. It has been known that by addition of methanol the emission of colloidal CdS can be strongly enhanced.[15]

At high pH, the surface of CdS QDs is covered with cadmium hydroxide, which is binding to sulfur anions. This mechanism may block the hole traps thus causing

excitonic fluorescence.[15] For this reason, the blue-shift of emission peak is observed at high pH. The trends can be seen by comparing Figure (B), (C), and (D).

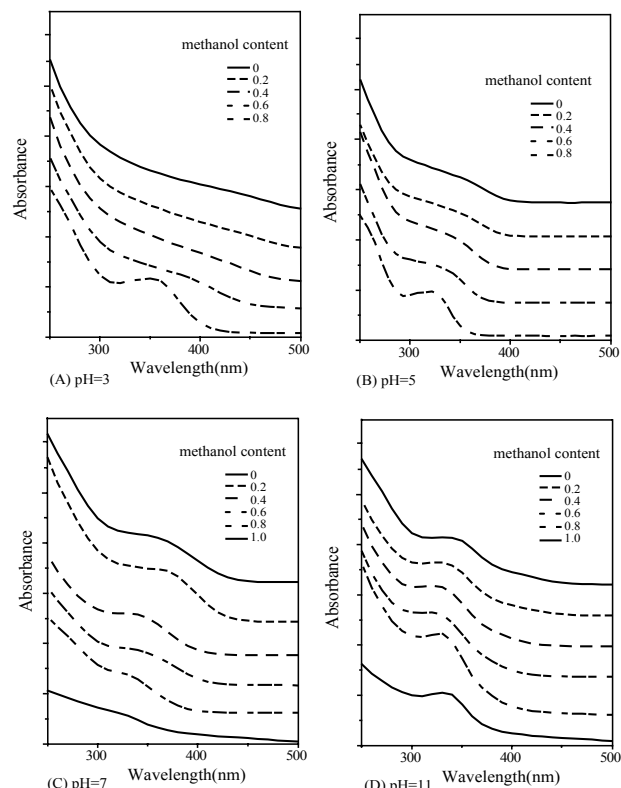


Figure 3. The comparison of UV-Vis spectra of the CdS QD colloids prepared at various pHs of the solvents with methanol volume fraction (f_M) of 0, 0.2, 0.4, 0.6, 0.8 and 1.

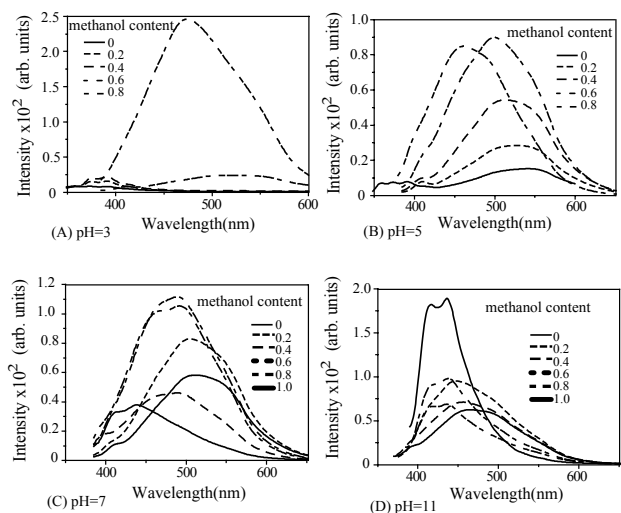


Figure 4. PL spectra for prepared colloidal CdS QDs at various solutions, which correspond to Figure 3(A) to (D)

4 CONCLUSIONS

PVAm can be utilized as the stabilizer for the preparation of colloidal CdS QDs in aqueous solution and mixed methanol/water solvents. The size of prepared colloidal QDs is affected by pH and the methanol content of the solution, therefore by the conformation of the PVAm in the corresponding solution. However, the PL properties of the prepared colloidal QDs are affected only by the surface properties of QDs, not by the size of QDs. The systematic study of the effect of pH and cosolvent composition on the PL properties of QDs provides a facile method of tuning photoluminescence of CdS QDs in solutions.

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