



Photo-luminescent characteristics of carboxyl-CdSe quantum dots synthesized with one-pot approach

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ABSTRACT

CdSe Quantum Dots have broad application prospects in many areas especially in biology due to the quantum effects. However, the CdSe QDs obtained by a traditional organic synthesis method are insoluble in water, which limits the application in biology. Also, the process of previous water system is more complicated and the time required is relatively long. Herein, we report a one-pot method to synthesize water-soluble CdSe QDs with excellent optical properties and structure. Importantly, the CdSe QDs exist in a mono-disperse state in water. We also examined the pH and temperature effect on the fluorescence intensity. This novel approach may improve the application of CdSe QDs used as a fluorescence probe in biology.

Keywords: CdSe QDs, one-pot method, water-soluble

INTRODUCTION

Generally Quantum Dots (QDs) refer to the nanoparticles composed of elements from Group II-VI or III-V. Based on quantum effects, QDs have broad application prospects in many areas. For example, Alivisatos' [1] applied the polymer-coated semiconductor Nano-crystals to the solar cell, making the full use of energy, which can save non-renewable resources. Peng [2] applied QDs to the photodiode, achieving a significant breakthrough in physics. Sanz-Medel [3-4] made the optical sensors with QDs, as optical biomarkers in biology.

CdSe QDs having excellent light-emitting properties usually prepared in organic systems, for instance, in Zhao's work [5], high-quality CdSe QDs with 30nm of FWHM emission peak and more than 60% of quantum yield were synthesized in paraffin system. However, since the quantum dots produced in the organic system is insoluble in water, the surface modification required if QDs needs to be used as a fluorescent probe. But the fluorescence quantum yield of quantum dots will reduce during the process of the surface modification. Compared with organic synthesis pathway, water phase synthesis method is simple, low cost and has good reproducibility. There are two ways in water phase synthesis method: heated to reflux [6] and microwave radiation [7], in which Se powder is mostly used as selenium source to prepare precursor: NaHSe or Na₂SeSO₃ and thioglycolic acid [8] or cysteine [9] used as stabilizer. These QDs has good water solubility, but its fluorescence quantum yield is low and the half width of the emission spectrum is large [6]. In addition, the preparation process with Se powder as selenium source to making CdSe quantum dots needs two steps, that is, firstly preparing NaHSe or Na₂SeSO₃ precursor and then injected into freshly prepared solution formed with cadmium and mercapto compounds. The process is more complicated and the time required is relatively long.

In this work, we prepared water-soluble Carboxyl-CdSe QDs via a one-pot method, using Cd(NO₃)₂, (NaPO₃)₆ and Selenium powder as reactants and thioglycolic acid (TGA) as stabilizer. The effects of pH and temperature on the spectral properties of CdSe quantum dots were also studied. Analytical methods such as UV-visible spectroscopy,

fluorescence spectroscopy and scanning electron microscopy were used to characterize the optical properties and structure of quantum dots.

EXPERIMENTAL SECTION

Materials: $\text{Cd}(\text{NO}_3)_2$, $(\text{NaPO}_3)_6$, Selenium powder, hydrazine hydrate and thioglycolic acid were purchased from KeWei (Tianjin, China)

Preparation of Carboxyl-CdSe QDs: Firstly, $\text{Cd}(\text{NO}_3)_2$, $(\text{NaPO}_3)_6$ and TGA were added sequentially into the 3-neck flask while stirring and then adjust the pH to 8 with sodium hydroxide solution (3 mol/L) to achieve the precursor solution of cadmium. Secondly, the Selenium powder was dissolved in an appropriate amount of HNO_3 (the concentration of 70% in volume), and then diluted with deionized water to achieve the precursor solution of Selenium, which would be added into the precursor solution of cadmium. Thirdly, hydrazine hydrate was added into the solution, the QDs would be achieved by heating reflux for 8 hours at 100°C . The supernatant should be removed by centrifugation (7500 rpm, 15 min), and the precipitation was dispersed in acetone. Repeat the procedures for three times. Finally, the precipitation was dissolved in deionized water to obtain purified water-soluble CdSe quantum dots.

RESULTS AND DISCUSSION

Characterization of CdSe QDs: The UV curve of the CdSe QDs displays well resolved absorption spectrum with a maximum absorption at 380 nm performed using U-3310 Spectrophotometer (Hitachi, Japan), meanwhile it showed the CdSe QDs exist in mono-disperse state due to the water-solubility. FL spectroscopy was performed by F-4500 fluorescence spectrophotometer (Hitachi, Japan) and was taken at the excitation wavelength $\lambda_{\text{ex}}=380$ nm with a 150 w Xenon lampas light source, slit width of emission channels was set to 10 nm and measuring wavelength range was 400 nm to 700 nm. The result showed it had a maximum excitation around 6500 at 550 nm (Fig.1) and the Stokes-shift is 170 nm, which means energy loss is relatively small. The mean diameter measured by Zetasizer analysis of 10 nm was confirmed by scanning electron microscopy. The SEM results showed that QDs is a lamellar structure nanomaterial, highlighting spherical morphology of QDs (Fig.2).

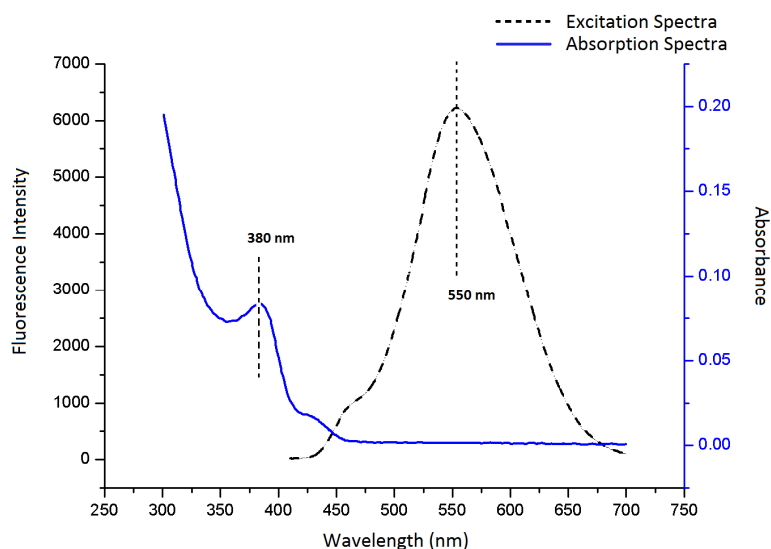


Fig.1 The UV Curve and Fluorescence Curve of CdSe QDs

pH effect on PL performances of Carboxyl-QDs

The fluorescence curve was obtained by dispersing the primary CdSe quantum dots in 10 mL of TE buffer at different pH adjustments (pH 6.3, 7.1, 7.4, 7.7 and 8).

The result showed (Fig.3) that with the rising of pH, the fluorescence intensity at 550 nm gradually increased. There are three reasons. Firstly, as the coordination effect of Cd^{2+} and R-SH, the Cd^{2+} -SR compound formed from TGA and Cd^{2+} will adhere to the surface of CdSe particles. Secondly, with the enhancement of alkaline solution, some Cd^{2+} become $\text{Cd}(\text{OH})_2$ with an excess of OH^- , covering the surface of the CdSe particles to form a composite structure. Meanwhile, under the acidic conditions, H^+ will neutralize the surface negatively charges, destroy the double-electricity layer structure, which might reduce the stability of the sol system and coagulation phenomenon appears, resulting the lower fluorescence intensity. Thus, the increased amount of thiol group coating the CdSe

nanoparticles, the formation of composite structure and the increased stability of the double-electricity layer structure which due to the increased pH are able to reduce surface defects CdSe nanoparticles, leading to the enhancement of fluorescence intensity. Meanwhile, the peak around 470 nm refers to the defect peak of the conjugation.

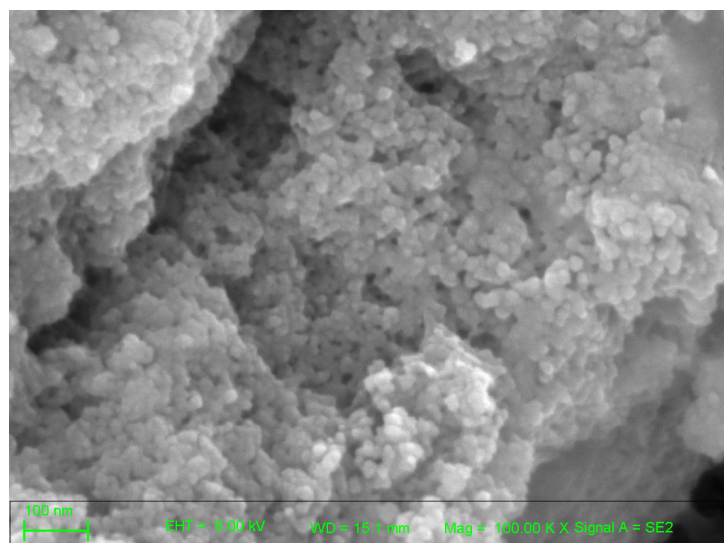


Fig.2 The SEM Image of CdSe QDs

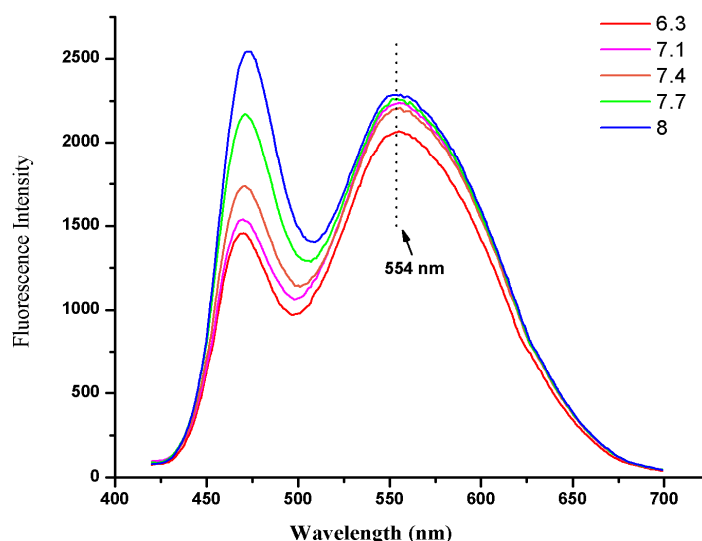


Fig.3 The pH Effect on the Fluorescence of CdSe QDs

Temperature effect on FL performances of Carboxyl-QDs

Also, the temperature effect on the fluorescence intensity of CdSe quantum dots was performed. The CdSe quantum dots were dispersed in 10 mL of TE buffer at pH 7.6 and measured the fluorescence intensity at different temperature (65°C, 70°C, 75°C, 80°C, 85°C and 90°C).

The fluorescence intensity decreases from 650 to 150 with temperature increases from 65 to 90°C (in Fig.4). The reduction of luminous efficiency and the decreasing of fluorescence intensity due to the fact that as the temperature increases, the phonon absorption increases, and because of the mechanism of Auger recombination and thermal excitation, the probability of non-radiative recombination increases. In conclusion, with the temperature rises, the fluorescence intensity decreases.

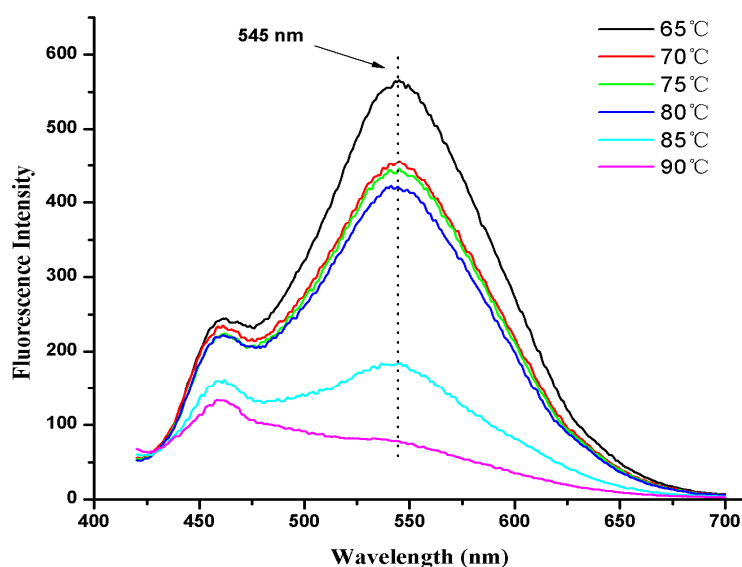


Fig.4 The Temperature Effect on the Fluorescence of CdSe QDs

CONCLUSION

In this work, we developed a one-pot method to prepare water-soluble CdSe QDs. We showed that it had a maximum absorption at 380 nm in UV spectroscopy and existed in mono-disperse state due to the excellent water-solubility. Also, it demonstrated a maximum excitation of 6500 at 550 nm with a 170 nm of Stokes-shift. In addition, we examined the pH and temperature effect to the fluorescence intensity. The results showed that with the rising of pH (from 6.3 to 8), the fluorescence intensity gradually increased, and that as the temperature increased, the fluorescence intensity decreased. In summary, the appropriate condition should be in a weak alkaline pH and room temperatures, which are the suitable conditions for follow-up applications in fluorescence probes.

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