Preparation and Characterization of CdSe QDs

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Abstract: An optimized synthesis route of CdSe quantum dots (QDs) in an aqueous solution was obtained. The shape, crystal structure and optical property of CdSe QDs were also characterized by XRD, UV-Vis and TEM. The result showed that the high-quality cubic CdSe QDs with 3 nm was obtained. The mechanisms about the influence factors were also presented.

Keywords: CdSe QDs; Optimized Synthesis; Characterization

1. Introduction

Quantum dots (also known as colloidal semiconductor nanocrystals, QDs) are generally composed of II-VI and III-V elements, which exhibit strongly size dependent optical and electrical properties[1-4]. Highly quality semiconductor nanocrystals have shown potential applications in thin film light-emitting devices, non-linear optical devices, solar cells and life science[5-8]. Quantum dots synthesized by organometallic approach have high quantum yield, sharp emission spectra, monodispersity and good crystallinity. However, key chemicals used in this route are toxic, expensive, pyrophoric, and even explosive. In this thesis, we synthesized a series quantum dots in aqueous solution by using thiols as the stabilizers. This method is simple and controllable; as-prepared quantum dots show good optical properties.

2. Experimental section

2.1 Reagents

Cadmium chloride (CdCl₂·5/2H₂O), Sodium hexametaphosphate ((NaPO₃)₆, HMP), Mercaptoacetic acid (MAA), Thioglycolic acid (TGA) and Se powders were purchased from...
Sinopharm Chemical Reagent Co. Ltd. Octyl-mercaptan (OMT) was purchased from J&K China Chemical Ltd. All the chemicals were of analytical grade and were used without further purification. Deionized water was used as a solvent.

2.2 Characterization

UV-Visible absorption spectra were measured with an UV-240 UV-visible spectrophotometer (Shimadzu, Japan). The morphology and size of the CdSe QDs were observed by a Hitachi Model-800 transmission electron microscope (TEM, Japan). The crystal structure of the as-prepared products were examined by Rigaku D/max-2200 X-ray diffraction (XRD) with Cu K\(_x\) radiation (\(\lambda = 0.15418\) nm).

2.3 Preparation of CdSe QDs

The preparation of CdSe QDs by the colloidal method had been described in detail elsewhere \(^{[9]}\), and we made a little modification. The black Se powders (0.001mol) were added into 100ml sodium sulfite (0.1M) solution and refluxed the solution under stirring with \(\mathrm{N}_2\) protecting for several hours to formation the 10\(^{-2}\) M sodium selenosulfate solution (\(\mathrm{Na}_2\mathrm{SeSO}_3\)). Then, several Cd precursors prepared by mixing 10 ml CdCl\(_2\) solution (10\(^{-3}\)M) with different stabilizer solution are adjusted to different pH values with 1M NaOH or HCl, respectively. And finally, designed volume as-prepared non-oxygen \(\mathrm{Na}_2\mathrm{SeSO}_3\) solution was added into the Cd precursor solution with stirring and refluxing 30 min under \(\mathrm{N}_2\) protection.

3. Results and discussion

3.1 Morphology analysis of CdSe QDs

The shape and size of CdSe QDs was observed by TEM. The TEM confirmed the spherical CdSe QDs were around 3 nm in size and dispersed well.

![Figure1 TEM image of CdSe QDs](image)
3.2 UV-Vis analysis

Generally, the electronic state is an important property and can be described in terms of valence and conductivity bands and a gap between these bands. However, as the particles become smaller, the wavelength of the electrons is closer to the range of the particle sizes and the laws of classical physics have to be substituted by quantum confinement or quantum size effect (QSE). Besides, the literature\cite{10} reported that the QSE in direct-gap semiconductors is well understood, such as a shift of the optical absorption edge to higher energies with decreasing size. And it could explain the PL and UV-Vis blue-shift effect.

The UV-Vis absorption spectrum showed that the absorption peak of as-obtained CdSe QDs in aqueous solution is 543 nm (2.28 eV), relative blue-shift to the band gap of bulk cubic CdSe (1.78 eV, 698 nm). The results clearly showed the effect of QSE. The estimated particle size was about 3 nm according to Brus-Equation.

![Figure 2](image.png)

**Figure 2** UV-Vis absorption spectra of CdSe QDs

3.3. X-ray diffraction analysis

The XRD patterns in Figure 3 indicated that the as-prepared CdSe QDs are of cubic crystal. According to the standard JCPDS card No. 19-0191, the diffraction peaks correspond to the (111), (220) and (311) crystal plane. The wide diffraction peaks suggested that the ultrafine particles were in poor crystallization. Average crystalline size of the CdSe QDs was estimated at 3 nm by Debye–Scherrer equation after modified instrument’s factors.
4. Measurement of quantum yield (QY) of CdSe QDs

The QY of CdSe QDs was measured according to the method described in Ref. [11,12]. Briefly, Rhodamine B was chosen as a reference standard, the absorbance for the standard and the as-prepared CdSe aqueous samples at the excitation wavelengths and the fluorescence spectra of the same solutions were measured, respectively. The integrated fluorescence intensity (IFI, which is the area of the fluorescence spectrum) from the fully corrected fluorescence spectrum was calculated. Six respective different concentration solutions of Rhodamine B (in ethylene glycol) and CdSe QDs aqueous solutions were used in the measurements. Optical densities of all solutions were adjusted to values between 0.1 and 0.25 at the excitation wavelength to avoid re-absorption effects. The areas of IFI VS absorbance were plotted. The plot obtained should be a straight line with a gradient, which was used to calculate the quantum yield according to the following equation:

\[
QY_u = QY_s \times \frac{F_u}{F_s} \times \frac{A_s}{A_u}
\]

Where the subscripts s and u denote standard (Rhodamine B) and test samples, respectively, and F is the IFI of the solvent. It should be noted that the excitation wavelength for measurements of the QY was set at the excitonic absorption peak of the CdSe QDs samples in our experiments. With the optimized routes, the maximum quantum yields of CdSe QDs up to 32.3%.

5. Conclusions

In this work, spherical cubic CdSe QDs with better FL properties and dispersedly had
been obtained successfully by an optimized and modified-synthesis process. The result showed that the high-quality cubic CdSe QDs with 3 nm was obtained. With the optimized routes, the maximum quantum yields of CdSe QDs up to 32.3%. The CdSe QDs has more possibilities for important implications in environmental, biological and other applications.

6. Acknowledgements

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