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Synthesis and fluorescence spectrum analysis of CdS nanocrystals

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Abstract An optimized synthesis route was applied for control the preparation of CdS nanocrystals (NCs) in an aqueous solution. Some key factors which influencing the characters of CdS NCs, such as stabilizers, ratio of reactant etc, were investigated. It was found that the fluorescence (FL) intensity of CdS NCs could be dramatically enhanced by refluxing. The size, shape, crystal structure and the optical properties of CdS NCs were also characterized by TEM, XRD, UV–Vis and FL spectra. The result showed that the well-disperse spheres CdS NCs with 6 nm in diameter were obtained.

Introduction

II–VI semiconductor nanocrystals (NCs) have attained a great research focus due to their advantages in optical properties including tunable emission spectra, high photostability, resistance to photobleaching and controllable surface characteristics. Studies on potential applications of II–VI NCs to life sciences [1] had been ignited since the pioneer work of Alivisatos [2], who fluorescently labeled 3T3 mouse fibroblast cells using two different size CdSe–CdS core-shell NCs enclosed in a silica shell, and Nie [3], who developed a classical method of nonisotopic detection labels by coupling luminescent CdSe–ZnS NCs to biological molecules in 1998. CdS, one of the most attractive metal chalcogenides, has been widely used as biomarkers owing to its excellent optical properties [4–6]. Nowayday CdS NCs could be prepared by a number of methods [7, 8]. Significant progresses had been made by Peng [9, 10] and coworkers, who synthesized strongly luminescent monodisperse CdS NCs by pyrolysis of precursor injection (organometallics method). The method, however, involves toxic reagents and intermediates (such as Cd $(CH_3)_2$, TOPO and so on), and the obtained NCs are soluble in just non-polar organic solvents because of the hydrophobic ligands unless their surfaces are modified. For biological and environmental applications, it is essential to prepare CdS NCs in water directly. In contrast to organometallics techniques, solution reaction growth method appears to be safer, lower cost and more convenient approach [11–14] because it does not involve special instrumentation, poisonous intermediates and the growing-rate can be easily controlled. In this work, we reported an optimized route to synthesize CdS NCs with improved FL properties.

Chemicals and instruments

Cadmium chloride ($CdCl_2$ $5/2H_2O$), Sodium sulfide (Na_2S $9H_2O$), Sodium hexametaphosphate ($(NaPO_3)_6$, HMP), Poly vinyl pyrrolidone (PVP, k = 30), Thiourea (Tu), and Mercaptoacetic acid (MAA) were purchased from Sinopharm Chemical Reagent Co., Ltd; 1-Dodecanethiol (DT) was purchased from J&K Chemical Ltd. All the chemicals were of analytical grade used without further purification. Deionized water was used as a solvent.

Shimadzu's UV-240 UV–Visible record spectrophotometer and Hitachi's F-4500 FL Spectrophotometer (Japan) were used to record the UV–Vis absorption spectrum and FL spectra of the products dispersed with water,

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respectively. FL Spectrophotometer parameters is PMT Voltage, 700 V, Scan speed, 2400 nm min^{-1} and excitation wavelength is at 350 nm unless noted specially. The crystal structure of the as-prepared products were examined by Rigaku D/max-2200 X-ray diffraction (XRD) with CuK_a radiation (λ = 0.15418 nm). The morphology and size of the CdS NCs were observed by a Hitachi Model-800 transmission electron microscope (TEM, Japan).

Experimental

CdS NCs were synthesized according to the modified-report pervious [11, 12]. Firstly, several Cd precursor solution prepared by mixing $CdCl_2$ solution with different stabilizer, which were adjusted to designed pH values with 1 M NaOH or HCl, respectively. Secondly, the sodium sulfide solution was added into the Cd precursor solution with stirring under N_2 protection. Then the solution was refluxed for 2 h to obtain the CdS NCs. The as-obtained colloidal CdS NCs were diluted to the same concentration for characterization and measurement.

Results and discussion

FL spectral characterizations of CdS NCs

Some key and uncared-for factors were investigated and an optimized synthesis route was applied for controllable preparation of colloidal CdS NCs with better FL property by FL spectroscopy.

Stabilizers effect on FL property

It is important to choose a proper stabilizer for preparing semiconductor NCs by wet chemical methods [15]. In order to choose the best stabilizer, this work analyzed the FL efficiency of CdS NCs with those stabilizers that HMP, PVP, Tu, MAA and DT. Figure 1 was the FL spectra of CdS NCs with above-mentioned stabilizers. It was clear that the FL properties of CdS NCs were affected differently, with the hydro-HMP and hydro-PVP being the lowest and Tu being the strongest because Tu molecules have very strong ability of losing electrons. CdS NCs could disperse well in water because the mercapto-group in Tu molecules reacts with Cd^{2+} to form complex compounds which were absorbed on the surface of the particles and prevented aggregating [11].

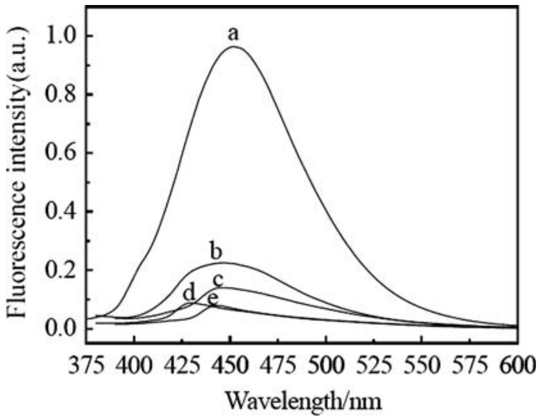

Fig. 1 FL spectra of CdS NCs with different stabilizers: (a) Tu, (b) MAA, (c) HMP, (d) PVP and (e) DT

Molar ratios of precursors effect on FL property

Molar ratios of precursors played an important role in preparation of CdS NCs. This work investigated FL efficiency of CdS NCs with the ratio of $[Cd^{2+}]/[S^{2-}]$ vary from 2:1 to 1:2 while others remained unchanged. The FL spectra of series of CdS NCs at different molar ratio were presented in Fig. 2. It was clear that the FL intensity decreased with the molar ratio decreasing because the CdS NCs surface had strongly to the Cd^{2+}–Tu composites in solution [16, 17] according to the Fajans' rule [18]. When the ratio increasing lead to more Cd^{2+}–Tu composites would aggregate on surface of the CdS NCs and prevent aggregation. But S^{2-} doesn't so.

Refluxing-depended on FL property

It was reported that II–VI NCs synthesized by wet chemical methods had incomplete crystallinity and structure defects [19]. Refluxing is of help in remedying for the regret. By changing just the synthesis temperature from room temperature (25 °C) to 100 °C, the effect of refluxing temperature on the FL properties could be understood.

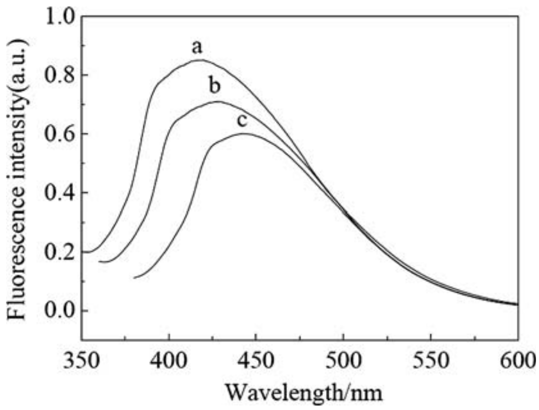

Fig. 2 FL spectra of CdS NCs with different ratio of $[Cd^{2+}]$ to $[S^{2-}]$: (a) $[Cd^{2+}]:[S^{2-}]$ = 2:1; (b) $[Cd^{2+}]:[S^{2-}]$ = 1:1 and (c) $[Cd^{2+}]:[S^{2-}]$ = 1:2

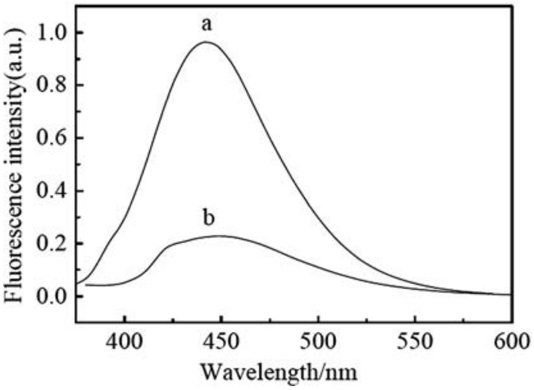

Fig. 3 FL spectra of CdS NCs with Refluxing: (a) 100 °C and (b) room temperature (25 °C)

Figure 3 showed that the FL intensity would enhance almost 5 times after refluxing 2 h because the crystal structure of the NCs was optimized, surface deficiency was decreased and Ostwald Ripening process was accelerated during refluxing.

UV–Vis absorption spectrum

The UV–Vis absorption spectrum showed that the absorption peak of as-obtained CdS NCs in aqueous solution is 417 nm (2.97 eV), relative blue-shift to the band gap of bulk cubic CdS (2.41 eV, 515 nm). The results clearly showed the effect of quantum confinement (quantum size effect, QSE). Reference [20] reported that the QSE in direct-gap semiconductors NCs were well understood, such as a shift of the optical absorption edge to higher energies with decreasing size, which can explain the PL and UV–Vis blue-shift effect (Fig. 4).

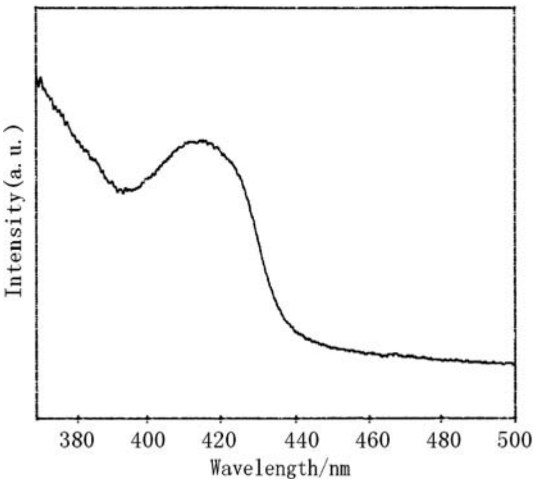

Fig. 4 UV–Vis absorption spectrum of CdS NCs

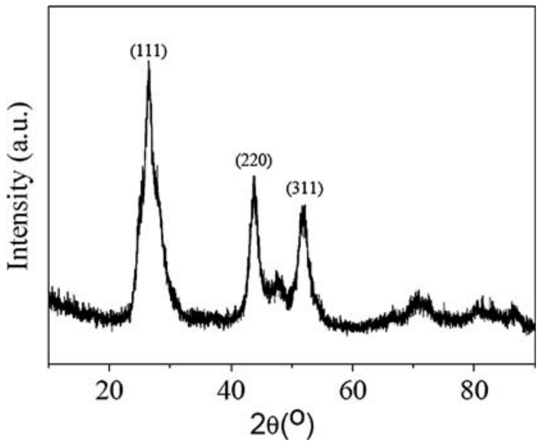

Fig. 5 XRD patterns of CdS NCs

XRD analysis

The XRD patterns in Fig. 5 indicated that the as-prepared CdS NCs were of cubic crystal. According to the standard JCPDS card No. 80-0019, the diffraction peaks correspond to the (111), (220) and (311) crystal plane respectively. The wide diffraction peaks suggested that the ultra-fine particles were in poor crystallization. Average crystalline size of the CdS NCs was estimated at 6 nm by Debye–Scherrer equation.

TEM measurement

The shape and size of CdS NCs was observed by TEM. Figure 6 showed that the typical Tu-modified CdS NCs synthesized with [Cd^{2+}]:[S^{2-}] = 2:1 and refluxing for 2 h. The TEM confirmed the spherical CdS NCs were around 6 nm in diameter and well-disperse. This result was good agreement with the XRD results.

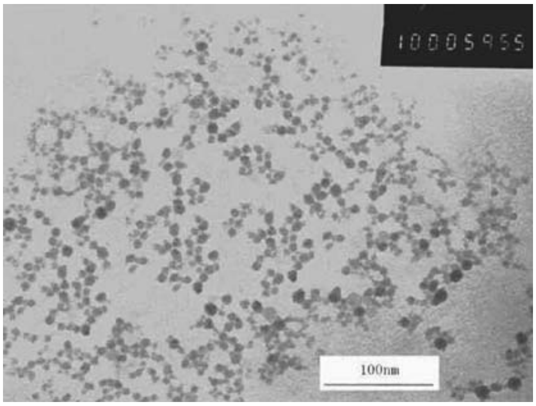

Fig. 6 The TEM photograph of CdS NCs

Conclusion

In this work, the CdS NCs were synthesized with an optimized modified preparing process. Spherical cubic CdS NCs with excellent FL properties had been obtained successfully. It was confirmed that $[Cd^{2+}]/[S^{2-}]$ is 2:1, 2 h refluxing under 100 °C, with the present of Tu is better conditions to obtain the high quality CdS NCs. The CdS NCs with excellent FL properties could be applied to environmental, biological and other applications.

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