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有机硫源溶剂热法合成 CdS 纳米晶体

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摘要:以二硫化四甲基秋兰姆((TMTD)作为有机硫源,分别在苯、水-苯溶剂中于不同温度、不同时间溶剂热法合成了 CdS 纳米晶体。采用 FE-SEM、XRD 和 FTIR 对晶体的结构和成形机理进行了研究。结果表明,溶剂热温度比反应时间对晶体形貌的形成影响更大。CdS 纳米晶体是立方与六角的混合晶型。此外,溶剂的种类也是影响 CdS 纳米晶体结构和成形的重要因素,并且对花形 CdS 纳米晶体进行了阴极发光(CL)光谱的研究。

关键词:二硫化四甲基秋兰姆;CdS 纳米晶体;合成
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Solvothermal Synthesis of CdS Nanocrystals with Organic Sulphur Source

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Abstract: CdS nanocrystals were synthesized by a solvothermal method with tetramethyl thiuram disulfide(TMTD) as a sulphur source in benzene or water-benzene solvent at different temperatures for different periods of time. The structure and formation mechanism of CdS nanocrystals were investigated by field emission -scanning electron microscope(FE-SEM), X-ray diffraction(XRD) and fourier transform infrared spectroscopy(FTIR), respectively. The results indicated that the solvothermal temperature played a more important role than reaction time in formation of crystal morphology. CdS nanocrystals were found to be a mixed phase of cube and hexagon. Furthermore, the type of solvent was also an important influencing factor for the structure and formation of CdS nanocrystals. The cathodoluminescence(CL) of the obtained flower-like CdS nanocrystals was also studied.

Key words: tetramethyl thiuram disulfide; CdS nanocrystals; synthesis

Synthesis of nanoscale inorganic crystals with controlled size, shape, and hierarchy has attracted intensive research interests, since they are potential building blocks for advanced materials and optoelectronic devices [1]. Ⅱ-Ⅵ nano-semiconductors have long been a research hot-topic because of their quantum size effects-related physical and chemical properties [2~4]. CdS, an Ⅱ-Ⅵ semiconductor with a direct band gap of 2.4 eV, has received considerable attention and is extensively studied because of its promising applications in photoelectricity, magnetism, and catalysis[5~7].

At present, many researches particularly emphasize on dimension effect. Various methods have

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been developed for the synthesis of one-dimensional nanostructured CdS [8~10]. Nevertheless, physical and chemical properties of inorganic crystals are related to not only dimension but also shape. Controllable and selective syntheses of these three-dimensional nanostructured materials are still a great challenge[11~13]. Among various synthetic approaches, the solvothermal method is an important synthetic method for the preparation of unique morphologies nanomaterials. The formation mechanism would be different, depending on the solvothermal conditions such as precursor, reaction temperature, reaction time, and solvent[14~16].

In recent years, sulphur source has been often inorganic or common organic sulphur compounds, such as sodium sulfide, thiourea etc. To the best of our knowledge, there have been few reports on preparation of CdS nanostructures with a specific structured organic sulphur source. In this work, we investigate the formation of CdS nanocrystals with tetramethgl thiuram disulfide (TMTD) as sulphur source, whose molecular structure may be favorable to the morphologically controlled growth of CdS crystals, and cadmium acetate as cadmium source via a solvothermal route in water-benzene as mixed solvent or benzene solvent at different reaction temperatures and reaction time. The products were characterized with FE-SEM, XRD, and FTIR.

The reaction temperature was above 140 ℃ because TMTD only slowly decomposes at 140 ℃.

1 Experimental

1.1 Synthesis of cadmium sulfide nanocrystallines

All chemicals were A. R. grades and used without further purification.

In a typical procedure, 5.0 mmol cadmium acet ate and 2.5 mmol of tetramethyl thiuram disulfide (TMTD, $N(CH_3)_2-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2$ were respectively added to 40 mL benzene or the mixed solvent of water and benzene under stirring at ambient temperature for 1 h. Then the solution was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 140~180 ℃ for 12~48 h and allowed to cool down to room temperature naturally. Subsequently, the resulting yellow precipitate was filtered and washed with deionized water and ethanol to remove excessive byproducts. The final product was dried in a vacuum box at 60 ℃ for 6 h.

1.2 Characterization

The morphologies of the products were investigated by field emission scanning electron microscopy (FE-SEM) with LEO 1550. The crystalline phases of the products were determined by powder X-ray diffraction (XRD) on a Bruker D8-ADVANCE diffractometer with monochromatic Cu $K\alpha$ radiation (λ=0.154 06 nm) at 40 kV and 40 mA. XRD patterns were recorded from 20° to 70°(2θ) with a scanning rate of 2~7°·min^{-1}. The reaction mechanism was studied by Fourier transform IR (FTIR) spectroscopy with NEXUS670. The local optical property of material was investigated by Cathodoluminescence(CL) with Moto 3^{+}(Gatan).

2 Results and discussion

The solvothermal temp erature plays an important role in crystalline phase of the samples. Fig.1 displays XRD patterns of the samples obtained in water-benzene at different reaction temperatures for 24 h. The diffraction peaks of the samples can be indexed as mixed phase of cube and hexagon which is in agreement with the values in the standard card(PDF Card No. 89-0440 and 41-1049). As the solvothermal temperature increases, the crystal forms of the samples change as indicated by the intensity of the diffraction peaks. However, the mixed phase is still remained. Compared

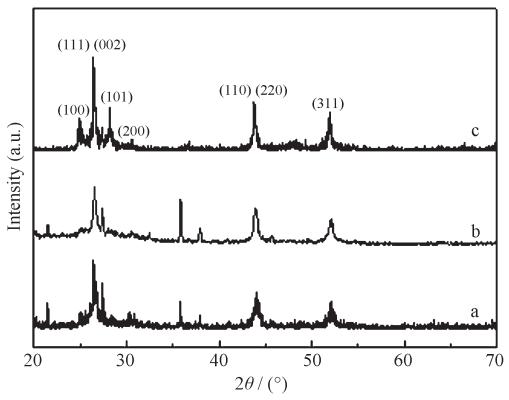


Fig.1 XRD patterns of CdS synthesized by solvothermal reaction in water-benzene at (a) 140 ℃, (b) 160 ℃, (c) 180 ℃ for 24 h

with those at 140 ℃, (100) and (101) peaks appear at 160 ℃and 180 ℃, while (111), (200), (220) and(311) peak still exist. It shows that hexagonal CdS wurizite structure gradually increases with the increase of solvothermal temperature. The relative intensity of (220) peak is higher than that of(110) peak at 180 ℃, whereas it reverses at 140 ℃ and 160 ℃. The relative intensity of the (002) peak(Fig.1c) is stronger than that of the other diffraction peaks of (100) and (101) for the sample obtained at 180 ℃, which represents relatively high crystalline order along(002). Moreover, many organic diffraction peaks at 140 ℃ and 160 ℃ appear, whereas they almost disappear at 180 ℃. This also indicates that TMTD adequately decomposes at 180 ℃.

Fig.2 displays XRD patterns of the samples obtained in water-benzene for different reaction time of 12~48 h at 180 ℃. As shown in Fig.2, the samples have the diffraction peaks of (100), (002), (101), (110), (111), (200), (220) and (311). The peaks of (100), (002), (101) and (110) are consistent with the major peaks of hexagonal CdS, and (111), (200), (220) and (311) are consistent with the major peaks of for cubic CdS. So CdS crystals obtained at 180 ℃ have always a mixed phase of cube and hexagon no matter what reaction time is. However, the relative intensity of the (002) peak is obviously stronger than that of the other diffraction peaks of (100) and (101). It shows that there is relatively high crystalline order along (002) and more crystal nucleus grows along the (002).

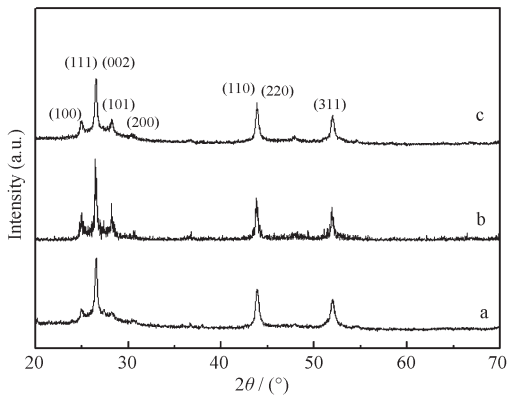


Fig.2 XRD patterns of CdS synthesized by solvothermal reaction in water-benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

Fig.3 displays XRD patterns of the samples obtained in benzene for reaction time of 12~48 h at 180 ℃. The samples have mixed phase of cube and hexagon with the increase of reaction time, which is in agreement with the values in the standard card(PDF No. 89-0440 and 41-1049). Miscellaneous peaks obviously disappear when the reaction time is 48 h, which shows that cadmium acetate and TMTD adequately decompose at 180 ℃ for 48 h. Moreover, the diffraction peaks are very weak and the sample has poor crystallinity when the reaction time is 12 h. As the solvothermal time increases, the crystallinity of the samples improves as indicated by stronger XRD peaks. It indicates that the reaction time influences the crystalline phase of the samples obtained in benzene at 180 ℃, which is different from the samples obtained in water-benzene.

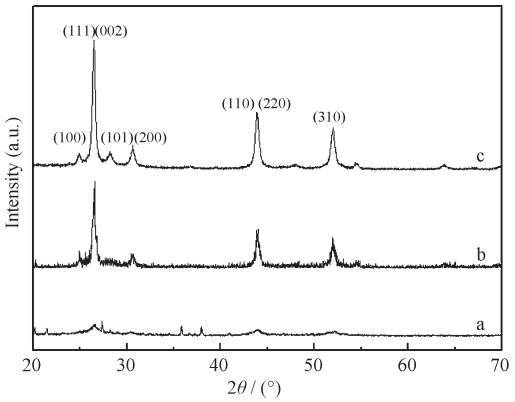


Fig.3 XRD patterns of CdS synthesized by solvothermal reaction in benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

It is well-known that the rearrangement of constituent atoms to generate new components and form crystals is thermodynamically controlled, as is the synthesis of colloidal inorganic nanocrystals [17,18]. The solvothermal temperature also plays an important role in formation of crystal structure, shape, and size. Fig.4 shows FE-SEM images of the samples prepared in water-benzene at various temperatures for 24 h. The development of CdS crystals obtained in the temperature range of 140~180 ℃ seems that flowers blossom out. The morphology of sample synthesized at 140 ℃ is observed to be particle aggregates with a diameter of ca. 50 nm, which is like flowers sprouting up on the lawn. As the solvothermal temperature increases, the samples seem to

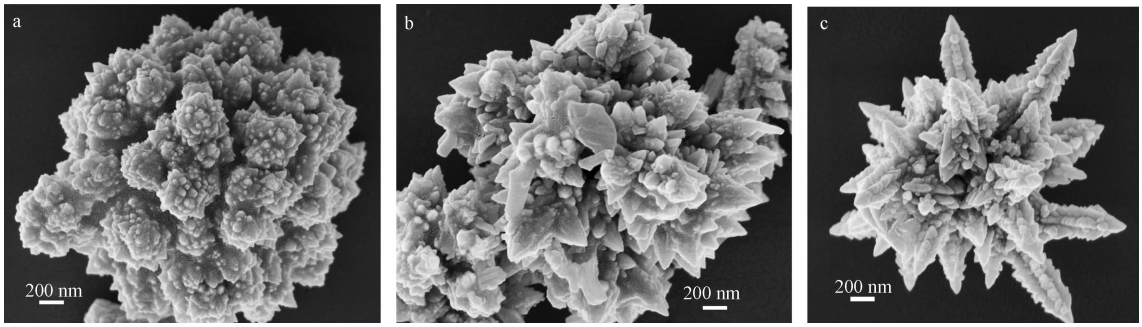


Fig.4 SEM images of CdS synthesized by solvothermal reaction in water-benzene at (a) 140 ℃, (b) 160 ℃, (c) 180 ℃ for 24 h

grow into flower with petals unfolding. The growth of the outside particles is faster than that of the inside particles, and the shapes of some particles change from microspheres to polygon. As the solvothermal temperature is 180 ℃, the sample appears to be blooming flower-like structure. The outer sphere of morphology is lamellar structure with hexagonal particle clusters, which is in agreement with Fig.1.

Kinetic factors have also been of great importance for the synthesis of inorganic nanocrystals[19]. Here the influence of reaction time on the shape-controlled syntheses of CdS nanocrystals was also studied. Fig.5 shows FE-SEM images of the samples prepared in water-benzene at 180 ℃ for different solvothermal reaction time. The solvothermal reaction time does not evidently influence the morphologies of products at 180 ℃, but it influences the growth of particles. As the solvothermal time is 12 h, flower-like particle aggregates and flower-like structure with petals unfolding exists at the same time. However, the number of particles aggregates decrease with the increase of solvothermal time, and the outside of crystals is lamellar structure with particle clusters in the middle part of laminae. The sample obtained at 180 ℃ for 48 h shows the morphology of more particle clusters growing into lamellar structure. Thus, the influence of solvothermal reaction time on the growth of crystals is less obvious than that of the solvothermal temperature. This result is in agreement with that of the XRD pattern of CdS samples(Fig.2).

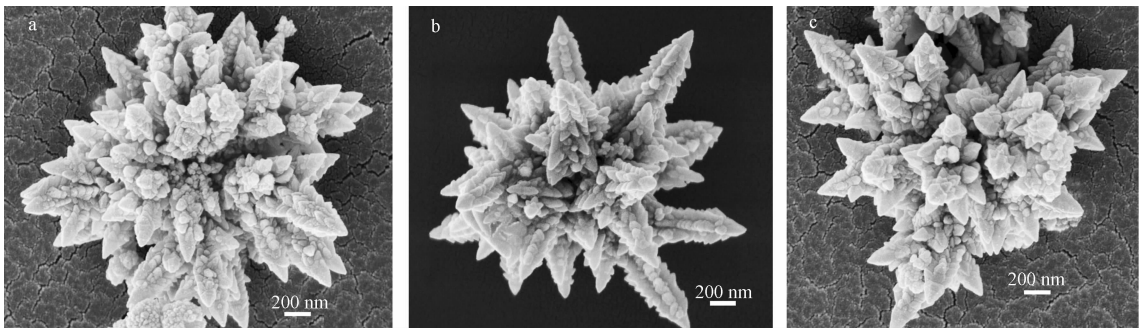


Fig.5 SEM images of CdS synthesized by solvothermal reaction in water-benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

Fig.6 shows FE-SEM images of the samples prepared in benzene at 180 ℃ for different solvothermal reaction time. It is found that the morphologies of samples obtained in benzene are nanoparticles structure with a diameter of 25~50 nm no matter what reaction time is. This is different from that of samples obtained in water-benzene. However, the nanoparticles are not uniformly dispersed.

In this work, FTIR spectroscopy is used to study the extent of participation of organic sulphur source and cadmium acetate in reaction and to also reveal the reaction mechanism. Fig.7 shows FTIR spectra of CdS synthesized by solvothermal reaction in water-benzene at different reaction temperatures for 24 h. These spectra exhibit characteristic bands of TMTD that are centred at 972 cm^{-1} and 848 cm^{-1}, assigned to C=S and

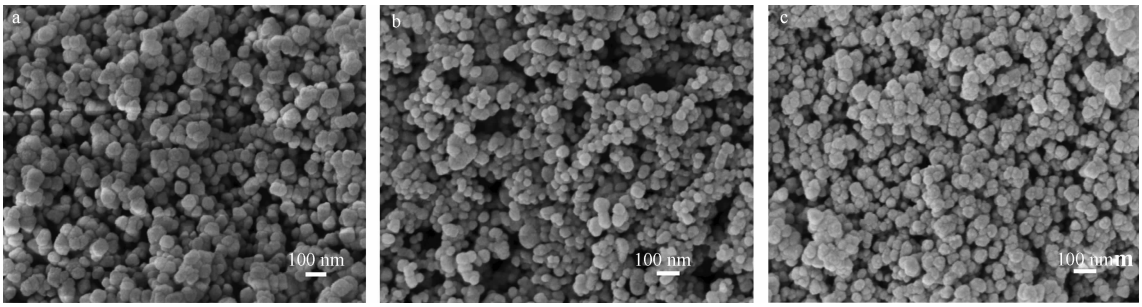


Fig.6　SEM images of CdS synthesized by solvothermal reaction in benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

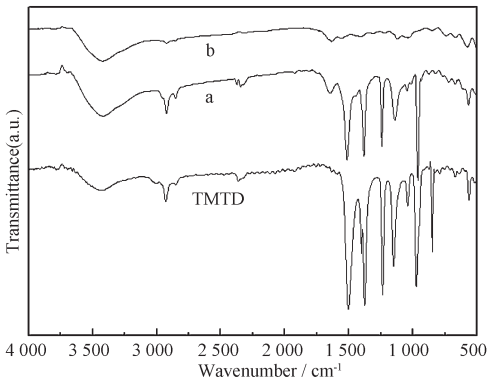


Fig.7　FTIR spectra of CdS synthesized by solvothermal reaction in water-benzene at (a) 160 ℃, (b) 180 ℃ for 24 h

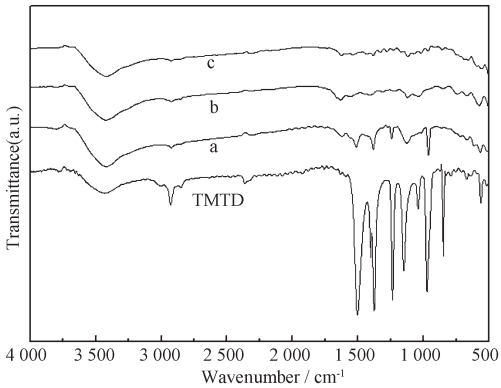


Fig.8　FTIR spectra of CdS synthesized by solvothermal reaction in water-benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

C-S, respectively. However, we observe a change in the strength of peaks with the increase of the solvothermal temperature. The ν(C-S) disappears at 160 ℃ and 180 ℃ compared with FTIR spectra of TMTD, and the ν(C=S) disappears at 180 ℃, which can be attributed to the participation of TMTD in reaction and the break of C-S and C=S.

Fig.8 shows FTIR spectra of CdS synthesized by solvothermal reaction in water-benzene for different reaction time at 180 ℃. Compared with FTIR spectra of TMTD, the strength of all characteristic peaks of CdS crystals is obviously weakened, which indicates that TMTD participates fully in solvothermal reaction and produces S^{2-} at 180 ℃.

Fig.9 shows FTIR spectra of CdS synthesized by solvothermal reaction in benzene for different reaction time at 180 ℃. Compared with FTIR spectra of TMTD, all characteristic peaks of CdS crystals obviously become weak, indicating participation of TMTD in solvothermal reaction at 180 ℃. However, as the solvothermal time is 24 h and 48 h, the relative intensity of characteristic peaks becomes weaker. As

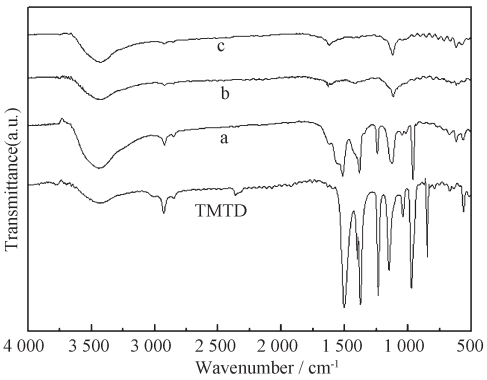


Fig.9　FTIR spectra of CdS synthesized by solvothermal reaction in benzene at 180 ℃ for (a) 12 h, (b) 24 h, (c) 48 h

mentioned previously, this is due to adequate decomposition of cadmium acetate and TMTD in solvothermal reaction at 180 ℃ for 24 h and 48 h.

Generally, the growth process of crystals can be divided into two steps: an initial nucleation stage and a subsequent crystal growth process. The critical factor that determines the morphology of crystals is the crystallographic phase of the initial crystal seeds formed in the nucleation stage. Once the preferential

crystalline phase is determined in the initial nucleation stage, the subsequent growth stage strongly governs the final architecture of the nanocrystals through the delicate balance between the kinetic growth and thermodynamic growth regimes[18,20].

In this experiment for mixed solvent, cadmium acetate is dissolved in water to produce cadmium ions, and TMTD is dissolved in benzene to slowly produce active sulfur anion above 140 ℃. The active Cd^{2+} reacts with the active S^{2-} on the interface of water-benzene to form CdS seeds. Once the CdS seeds are formed, CdS crystals grow on the surface of CdS seeds. At first, the concentration of S^{2-} on the interface is so low that the development of CdS crystals slows down. More active S^{2-} ions are released and the reaction between Cd^{2+} and S^{2-} goes on, as both the temperature and the reaction time are increased. In the final stage, it results in the formation of CdS nanocrystals with flowerlike structure, as shown in Fig.1. There are organic substances on the surface of CdS crystals because TMTD does not drastically decompose at relatively low temperature. Organic diffraction peaks are observed as shown in Fig. 1a ~b, whereas organic diffraction peaks basically disappear at 180 ℃ as shown in Fig.1c, which indicates that the rapid decomposition of TMTD is in favor of the development of CdS crystals. In a word, the growth of 3D CdS nanocrystals was thermodynamically and kinetically controlled, namely, temperature and time dependent.

However, in this experiment for benzene solvent, cadmium acetate is not dissolved in benzene, while TMTD is dissolved in benzene. S^{2-} and Cd^{2+} are released from TMTD and cadmium acetate by high temperature decomposition in solvothermal conditions. As a result, the concentrations of S^{2-} and Cd^{2+} are maintained at a stable level, which is in favor of anisotropic growth[21]. More Cd^{2+} ions are combined with S^{2-} ions with the increase of the reaction temperature, and CdS crystals quickly grow. The anisotropic growth of the CdS crystals is completely stopped and instead irregular polycrystalline nanoparticles are produced, as shown in Fig.6. There are still many miscellaneous peaks at 180 ℃ for 12 h, which may be due to inadequate decomposition of cadmium acetate.

Cathodoluminescence(CL) is the emission of light as a result of electron bombardment. We explored the optical properties of flower-like nanocrystal by employing high spatial resolution CL spectroscopy. Fig.11 displays a typical CL spectrum acquired from a flower-like CdS nanocrystal synthesized at 180 ℃ for 24 h (SEM image shown in Fig.10). The spectrum consists of a slight UV peak centred at 412 nm(3.0 eV) and a broad and strong green emission, respectively, centred at 524 nm((2.36 eV) and 532 nm(2.33 eV), as shown in Fig. 11a. However, the spectrum excitated from the laminae only shows a narrow and strong peak centred at 520 nm (2.38 eV).

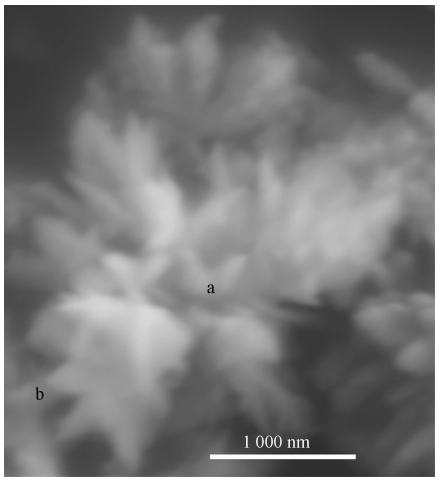
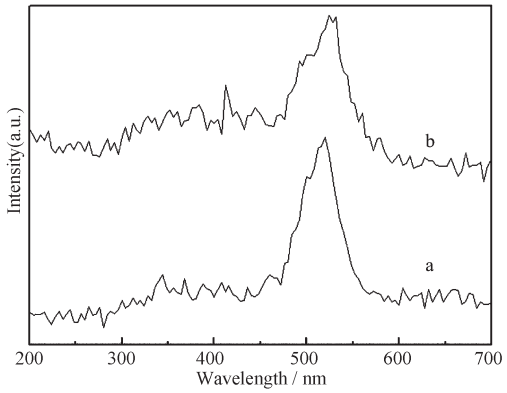


Fig.10 Mapping of the flower-like CdS

CdS nanocrystals typically have two characteristic emissions. The emission at 520~540 nm is assigned to hole-electron recombinations at surface traps, while the higher energy emission at 412 nm is attributed to recombination from the excitonic state in the crystallite interior[22,23]. Compared to Fig.11a, the slight UV peak in Fig.11b may be due to favorable dispersion of CdS nanocrystal in the flower interior. It is also observed that there is defect-related red shift originated from the trapped states at low-energy emission. The fluctuation in the surface charge density and local fields result in the inhomogeneous broadening of the excitonic peaks.[24] The influence of surface is revealed from the broad asymmetric emission toward the higher wavelength, and these emissions are originated from the surface donor-acceptor pair (DAP) recombinations [24]. All emission demonstrates that the CdS nanocrystals with flower-like



(a) excitated from the laminae;
(b) excitated from the centre of flower

Fig.11　CL spectra recorded from the flower-like CdS nanocrystal

morphology in this work possesses excellent optical property, implying potential applications for the CdS nanocrystals as building blocks in optoelectronic devices.

3　Conclusions

A special structured organic sulphur source TMTD was used to synthesize CdS by solvothermal route. The morphologies of CdS nanocrystals could be controlled by solvent, reaction temperatures and time. The morphologies are transformed from particle aggregates to blooming flower-like structure with the increase of solvothermal temperature, while the morphologies are always kept blooming flower-like structure with the increase of reaction time at 180 ℃ in water-benzene. However, the morphologies are always in nanoparticle structure with the increase of reaction time at 180 ℃ in benzene. Furthermore, CdS nanocrystal has mixed phase of cube and hexagon regardless of in water-benzene or in benzene solvent. The possible formation mechanism of the CdS nanostructures obtained in water-benzene and benzene is also suggested. The synthesis of crystals is thermodynamically and kinetically controlled. The number of sulfur ions and cadmium ions has effect on the development of CdS crystals. CL spectra demonstrate that the CdS nanocrystals with flower-like morphology possess excellent optical property.

The formation mechanism of the CdS nanostructures obtained in other solvents may need further study.

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