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Morphology control of CdSe nanocrystallines

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CdSe nanocrystallines with different micromorphology were synthesized by inverse microemulsion method. X-ray diffraction and transmission electron microscopy were used to characterize the micromorphology, phase and ingredient compositions of nanocrystallines. The results indicate that nanosphere, necklace-shaped and bamboo-likeCdSe nanocrystals were successfully prepared. The bamboo- like nanotubes have the best crystallization performance. The red shift of the fluorescence peak can be observed clearly, and bamboo-shaped nanotubes have stronger fluorescence emission. Detailed study on the formation of bamboo-like nanotubes was performed. The mechanism is as follows: the difference of the bound water content at the interface and the free water content in the water core leads to the density difference between outer layer and the center. The diffusion of Se^{2-} and Cd^{2+}induces hollow structure of CdSe nanospheres. Due to the small size effect, hollow nanospheres grow into necklace-shaped and bamboo-structure finally.

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Keywords: Microemulsion, Nanosphere, Nanotube, Nanocrystalline

1. Introduction

Among all semiconductor nanocrystals, CdSe nanocrystallines have attracted the most widespread interest due to their narrow fluorescence peaks and larger exciton bohr radius [1]. The morphological correlation and size correlation have important influence on the properties of nanocrystallines. The micromorphological adjusting can change the electronic structure more effectively than the size adjusting. For example, spherical CdSe quantum dots emit plane-polarized light, while rod-shaped CdSe nanocrystallines emit linearly polarized light along the long axis. This feature will be applied in some orientation-sensitive field, such as molecular markers. Therefore, it is very important to control the morphology of nanocrystallines during the preparation process. So far, there have been a large number of reports on CdSe nanomaterials with different morphologies such as zero-dimensional quantum dots, one-dimensional nanowires, rods, two-dimensional nanosheets, films, three-dimensional nanoparticles and core-shell structure nanospheres[2-3].With the in-depth research, dendritic[4], four-cornered pod-shaped[5], ribbon-shaped[6], needle-shaped[7], jagged[8] nanocrystallines and nanoclusters are all successfully prepared[9], the application field of CdSe is expanded greatly.The optical property was controlled by the size and morphology of nanocrystallines. The microemulsion method can control the size and morphology of nanocrystallines by adjusting the concentration of water and surfactants in the system and the types of surfactants, which is widely used to prepare various inorganic functional nanomaterials[10-12]. In this project, CdSe nanocrystallines with different morphologies were prepared by the inverse microemulsion method, and the formation mechanism was studied from the crystallographic point of view.

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2. Experimental

1) Cd^{2+} complex solution was prepared by adding excessive ammonia water to $Cd(NO_3)_2$ aqueous solution, Then a quantitative Cd^{2+} complex solution was added to CTAB/n-hexane/isobutanol mixture liquid. After stirring magnetically, a microemulsion with the Cd^{2+} complex as the water phase was obtained;

2) Na_2SeSO_3 solution was prepared by reverse microemulsion method, using sodium sulfite, selenium powder and chromium nitrate as raw materials, dodecyl trimethyl amine bromide (CTAB) as surfactant, isobutanol as co-surfactant, and n-hexane as oil phase.A quantitative Na_2SeSO_3 solution was add toCTAB/n-hexane/isobutanol mixture liquid, and then a microemulsion with Na_2SeSO_3 solution as the aqueous phase was prepared;

3) Mixed the microemulsion prepared in 2) into the microemulsion prepared in 1);

4) The product of 3)was washed with distilled water and absolute ethanol. CdSe precipitates were obtained after magnetically stirring the product for 1h and centrifugation;

X-ray diffraction analysisof the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX 2500, Rigaka) with Cu Kα radiation (λ =0.154056 nm). The morphology ofthe as-prepared products was characterized by transmission electron microscopy (TEM, JEOL-2010, operating voltage of 200 kV) and scanning electron microscopy (SEM, S-4800). Fluorescence spectra and ultraviolet-visible spectra were recorded by an LS55 fluorospectrophotometer (Pekin Elmer, America)and a Lambda 750S UV-Visible-NIR spectrophotometer (Hitachi, Japan) respectively.

3.Results and discussions

Three different morphologies of nanocrystals were synthesized by microemulsion method under different preparation conditions. The result of XRD analysis is showed in Figure 1. The phase compositions of nanocrystals are CdSe. The phase composition of the three morphologies of nanocrystals are all CdSe, among which the bamboo-shaped nanotubes have the strongest and sharpest diffraction peaks, indicating that the bamboo-shaped nanotubes have the best crystallization performance.

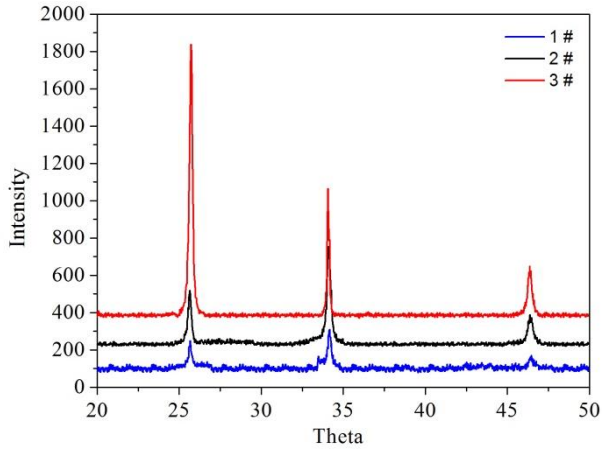

Fig.1. XRD patterns of nanocrystals.

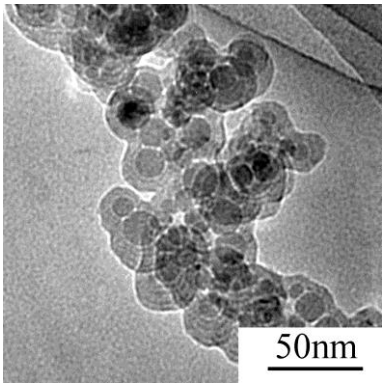

Fig.2. TEM pattern of nanospheres(1#).

Figure 2 shows the TEM pattern of nanospheres. When W=[H_2O] / [CTAB] =40 mol/L, [CTAB]=0.044 mol/L, [$Cd(NO_3)_2$]=0.2 mol/L, [Na_2SeSO_3]=0.2 mol/L, standing for 10 minutes, nanocrystals are nanospheres with the diameter of 20nm. The nanosphere is wrapped with a thick film.

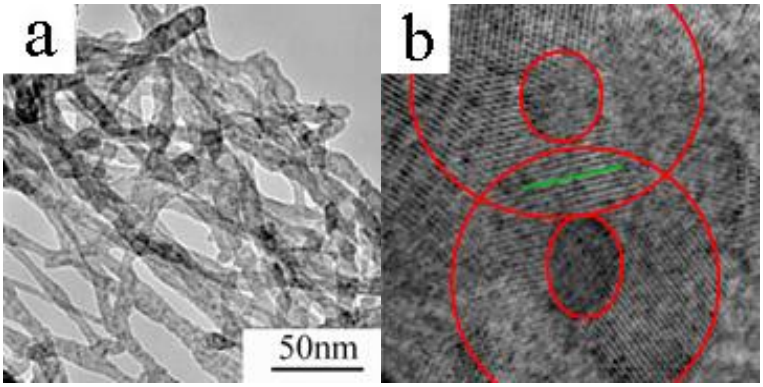

Fig.3.TEM patterns of (a)necklace-like nanotubes(2#); (b) HRTEM of the grain boundary.

Figure 3 shows the TEM patterns of necklace-like nanotubes. When W=[H_2O] / [CTAB]=40, [CTAB]=0.045 mol/L, [$Cd(NO_3)_2$]=0.4 mol/L, [Na_2SeSO_3]=0.4 mol/L, standing for 24h, nanocrystals are necklace-shaped nanotubes with the diameter of 6nm and rough surface. The necklace-shaped nanotubes are formed by epitaxial hollow nanospheres. The two hollow spheres have the same lattice orientation at the junction, which provides evidence for epitaxial growth [13].

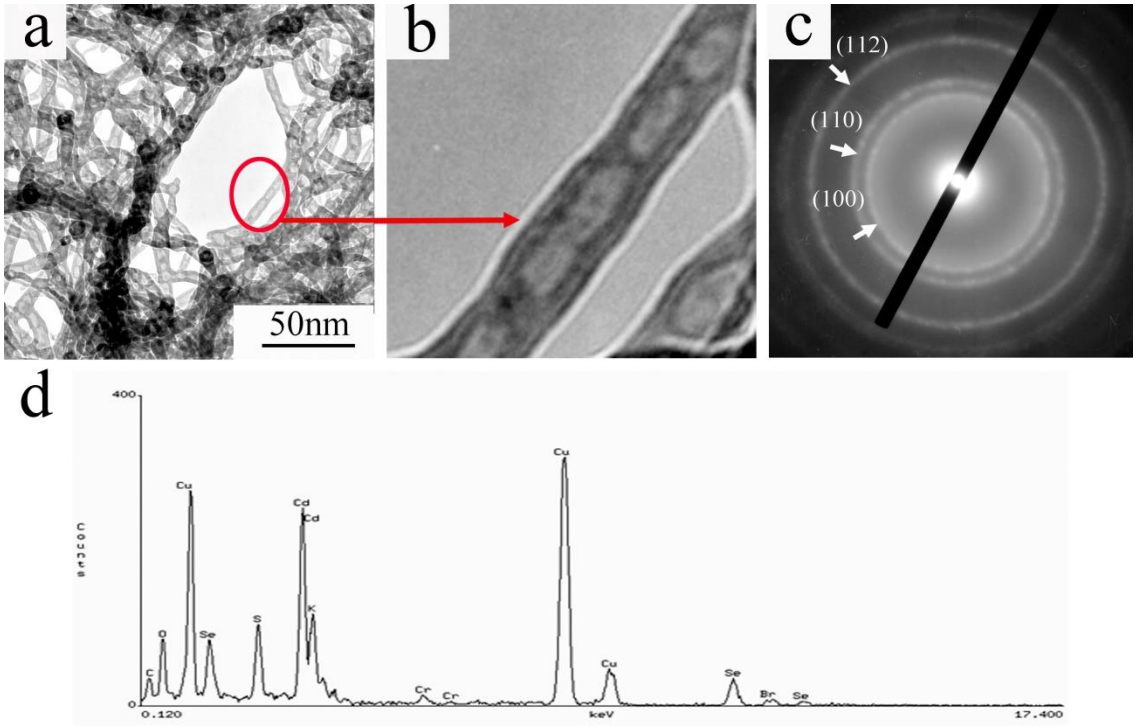

Fig.4. TEM patterns of bamboo-like nanotubes(3#).

When W=[H_2O] / [CTAB]=40 mol/L, [CTAB]=0.045 mol/L, [$Cd(NO_3)_2$]=0.4 mol/L, [Na_2SeSO_3]=0.4 mol/L, standing for 72 hours, nanocrystals grow into bamboo-shaped nanotubes witha diameter of 18nmand smooth surface, showed in Figure 4(a). The enlarged image of the field marked with circle in the figure 4(a) shows the smooth surface, showed in Figure 4(b).The electron diffraction pattern showed in Figure 4(c) indicates good crystallinity. Figure 4d shows the EDS spectrum of bamboo-shaped nanotubes. It can be seen from the spectrum that the nanocrystals are mainly Cd and Se. It is concluded that CdSe bamboo-shaped nanotubes are prepared successfully.

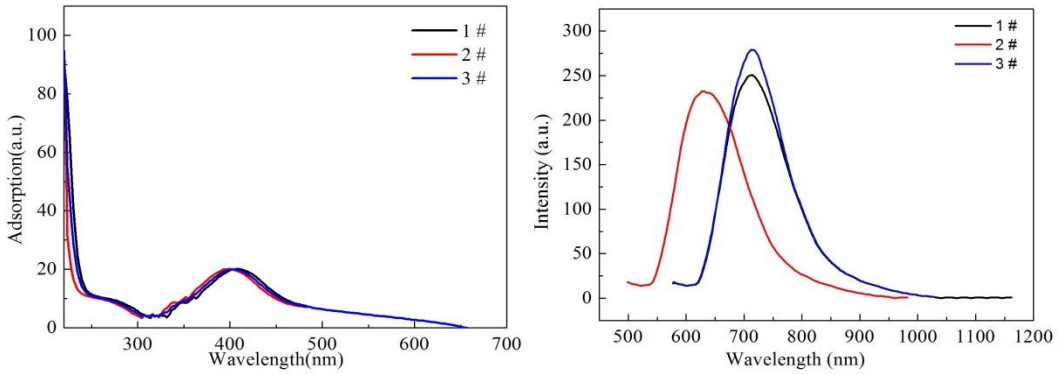

Fig.5.UV-Vis spectrums and fluorescence spectrums ofnanospheres;necklace-like nanotubes and bamboo-like nanotubes.

The above figure shows the ultraviolet-visible absorption spectrums and fluorescence spectrum of the synthesized CdSe nanomaterials with different morphologies. It can be seen from UV absorption spectrums that three types of CdSe nanomaterials have significant absorption peaks near 467nm, which proves that the CdSe nucleus is generated instantly when the Cd^{2+} complex solution is added to the CTAB/n-hexane/isobutanol mixture. The same excitation light is used to

simultaneously excite nanomaterials with different morphologies, and the fluorescence of different wavelengths is emitted respectively. The position of the fluorescence peak is related to the physical size of nanomaterial. We can clearly observe the red shift of the fluorescence peak. Necklace-shaped nanotubes have the smallest size as an intermediate product. Surface defects of bamboo-shaped nanotubes are reduced, so stronger fluorescence emission is obtained.

4. Mechanism analysis

The formation mechanism of bamboo-shaped CdSe nanotubes is explained as follows: when the microemusion containing Cd^{2+} and the microemulsion containing $SeSO_3^{2-}$ are mixed, a reaction channel forms at interface membrane ruptures in the collision process. The micelles exchange reaction substances through the reaction channel [14]. The micelles containing Cd^{2+}, $SeSO_3^{2-}$, and CdSe continuously collide, fuse, and split. $SeSO_3^{2-}$ decomposes into Se^{2-} in an alkaline environment. And then Se^{2-} and Cd^{2+} react to form CdSe crystal nucleus. In this process, when the size of crystal nucleus exceeds the critical size, it will grow up to form CdSe nanocrystals. Under the action of the micelle template, CdSe nanospheres form [15]. Because the bound water content at the interface film is less than the free water content inside the water core, the solubility of the CdSe crystal nucleus near the interface film is less than the solubility inside the water core, that is, the density of the outer layer of CdSe nanospheres is less than the central density. The difference of concentration drives Se^{2-} and Cd^{2+} to diffuse to the outer layer. Due to the Kirkendall effect, a lot of holes are formed in the center of the CdSe nanospheres. As the process develops, these holes fuse to form larger holes, hollow CdSe nanospheres form finally[16-18]. Due to the small size effect, hollow CdSe nanospheres oriented attach to form necklace-shaped nanotubes [19]. The surface tension gradient tends to transfer the mass from the tips to sides, the surface of the necklace-shaped nanotube become smoother in the surface mass diffusion motion [20-22], and finally the bamboo-shaped nanotube forms [23-24], the schematic diagram is shown in Figure 6.

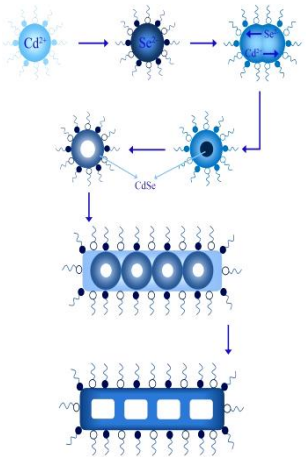

Fig.6.Schematic diagram of formation mechanism of bamboo-like nanotube.

5. Conclusions

In this paper, the nanosphere, necklace-shaped and bamboo-like CdSe nanocrystals were successfully prepared by the reverse microemulsion method under different conditions.The bamboo-shaped nanotubes have the best crystallization performance and stronger fluorescence emission. The formation mechanism is as follows: because the bound water content at the interface film is less than the internal free water content, the density of the outer layer of the CdSe nanospheres is lower than the central density. Due to the Kirkendall effect, holes formed in the

center of the CdSe nanospheres. Holes mergerto hollow structure. Due to the small size effect, hollow CdSe nanospheres oriented to form necklace-shaped nanotubes and bamboo-shaped nanotubes.

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