Preparation of CdS semiconductor nanomaterials with different morphologies

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Abstract Cadmium sulfide (CdS) nanocrystals were successfully prepared by hydrothermal method, and chromium nitrate [Cd(NO$_3$)$_2$] was used as the source of cadmium, thiourea as the source of sulfur, and hexamethylenetetramine [(CH$_2$)$_6$N$_4$, HMT] as a capping agent. In this paper, the shape and size of nanocrystals were regulated by adjusting the preparation process, such as the proportion of raw materials and the amount of capping agent. The X-ray diffraction (XRD) was used to identify structure of CdS nanostructures, and morphologies were examined by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

1. Introduction
In recent years, nanocrystalline materials have attracted much attention because of their potential application value in the field of new energy, mainly focusing on solar cells, nonlinear optics, photoelectron chemical batteries and photocatalysis. In the past decades, the preparation and application of semiconductor nanomaterials (ZnO, ZnS, CdS, CdSe, etc.)$^{[1,2,3]}$ have made amazing progress. In the design of nanomaterials, it is gradually recognized that the factors affecting the properties of nanomaterials include not only the chemical composition and size effect, but also the morphology (i.e. the exposed crystal surface).

As a common semiconductor material, CdS is a typical direct-wideband gap II-VI semiconductor material, with a band gap of 2.42 eV at room temperature, and excellent physico-chemical properties such as photoelectric conversion and luminescence performance. It is found that with the change of size and morphology, the gap width of CdS nanostructures will change significantly, leading to great differences in their photoelectric and photocatalytic properties. There are many ways to synthesize different morphologies of CdS nanocrystals, such as solid phase method$^{[4]}$, water-solvent hot method$^{[5]}$, microemulsion method$^{[6]}$, sol-gel$^{[7]}$, and through these methods successfully create nanostructures with different morphology and size, such as nanowires, nanoparticles and nanorods$^{[8,9]}$. Many researches successfully prepared three-dimensional CdS nanocrystals via thermal evaporation and solvothermal approach$^{[10]}$. Although these preparation methods can successfully prepare CdS nanocrystals, the preparation process is complex and the particle size is difficult to control, which limits the further application.

The hydrothermal approach can control the morphology, size, crystallinity and fewer defects of the reaction products, and has many advantages, such as low synthesis temperature, mild reaction
conditions, stable solvent system, non-volatile components, and no impurities. Moreover, the reaction process is simple and repeatable because it is carried out in a confined space, avoiding the emission of toxic substances. Therefore, as a simple and safe synthesis technology, it will be further developed. So et al. [11] successfully prepared cadmium sulfide nanoparticles and nanorods by traditional hydrothermal method, and studied the effects of reaction time and temperature on the morphology and crystal morphology of samples.

In this paper, high performance CdS nanocrystals with controllable morphology were prepared by hydrothermal solvent thermal method and process parameters were strictly controlled. The cheap raw materials such as cadmium chloride, cadmium nitrate and sodium thiosulfate were used as cadmium and sulfur sources. On this basis, the effects of hydrolysis time, reaction temperature, solvent and other factors on the morphologies and structure of CdS nanomaterials were explored.

2. Experimental Section

2.1 Preparation of CdS nanocrystals

The different CdS nanomaterials were synthesized by hydro-thermal solvent thermal method. The detailed steps as follows, the raw materials of cadmium nitrate tetrahydrate (Cd(NO3)2·4H2O) and thiourea (CH4N2S), and the capping agent hexamethylenetetramine [(CH2)6N4), HMT] were added into a certain amount of deionized water, respectively. In order to obtain nanocrystals with different morphologies, the ratio of raw material Cd to S precursor can be changed. And the dendritic-like CdS (D-CdS), branched-like CdS (B-CdS), petaloid-like CdS (P-CdS) were produced by regulating the ratio of Cd(NO3)2•4H2O, CH4N2S and HMT at 1:1:0, 1:3:1, 1:1:1, respectively. The resulting mixture is transferred to a teflon-lined stainless steel autoclave, which is then sealed and kept at 200 ℃ for 12 hours. After the mixture was cooled to room temperature, the finished product was collected, washed several times with ultrapure water and ethanol, vacuum-dried and preserved for further identification.

2.2 Characterization

The microstructures and morphologies of the CdS nanocrystals were characterized by a field emission scanning electron microscopy (FE-SEM; JEOL, JSM-6701F, Japan) and a high-resolution transmission electronic microscopy (TEM; JEOL, JEM-2100, Japan). The X-ray diffraction (XRD; Bruker, D8 ADVANCE, Germany) were identified the crystal microstructures of the samples.

3. Results and Discussion

By changing the molar ratio of Cd to S precursor (Cd/S), CdS nanocrystals of different sizes and shapes were prepared. The proportions of Cd(NO3)2•4H2O, CH4N2S and HMT were adjusted to 1:1:0, 1:1:1 and 1:3:1 respectively to synthesize A, B and C samples. Figure 1 shows the XRD pattern of CdS samples prepared by using different proportions of Cd and S precursor. As can be seen from the Figure 1, the diffraction peak is strong and sharp, indicating that the product crystallizes well. Meanwhile, all diffraction peaks can be labeled as the pure hexagonal structure of CdS, which are consistent with the literature values (JCPDS card number 41-1049), and do not show impurities. Compared with the standard card, the intensity of the diffraction peak becomes stronger, which can be attributed to the preferred growth orientation of the crystal along the C axis.
Figure 1 XRD pattern of samples synthesized with different ratios of Cd, S and HMT: A, B, C of 1:1:0, 1:3:1, 1:1:1

Figure 2 shows the SEM images of different morphologies of the synthesized CdS nanocrystals. By regulating the added ratio of cadmium precursor to sulfide precursor (abbreviated as Cd/S), the morphology of the CdS nanocrystals varied, in which the dendritic-like CdS (D-CdS, Figure 2A), branched-like CdS (B-CdS, Figure 2B), petaloid-like CdS (P-CdS, Figure 2C) were prepared by adjusting the ratio of Cd(NO$_3$)$_2$•4H$_2$O, CH$_3$N$_2$S and HMT at 1:1:0, 1:3:1, 1:1:1, respectively. Interestingly, we found that the structural evolution of cadmium crystals is more dependent on HMT concentration than on cadmium ion concentration. In the absence of HMT, only D-CdS with micrometer scale are obtained. Compared with concentration of Cd, when HMT concentration increases to the same level, CdS grows into nanometer scale structure. When the molar ratio of Cd/S was 1:1, the morphology of CdS nanocrystals changed into an approximate P-CdS structure (Figure 2C). Interestingly, we found that CdS nanocrystals (Figure 2B) with branched structure were formed when the Cd/S molar ratio was 1:3.

Figure 2 SEM images of CdS nanocrystals with different shape
To further characterize the microstructure of nanocrystals, transmission electron microscopy (TEM) characterization was used. From Figure 3b, it clearly indicates that B-CdS is composed of five to eight pods, and it is consistent with the previous SEM data.

![Figure 3 SEM images of CdS nanocrystals with different shape](image)

Figure 3 SEM images of CdS nanocrystals with different shape

4. Conclusions
In summary, a simple hydrothermal method is used to synthesize CdS nanocrystals with controllable shapes. And no organic solvents are used throughout the process, which is environmentally friendly. By changing the parameters such as precursor ratio and capping agent, it was found that the morphology of nanocrystals could be effectively regulated. XRD data show that the synthesized CdS nanocrystals have high crystal quality.

In this paper, CdS nanocrystals with controllable morphology and better crystal shape were successfully prepared by a simple and environment-friendly one-step hydrothermal method, paving the way for the potential application of CdS nanocrystals in photoelectric devices.

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