Research Article

Synthesis of Co-Doped CdS Nanocrystals by Direct Thermolysis of Cadmium and Cobalt Thiolate Clusters

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Co-doped CdS (Co:CdS) nanocrystals with controllable morphology (quantum dots and nanorods) were easily synthesized by direct thermolysis of (Me₄N)₂[Co₄(SC₆H₅)₁₀] and (Me₄N)₄[S₄Cd₁₀(SPh)₁₆] under different precursor concentration, in virtue of the ions exchange of molecular clusters. The Co:CdS quantum dots were produced under low precursor concentration, and the Co:CdS nanorods could be obtained under higher precursor concentration. The Co-doping effect on the structure, growth process, and property of CdS nanocrystals was also investigated. The results indicated that the Co-doping was favorable for the formation of the nanorod structures for a short reaction time. In addition, the Co-doping in the CdS lattice resulted in the ferromagnetic property of the Co:CdS quantum dots at room temperature. Moreover, compared with the CdS quantum dots, the Co:CdS quantum dots exhibited obvious quantum confinement effect and photoluminescence emission with slightly red-shift.

1. Introduction

The doping of magnetic ions into semiconductor nanoparticles potentially gives a new class of materials, diluted magnetic semiconductors (DMSs) [1]. In II–VI materials, the magnetic coupling for Mn and Co ions in bulk semiconductors has been observed [2, 3]. DMSs are currently receiving much attention due to their potential applications in magnetic, electronic [4], and biological labeling fields [5], especially in the emerging field of spin-based electronics, or “spintronics.” The objective of spintronics is to control electron spins in order to transmit information and provide new functionality to semiconductor devices, for example, semiconducting alloys [6], semiconducting film [7], and nonmagnetic semiconductor [8, 9]. The potential applications and the possibility of novel magneto-optical phenomena in these materials have motivated the exploration about the synthesis techniques of magnetic ions doped nanocrystals (NCs).

CdS is a popular II–VI semiconductor material and can be easily synthesized, which makes it an effective test vehicle in training as well as in the demonstration of innovative technologies [10]. Furthermore, CdS has a large band gap (2.42 eV) and can form a doped semiconductor by adding a third element. Much effort of magnetic ions doping has focused on CdS NCs such as Mn [11,12]. Mn can easily replace Cd because the radius of Mn ion is close to that of Cd ion. In addition, the incorporation of Mn in CdS crystal lattice slightly disturbs CdS crystal structure. In previous reports [11, 13], Mn²⁺-doped CdS NCs have been synthesized by colloidal route based on the simultaneous precipitation of CdS and MnS or by a coprecipitation reaction in reverse micelles using Na₂S as the sulfur source. However, the results show that only a small fraction of the initial Mn²⁺ added can be incorporated into the crystal lattice, while a large proportion of the Mn²⁺ remain on the surface or form MnS precipitates. Consequently, in the case of nanostructured materials, the small size and large surface area-to-volume ratio present a significant challenge to impurity doping.

Co²⁺-doped II–VI systems could exhibit stronger coupling than that of Mn-doped NCs, due to the increased Co d-orbital mixing with the valence band and conduction band of the II–VI host. It is possible for the Co-doped CdS NCs to induce novel magneto-optical phenomena which could open new possibilities for spintronics studies and applications. Recently, room-temperature ferromagnetism
has been reported for some Co\(^{2+}\)-doped NCs, such as TiO\(_2\) [14, 15] and ZnO [16]. For Co\(^{2+}\)-doped NCs, doping occurs primarily at the surface or near-surface sites in these materials by simple coprecipitation [17] and standard inverted micelle coprecipitation methods [18]. Radovanovic and Gamelin [18] have shown that normal soft chemical processing does not render cobalt substitution in a CdS matrix and that the dopants are diverted to the surface. It is attributed to the large mismatch between the radius of Co and Cd ions, which is responsible for exclusion of Co ions during CdS NCs growth. They have proposed an interesting core/shell strategy to solve this problem. Unfortunately, no magnetic properties are examined. Bogle and coworkers [19] synthesized CdS:Co NCs via a route of pulsed high energy electron induced synthesis, and the incorporation of Co is realized in the CdS NCs under stoichiometric proportion in liquid medium condition. Nevertheless, the method needs special instrument and is less controllable especially for the NCs morphology and optical properties. The difficulty of controlling doping is to develop convenient methods for the preparation of high-quality Co-doped CdS NCs.

To obtain magnetic ions internal doped NCs, the chemical synthesis of molecular clusters is another possible strategy, and this synthesis method has ability to exchange metal and chalcogenide atoms among each other [20]. The character is explored during the synthesis of Co ions doped CdS [21] and Mn ions doped ZnSe NCs [22]. Inorganic clusters such as \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\) are a class of materials that exist as discrete units related to a fragment of a bulk lattice [23, 24]. As the metal-chalcogen bond has already existed in the \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\), thermolysis of the cluster provided a preformed template for the construction of nanocrystals (which has been synthesized in our previous work [25]). Application of molecular-cluster-based precursors for NCs growth offered an alternative synthetic methodology for material preparation with novel properties.

In this work, Co-doped CdS NCs with different morphologies (quantum dots and nanorods) were synthesized in virtue of the ions exchange of molecular clusters. By direct thermal decomposition of two clusters, \((\text{Me}_4\text{N})_2\text{Cd}_6(\text{SC}_6\text{H}_5)_16\) and \((\text{Me}_4\text{N})_2\text{Cd}(\text{SPh})_6\), in hexadecylamine (HDA), uniform CdS:Co quantum dots were obtained under low precursor concentration and CdS:Co nanorods were formed by increasing the cluster concentration. The morphology and structure of the Co-doped CdS NCs were thoroughly characterized by TEM, HRTEM, and XRD. The luminescent and ferromagnetic properties of the nanocrystals were further investigated by ultraviolet-visible (UV-vis) absorption spectroscopy, photoluminescence (PL) spectroscopy, and physical properties measurement system (PPMS).

2. Materials and Methods

2.1. Materials. Cd(NO\(_2\))\(_2\)-4H\(_2\)O, Co(NO\(_3\))\(_2\)-6H\(_2\)O, triethylamine, acetonitrile, sulfur powder, tetramethylammonium chloride, and hexadecylamine (HDA) were purchased from Aldrich Chemical. Pyridine, methanol, and toluene used in research were of analytical grade. \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\) and \((\text{Me}_4\text{N})_2\text{Cd}_6(\text{SC}_6\text{H}_5)_16\) were prepared according to the reported methods [23, 26].

2.2. Synthesis of Co-Doped CdS Quantum Dots. In the typical synthesis of the CdS:Co quantum dots, the cadmium thiolate cluster \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\) (1.2 g) and the cobalt thiolate cluster \((\text{Me}_4\text{N})_2\text{Cd}_6(\text{SC}_6\text{H}_5)_16\) (0.2 g and 0.5 g) were added in 80 g HDA at 80°C under an atmosphere of nitrogen. The temperature of the reaction mixture was raised to 220°C and the growth of the CdS quantum dots was monitored by recording the optical absorption spectra. At the desired crystal size, the crystalline growth was subsequently terminated by cooling the reaction mixture to approximately 60°C, followed by precipitation from HDA via the addition of anhydrous methanol to produce precipitated samples. The purification of the CdS:Co quantum dots was carried out by suspension in toluene followed by reprecipitation in methanol and isolation by centrifugation. After purification, the dried samples are about 10.8 and 12.4 g/L (with 0.2 g and 0.5 g cobalt thiolate cluster, resp.). To efficiently eliminate those Co ions which may be physically adsorbed on the surface of NCs, the as-prepared samples were stripped with pyridine to perform the ligand exchange [27]. Particle size for the Co:CdS samples was determined by UV-vis absorption and TEM measurements. As a reference, CdS NCs were prepared by the similar method without addition of cobalt thiolate cluster.

2.3. Synthesis of Co-Doped CdS Nanorods. Synthesis of Co-doped CdS nanorods was performed by using the parallel methodology by thermolysis of 1.2 g \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\) and of 0.2 g or 0.5 g \((\text{Me}_4\text{N})_2\text{Cd}_6(\text{SC}_6\text{H}_5)_16\) in different contents of HDA. The following process and purification of CdS:Co nanorods are the same as those of quantum dots.

2.4. Characterization. TEM and HRTEM were performed on a Tecnai S-Twin electron microscope operating at 200 kV. ICP was performed on an Optima 5300 DV (Perkin Elmer Inc.). Samples were dissolved in a 2% HNO\(_3\) solution, and the Cd and Co concentrations were measured against known Cd and Co standards (High Purity Standards). XRD patterns of the nanocrystals were recorded with a Rigaku D/max-\(\gamma\)B diffractometer equipped with a rotating anode and a Cu Ka source (\(\lambda = 0.154056 \text{ nm}\)). UV-vis absorption spectra were recorded at room temperature on a UV-2550 spectrophotometer. Photoluminescence (PL) spectra were recorded at room temperature on a FP-6500 spectrophotometer. Magnetic measurements were carried out using the physical properties measurement system (PPMS) of Quantum Design with a magnetic field up to 5 T.

3. Results and Discussion

3.1. Synthesis of Co-Doped CdS Quantum Dots. The thiopehtolate complex of \((\text{Me}_4\text{N})_4\text{S}_4\text{Cd}_{10}(\text{SC}_6\text{H}_5)_16\) is used as the precursor, and metal ion exchange reactions in the clusters
have been revealed [20, 28, 29]. For example, metal exchange has been shown to occur in \( [S_4M_{10}(SPh)_{16}]^{16−} \) (M=Cd, Zn) for Zn\(^{2+}\)/Cd\(^{2+}\) by NMR analysis [28]. Løver et al. [29] have also investigated the metal ion exchange process using electrospray mass spectrometry in the thiophenolate-capped clusters, such as \( (\text{Me}_4\text{N})_4[E_4\text{Cd}_{10}(\text{SC}_{6}\text{H}_5)_{16}] \) (E=S, Se), and generated mixed-metal clusters of cadmium and zinc. Even at room temperature, such metal ion substitution process could be easy to achieve because the ion radius of Zn\(^{2+}\) and Cd\(^{2+}\) is close. However, between the radii of Co and Cd ions large mismatch existed, resulting in the Co ions doping occurring primarily at the surface or near-surface sites in NCs [17, 18]. The cobalt thiophenolate cluster \( (\text{Me}_4\text{N})_2[\text{Co}_4(\text{SC}_{6}\text{H}_5)_{10}] \) is used as the Co precursor. The complexation of Co with thiophenolate could improve the reactivity of Co\(^{2+}\), which has been shown to undergo rapid metal ion exchange within similar clusters such as Fe\(^{2+}\)/Co\(^{2+}\), Co\(^{2+}\)/Zn\(^{2+}\), and Co\(^{2+}\)/Cd\(^{2+}\) exchange that occurred in \( [M_4(SPh)_{10}]^{12−} \) (M=Fe, Co, Zn, Cd) complex [20, 29]. For the formation of Co-doped CdS nanocrystals, the supposition was performed by direct thermolysis of \( (\text{Me}_4\text{N})_4[S_4\text{Cd}_{10}(\text{SC}_{6}\text{H}_5)_{16}] \) and \( (\text{Me}_4\text{N})_2[\text{Co}_4(\text{SC}_{6}\text{H}_5)_{10}] \) in HDA.

Figures 1 and 2 show the TEM image, histogram of size distribution, and HRTEM image of the prepared CdS NCs doped with different Co concentration (the Co concentration was determined by ICP in the next section).

The Co-doped CdS (CdS:Co) quantum dots are well-defined and nearly spherical nanoparticles, and the quantum dots are prepared by thermolysis of \( 1.2 \text{ g} (\text{Me}_4\text{N})_4[S_4\text{Cd}_{10}(\text{SC}_{6}\text{H}_5)_{16}] \) and \( 0.2 \text{ or } 0.5 \text{ g} (\text{Me}_4\text{N})_2[\text{Co}_4(\text{SC}_{6}\text{H}_5)_{10}] \) at 80°G HAD.

The size distribution of the samples is demonstrated in Figures 1(b) and 2(b). The average particle size is 3.8 nm ± 10% for Cd\(_{0.924}\)Co\(_{0.076}\)S NCs and 4.1 nm ± 12% for Cd\(_{0.915}\)Co\(_{0.085}\)S NCs, respectively. Figure 1(c) shows a typical HRTEM image of Cd\(_{0.924}\)Co\(_{0.076}\)S NCs, and the products
are nearly spherical particles with slight prolate deviations. The space between adjacent planes is 0.336 nm, which is consistent with the interplanar distance of the (002) planes of hexagonal CdS. Figure 2(c) demonstrates the HRTEM image of Cd$_{0.815}$Co$_{0.185}$S NCs along with (002) plane. The particles are also nearly spherical with slight prolate deviations. Figure 3 shows the room-temperature UV-vis absorption and photoluminescence (inset) spectra of the CdS:Co quantum dots.

The excitonic absorption peaks are well-defined and rather sharp indicative of narrow size distribution of the NCs. The excitonic absorption peak is associated with the lowest optical transition and provides a simple way to determine the band gap of NCs. The maximum absorption peaks as shown in Figure 3 are 418 nm (for CdS), 415 nm (for Cd$_{0.924}$Co$_{0.076}$S), and 413 nm (for Cd$_{0.815}$Co$_{0.185}$S), corresponding to the band gap of 2.97, 2.99, and 3.00 eV, respectively. The band-gap energy of the synthesized NCs is higher than that of CdS bulk crystal (2.42 eV) [30], indicating quantum confinement of the CdS:Co quantum dots.

The similar absorption spectra of the NCs demonstrate that the incorporation of Co ions in the CdS NCs lattice does not significantly change the absorption edge of the NCs. The average particle size could be estimated from the first excitonic absorption peak [31], which is all about 4.0 nm for the Co ions doped samples. This is in agreement with the value of TEM results. In the PL spectra as shown in Figure 3, the emission band is red-shifted compared with the absorption band, which is frequently observed for CdS NCs [32–34]. Bulk CdS is reported to have a broad emission with the emission maximum in the 500–700 nm region of the luminescence spectrum, which is attributed to the recombination from surface defects (predominantly sulfur vacancies) [35]. For the NCs, the photoluminescence arises from the radiative recombination of electrons and holes at defect levels brought about by surface trap, and red-shifted
photoluminescence is observed. No deep trap emission is observed in the long wave region, indicating that HDA is an effective passivating agent. The particles of CdS and CdS:Co NCs were prepared using the same process, and the size of the CdS:Co NCs was consistent with that of the CdS NCs (as shown in Figure 4, 4.2 nm for CdS quantum dots).

Consequently, the absorption peaks of CdS:Co NCs are consistent with that of CdS NCs. Compared with the PL spectrum of CdS NCs, the spectra of Co ions doped NCs are slightly red-shifted in the similar size regime. The observed shift in PL spectra implies that perhaps the initial Co-doping induces defects due to self-contraction.

### 3.2. Proof of Co Internal Doping in CdS Nanocrystals

Inductively coupled plasma (ICP) is used to measure the Co ions concentration of the prepared NCs. To further confirm that the Co ions concentration measured reflects substitution of internal Cd sites, the method of pyridine stripping is adopted. This method has previously been used to remove surface-bound contamination in doped NCs [36]. The Co ions concentration after pyridine stripping yields doping concentrations of $x = 0.076$, 0.185 moles of cobalt in Cd$_{1-x}$Co$_x$S and 0.082, 0.196 moles of cobalt prior to ligand exchange, respectively. The differences between Co ions concentrations in as-grown and pyridine-capped NCs are about 7% and 6% for the two samples, indicating that pyridine stripping can remove surface-adsorbed Co ions. The Co ions were internally doped in the NCs based on the ICP measured results.

Figure 5 shows the XRD patterns of the synthesized CdS and Co-doped CdS NCs with similar method. The XRD data are given in Table I.

The diffraction patterns show broad peaks typical of particles in the nanosize. The XRD patterns are consistent with the hexagonal phase of CdS. The (110), (103), and (112) planes of wurtzite NCs are clearly distinguishable in the patterns (JCPDS file number 41-1049). From the CdS XRD pattern (Figure 5(a)), a strong (002) peak is observed in contrast to other peaks, while the (102) peak is low and broad. For the Co-doped CdS NCs, the (002) peaks are much stronger than that of CdS NCs as shown in Figures 5(b) and 5(c).

### Table I: Comparison of $d$-spacing values of the as-synthesized samples with standard JCPDS CdS: (a) CdS, (b) Cd$_{0.924}$Co$_{0.076}$S, and (c) Cd$_{0.815}$Co$_{0.185}$S quantum dots.

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Note: (a) CdS, (b) Cd$_{0.924}$Co$_{0.076}$S, (c) Cd$_{0.815}$Co$_{0.185}$S, and (lit) standard JCPDS value of CdS.
After pyridine stripping, the Co ion concentrations measured by ICP are 0.079 and 0.180, respectively. Compared to low synthesis temperature, and the result is similar to Cd of ferromagnetism, and the coercive field and remnant sample measured at 300 K. There is a hysteresis loop because field dependence of magnetic moment (M-H) curve of the system (PPMS) of Quantum Design. Figure 6 shows the absorption spectra of CdS:Co NCs is associated with the substitutional Co-dopants characterized in the previous sections. Further investigation is in progress for the magnetism of CdS:Co NCs.

3.3. Influence of Co-Doping on Growth Process of Quantum Dots. In order to investigate the influence of Co-doping on growth process of quantum dots, the growth process of Cd$_{0.924}$Co$_{0.076}$S quantum dots was monitored by UV-vis spectrum. All the samples for absorption experiments were used as prepared, without any further purification. Figure 7(a) shows the absorption spectra of Cd$_{0.924}$Co$_{0.076}$S quantum dots obtained at different reaction temperatures.

No obvious absorption peak is observed at temperature below 120°C. When the reaction temperature is raised to 120°C, the absorption peak appears, implying that nuclei are formed massively. With the temperature rising from 120°C to 190°C, the absorption peaks are slowly red-shifted from 370 nm to 384 nm. When the reaction temperature is increased above 190°C, the absorption peaks are red-shifted largely from 384 nm to 424 nm. The large shift of the absorption peaks indicates that the quantum dots grow rapidly as the temperature exceeds 190°C [25]. Figure 7(b) demonstrates the change of absorption peaks with reaction temperature. The absorption peak increases slightly from 100°C to 150°C, but the absorption peak increases rapidly when the temperature is raised above 190°C. Figure 8 shows the absorption spectra of Cd$_{0.924}$Co$_{0.076}$S quantum dots at 220°C with different reaction times. The absorption peak increases with prolonging time at 220°C.

Based on the above results, the growth process of quantum dots could be divided into two stages, including nucleation and rapid growth. During the nucleation stage (below 190°C), the quantum dots grow slowly and the nucleation is dominant. As the temperature is increased above 190°C, a rapid growth stage of quantum dots occurred. The growth process of Co-doped quantum dots is similar to that of CdS quantum dots [25]. This similarity reveals that the Co-doping in the quantum dots does not change the growth process of NCs. It can be reasonably concluded that the Cd/Co ion exchange between clusters is rapid under lower temperature and is accomplished before the formation of quantum dots. The rapid exchange ability of Cd/Co ion leads to the formation and growth of Co-doping NCs consistent with that of CdS NCs. Thus, the way of preparing Co-doping NCs by inorganic clusters does not disturb the growth process of NCs and can be easy to achieve.

3.4. Synthesis of Co-Doped CdS Nanorods. Based on our previous works [25, 42] and other research results [43], the reaction conditions especially precursor concentration significantly affect the morphology of NCs. The effect of precursor concentration on NCs morphology with Co-dopant is explored by reducing HDA dosage.

Figures 9 and 10 show the sample TEM images prepared by thermal decomposition of 1.2 g (Me$_{4}$N)$_{2}$[Sc$_{2}$Cd$_{10}$$(\text{SC}$_{6}$H$_{5}$)$_{10}$] and 0.2 g or 0.5 g (Me$_{4}$N)$_{2}$[Co$_{2}$$(\text{SC}$_{6}$H$_{5}$)$_{10}$] in 25 g HDA at 220°C for 1h.

After pyridine stripping, the Co ion concentrations measured by ICP are 0.079 and 0.180, respectively. Compared
with the results of CdS:Co quantum dots, the Co-doping concentration in CdS NCs is identical under the same content of (Me$_4$N)$_4$[S$_4$Cd$_{10}$(SC$_6$H$_5$)$_{16}$] and (Me$_4$N)$_2$[Co$_4$(SC$_6$H$_5$)$_{10}$]. The morphology of the NCs changes obviously with HDA dosage reducing. The products are straight nanorods by thermolysis of 1.2 g (Me$_4$N)$_4$[S$_4$Cd$_{10}$(SC$_6$H$_5$)$_{16}$] and 0.2 g (Me$_4$N)$_2$[Co$_4$(SC$_6$H$_5$)$_{10}$] in 25 g HDA (as shown in Figure 9). The nanorods sizes are an average diameter of 3.9 nm and length of 42 nm, and no aggregation can be observed. Furthermore, the interplanar distance along the growth axis of the nanorods is about 0.336 nm (the HRTEM image), which is consistent with the interplanar distance of the (002) plane in the wurtzite structure of CdS [44]. Thus, the results confirm that the nanorods are lengthened along the axis. For the NCs obtained by thermolysis of 1.2 g (Me$_4$N)$_4$[S$_4$Cd$_{10}$(SC$_6$H$_5$)$_{16}$] and 0.5 g (Me$_4$N)$_2$[Co$_4$(SC$_6$H$_5$)$_{10}$] in 25 g HDA, the products are the mixture of straight and branched nanorods (small quantity) as shown in Figure 10. The branched nanorods with small quantity are formed by increasing (Me$_4$N)$_2$[Co$_4$(SC$_6$H$_5$)$_{10}$] usage to 0.5 g under other same conditions.

The precursor concentration significantly influences the morphology of the CdS:Co NCs, and the morphology of NCs changes from quantum dots to nanorods with precursor concentration increase. In order to further prove such results, cluster of 1.2 g (Me$_4$N)$_4$[S$_4$Cd$_{10}$(SC$_6$H$_5$)$_{16}$] and 0.5 g (Me$_4$N)$_2$[Co$_4$(SC$_6$H$_5$)$_{10}$] is thermolysized in different contents of HDA. It has been shown in Figure 1 that the products obtained are quantum dots by thermal decomposition of the same clusters in 80 g HDA. Decreasing HDA mass to 40 g,
Figure 9: The sample synthesized by thermolysis of 1.2 g (Me₄N)₄[S₄Cd₁₀(SPh)₁₆] and 0.2 g (Me₄N)₂[Co₄(SC₆H₅)₁₀] in 25 g HDA: (a) TEM image, (b) HRTEM image, (c) diameter, and (d) length distribution histogram of the nanorods.

Figure 10: The sample synthesized by thermolysis of 1.2 g (Me₄N)₄[S₄Cd₁₀(SPh)₁₆] and 0.5 g (Me₄N)₂[Co₄(SC₆H₅)₁₀] in 25 g HDA: (a) TEM image and (b) enlarged image of (a).
straight nanorods are formed as shown in Figure II(a). By use of 35 g HDA, straight nanorods with a small quantity of branched nanorods are obtained as shown in Figure I1(b).

Based on the evolution of NCs morphology with precursor concentration, it can be concluded that the nanorods could be formed by aggregation of nanoparticles. The nanoparticles are formed first in the process and then aggregate together along the (002) plane of CdS wurtzite crystal lattice to form nanorods [44]. Thus, the formation of Co-doping CdS nanorods follows oriented attachment mechanism [45]. The diameters of the nanoparticles and nanorods are almost identical at the same reaction conditions. The appearance of small quantity of nanoparticles in Figure 9(b) also approves the mechanism. The reaction time has to be 5 h or even longer for the formation of CdS nanorods without Co-doping by thermolysis of (Me₄N)₂[S₄Cd₁₀(SC₆H₅)₁₆] [42]. Compared with the fabrication of Co-doping and pure CdS nanorods, the addition of (Me₄N)₂[Co₄(SC₆H₅)₁₀] cluster means Co-doping in CdS NCs and is favorable for the formation of nanorods, even the reaction time is shortened. It has been shown that the nanorods are obtained at 220°C for just reacting 1 h by addition of 0.2 g (Me₄N)₂[Co₄(SC₆H₅)₁₀]. Table 2 shows the products obtained at different conditions for comparison of doping and undoping nanorods.

The products are quantum dots only by thermal decomposition 1.0 g (Me₄N)₄[S₄Cd₁₀(SC₆H₅)₁₆] in 40 g HDA for 3 h, while the nanorods are formed by addition of 0.5 g (Me₄N)₂[Co₄(SC₆H₅)₁₀], and the reaction time is just 1 h. The above results demonstrate that the dopant of Co ions in the CdS is favorable for the formation of nanorods. It has been shown [46] that magnetic particles such as Fe₃O₄ are easy to be aggregated as one-dimensional chain structure in organic solvent. For magnetic Fe₃O₄ nanoparticles behaving like magnetic dipoles, the effect of interparticle forces plays principle role in ordering of the nanoparticles in one-dimensional structures. According to the phenomenon, the Co-doped CdS nanoparticles could be considered as magnetic dipoles in HDA and maybe there are similar magnetic interparticle interactions. The interaction between Co-doped CdS particles is favorable for the oriented aggregation of particles, further promoting the formation of the nanorods.

4. Conclusions

In summary, Co-doped CdS NCs were successfully synthesized by direct thermolysis of (Me₄N)₂[Co₄(SC₆H₅)₁₀] and (Me₄N)₄[S₄Cd₁₀(SPh)₁₆] molecular clusters in HDA.
Uniform Co:CdS quantum dots were obtained under low precursor concentration, and Co:CdS nanorods were formed by increasing the precursor concentration. It was revealed that the formation of the Co:CdS nanorods followed an oriented attachment mechanism. The Co-doping facilitated the morphology evolution of resulting product to nanorod structures, even in shorter reaction time. Additionally, the multifunctionality of the Co:CdS NCs including luminescence and ferromagnetism at room temperature was achieved due to the Co-doping. These Co:CdS NCs with controllable morphology were considered to have potential applications in spintronic devices and biological labeling fields, and this feasible synthesis method could be anticipated to be employed in industry manufacturing of Co:CdS NCs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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