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Controlled Synthesis and Luminescence of Semiconductor Nanorods

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Abstract: A variety of nearly monodisperse semiconductor nanocrystals, such as CdS, ZnS, and ZnS:Mn, with controllable aspect ratios have been successfully prepared through a facile synthetic process. These as-prepared nanocrystals were obtained from the reactions between metal ions and thioacetamide by employing octadecylamine or oleylamine as the surfactants. The effects of reaction temperature and time, ratios of thioacetamide to inorganic precursors, and the reactant content on the size and crystal purity of the nanorods, have been systematically investigated. The optical properties and the formation mechanism of the nanorods have also been discussed. For the next biolabel applications, these hydrophobic nanocrystals have also been transferred into hydrophilic colloidal spheres by means of an emulsion-based bottom-up self-assembly approach.

Keywords: hydrophilicity • luminescence • nanorods • semiconductors • solvothermal synthesis

Introduction

In recent decades, semiconductor nanocrystals (NCs) have attracted a great deal of interest, owing to their dimension-dependent optical and electrical properties, which have made them ideal building blocks in many fields, such as solar cells,[1] biological labels,[2–3] light-emitting diodes,[4–6] electronics,[7–9] and lasers.[10–12] Owing to the quantum confinement effect, control of the size and shape of semiconductor NCs plays an important role in tailoring the properties of these materials and offers deep insight for understanding the important physical phenomena. Recently the synthesis and self-assembly of one-dimensional nanostructures of semiconductors have become a research attraction, owing to their potential applications in electronic, optical and sensorial device construction. At present, a number of methods including VLS (vapor-liquid-solid),[13] template-assisted,[14–15] solvothermal,[16–17] hydrothermal[18–21] and MWI (microwave irradiation)[22] methods have been developed for the shape-controlled synthesis of colloidal semiconductor NCs. However, most of the synthetic routines are based on the high-temperature thermolysis of organometallic precursors. To avoid employing these organometallic precursors, which are toxic, expensive, and unstable, several green chemical approaches employing common inorganic salts have been developed.[23–25] There is still a challenge to synthesize monodisperse semiconductor nanorods by using stable inorganic precursors such as nitrates and chlorides. Recently, a facile strategy for cell imaging by using luminescence of semiconductor nanorods has been reported.[26] In the present work, semiconductor NCs of CdS, ZnS, and ZnS:Mn with controllable aspect ratios have been prepared through a facile synthetic process under mild experimental conditions. The effects of reaction temperature and time, ratios of thioacetamide to inorganic precursors, and the reactant content have been discussed in detail. The as-prepared NCs were obtained from the reactions between stable inorganic salts and thioacetamide by employing octadecylamine or oleylamine as capping agents. For the biolabel applications, these hydrophobic NCs dispersed in cyclohexane were transferred into water by means of an emulsion-based bottom-up self-assembly approach.

Results and Discussion

The semiconductor nanorods were prepared by employing metal nitrates (or chlorides) and thioacetamide as reactants under optimum conditions. The sizes and morphologies of

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the as-prepared NCs are mainly affected by the following conditions, such as precursor concentration, temperature, and growth time. All the above effects have been investigated in detail.

Synthesis of CdS nanocrystals: In the current synthesis, the effect of the thioacetamide content has been discussed. The amount of thioacetamide is very important to the formation of nanorods. If thioacetamide (1.0 mmol) and $Cd(NO_3)_2{\cdot}4H_2O$ (1.0 mmol) are combined, only nanoparticles rather than nanorods are obtained after 12 h at $T = 160\,^{\circ}C$. Figure 1 shows the transmission electron microscopy (TEM) images of the semiconductor NCs prepared in oleylamine under the conditions listed in Table 1. The various as-prepared NCs shown in Figure 1 are created by changing the content of thioacetamide from 1.2 to 2.0 mmol. The effects of temperature and reaction time were also considered. Figure 1a shows the TEM image of CdS nanorods obtained at the temperature of 160 °C for 12 h, by using a 1:1.2 Cd/thioacetamide molar ratio. Analysis of the TEM shows that most of the CdS nanorods are less than 20 nm long. Prolonging the reaction time to 24 h (Figure 1 d) led to an increase in the average length of the nanorods (≈25 nm). These nanorods were also characterized with high resolution TEM (HRTEM). Figure 2 clearly indicates that the nanorods are single-crystal and the lattice fringe spacing is in correspondence with the (002) plane of wurtzite CdS.

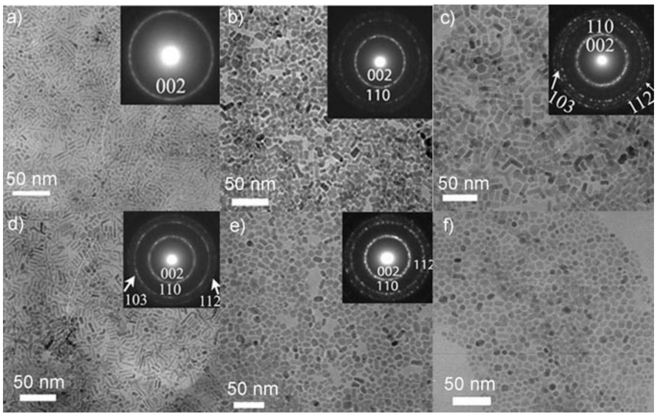

Figure 1. TEM images of the CdS NCs by using different amount of thioacetamide. All the samples are prepared according to the conditions presented in Table 1.

Table 1. Synthesis, conditions and resulting morphologies.

$Cd(NO_3)_2{\cdot}4H_2O$ [mmol]	CH_3CSNH_2 [mmol]	Solvent [mL]	T [°C]	t [h]	Figure, shape and size
1	1.2	25	160	12	Figure 1a, nanorods, ≈20 nm,[a] ≈5 nm[b]
1	1.2	25	160	24	Figure 1d, nanorods, ≈25 nm,[a] ≈5 nm[b]
1	1.6	25	160	12	Figure 1b, rodlike nanoparticles, ≈14 nm
1	1.6	25	160	24	Figure 1e, rodlike nanoparticles, ≈15 nm
1	1.6	25	200	12	Figure 1f, spherical, ≈9 nm
1	2.0	25	160	12	Figure 1c, nanorods, biopods, and tripods, ≈17 nm,[a] ≈8 nm[b]

[a] Rod length, [b] Rod diameter.

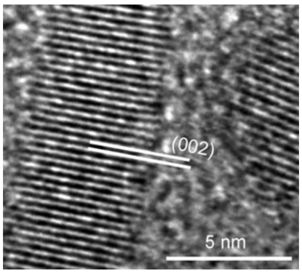

Figure 2. HRTEM image of CdS nanorod.

If a 1:1.6 molar ratio of cadmium to thioacetamide is used in the reaction system (in 25 mL of oleylamine), the length-to-diameter ratio of the as-prepared nanorods decreased, and rodlike nanoparticles were obtained at 160 °C. As shown in Figure 1, the average sizes of the NCs were about 14 nm for 12 h (b) and 15 nm for 24 h (e), respectively. However, upon increasing the temperature from 160 to 200 °C, and keeping the other conditions unchanged, spherical nanoparticles were presented (Figure 1 f). To further investigate the effects of precursor concentrations, $Cd(NO_3)_2{\cdot}4H_2O$ (1 mmol) and thioacetamide (2 mmol) were added to the reaction system and kept at 160 °C for 12 h. Figure 1c depicted the TEM image of CdS. From the image, a mixture of the obtained rods, bipods, and tripods can be clearly observed.

The as-prepared NCs were characterized by power X-ray diffraction (XRD). The XRD patterns of the CdS nanorods prepared in oleylamine are shown in Figure 3. As shown in Figure 3, the XRD pattern of nanoparticles (line 1) was indexed to the (111), (220) and (311) reflections of the cubic structure of CdS (JCPDS, 10–0454). Notably, these diffrac-

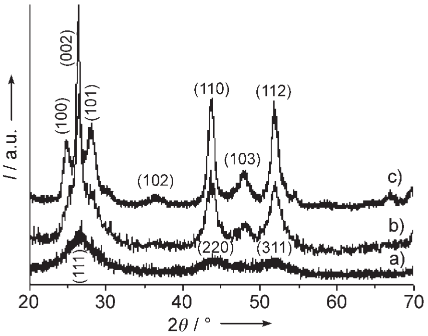

Figure 3. XRD patterns of as-prepared CdS NCs. The pattern for a) nanoparticles and b,c) nanorods.

tion peaks can also be assigned to the (002), (110) and (112) reflections of hexagonal structure of CdS (JCPDS, 41–1049). The results imply that these nanoparticles may be the composites of cubic and hexagonal CdS NCs. Indeed, the XRD patterns of nanorods (line 2 and 3), confirmed the hexagonal structure of wurtzite CdS (JCPDS, 41–1049).

Synthesis of ZnS and ZnS:Mn nanorods: The effect of the incorporation of Mn^{2+} ions in the Mn^{2+} doped ZnS NCs are discussed first. By increasing the concentration of Mn from 0 to 10%, as shown in Table 2, the morphologies of the as-prepared nanorods had no obvious change. From Figure 4, it can be seen that the length of the nanorods is less than 70 nm with diameters of less than 5 nm. The influence of temperature and growth time has also been investigated. The TEM image of the ZnS:Mn (10%) nanorods prepared in oleylamine, with a 1:1.2 molar ratio of Cadmium to thioacetamide is used, for 12 h (or 24 h) at 160°C can be seen in Figure 4. The length of the as-prepared nanorods is about 100 nm for 12 h (a) and 150 nm for 24 h (c). However, there is no apparent change in the average diameter of the nanorods. If the temperature is increased from 160 to 200°C, short ZnS nanorods were inclined to form, and the length decreased from 64 to 34 nm. Additionally, the effect of the amount of thioacetamide used in the synthetic system is also very important. Just as CdS, if $Zn(NO_3)_2{\cdot}6H_2O$ and thioacetamide (1:1 ratio 12 h, 160°C) was used, only ZnS nanoparticles were obtained.

Table 2. Effect of Mn^{2+}-doped concentration on the nanorods.[a]

$Zn(NO_3)_2{\cdot}6H_2O$ [mmol], [%]	$MnCl_2{\cdot}4H_2O$ [mmol], [%]	CH_3CSNH_2 [mmol]	*T* (°C)	*t* (h)	Figure, shape and size
1	0	1.2	160	12	Figure 4h, nanorods, l≈64 nm
1	0	1.2	200	12	Figure 4g, nanorods, l≈34 nm
0.975, 97.5	0.025, 2.5	1.2	160	12	Figure 4e, nanorods, l≈70 nm
0.95, 95	0.05, 5	1.2	160	12	Figure 4b, nanorods, l≈70 nm
0.95, 95	0.05, 5	1.2	160	24	Figure 4d, nanorods, l≈70 nm
0.9, 90	0.1, 10	1.2	160	12	Figure 4a, nanorods, l≈100 nm
0.9, 90	0.1, 10	1.2	160	24	Figure 4c, nanorods, l≈150 nm

[a] The nanorods synthesized in 25 mL of oleylamine. All the rod diameters are less than l=5 nm (l:Rod length).

The electron diffraction patterns of ZnS:Mn nanorods, shown in Figure 5, can be attributed to hexagonal wurtzite ZnS (JCPDS, 36–1450) structure. The XRD patterns of the ZnS:Mn NCs prepared in oleylamine shown in Figure 5, match well with those from the JCPDS card (JCPDS, 36–1450). The XRD patterns of ZnS nanorods were readily indexed to the (100), (002), (101), (102), (110), (103), and (112) reflections of hexagonal structures of wurtzite ZnS (JCPDS, 36–1450). The HRTEM was further used to characterize the as-prepared nanorods. As shown in the Figure 5, the XRD pattern of ZnS:Mn nanoparticles (line 1) was partly indexed to the (111), (220) and (311) reflections of the cubic structure of ZnS (JCPDS, 05–0566). Meanwhile, the XRD pattern of the ZnS:Mn nanoparticles also partly confirmed the hexagonal structure of ZnS (JCPDS, 36–1450), which indicated that the ZnS:Mn nanoparticles consisted of cubic and hexagonal structures of ZnS. Moreover, the XRD pattern of ZnS nanorods, shown in Figure 6, can also be assigned to hexagonal wurtzite ZnS (JCPDS, 36–1450).

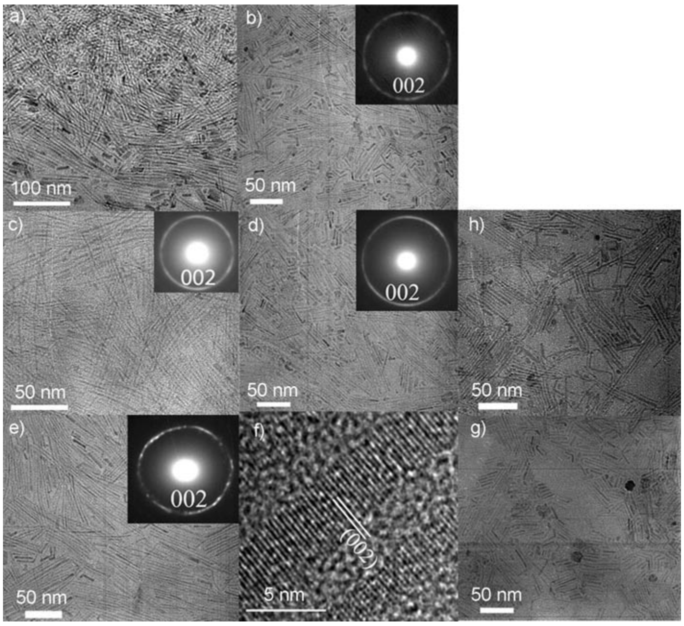

Figure 4. TEM images of the ZnS:Mn (a–e) and ZnS (g,h) nanorods obtained according to the conditions presented in Table 2. f) An HRTEM image of ZnS:Mn nanorods.

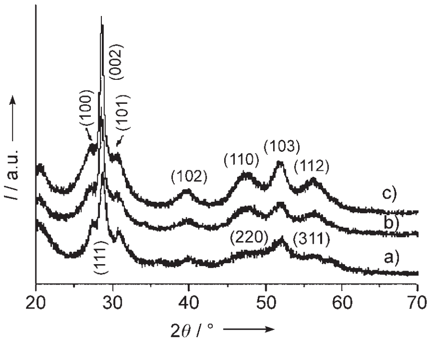

Figure 5. XRD patterns of as-prepared ZnS:Mn nanorods. The pattern of a) nanoparticles and b,c) nanorods.

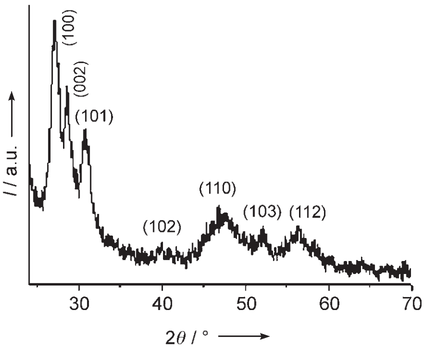

Figure 6. XRD pattern of as-prepared ZnS nanorods.

Synthesis of $Cd_xZn_{1-x}S$ nanocrystals: Typically, different amounts of precursors were mixed into oleylamine (25 mL), followed by thioacetamide (1.2 mmol). The mixture was then heated at $T=160$ °C for 24 h. As shown in the TEM images (Figure 7 and Table 3), the morphologies of the as-prepared NCs changed from nanorods to rodlike nanoparticles concurrently with the increase of the ratio of Cd^{2+}. For the amount of precursor ($x=0.2$, 0.5, 0.8 mmol) used, only mixtures of CdS and ZnS are obtained (Table 3). However, if $Cd(NO_3)_2$·$4H_2O$ (1 mmol) and $Zn(NO_3)_2$·$6H_2O$ (1 mmol) are reacted with thioacetamide (2.4 mmol) at 160 °C for 24 h, $Cd_xZn_{1-x}S$ NCs can be obtained. Thus, the amount and the concentration ratio of the precursors can strongly affect the formation of $Cd_xZn_{1-x}S$ NCs. Moreover, the as-prepared NCs of different morphologies were characterized by XRD. In Figure 8 the XRD patterns of the as-prepared NCs are depicted.

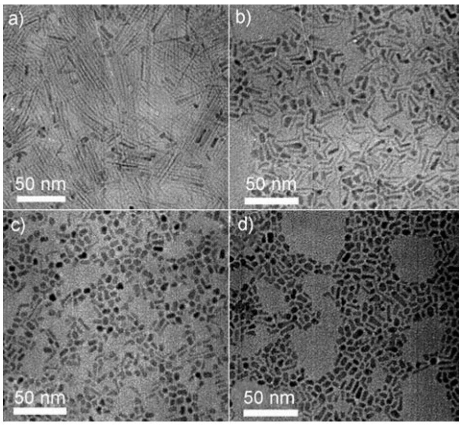

Figure 7. TEM images of the as-prepared NCs.

Table 3. Synthesis conditions and resulting morphologies.

$Cd(NO_3)_2$ ·$4H_2O$ [mmol]	$Zn(NO_3)_2$·$6H_2O$ [mmol]	CH_3CSNH_2 [mmol]	T [°C]	t (h)	Figure, shape and size
0.2	0.8	1.2	160	24	Figure 7a, CdS + ZnS nanorods, l≈54 nm
0.5	0.5	1.2	160	24	Figure 7b, CdS + ZnS bipods
0.8	0.2	1.2	160	24	Figure 7c, CdS + ZnS rod-like nanoparticles, ≈7 nm
1.0	1.0	2.4	160	24	Figure 7d, $Cd_xZn_{1-x}S$ rod-like nanoparticles, ≈10 nm

[a] The NCs synthesized in 25 mL of oleylamine. All the rod diameters are less than $l=5$ nm (l:rod length).

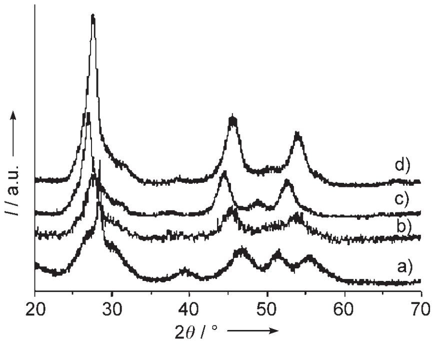

Figure 8. XRD patterns of the as-prepared NCs. All samples were synthesized in oleylamine at 160 °C for 24 h witth a 1:1.2 molar ratio of metal ions and CH_3CSNH_2; a) with a mixture of 0.2 mmol Cd^{2+} and 0.8 mmol Zn^{2+}; b) with a mixture of 0.5 mmol Cd^{2+} and 0.5 mmol Zn^{2+}; c) with a mixture of 0.8 mmol Cd^{2+} and 0.2 mmol Zn^{2+}; d) with a mixture of 1.0 mmol Cd^{2+} and 1.0 mmol Zn^{2+}.

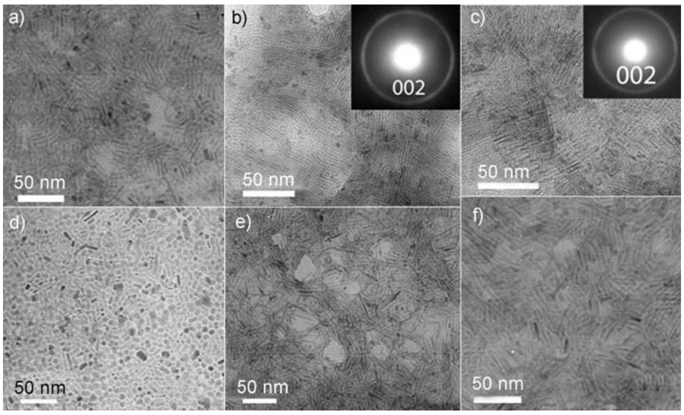

Figure 9. TEM images of the CdS (a,d), ZnS (b,e), and ZnS:Mn (c,f) NCs prepared in octadecylamine. a–c) $T=160$ °C, and d–f) $T=180$ °C.

Effect of surfactants: To investigate the dependency of surfactant on the epitaxial growth of the NCs, octadecylamine was used to replace oleylamine. The TEM images in Figure 9 show the semiconductor nanorods prepared in octadecylamine at $T=160$ and 180 °C. All the products were obtained by heating the solution for 12 h. The structure and composition of the nanorods have been characterized by using TEM and electron diffraction. Short CdS nanorods were prepared upon heating at $T=160$ °C (Figure 9a) and $T=180$ °C (Figure 9d) for 12 h by using thioacetamide

(1.2 mmol). Under the same conditions, the corresponding long ZnS (Figure 9b,e) and ZnS:Mn nanorods were obtained (Figure 9c,f). Analysis of the TEM observations revealed that most of the CdS nanorods were less than ≈20 nm long and the ZnS:Mn nanorods were less than ≈50 nm long. It is worth noting that the as-prepared CdS and ZnS:Mn nanorods are shorter than those prepared in oleylamine. As we know, there is a double bond (C=C) in the alkyl chain of oleylamine, which makes the oleylamine more flexible than octadecylamine. The results imply that the flexible structure of oleylamine may be also ready for the formation of nanorods.[26] It should be mentioned that the NCs prepared in octadecylamine have the similar crystal structures that are not shown here.

Formation mechanism of the nanorods: The experimental results described here indicate that a higher concentration of thioacetamide, as well as an appropriate solvothermal temperature and time are suitable for the formation of semiconductor nanorods. Hyeon and his co-workers[27] have reported the synthesis of ZnS nanorods and discussed the formation mechanism. They found that excess sulfur should be used to maintain high chemical potential, and to obtain nanorods. In our report, similarly, the excess thioacetamide, as the sulfur source, is favorable for the formation of CdS (or ZnS) nanorods. Furthermore, the reasonable choice of surfactants in the experiment was also an important factor for the preparation of the nanorods. We speculate that the alkylamine (octadecylamine or oleylamine) is an appropriate surfactant binding to Cd^{2+} (or Zn^{2+}) to generate the elongated NCs. As shown in Figure 2 and Figure 4f, the HRTEM image clearly shows that the alkylamines selectively bind to the surfaces of crystallites, and render the epitaxial growth along the (001) directions, this confirms our speculation.

Optical properties of the semiconductor nanocrystals: The fluorescence spectra of as-prepared CdS NCs with different sizes is displayed in Figure 10a. As shown above, the CdS NCs formed in this work had mean sizes from ≈5 to ≈25 nm. In the present work, the emission spectra were obtained under $\lambda = 365$ nm excitation. The multicolor luminescence photos of the CdS NCs that show strong emissions from blue to green, indicate the size-dependent quantum confinement effects. The luminescence spectra of the as-prepared ZnS:Mn NCs and the response to Mn^{2+}-doping and the lengths of the as-prepared nanorods is shown in Figure 10b. The fluorescence intensity becomes stronger if the precursors $Zn(NO_3)_2{\cdot}6H_2O$ (1 mmol) and thioacetamide (1 mmol) are doped with Mn^{2+} (10%). However, by increasing the content of thioacetamide, the fluorescence intensity of the as-prepared long nanorods decreased lightly. The obtained emission spectra of ZnS: Mn NCs are assigned to the emission of Mn^{2+} that corresponds to the $^4T_1$–$^6A_1$ transition within the $3d^5$ configuration of Mn^{2+}. The visual image of the samples show strong red emission is obtained by using $\lambda = 254$ nm irradiation. The fluorescence emission spectrum of as-prepared ZnS NCs dispersed in cyclohexane is displayed in Figure 10c. The ZnS NCs exhibit a strong blue emission. The fluorescence spectra of the $Cd_xZn_{1-x}S$ NCs are shown in Figure 10d.

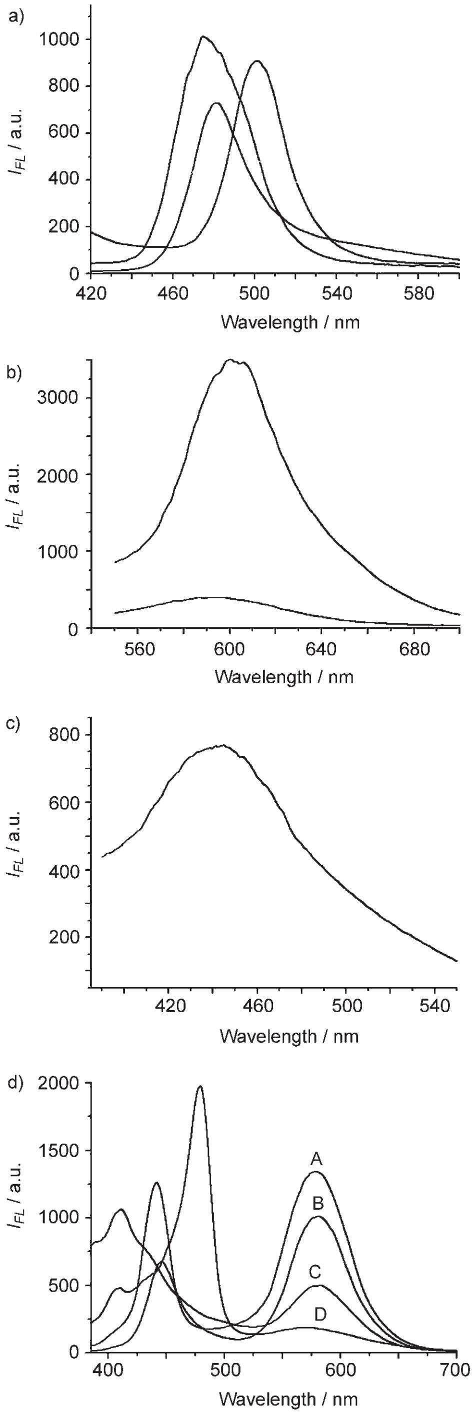

Figure 10. Room-temperature fluorescence spectra and luminescence photos of the as-prepared NCs. a) fluorescence emission spectra of CdS NCs excited at $\lambda = 365$ nm; b) fluorescence spectra of ZnS:Mn NCs excited at $\lambda = 254$ nm; c) fluorescence emission spectrum of ZnS NCs excited at $\lambda = 365$ nm; d) fluorescence spectra excited at $\lambda = 365$ nm, A–C) mixtures of CdS and ZnS, and D) $Cd_xZn_{1-x}S$ NCs, corresponding to those given in Table 3 for Figure 7a)–d), respectively.

Formation of hydrophilic colloidal nanospheres: For bioapplications such as fluorescence labels, the as-prepared nanorods that are dispersed in cyclohexane should be transferred to water. In this work, a facile emulsion-based bottom-up self-assembly approach was employed for the transfer of the hydrophobic NCs into aqueous solution.[28] The TEM images of CdS and ZnS:Mn nanospheres coated with CTAB can be seen in Figure 11; all of which are water-soluble and favorable for bioapplications.

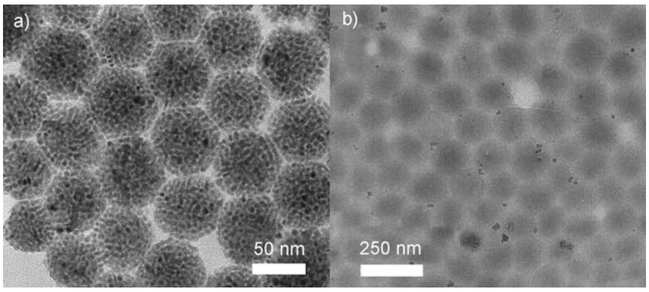

Figure 11. TEM images of a) the CdS, and b) the ZnS:Mn colloid nanospheres with CTAB as a surfactant.

Conclusion

In summary, we have developed a facile solvothermal method to prepare luminescent semiconductor nanorods by using common inorganic salts as precursors. By tuning the synthetic conditions such as thioacetamide content, dopant concentration, as well as reaction temperature and time, nearly monodisperse semiconductor nanorods were obtained. The luminescence and formation mechanism of as-prepared nanocrystals (NCs) have also been investigated in detail. Moreover, these hydrophobic NCs are transformed into hydrophilic colloidal nanospheres, which would facilitate their use in bioapplications, such as fluorescence imaging and immunoassays.

Experimental Section

Chemicals: All chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout. Oleylamine was supplied by Zhejiang Ningbo Chemical Factory, China. Octadecylamine, thioacetamide, ethanol, cyclohexane, $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$ were purchased from the Beijing Chemical Reagent Company, China.

Solvothermal synthesis of semiconductor nanocrystals: In a typical synthesis, oleylamine or octadecylamine (25 mL) was heated to 120 °C. To this, $Cd(NO_3)_2{\cdot}4H_2O$ or $Zn(NO_3)_2{\cdot}6H_2O$ (1.0 mmol) or certain ratios of $Zn(NO_3)_2{\cdot}6H_2O$ with $MnCl_2{\cdot}4H_2O$ were added, and the mixture stirred for 10 min. Then specific amounts of thioacetamide were added and stirred for another 15 min. The solution was then transferred into a Teflon-lined autoclave (50 mL) and heated at different temperatures over a range of different times. The final products were collected by centrifuging and washing the powder with ethanol and cyclohexane.

Characterization: The samples were characterized by using an X-ray diffractometer (Rigaku D/max 2500Pc, $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å). The operation voltage and current were kept at 40 kV and 250 mA, respectively. The sizes and morphologies of the NCs were obtained by using a transmission electron microscope (JEOL JEM-1200EX) and a high-resolution transmission electron microscope (Tecnai F20). Fluorescent spectra were recorded by using a Fluorescence Spectrophotometer (Hitachi F-4500).

Acknowledgements

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