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Synthesis, optical properties, and superlattice structure of Cu(I)-doped CdS nanocrystals

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High quality Cu(I)-doped CdS [CdS:Cu(I)] nanocrystals were synthesized by thermolysis of metal acetylacetonate complexes in *n*-dodecanethiol. The optical emission of the doped nanocrystals was observed to change from surface trap-dominant emission to Cu(I)-dominant emission with respect to the reaction time and the doping levels of Cu(I) ions in CdS particles. The maximum photoluminescence quantum yields of the CdS:Cu(I) nanocrystals could reach 15.8%. More interestingly, these doped nanocrystals could self-assemble into highly ordered superlattices depending on the doping levels of the Cu(I) ions. A possible explanation for the formation of the CdS:Cu(I) nanocrystal superlattices is dipole–dipole interactions between the adjacent nanocrystals. © *2010 American Institute of Physics*. [doi:10.1063/1.3466664]

Semiconductor nanocrystals have received enormous attention in the past decades due to their dramatic size-dependent optical and electronic properties,[1,2] as well as their wide applications in the fields of optoelectronic and biological technology.[3–6] Doped semiconductor nanocrystals, as an important family of semiconductor nanocrystals, have attracted much attention due to their apparent merits, such as larger ensemble Stokes shift to reduce self-quenching and insensitivity to thermal and photochemical disturbances.[7] To date, many efforts have been made to prepare well-formed semiconductor nanocrystals doped with various transition metal or rare earth ions.[8,9] Following extensive studies on the potential applications of solar cells and radiation detector,[10] considerable work on the synthesis of Cu(II)-doped ZnS or ZnSe nanocrystals and their optical properties have been reported recently.[11–14] Until now, however, the reports about the synthesis and optical properties of Cu(I)-doped CdS nanocrystals are relatively few.

In the past decades, assembling nanocrystals into two- or three-dimensional (2D or 3D) superlattice structures has gained more and more attention for the study of the collective properties of semiconductor nanocrystals. These highly ordered superstructures exhibit collective physical and chemical properties which are different from those of isolated nanocrystals and the bulk counterparts.[15,16] Currently, a wide range of monodispersed nanocrystals have been used as building blocks for fabricating 2D or 3D superlattices.[17–20] Among these candidates, semiconductor nanocrystals have undoubtedly become the most popular due to their distinguished chemical and physical properties. Research on semiconductor nanocrystals as building blocks has been mainly focused on the undoped nanocrystals (such as CdSe and CdS), while the assembly of doped semiconductor nanocrystals into superlattices has been rarely reported. In this paper, we reported a one-pot approach for preparing high quality CdS:Cu(I) nanocrystals by the decomposition of metal-dodecanethiol complexes in *n*-dodecanethiol. The doping-level dependent optical properties and self-assembly behaviors of the resultant nanocrystals were investigated. The possible mechanism for the formation of CdS:Cu(I) nanocrystal superlattices was also discussed.

For a typical preparation, 5 mmol of cadmium acetylacetonate [$\mathrm{Cd(acac)_2}$] and 5 mmol of copper (II) acetylacetonate [$\mathrm{Cu(acac)_2}$] in 30 ml *n*-dodecanethiol were heated to 200 °C for 23 h, then cooled down to room temperature naturally. In addition, undoped CdS nanocrystals and other CdS:Cu nanocrystals with the molar ratios of $\mathrm{Cd(acac)_2}$ to $\mathrm{Cu(acac)_2}$ of 7:3, 9:1, and 9.5:0.5 were also prepared under the same conditions as mentioned above by maintaining a constant concentration of the metal precursors. Regarding the molar ratios of $\mathrm{Cd(acac)_2}$ to $\mathrm{Cu(acac)_2}$ of 9.5:0.5, 9:1, 7:3, and 5:5, the resultant samples are denoted as sample A, sample B, sample C, and sample D, respectively. Inductively coupled plasma optical emission spectrometer analysis of the samples reveals that the as-prepared Cd/Cu [$\mathrm{Cd(acac)_2/Cu(acac)_2}$] molar ratios of 5:5, 7:3, 9:1, and 9.5:0.5 result in nanocrystal compositions (Cd/Cu) of 5.6:1, 7.1:1, 13.7:1, and 35.2:1, respectively. The experimental details are shown in Ref. 21.

In order to study the growth process of the CdS:Cu nanocrystals, the temporal evolutions of absorption and photoluminescence (PL) spectra of sample D were carefully recorded. As shown in Fig. 1(a), an absorption band at 323 nm appears after the reaction proceeds for 1 h and then disappears 3 h later. Additionally, another characteristic absorption band at 385 nm appears and evolves from an absorption shoulder to a clear absorption peak as the reaction goes on. It has been reported that the metal precursors can react with dodecanethiol to form an intermediate complex upon heating, which could be responsible for the appearance of the first absorption peak. Upon decomposition of the complex,

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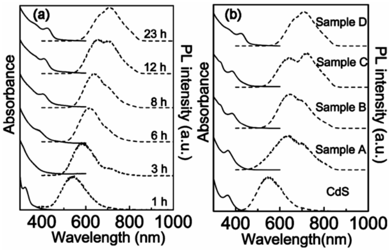

FIG. 1. PL (dashed line) and UV-vis absorption (solid line) spectra of (a) sample D for different reaction time and (b) undoped CdS and CdS:Cu nanocrystals with different doping levels.

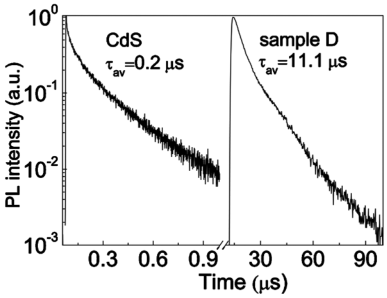

FIG. 2. PL decay curves of CdS nanocrystals and sample D monitored at the PL peaks excited at a wavelength of 350 nm at room temperature.

nanoparticles are formed at the cost of the initially formed complex.[22] Consequently, the absorption peak appears at longer wavelength. Accompanying the changes in absorption spectra, the PL peak position shifts gradually to red. Meanwhile, another emission band at around 707 nm starts to appear after 8 h of reaction and becomes dominant till the end of the reaction. The wide emission feature of the first sample (1 h) suggests that surface-trap emission is dominant in the early samples. But the further broadening of the emission band, together with the appearance of the emission band at around 707 nm, implies that Cu ions involve in the emission, possibly as a dopant.[23]

The optical properties of the CdS:Cu nanocrystals with different doping levels and the undoped CdS were investigated by conventional electron spectroscopies, which are shown in Fig. 1(b). The undoped CdS nanocrystals present a redshift PL peak with respect to the absorption onset, indicating that the PL emission of the undoped CdS nanocrystals is dominated by surface-trap emission. The surface-trap emission originates from structural defects which may arise from the excess sulfur due to the extra dodecanethiol used in our experiments. As the Cu doping levels increase, the absorption peak of the CdS:Cu nanocrystals shifts to longer wavelengths. According to the transmission electron microscopy (TEM) results (shown in Fig. 4), the size of the doped nanocrystals is relatively independent of the Cu doping levels, which suggests that the redshift in the absorption peak is strongly associated with the doping levels of Cu ions in the lattice of CdS particle matrix, similar to what has been observed with Cu-doped CdSe nanocrystals.[24] This explanation is also supported by following observation on PL properties of the Cu-doped CdS nanocrystals against the doping levels. For example, the PL emission band at 707 nm becomes dominant in the PL spectra with the increase in the Cu doping levels, which indicates that the photoemission is gradually transforming from surface-trap emission to deep dopant-related emission with respect to the increase in doping levels due to the recombination of an excited electron in the conduction band of the CdS nanocrystals and a hole from the *d*-orbital of Cu ions.[7] The room temperature PL quantum yields (QYs) of the CdS:Cu nanocrystals with different Cu doping levels are in the range of 8%–16% (shown in Table S1 in Ref. 21), which is much higher than that of the CdS:Cu nanocrystals reported previously.[12] The details of the PL QYs measurement are shown in Fig. S1 in Ref. 21.

The PL lifetime is another important optical property of semiconductor nanocrystals that deserves concern. Figure 2 shows the PL decay curves of undoped CdS and CdS:Cu nanocrystals (sample D). The average lifetime of sample D (11.1 μs) is much greater than that of undoped CdS nanocrystals (0.2 μs), due to the Cu ions doped into CdS lattices (see Table S2 in Ref. 21). In fact, the PL lifetime of the transition metal ions (such as Mn^{2+}, Cu^+, etc.) is very long as stated in previous reports.[25]

In order to reveal the details on the valence state of the Cu ions, x-ray photoelectron spectroscopy (XPS) analysis was performed. The XPS spectrum of Cu 2*p* signal shown in Fig. 3(a) reveals that the Cu $2p_{3/2}$ signal is centered at 932.6 eV, while the Cu $2p_{1/2}$ signal is located at 952.4 eV, suggesting that Cu ion exists in +1 state according to previous reports.[24] The Cu(I) ion is formed by the reaction between $Cu(acac)_2$ and *n*-dodecanethiol, which leads to the formation of $Cu_{1.94}S$ nanocrystals.[26] With respect to the current preparations, the precipitates collected from the reaction mixture by centrifugation are also identified as $Cu_{1.94}S$ nanocrystals as shown in Fig. S2 in Ref. 21. The crystalline phase structure of sample D was characterized by x-ray diffraction (XRD) patterns. The results shown in Fig. 3(b) demonstrate that the resultant nanocrystals possess a cubic zinc blende structure similar to the cubic CdS structure [Ref. 27, the lines at the bottom of Fig. 3(b)]. The XRD peaks can be assigned to the (111), (200), (220), and (311) planes of cubic CdS, respectively. The mean particle size of the products (sample D) estimated by Debye–Scherrer's formula based on the (111) plane is about 3.1 nm.

Figure 4 shows the TEM images of the CdS:Cu(I) nanocrystals with different Cu(I) doping levels. It is difficult to resolve the individual character of the nanocrystals in sample A shown in Fig. 4(a). However, when the molar ratio of Cu to Cd is increased to 1:9, as shown in Fig. 4(b), the resultant nanocrystals are generally spherical with uniform sizes, and start to self-assemble into ordered structures. The ordering degree and domain size of the superlattice structure are greatly increased when the molar ratio of Cu to Cd is further increased to 3:7 (sample C) [as shown in Fig. 4(c)]. Quite unexpectedly, sample D in Fig. 4(d) shows that the resultant CdS:Cu(I) nanocrystals can form a highly ordered superlattice structure, and the size of the superlattice domains can reach up to several micrometers. The fast Fourier transform

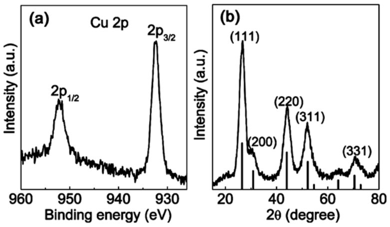

FIG. 3. (a) XPS spectrum of Cu 2*p* for sample D; (b) XRD pattern of sample D, which can be indexed to cubic bulk CdS (Ref. 27, bottom lines).

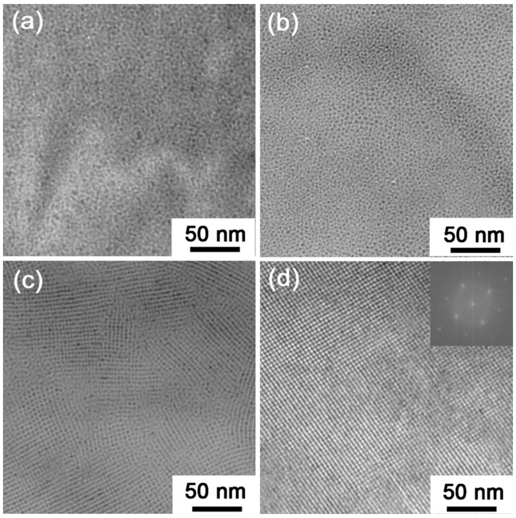

FIG. 4. TEM images of CdS:Cu(i) nanocrystals with different doping levels: (a) sample A; (b) sample B; (c) sample C; and (d) sample D, and the inset shows the FFT of sample D.

(FFT) pattern shown in the inset of Fig. 4(d) demonstrates that the superlattice structure possesses a long-range order with a quasicubic symmetry.[17] The results clearly demonstrate that the formation of the superlattice structure is strongly related to the Cu(I) doping levels. As stated in previous studies that *n*-dodecanethiol-capped noble metal nanocrystals could often form highly ordered superlattice structures, due to the cohesive interaction through interdigitation or interpenetration of alkyl chain.[28,29] According to Per Bain's empirical equation, the length of *n*-dodecanethiol is about 1.77 nm.[29] Based on the superlattice structure shown in Fig. 4(d), the mean inter-particle spacing is estimated to be about 3.8 nm, close to the twofolds of the length of *n*-dodecanethiol, suggesting that the surface-capping molecules from adjacent particles do not interdigitate with each other. Therefore, the interactions between the surface-capping molecules may not be responsible for the spontaneous superlattice formation.

Although the particle size distribution is also a key factor for forming superlattices of monodispersed nanocrystals,[17,30] the nearly identical particle size distributions (shown in Fig. S4 in Ref. 21) for samples A–D present quite different self-assembling behavior, which suggests that narrow particle size distribution makes it difficult to control the formation of the superlattices from the CdS:Cu(I) nanocrystals. Previous studies have pointed out that the nanocrystals capped by alkyl ligands become polar through direct addition of other species such as hydrochloric acid, which in turn promotes the spontaneous superlattice formation.[17,31] The Cu dopant is in +1 state in the current nanocrystal systems, and the ordering degree and domain size of the superlattice structure are strongly dependent on the Cu(I) doping levels. Therefore, it can be concluded that the dipole–dipole interactions between adjacent particles promote the spontaneous superlattice formation.[30,31]

In conclusion, CdS:Cu(I) nanocrystals with different Cu(I) doping levels were prepared by the pyrolysis of both Cu(acac)$_2$ and Cd(acac)$_2$ in *n*-dodecanethiol. The photoemissions of the CdS:Cu(I) nanocrystals could be tuned from surface trap-dominant emission to Cu(I) dopant-related emission by controlling the reaction time and the Cu(I) doping levels. The resultant CdS:Cu(I) nanocrystals could self-assemble into highly ordered superlattices with adjustment of the Cu(I) doping levels, which may be attributed to the electrostatic interactions between the adjacent particles created by the excess amount of Cu(I) ions on the nanocrystal surface. Furthermore, the current synthetic method can be extended to prepare Cu(I) doped ZnS nanocrystals (Fig. S6 and Fig. S7 in Ref. 21).

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