Transactions of the Materials Research Society of Japan 30[4] 1227-1230 (2005)

Surface Functionalization of Mixed Monolayer-Protected Semiconductor Nanocrystals

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A study aimed at synthesizing mixed monolayer-protected semiconductor nanocrystals is described. We prepared CdSe/ZnSe nanocrystals protected by surfactants and used them as starting materials. Decanethiol molecules were added into the toluene solution containing these semiconductor nanocrystals to initiate ligand exchange reaction. In order to obtain mixed monolayer-protected nanocrystals, mercaptoundecanol molecules were mixed into the solution containing decanethiol-protected nanocrystals. The degree of surface modification could be controlled by the concentration of thiolates and the reaction time. The obtained CdSe nanoparticles were characterized by FT-IR, UV-vis spectroscopy. The surface coverage could be systematically controlled through concentration of thiolate molecules, thus providing mixed monolayer-protected semiconductor nanocrystals with diverse surface functionalities.

Key words: Semiconductor nanocrystals, Surface functionalization, PL property

1. INTRODUCTION

Semiconductor nanocrystals, also known as quantum dots (QDs), have attracted much attention because of novel size-tunable properties. The development of reliable and reproducible methods for generating large amounts of highly luminescent semiconductor nanocrystals is a major problem over the several years. Recently, the TOPO/TOP hot injection technique has become one of the most successful methods for preparing highly luminescent semiconductor nanocrystals [1-3]. Moreover, shell formation is widely recognized as an effective passivation method that produces nanocrystals with high quantum yields up to 70 % [4-6]. These highly luminescent semiconductor NCs are expected for potential applications such as light-emitting diodes (LEDs) [7,8], solar cell [9], single-electron transistors (SETs) [10] and biological labels [11,12]. For these applications, it is essential to invert the reactivity and solubility of nanocrystals against various organic solvents or water. However, the TOPO/TOP method provides TOPO-stabilized nanocrystals with hydrophobicity (the terminal group: -CH_3), which to some extent limits applications. Therefore, a key subject for many applications is the surface functionalization of nanocrystals by the introduction of functional groups such as amine, carboxyl, and hydroxyl groups.

There are a wide variety of methods for surface modification of the nanocrystals using, for example, thiol molecules bearing functional groups, silica, polymer, and phospholipids. However there are few examples of methods for preparing mixed monolayer-protected nanocrystals. The nanocrystals protected by different kind of molecules are recognized to be useful for various applications because they have diverse functionality that can be tuned by controlling composition of the molecules. Here we report a simple method for chemical functionalization of CdSe nanocrystals in order to form mixed monolayer-protected nanocrystals. The process involves preparation of luminescent CdSe/ZnSe nanocrystals using TOPO/TOP method, and the surface modification with alkanethiols and partial introduction with thiol molecules bearing hydroxyl group by place-exchange reaction. We also investigate the changes in photoluminescence quantum yields of CdSe/ZnSe nanocrystals during ligand exchange reaction.

2. EXPERIMENTAL

Synthesis of CdSe/ZnSe nanocrystals

Synthesis of CdSe/ZnSe nanocrystals was performed following recently reported methods [5]. Briefly, a mixture of CdO (51.4 mg, 0.4 mmol), TOPO (5 g, 13 mmol), octadecylamine (5 g, 19 mmol), and *n*-octylphosphonic acid (0.16 g, 0.8 mmol) was heated to 270 °C. A TOPSe stock solution (0.2 M, 2.5 mL) was prepared by dissolving Se powder dissolved in TOP solution, which was then rapidly injected into hot Cd precursor solution, and then reaction mixture allowed to 250 °C for nanocrystals growth. After the growth reaction was carried out for several minutes, nanocrystals were precipitated and purified with mixture

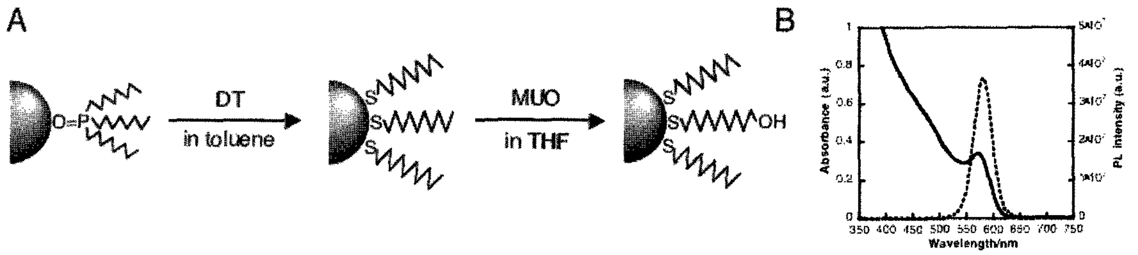

Figure 1. (A) Schematic illustration of the surface functionalization process producing the hydroxyl group-functionlized CdSe/ZnSe nanocrystals. (B) Optical absorption and PL spectrum of the hydroxyl group-functionlized CdSe/ZnSe nanocrystals.

of methanol and toluene. The ZnSe shell around the CdSe nanocrystals was grown by slow addition of zinc stearate and TOPSe solution into the solution of the purified CdSe nanocrystals in TOPO-octadecylamine at 190-200 °C. The resulting crude nanocrystals were purified with mixture of methanol and toluene.

Surface modification using place-exchange reaction.

A toluene solution containing 1-decanethiol (0.43 M, 0.2 mL) was added into toluene containing CdSe/ZnSe nanocrystals (20 mg, 10 mL) at room temperature to obtain DT-protected CdSe/ZnSe nanocrystals. After the purification, nanocrystals were dispersed in THF, and 11-mercapto-1-undecanol (MUO) molecules in THF (0.47 M, 5 mL) was then added into nanocrystals solution (20 mg, 10 mL). The resulting products were characterized by FT-IR, EDX, TEM, UV-vis, and photoluminescence. The PL quantum yields of CdSe/ZnSe nanocrystals was estimated using Rhodamine 6G (95 %) as PL reference.

3. RESULTS AND DISCUSSION

Preparation and PL characterization of DT-protected CdSe/ZnSe nanocrystals.

Figure 1A shows the overall procedure for the preparation of the DT/MUO-protected CdSe/ZnSe nanocrystals. Surface modification of TOPO with DT can be controlled by factor that include the mole ratio of DT to TOPO molecules because ligand exchange reaction is dynamic equilibrium between the added molecules and molecules bound on nanocrystals. An exchange of protective molecules from TOPO to DT can be characterized by the FT-IR spectra presented in Figure 2. The C-H stretching bands of the methylene groups of alkyl chain in TOPO arise at 2925 and 2852 cm^{-1} in agreement with the free TOPO molecules, except for the P-O stretching (1098 cm^{-1}) with a shift to lower energy (Figure 2a) [13]. Figure 2b shows the spectrum of the obtained products after ligand exchange reaction using DT molecules. The peaks assigned to alkyl chains remain unchanged and the intensity of P-O stretching band becomes weaker as compared to initial TOPO-protected nanocrystals. This result indicates that CdSe/ZnSe nanocrystals are protected with DT molecules. However, a weak band assigned to P-O stretching is still remained, indicating that the ligand exchange is not complete. To confirm the more detail for exchange with DT, we performed EDX elemental analysis for purified nanocrystals and the results are given in Table 1. The S content increases remarkably at the initial stage followed by a gradual increase. During exchange for 3 days, the S content in the CdSe/ZnSe nanocrystals reaches up to 9.34 %. Simaltaneously, the P content (arises from TOPO molecules) decreases and the other contents (Cd, Zn, and Se) remain unchanged. These results also indicate that the protective molecules

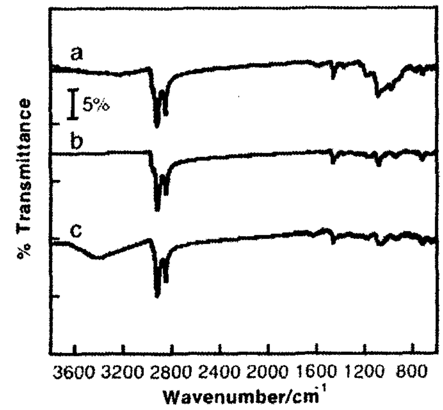

Figure 2. FT-IR spectra of initial TOPO-protected CdSe/ZnSe nanocrystals (a), the products after place-exchange with DT for 3 days (b), and the products after the introduction of MUO for 3 h(c).

Table 1. Changes in elemental composition of CdSe/ZnSe nanocrystals during exchange with DT

Reaction Time (h)	Cd (%)	Zn (%)	Se (%)	P (%)	S (%)
0	29.71	20.35	38.25	11.69	-
24	30.58	20.21	37.38	7.83	3.55
48	29.25	19.86	36.99	5.98	7.92
72	30.33	20.35	37.50	2.48	9.34

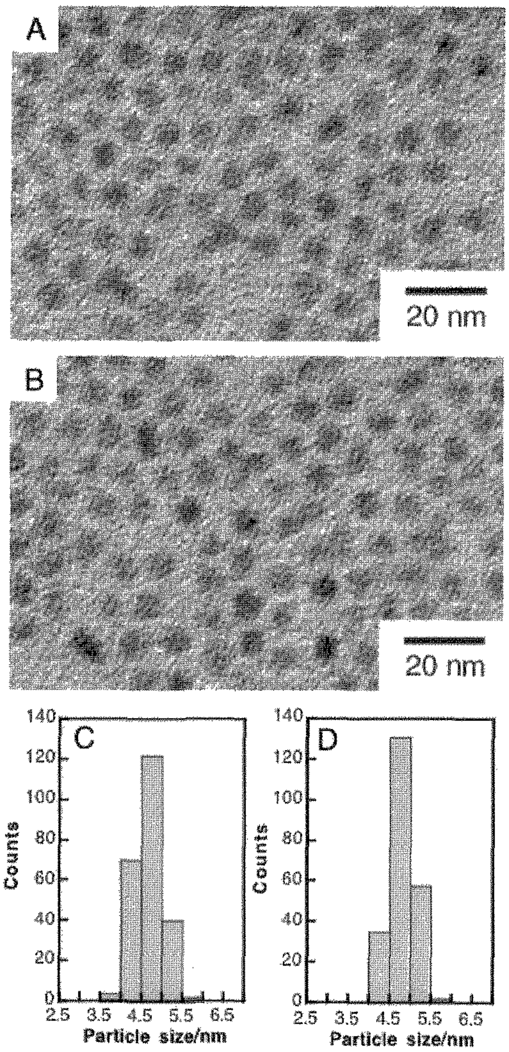

Figure 3. TEM images of CdSe/ZnSe nanocrystals before (A) and after exchange with DT (B) using ligand exchange reaction. (C, D) Size histograms of nanocrystals shown in (A) and (B), respectively.

are exchanged with DT. During the reaction, sum of P and S is almost constant, indicating 1:1 stoichiometric exchange of TOPO with DT molecules.

Figure 3 shows TEM images and size histograms of the nanocrystals before and after ligand exchange reaction with DT. The particle size and standard deviation of initial TOPO-protected CdSe/ZnSe nanocrystals are 4.7 and 0.3 nm, respectively. The electron diffraction pattern of TOPO-protected CdSe/ZnSe nanocrystals indicates CdSe with wurtzite structure. After the exchange reaction from TOPO to DT, the TEM observation show that the particle size (4.8 nm), crystallinity (wurtzite), and monodispersity (standard deiation = 0.4 nm) remains unaltered as compared to those of the TOPO-protected nanocrystals (Figure 3B).

Figure 4 shows changes in fluorescent quantum yields of CdSe/ZnSe nanocrystals during exchange of TOPO with DT. The initial TOPO-protected CdSe/ZnSe nanocrystals has high quantum yields (64 %). After the ligand exchange reaction for 72 h, the quantum yields of DT-protected CdSe/ZnSe nanocrystals decreases to 12 %, presumably due to formation of surface defects during surface modification [14,15]. No changes in optical absorption spectra and PL peak wavelength are observed.

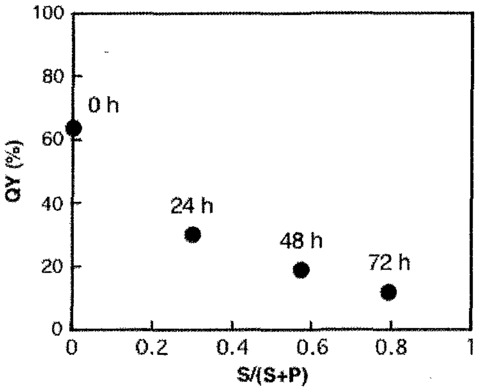

Figure 4. Changes in quantum yields of CdSe/ZnSe nanocrystals during ligand exchange reaction.

Surface functionalization of CdSe/ZnSe nanocrystals by partial introduction of MUO molecules.

The place exchange reaction can be further used to modify the nanocrystals with MUO molecules. The presence of the MUO molecules bearing hydroxyl group can be identified in the spectrum shown in Figure 2c. The C-H stretching bands around 2900 cm^{-1} remain unchanged, and a characteristic of O-H stretching band at 3400 cm^{-1} is newly observed. The resulting nanocrystals are solble in polar solvents such as THF, ethanol, methanol, and dimethylformamide, while TOPO- or DT-stabilized CdSe/ZnSe nanocrystals are only dispersed into non-polar solvents such as hexane, toluene, and chloroform. This behavior also indicates the partial introduction of MUO molecules with polar terminal group. After place exchange, the resulting nanocrystals had the S content nearly the same to that for DT-protected CdSe/ZnSe nanocrystals. Therefore, the partial introduction of MUO molecules onto the nanocrystal surface can slso be achieved by 1:1 exchange of surface-bound DT with MUO molecules.

The DT/MUO-protected CdSe/ZnSe nanocrstals show a strong PL peak at 582 nm, close to the emission peak of the TOPO-, and DT-protected nanocrystals (Figure 1B), suggesting that there is no significant aggregation of nanocrystals upon surface modification. The quantum yield of DT/MUO-protected CdSe/ZnSe nanocrystals was found to be 11 %, which is comparable to that of

DT-protected nanocrystals. This result indicates that no additional surface defects are formed during introduction of MUO molecules to nanocrystals.

4. CONCLUSION

In this paper, we presented a surface modification approach to prepare monolayer-protected CdSe/ZnSe nanocrystals and investigated the changes in optical property of nanocrystals during surface modification. TOPO-protected CdSe/ZnSe nanocrystals were used as a starting material for the preparing DT-protected CdSe/ZnSe nanocrystals using ligand exchange reaction. The size, size distribution, and crystal structure preserved before and after the exchange with DT. During the ligand exchange reaction, the quantum yields of nanocrystals gradually decreased presumably due to the formation of surface defects. Additionally, the partial introduction of MUO molecules to DT-protected CdSe/ZnSe nanocrystals can be achieved by adding MUO molecules in THF solution. The obtained nanocrystals are soluble in various organic solvents and the solubility is controlled by concentration of adding MUO solution or exchange reaction time. Although quantum yield of CdSe/ZnSe nanocrystals decreases during surface modification, over 10 % quantum yield was achieved after ligand exchange for 3 days. The process presented here allows one to prepare luminescent semiconductor nanocrystals with controlled surface functionalities, enabling one to use them as building blocks for novel optoelectronic devices such as LEDs.

ACKNOWLEDGMENT

This work was supported in part by Hyogo Science and Technology Association. T. T. is grateful for research fellowship support from Japan Society for the Promotion of Science.

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(Received December 24, 2004; Accepted June 30, 2005)