

## Fabrication of Fluorescent Multilayers Consisting of CdTe Nanocrystals through Carbamate Bond Forming Reaction

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Herein, we present an approach for the fabrication of three-dimensional structures based on highly luminescent CdTe nanocrystals through carbamate bond forming reaction. Highly luminescent CdTe nanocrystals functionalized with 1-decanethiol (DT) molecules were initially prepared in solution and the reactive molecules, 11-mercapto-1-undecanol (MUO), were then introduced in part into these monolayer-functionalized nanocrystals by place-exchange reaction. The immobilization process relies on reaction between hydroxyl group onto nanocrystals and isocyanate group pre-deposited on solid substrates. The CdTe nanocrystals could be successfully immobilized on solid substrates and could be further utilized for multilayer construction in layer-by-layer fashion. The emission properties of immobilized CdTe nanocrystals are nearly consistent with those of CdTe nanocrystals dispersed in THF. In addition, the CdTe nanocrystals could be selectively immobilized on solid substrate, providing fluorescent patterns of nanocrystals.

Key words: Semiconductor nanocrystals, Surface functionalization, Nanostructures, Carbamate bond

### 1. INTRODUCTION

Semiconductor nanocrystals are being extensively studied because of their size-dependent electrical and optical properties [1]. In particular, cadmium chalcogenide (CdS, CdSe, and CdTe) nanocrystals are probably the most studied and best established systems, and a variety of procedures have been developed to produce monolayer-protected nanocrystals with high quantum yields up to 50 % [2-7]. These highly luminescent cadmium chalcogenide nanocrystals are promising candidates for next generation devices including light-emitting diodes [8,9], quantum dot lasers [10], photovoltaic cells [11], and biological probes [12,13].

The successful optoelectronic devices based on semiconductor nanocrystals require the ability to fabricate two- or three-dimensional nanostructures. There are many approaches for preparing nanocrystals-based three-dimensional structures, utilizing self-assembly, electrostatic interaction, and covalent bonding. The covalent bond forming reaction can be used for preparation of the three-dimensional structures with high chemical and physical stability, but the major limitation of this approach is the reactivity of monolayer-protected semiconductor nanocrystals. Highly luminescent semiconductor nanocrystals have typically been prepared in high temperature medium containing protective molecules such as aliphatic phosphine, phosphine oxide, and alkylamines [2-7].

Although these ligands are essential to prevent the nanocrystals from aggregation, they also cause the nanocrystals to be only soluble into non-polar solvents and less reactivity. Therefore, for the fabrication of three-dimensional structures of semiconductor nanocrystals linked by covalent bonds, it is important to control the surface functionality of nanocrystals by the introduction of highly reactive functional 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. Here we report a simple method for chemical surface modification of CdTe nanocrystals in order to form highly luminescent, surface functionalized nanocrystals. The process involves preparation of CdTe nanocrystals in noncoordinating solvent, and the surface modification of nanocrystals with mixed monolayers of thiol molecules by place-exchange reaction. Fabrication of fluorescent multilayers consisting of CdTe nanocrystals on a quartz substrate was achieved through a carbamate bond forming reaction between hydroxyl groups on the surface of nanocrystals and isocyanate groups on the quartz substrate. In addition, we also report the fabrication of fluorescent patterns by selective immobilization of the nanocrystals.

## 2. EXPERIMENTAL

### Synthesis of CdTe Nanocrystals

Synthesis of CdTe nanocrystals was performed following recently reported methods [14]. Briefly, a mixture of CdO (12.8 mg, 0.1 mmol), *n*-octylphosphonic acid (39.8 mg, 0.2 mmol), octadecene (3.93 g, 16 mmol) was heated to 260 °C. A Te precursor solution containing Te powder (25.0 mg, 0.2 mmol), tributylphosphine (TBP: 0.475 g, 2.3 mol), and octadecene (1.5 g, 5.9 mmol) was then rapidly injected into hot Cd precursor solution, and reaction mixture heated at 260 °C for nanocrystals growth. After the reaction was carried out for several minutes, the resulting solution was cooled to room temperature.

### Surface Modification Using Place-Exchange Reaction.

A toluene solution containing 1-decanethiol (DT: 4.3 M, 2.0 mL) was added into toluene containing CdTe nanocrystals (50 mL), and then this solution was refluxed for 3 h to obtain DT-protected CdTe nanocrystals. After the purification using acetone, nanocrystals were dispersed in THF, and 11-mercapto-1-undecanol (MUO) molecules in THF were then added into the nanocrystals solution. The resulting products were characterized by FT-IR, UV-vis, and photoluminescence measurements.

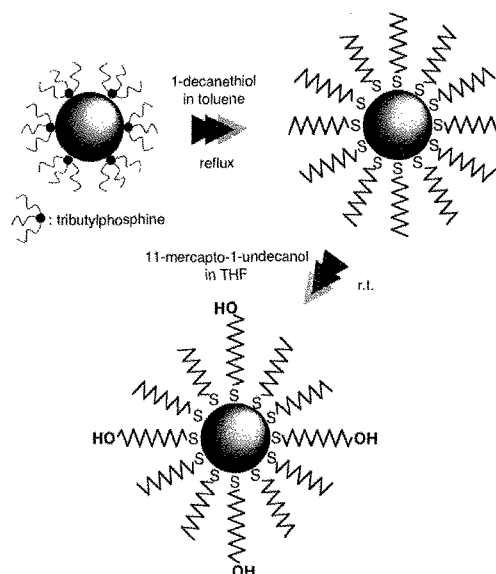
### Fabrication of Nanocrystals-Based Fluorescent Multilayer Films.

The quartz substrate was cleaned by irradiation of vacuum ultraviolet (VUV) light (wavelength: 172 nm) for 20 min and then immersed in toluene containing hexamethylene diisocyanate (IM, 5 mL) at room temperature for 4 h, followed by rinsing with toluene under ultrasonication. The isocyanate-functionalized quartz substrate was immersed in THF containing hydroxyl-functionalized CdTe nanocrystals for 2 h. After the quartz substrate was rinsed with THF under ultrasonication, the quartz substrate with the first CdTe monolayer was again immersed hexamethylene diisocyanate for 1 h. This process was repeated in order to form three-dimensional multilayered film.

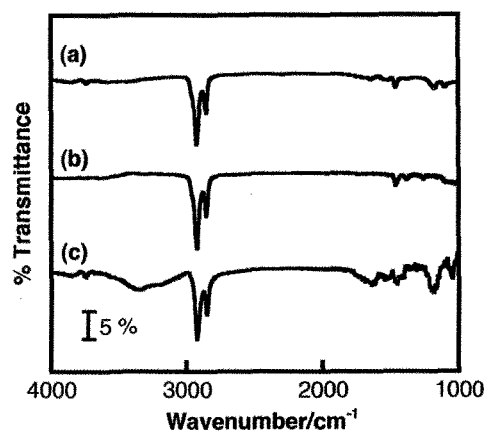
## 3. RESULTS AND DISCUSSION

### Surface Modification of CdTe Nanocrystals by Partial Introduction of MUO Molecules.

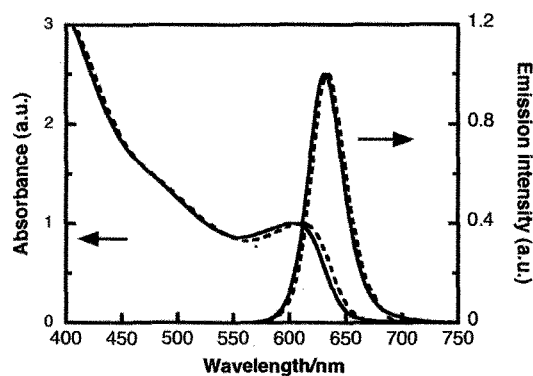
Figure 1 schematically describes the procedure for the preparation of the mixed-monolayer-protected CdTe nanocrystals. These surface modification processes were used to obtain CdTe nanocrystals protected by both DT and MUO molecules. The ligands at each modification process were characterized by FT-IR, as shown in Figure 2. The FT-IR spectrum of as-prepared nanocrystals clearly shows the C-H stretching bands around 2900  $\text{cm}^{-1}$ , which are assigned to alkyl chains of TBP molecules. After surface modification with DT, the



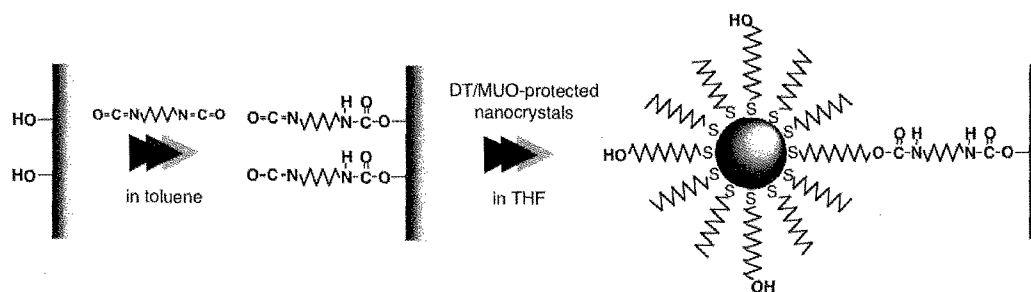
**Figure 1.** Schematic illustration for preparation of DT/MUO-protected CdTe nanocrystals.



**Figure 2.** FT-IR spectra of initial TBP-protected CdTe nanocrystals (a) and the nanocrystals obtained after surface modification with DT (b) followed by place exchange with MUO (c).



**Figure 3.** UV-vis and PL spectra of CdTe nanocrystals before (solid line) and after surface modification with DT (dashed line).



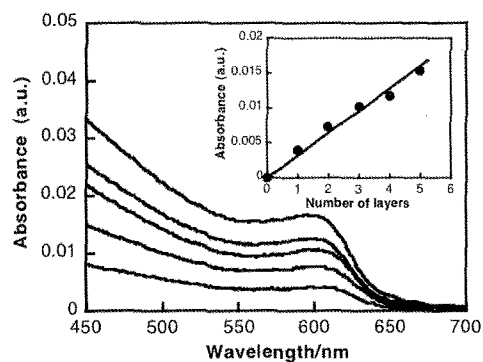
**Figure 4.** Schematic illustration for immobilization of DT/MUO-protected CdTe nanocrystals on the isocyanate-bearing substrate through carbamate bond-forming reaction.

spectrum of the resulting nanocrystals is almost the same as that of initial TBP-protected nanocrystals because DT-protected nanocrystals shows only C-H stretching band in FT-IR spectrum. However, EDX elemental analysis for the purified nanocrystals provided the indication of ligand exchange during this process. Although the sulfur was not detected for the initial TBP-protected nanocrystals, the sulfur content increased after surface modification with DT. This result indicates that DT-protected CdTe nanocrystals were formed by surface modification. The absorption maximum and emission peak wavelength of the resulting nanocrystals remains unchanged as shown in Figure 3.

The place exchange reaction can be further used to modify the nanocrystals with MUO molecules. The nanocrystals obtained after place-exchange reaction were soluble in THF but were found to be insoluble in non-polar solvents such as toluene and chloroform. The FT-IR spectrum of the products is shown in Figure 2c. The C-H stretching bands remain unchanged, whereas new absorption bands are observed around  $3400\text{ cm}^{-1}$  and at  $1150\text{ cm}^{-1}$  which are associated with the O-H stretching and C-O stretching bands. These results indicate that partial introduction of MUO molecules was achieved by a place-exchange reaction. The optical properties of the DT/MUO-protected CdTe nanocrystals are almost the same as those for DT-protected nanocrystals.

#### Immobilization of Highly Luminescent, DT/MUO-protected CdTe Nanocrystals.

The hydroxyl group onto the nanocrystal surface can be used to immobilize the nanocrystals on the isocyanate-bearing quartz glass substrate through carbamate bond-forming reaction (Figure 4) that could be further utilized for multilayer growth in layer-by-layer approach. UV-vis absorption spectroscopy was carried out to monitor the multilayer construction as a function of number of CdTe nanocrystal layers. In Figure 5, the absorbance increased as the number of immobilization cycle increased

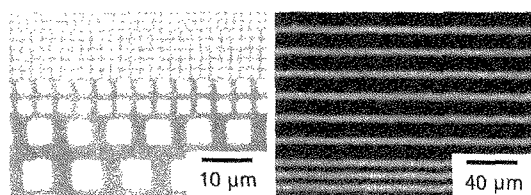


**Figure 5.** Absorption spectra of CdTe nanocrystals-based multilayer films on the quartz substrate. Layers 1-5 of the nanocrystals are shown from the lower to the upper spectrum. Inset: Plots of absorbance at 610 nm for films as a function of the number of layers.

whereas the band onset wavelength was observed to remain unchanged. The absorbance at 610 nm increased almost linearly with the number of immobilization cycle (Figure 5 inset), indicating a uniform immobilization on the quartz substrate.

We also performed photoluminescence (PL) measurement of CdTe nanocrystals immobilized on the quartz substrate. The emission wavelength of CdTe nanocrystals immobilized on the substrate was slightly red-shifted compared with that of nanocrystals dispersed in THF (from 615 nm to 620 nm). Similar PL red-shift have been reported by other groups [14] and is usually attributed to energy transfer from smaller to larger nanocrystals due to decreased interparticle distance after immobilization onto substrate.

One of the advantages of the present immobilization process is the fabrication of micropatterns consisting of luminescent nanocrystals. In order to generate patterns of nanocomposites, template hexamethylene diisocyanate monolayer patterns on the quartz substrate was prepared by VUV lithography using a photomask [15]. We first prepared *n*-octadecyl trimethoxysilane



**Figure 6.** Fluorescent images of patterns of immobilized nanocrystals on the quartz substrate. The brighter area corresponds to the immobilized nanocrystals.

(OTS) monolayer modified substrate. The OTS-modified substrate was then irradiated by VUV light through a photomask because it is possible to selectively decompose OTS monolayers in specific regions irradiated by UVU light. After VUV illumination, the resulting substrate was immersed into toluene solution containing hexamethylene diisocyanate, providing patterns of hexamethylene diisocyanate on the quartz substrate. This template was utilized for the selective immobilization of nanocrystals on the substrate. Consequently, fluorescent micropatterns of CdTe nanocrystals can be successfully fabricated on the quartz substrate (Figure 6).

#### 4. CONCLUSION

In summary, we have successfully prepared DT/MUO-protected CdTe nanocrystals and fabricated fluorescent multilayer films consisting of CdTe nanocrystals through carbamate bond-forming reaction. The hydroxyl groups onto the nanocrystal surface can readily react with the isocyanate groups onto the quartz substrate, resulting in the immobilization of CdTe nanocrystals onto the substrate through carbamate bond-forming reaction. The residual hydroxyl groups onto the substrate can be used to construct the fluorescent multilayers consisting of the nanocrystals. Additionally, we could also prepare fluorescent micropatterns of CdTe nanocrystals using the template patterns of hexamethylene diisocyanate monolayers. This method enable to fabrication of nanocrystals-based three-dimensional nanostructures through covalent bond-forming reaction, the ability of which is expected to be useful for fabrication of optoelectronic devises.

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