Preparation and Photoluminescence of SiO$_2$-CdTe multilayer film by layer-by-layer self-assembly

Ping Yang, Norio Murase
Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka, Ikeda-city, Osaka, 563-8577, Japan

E-mail: n-murase@aist.go.jp

Abstract. Preparation parameters of layer-by-layer self-assembled films consisting of functional SiO$_2$ layers and emitting CdTe quantum dots (QDs) layers were investigated. A surface-treated plate was successively dipped into three different solutions: surfactant (thioglycolic acid, TGA), colloidal QDs, and functional silicon alkoxide. Since the free TGA molecules in the first solution became linkers between the two kinds of layers, the condition of the first solution (TGA and Cd$^{2+}$ ion concentrations and pH) affected the properties of the film. Under optimal conditions, the QDs were dispersed at a high concentration (0.01 M) in a closely packed manner without agglomeration. This resulted in a narrowing of the photoluminescence (PL) spectrum and a red shift of the peak wavelength due to reabsorption of the emission. The PL efficiency of films thus prepared with ten double layers (ca. ~50 nm thick) was 25%. This high efficiency together with the high concentration resulted in a brightness much higher than that of a commercial phosphor when their thickness was same. However, when there were excess free TGA molecules in the first solution, the film had a higher concentration (0.02 M) and lower PL efficiency due to agglomeration of the QDs.

1. Introduction
Layer-by-layer (LbL) assembly techniques have been extensively studied using various driving forces such as electrostatic, hydrogen bonding, charge transfer interaction, and coordination bonding [1, 2]. LbL assembly has been achieved for a wide variety of materials including polymers, inorganic nanoparticles, nanowires, organic components, carbon nanotubes, and biological macromolecules such as proteins, viruses, and DNA [3–14]. Such assembly requires control of the molecular orientation and organization at the nanometer level, so it is essential to investigate and develop methods for the controlled assembly of multi-component nanostructures [15]. LbL self-assembly, based on sequential adsorption of oppositely charged components, is one of the most established methods for the preparation of thin films with controlled properties [16]. The potential applications of such LbL-assembled films range from drug delivery and cell resistant coatings to antireflection coatings, batteries, and electrochromic devices [17].

Thin films of quantum dots (QDs) are emerging as an important class of materials for electronic and optoelectronic devices such as field-effect transistors, photodetectors, light-emitting diodes, and solar cells [18]. The incorporation of QDs into the films using LbL assembly has been accomplished using different approaches. For example, a novel type of composite thin film consisting of gold QDs and polyimide was prepared through binding based on the combined effect of metal-ligand coordination and electrostatic interaction [19]. Kotov’s group reported free-standing LbL-assembled...
films of magnetite QDs [20]. They also reported LbL films of semiconductor QDs and a polymer with multicolor capability [21]. Hybrid thin films of a conjugated polymer and CdSe QDs have been fabricated using a LbL assembly method based on covalent coupling reactions [22]. A graded semiconductor film with rainbow-like luminescence was prepared using CdTe QDs [23]. In short, LbL assembly is a promising method for fabricating structured and functional films for the construction of nano-devices.

We previously developed a novel method for preparing multilayer films of CdTe QDs by LbL self-assembly using very thin functional SiO$_2$ layers for linkage [24]. The films have intense photoluminescence (PL) and a high QDs concentration. They have a PL efficiency of 24% and are 40 times brighter than a conventional rare-earth phosphor of the same thickness when excited at the same intensity at 365 nm [25]. This high brightness should lead to a new variety of applications with a functional SiO$_2$ layer composed of amino or mercapto groups.

We have now investigated the relationship between the preparation conditions and properties of SiO$_2$-CdTe multilayer films prepared by LbL self-assembly. We found that free thioglycolic acid (TGA) molecules (without connected Cd$^{2+}$ ions) in the TGA and Cd$^{2+}$ ion solution play an important role in the arrangement of the CdTe QDs in the film. This arrangement affects drastically the PL properties of the film.

2. Experimental section

A colloidal solution containing TGA-capped red-emitting CdTe QDs was prepared using a procedure described in detail elsewhere [26]. The QDs had a diameter of 3.9 nm and a PL efficiency of 70%. SiO$_2$-CdTe multilayer films were prepared using LbL self-assembly [24]. We reduced the dipping time at each step in accordance with the optimal preparation procedure. Briefly, a glass slide (Matsunami, No. S8111) coated with a 3-aminopropyltrimethoxysilane (APS) layer was first dipped in the solution of TGA and Cd$^{2+}$ ($\text{Cd(ClO}_4)_2$) for 0.5−1 min. The sample was then dipped in the colloidal solution of CdTe QDs for 1−2 min. Finally, the sample was immersed in the solution of APS and toluene (volume ratio of APS to toluene of 0.33) for 1−2 min. The cycle was repeated until the desired number of layers was obtained. After each cycle, the sample was rinsed with Milli-Q water and dried under N$_2$.

Scheme 1 illustrates the steps in the formation process.

Scheme 1. Preparation of SiO$_2$-CdTe multilayer film by LbL self-assembly.
Because the free TGA molecules act as linkers between the QDs and SiO₂ layers, we investigated the relationship between the first solution conditions (TGA and Cd²⁺ ion concentrations, pH) and the PL properties. The molar ratio of TGA to Cd²⁺ ranged from 2 to 8. The concentration of TGA ranged from 0.01 to 0.20 M. The pH was changed from 7 to 11 by adding a NaOH solution.

The absorption and PL spectra were measured with conventional spectrometers (Hitachi U-4000 and F-4500). Transmission electron microscopy (TEM) analysis was performed using a Hitachi H-9000 microscope. Optical images of the films under visible light and UV irradiation (365 nm) were taken by a digital camera. The film thickness was measured with a surface roughness measuring instrument (Mitutoyo SurfTest SV-624) or an atomic force microscope (Digital Instruments Nanoscope). The PL efficiencies of the colloidal solution were estimated by comparison with a solution of quinine sulfate in 0.5 M H₂SO₄. Because the prepared films were transparent, their PL efficiencies were estimated by comparison with solutions of standard dye having a similar optical path length and optical density. The details are described elsewhere [27].

3. Results and discussion

Figure 1 shows the absorption and PL spectra of a SiO₂-CdTe multilayer film with five double layers. It was prepared using a TGA and Cd²⁺ solution with a molar ratio of TGA to Cd²⁺ of ~5, a pH of ~10, and a TGA concentration of ~0.1 M. Comparing with the CdTe colloidal solution, the film revealed a decreasing (~10 nm) of full-width at half maximum (FWHM) of PL spectrum and a red-shift (~17 nm) of PL peak. This phenomenon is ascribed to the reabsorption of the emissions from the smaller QDs by the larger QDs in the matrix. The PL efficiency of the film was 25% while that of the QDs in the colloidal solution was 70%. The brightness of the film was estimated to be more than 40 times that of a commercial rare-earth phosphor (P22-RE3) on the basis of previous quantitative analysis [25]. This much higher brightness means that the film is attractive for various potential applications.

![Figure 1. Absorption and PL spectra of SiO₂-CdTe multilayer film with five double layers. Inset shows color image of film (lower) under UV light and optical picture of it (upper) under visible light. Absorption and PL spectra of CdTe colloidal solution are shown for comparison.](image)

Figure 2 shows the TEM photograph of a SiO₂-CdTe multilayer film with ten double layers. The QDs, with a mean diameter of ~4 nm, were uniformly dispersed in the film. Their concentration was estimated to be 0.01 M on the basis of the absorbance at the first absorption peak and the thickness
(~50 nm) of the film. Furthermore, calculation using the thickness of the film and the absorbance at the first absorption peak revealed that the immobilized QDs (3.9 nm in diameter as estimated from the first absorption peak) were arranged in a closely packed manner with a thin functional sol-gel SiO$_2$ layer.

The formation of a Cd-thiol layer on the surface of aqueous CdTe QDs effectively passivates them, resulting in high PL efficiency. The Cd$^{2+}$ ions were added to the TGA solution to maintain the initial surface state of the QDs during film preparation. Because the carboxyl and mercapto groups in free TGA (without connection to Cd$^{2+}$ ions) act as interaction mediums between the QDs and the functional SiO$_2$ layers consisting of condensed APS, the form of the TGA molecules in the TGA and Cd$^{2+}$ solution affected the arrangement of the QDs in the film. According to previous reports on CdTe QDs, a variety of Cd-TGA complexes formed depending on the molar ratio of TGA molecules to Cd$^{2+}$ ions in the solution. When the molar ratio is less than 2, a dithio-complex is formed in two consecutive steps, as described by eqs. 1 and 2, through the reaction between Cd$^{2+}$ ions and TGA molecules [28].

$$\begin{align*}
\text{Cd}^{2+} + \overline{\text{SR}} & \leftrightarrow (\text{Cd-SR})^+ \\
(C\text{d-SR})^+ + \overline{\text{SR}} & \leftrightarrow \text{Cd(SR)}_2
\end{align*}$$

Additionally, the dithio-Cd complex (a molar ratio of TGA molecules to Cd$^{2+}$ ions of more than 2) has better stabilization than that of a monothio-Cd complex (a molar ratio close to 1). In our experiments (with an alkaline condition), the molar ratio ranged from 2 to 8. Therefore, there were two main forms of TGA molecules in the solution. One was the thio-Cd complex form, and the other was the ionization state form.

Scheme 2 illustrates the morphology of the SiO$_2$-CdTe multilayer film prepared by LbL self-assembly for three different concentrations of free TGA in the solution. The optimal concentration resulted in the formation of layers of CdTe QDs in a closely packed manner (Scheme 2, middle). This means that the average distance between QDs is ~5.5 nm fored-emitting CdTe QDs with a thickness of the functional SiO$_2$ layer of 1–2 nm [24]. With the low concentration (Scheme 2, left), there were fewer QDs in each layer. With the high concentration (Scheme 2, right), the number of free TGA molecules connected with a functional SiO$_2$ layer was higher. This resulted in an increased number of CdTe QDs assembled into each layer. The results of additional experiments support these findings, as we explain in detail below. All the films had five double layers (CdTe QDs layer and functional SiO$_2$ layer) unless otherwise noted.
Scheme 2. Morphologies of SiO₂-CdTe multilayer films prepared with different concentrations of free TGA in solution. Number of CdTe QDs in each monolayer increased with the concentration.

Figure 3 shows the effect of the molar ratio of TGA to Cd²⁺ in the solution on the PL efficiency and the peak wavelength of the PL spectra of SiO₂-CdTe multilayer films. The inset shows the absorption and PL spectra for three molar ratios. The absorbance at the first absorption peak and the red shift of the PL peak increased with increasing the ratio. This means the number of QDs assembled in the film increased. Additionally, the films had relatively high PL efficiency when the ratio was 5–6. Beyond a ratio of 7, the efficiency decreased quickly. This phenomenon was ascribed to the number of free TGA molecules in the solution. With an increasing molar ratio of TGA to Cd²⁺ in the solution, the amount of thio-Cd complex decreased and the number of free TGA molecules increased because the concentration of TGA remained unchanged and the concentration of Cd²⁺ decreased. Therefore, many free TGA molecules connected with a functional SiO₂ layer due to the formation of a hydrogen bond between the amino group in APS and the carboxyl group in TGA. The large number of mercapto groups in each layer resulted in an increased number of QDs. This high QD concentration led to an increased red shift of the PL peak and lower PL efficiency. In addition, when the ratio was more than 7, the number of Cd²⁺ ions in the solution was less because the ions on the surface of the QDs escaped into the solution. This change in the surface state resulted in reduced PL efficiency.

Figure 4 shows the effect of the concentration of TGA in the solution on PL efficiency and on absorbance at the first absorption peak for SiO₂-CdTe multilayer films. When the concentration was less than 0.1 M, the films had relatively high efficiency. Above 0.1 M, it decreased dramatically with an increasing concentration. The absorbance at the first absorption peak increased linearly with the
concentration. When the concentration was 0.1 and 0.2 M, the concentration of QDs in the film was 0.01 and 0.02 M, respectively, estimated from the thickness and absorbance at the first absorption peak. This increase in QDs concentration was associated with the increase in the number of free TGA molecules in the solution. The QDs were arranged in a closely packed manner when the concentration was 0.01 M. At the higher concentration (0.2 M), the QDs aggregated. The resulting concentration quenching caused the PL efficiency of the film to decrease remarkably.

**Figure 4.** Effect of concentration of TGA in solution (molar ratio of TGA to Cd\(^{2+}\) \(\sim 5\), pH \(\sim 10\)) on PL efficiency and absorbance at first absorption peak of SiO\(_2\)-CdTe multilayer films: (a) PL efficiency against concentration of TGA; (b) absorbance at first absorption peak against concentration of TGA.

Figure 5 shows the effect of the pH of the TGA and Cd\(^{2+}\) ion solution on the PL efficiency and on the absorbance at the first absorption peak for SiO\(_2\)-CdTe multilayer films. The PL efficiency was relatively high when the pH was from 7 to 10. Furthermore, the absorbance at the first absorption peak was relatively high in this range. When the pH was about 11, both the efficiency and absorbance at the first absorption peak were lower. These results are related to the pH dependence of the formation of sol-gel derived SiO\(_2\) layers because such layers are partly dissolved when the pH is high [29].

**Figure 5.** Effect of pH of solution (molar ratio of TGA to Cd\(^{2+}\) \(\sim 5\), concentration of TGA \(\sim 0.05\) M) on PL efficiency and absorbance at first absorption peak of SiO\(_2\)
4. Conclusion
To clarify the effect of the preparation conditions on the properties of LbL self-assembled films, we prepared SiO$_2$-CdTe multilayer films by LbL self-assembly. Because the mercapto and carboxyl groups in the TGA were linkers between the CdTe QDs and functional SiO$_2$ layers, the free TGA molecules (not connected with Cd$^{2+}$) in the aqueous solution of TGA and Cd$^{2+}$ ions used for a successive dipping during preparation played an important role in determining the properties of these films, such as the concentration of CdTe QDs, the efficiency of the PL, and the peak wavelength of the PL spectra. When the molar ratio of TGA to Cd was 5–6, the pH was 7–10, and the concentration of TGA was 0.01–0.1 M, the PL efficiency was relatively high. The optimal QD concentration (0.01 M) was obtained by optimizing the preparation conditions. The resulting PL efficiency was 25%, and the QDs were arranged in a closely packed manner. This close-packed arrangement resulted in a red-shifted PL peak and a narrowed PL spectrum. Further work will address the use of these films as biodetectors and optical devices, making use of their higher PL brightness compared with that of a commercial phosphor.

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