Formation of Quantum Dot Fluorescent Monolayer Film using Peptide Bond

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Abstract

We present a method for preparing a quantum dot fluorescent monolayer film on a glass substrate. Since nanoparticles aggregate easily, it is difficult to prepare a nanoparticle monolayer film. We have used a covalent bond, the peptide bond, to fix quantum dots on the glass substrate. The surface of the quantum dot was functionalized with carboxyl groups, and the glass substrate was also functionalized with amino groups using a silane coupling agent. The carboxyl group can be strongly coupled to the amino group. We were able to successfully prepare a monolayer film of CdSe quantum dots on the glass substrate.

Key Words : Display, Fluorescent monolayer film, Peptide bond, Quantum dot

1. Introduction

Quantum dots are parts of matter whose excitons are confined in all three spatial dimensions. As a result, their electronic properties are between those of bulk semiconductors and those of discrete molecules. Research interest in quantum dots has tremendously increased in recent years because they are extremely promising materials that can be applied to various fields such as lasers1-3, light emitting diodes3-6, display7,8, transistors9, fluorescent dyes for life science10,11, solar cells12 and so on13-15. Quantum dots have many advantages such as tunability of emission color with a single-excitation light source, wide color reproduction range, and long-term photostability. The emission wavelength of a quantum dot can by controlling its size: further the emission wavelength range is extremely wide and encompasses ultraviolet to near infrared (350-1300nm).

A promising application of quantum dots is display devices, because the colors can be easily tuned by mixing several quantum dots and the emission can be excited by a single light source. A quantum dots thin film with a thickness of several tens of nanometers can realize ultra-thin flexible displays.

However, it is difficult to prepare a nanoparticle monolayer film because nanoparticles aggregate easily. Self-organization processes can solve the aggregation problem. The Langmuir-Blodgett (LB) technique16,17, convective assembly method18,19, electrophoresis20, and magnetrophoresis21 are well-known methods of arranging of nanoparticles on a substrate. The nanoparticles can be easily removed from the substrate, because the nanoparticles and substrate are not bonded strongly with the self-organization process. The bonding is non-covalent bond, whose strength is considerably weaker than that of a covalent bond.

In this paper, we present a method for preparing quantum dot fluorescent monolayer films on surface of a glass substrate surface using covalent bonding. Peptide bonds22 are used to fix the quantum dots on the surface of the surfaces. The peptide bond is a covalent bond that is formed between carboxyl groups and amino groups by dehydration synthesis. The surfaces of the quantum dots were functionalized with carboxyl groups, and the glass substrate is functionalized with amino groups by a silane coupling agent. The reaction time and concentration of the quantum dot solution are also optimized. We were able to successfully prepare 10- and 20-nm quantum dot monolayer films on a glass substrate.

2. Experiment

Figure 1 shows our method for fixing quantum dots on a substrate by using the peptide bond. Amino groups are
formed on the surface of a glass substrate by using a silane coupling agent. Quantum dots with polymer coating have carboxyl groups. The carboxyl groups of quantum dots react with the amino group of the surface glass substrate by dehydration synthesis, thereby releasing water. Peptide bonds are formed between the quantum dots and the glass substrate. The residual quantum dots that did not attach to the glass substrate can be removed by a rinsing process. In this manner, we can finally obtain a monolayer film of quantum dots.

Figure 2 shows our procedure for obtaining a quantum dot fluorescent monolayer film. The process consists of silanizing a glass surface, achieving coupling between quantum dots and the substrate, and rinsing procedure. First, amino groups were formed on a glass substrate surface by using a silane coupling agent. The glass substrate (Matsunami, C218181, 18x18mm) was then washed with Scat 20X PF (Daichi Clean Chemical, Inc.) detergent in an ultrasonic bath for 30 min. Amino groups were formed on the surface of the glass substrate by immersing the glass film in a silane coupling agent for 5 min. The silane coupling agent was prepared by mixing 200 µL of 3-aminopropyltriethoxy silane (APTES, Sigma, A3468) and 10 mL of acetone (Wako, 018-17815). In order to wash the extra silane coupling agent from the glass substrate, the substrate was immersed in acetone in a plastic test tube and shaken. The substrate was then immersed in pure water to remove the acetone from the substrate surface. The rinsing process was performed twice.

The quantum dots that were functionalized with carboxyl groups were fixed on the surface of the glass substrate. A solution including the quantum dots was dropped on the glass substrate. The solution was prepared by adding 10.0 mg of EDC (N-(3-dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (Sigma E6383)) to 1.0 mL of phosphate buffered saline (PBS; pH 7.4 (Sigma, P5368)). After EDC was completely dissolved in PBS, 10 µL of a solution of quantum dots was added to the solution. The concentration of the prepared quantum dot solution was 80 nM. We prepared a parafilm bank around the substrate to store the quantum dot solution on the substrate. The quantum dots were fixed on the substrate by the formation of a peptide bond between the quantum dots and the substrate.

Finally, the glass substrate was washed in order to remove the residual quantum dots from the substrate surface. The parafilm was removed and the glass substrate was immersed in PBS solution. Subsequently, the glass substrate was immersed in pure water. The rinsing procedure was performed twice. The glass substrate was successively immersed in 50% and 100% ethanol successively and dried at room temperature.

3. Results and discussion

Figure 3(a) shows the observation results of the fluorescent monolayer film of quantum dots. We used Qdot 655 ITKTM Carboxyl Quantum Dots (Invitrogen) prepared from nanometer-scale crystals of a semiconductor material (CdSe). The diameter of the quantum dot we used was 20 nm. We observed the topography of the monolayer film by using an atomic force microscope (AFM; Seiko Instruments, SPA300). The scanning area was 1x1 µm. The reaction time and the concentration of the quantum dot solution were 1 h and 80 nM, respectively. As shown in Fig. 3(a), a monolayer quantum dot film was formed with some particles having diameters larger than 20 nm.

Figure 3(b) and (c) show the line profiles along lines (A) and (B), respectively, in Fig. 3(a). Figure 3(b) shows peaks of two different sizes: 21.9 nm and 54.1 nm. The peak of 21.9 nm width represents a single quantum dot while the peak of the 54.1 nm width represents an aggregation of quantum dots. Some aggregations of quantum dots can be observed in Fig. 3(a). The height of the observed quantum dots in Fig. 3(b) and (c) was approximately 8 nm even though we had used quantum dots with a diameter of 20 nm. We believe that this was because the quantum dot that formed on the substrate "sank" into amino groups whose thickness was 10 nm.