Silica-Coating of Quantum Dots by Using Water Glass and Their Photo-Bleaching Properties

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Abstract: An uncomplicated, secure, and low environmental load method for suppressing the oxidation and aggregation of luminescent semiconductor nanoparticles like spherical nanoparticles comprising of cadmium compounds, *or* quantum dots (QD), is awaited to be developed. This paper expresses silica-coating of the QDs in water by means of a method using sodium silicate, and their fluorescence properties. The QDs were silica-coated by adding sodium silicate to the QDs with a size of 9.3±1.2 nm dispersed in water. A structure of the silica-coated QDs (QD/SiO₂) was a core-shell type with the QDs as core and the silica as shells, and had a particle size of 28.6±2.7 nm. IVIS images with intensities larger than those of uncoated QDs were taken for the QD/SiO₂. Although fluorescence intensity of the QD/SiO₂ measured by a conventional fluorescence spectroscopy decreased with aging at room temperature in a dark box open to the atmosphere, the fluorescence intensity was stable after the drastic decrease in fluorescence intensity.

Key words: Quantum dot, Cadmium-related semiconductor, Core-shell, Silica-coating, Sol-gel, fluorescence.

1. Introduction

Luminescent semiconductor nanoparticles, which are called quantum dots (QDs), are one of luminescent materials. Among various QDs, cadmium-related QDs such as CdS, CdSe and CdTe have been focused on for various applications.

Cadmium contained in the cadmium-related semiconductors harms living bodies. The harm of the cadmium-related semiconductors must be weakened to ensure safety. Weakening of harm can be realized by coating the cadmium-related semiconductor nanoparticles (core) with materials (shell) that are harmless to living bodies. The coating prevents the cores from making contact with living tissues because of a physical barrier function of shells. Accordingly, the formation of core-shell structures is a candidate method for weakening the cadmium harm.

Aggregation of QDs or shortening of interparticle distances between QDs may lower the luminescence intensity. Therefore, the luminescent semiconductor nanoparticles are demanded to unaggregate. The core-shell structure formation has another function besides weakening harm, which includes the control of aggregation; the cores are prevented from aggregating and succeeding colliding due to the physical barrier function of shells. Hence, the core-shell structure formation keeps the luminescence intensity of the

semiconductor nanoparticles.

The semiconductor nanoparticles are desired to emit strong and stable intensity fluorescence for a long time. Such strong and stable intensity fluorescence is dependent on environment around the semiconductor nanoparticles. For example, photo-oxidation of them is induced at their surface by the action of oxygen around the nanoparticles and of light irradiated to the nanoparticles, which might provide their optical unstability, as suggested by several researchers [1]-[3]. The formation of core-shell particles is promising for controlling the photo-oxidation, because the shell materials can prevent them from contacting oxygen molecules.

Silica is suitable as a shell material because it is chemically stable in various solvents and harmless compared with other materials. Several methods for silica-coating the QDs have been developed [4]-[8]. They are on a basis of a sol-gel process using alcohol as a solvent. From a viewpoint of cost reduction for production, it is desirable not to use alcohol or reduce its amount used.

Our research group has proposed methods for silica-coating of metallic copper nanoparticles in water phase by using a water glass [9], [10]. In the present work, our silica-coating technique for nanoparticles, which does not use alcohol, is applied to QDs ($CdSe_xTe_{1-x}$ nanoparticles coated with ZnS) in order to develop an uncomplicated, secure, and low environmental load method for silica-coating of QDs. This article concentrates on the photostability of fluorescent materials, and the photo-bleaching of the QDs within the SiO₂ nanoparticles was also investigated by measuring their fluorescence in the particle colloid solution.

2. Experimental

2.1. Preparation

In order to increase the affinity between the QD particle surface and the sodium silicate, hydroxyl groups were introduced onto the QD surface by adding (3-aminopropyl)triethoxysilane (APES) to a 3.3×10^{-9} M QD aqueous solution obtained by diluting the 8×10^{-6} M QD solution with water (QD/APES). The concentrations of QD and APES in the final QD/APES solution were 3.5×10^{-9} and 9.0×10^{-4} M, respectively. The 38 wt% sodium silicate solution was diluted with water until a Na₂SiO₃ concentration became 0.33 wt%. Adjustment of pH of the 0.33 wt% sodium silicate solution to ca. 10.5 was made with the addition of 1.0 M HCl. Then, the pH-adjusted sodium silicate solution was added to the QD/APES aqueous solution to carry out silica-coating of the QD/APES nanoparticles (QD/SiO₂). Adjustment of pH of the mixture to ca. 8.5 was made by using 1.0 M HCl to accelerate the silica-coating. The concentrations of QD and Na₂SiO₃ in the final solution were 3.2×10^{-9} M and 2.6×10^{-2} wt%, respectively. The time and the reaction temperature for the silica coating process were 24 h and 25° C, respectively.

2.2. Characterization

The particle morphology was studied by a transmission electron microscope (TEM) (JEOL JEM-2100) operating at 200 kV and a scanning transmission electron microscope (STEM) (Hitachi HD-2700) operating at 200 kV. Secondary electrons (SE) and high-angle annular dark-field (HAADF) images were taken with the STEM. Samples for TEM and STEM were prepared by dropping nanoparticle colloid solutions on a collodion-coated copper grid and evaporating their dispersants. The volume-averaged particle size was determined by measuring diameters of dozens of particles on images with a caliper and processing the measured diameters statistically. The surface composition of particles was studied using X-ray photoelectron spectroscopy (XPS), which was performed using a JEOL JPS-9010 equipped with a monochromatic Mg Ka radiation source (200 W, 10 kV, 1253.6 eV). The XPS samples were powders of the nanoparticles. The nanoparticles in colloidal solutions were washed by centrifugation, decanted to remove the supernatant, and redispersed in water by shaking with a vortex mixer. The washing process was repeated three times, and the nanoparticle powder

was obtained by centrifuging and removing the supernatant by decantation after the third washing process and then by drying the nanoparticle powders in vacuo. To study the composition below the surface, the particles were etched using 500 kV Ar⁺ sputtering for 1 min. The fluorescence properties of particles were characterized by in vivo imaging system (IVIS) and fluorescence spectroscopy using a conventional fluorometer. The fluorescence images were taken using a Xenogen IVIS 100 fluorometer IVIS, and fluorescence intensities of particle colloid solutions were estimated from dark and light contrast of the images. Samples for the fluorescence spectroscopy using the conventional fluorometer were prepared by aging the particle colloid solutions at room temperature in a dark box open to air. Their fluorescence spectra were recorded with a Hitachi F-4500 spectrometer. The particle colloid solutions were excited with irradiation by a light with a wavelength of 405 nm.

3. Results and Discussion

3.1. Morphology of Particles

Fig. 1 (a) gives a photograph of the colloid solution of QD/SiO_2 nanoparticles. No sediments were observed by naked eyes even after the silica-coating process, which indicated that the colloidal stability of the particles was not influenced with the silica-coating process.

A TEM image of QD/SiO_2 nanoparticles is given in Fig. 1(b). The QDs and silica were indicated as the darker and lighter areas of the particles, respectively, because electron densities of elements of QD were larger than those of silica. In most and a few silica-coated particles, silica enclosed single QD cores and a few QD cores, respectively, which indicated that such core-shell structure was successfully created with the method proposed in the present work. An average particle size of the QD/SiO₂ nanoparticles was 28.6±2.7 nm, and the QD contained as core in the particles had an average size of 7.1±1.1 nm.



Fig. 1. Images of QD/SiO₂. Images (A) and (B) are a photograph of the QD/SiO₂ nanoparticle colloid solution and a TEM image of the QD/SiO₂ nanoparticles in the colloid solution, respectively.

Fig. 2(a) gives an SE image of the QD/SiO₂ nanoparticles. Spherical nanoparticles were caught in the SE observation, and their spherical structure in the SE image was quite resembling that in their TEM image. The QD and the QD/SiO₂ had particle size of 7.2±1.1 and 32.4±3.7 nm, respectively. The QD/SiO₂ particle size of 32.4 nm was to some extent larger than that obtained with estimation by the TEM observation. The particle colloid solution used for preparation of the SE sample was not the same as that for the TEM sample, although both methods for preparing the particle colloid solutions were not different. Accordingly, in the present work, the difference in particle size was regarded as an individual difference, *or* there was considered to be no large difference in particle size between the estimations by TEM and SE. The comparability between the SE and TEM observations indicated that the particles, which supported that the QDs recognized with the TEM observation were present not on the particles but inside them. A BF image of the QD/SiO₂ nanoparticles is given in Fig. 2 (b). The regions of the particles observed darkly and brightly were attributed to the QDs and

the silica, respectively. Most particles enclosed single QD cores, and a few QD cores were contained in a few particles, which was similar to the TEM image (Fig. 1 (b)). Accordingly, the BF observation also indicated the successful fabrication of core-shell particles, and supported the consideration given in the SE observation (Fig. 2(a)). Fig. 2(c) gives a HAADF image of QD/SiO₂ nanoparticles. The area of HAADF image was the same as those taken in the observations of SE and BF. The regions of silica and QD were observed in the particles darkly and brightly, respectively, because HAADF contrast depends on atomic number; a substance composed of an element with a large atomic number exhibits a bright contrast. Brighter parts were observed as dots inside darker parts, of which structure was quasi-spherical. The HAADF image was quite similar to the BF image except for inversion of brightness and darkness. Consequently, the observations by TEM and STEM resulted in the conclusion of successful fabrication of core-shell particles comprising of QDs as cores and silica as shell.



Fig. 2. STEM images of QD/SiO₂ nanoparticles. Detector: (A) SE, (B) BF, (C) HAADF.

Fig. 3 shows the Cd + Si atomic ratios. Estimation using the XPS peak area intensity gave the atomic ratios. In all the samples, peaks due to Cd $3d_{5/2}$ and Si $2p_{1/2}$ were detected. They were attributed to Cd and Si elements composing the QD and SiO₂ shells, respectively. For the as-prepared QD/SiO₂ particles (etching number: 0), the atomic ratios of Cd and Si were 1.8 and 98.2 atom%, respectively. The atomic ratio of Cd exceeded 2 atom% with the etching, and tended to increase as the etching time increased. In contrast, the Si ratio fell below 97.9 atom% with the etching, and tended decreased with the increase in etching time. This result indicated that the silica shells existed on the QD surfaces, and the QD surfaces appeared with removal of silica shells by the etching. Consequently, the XPS measurements further strengthened the successful performance of silica-coating of the QDs that was proved by the TEM and STEM.



Fig. 3. Atomic ratios of Cd + Si for the surfaces of the QD/SiO₂ particles as a function of the number of Ar⁺ etching steps. (●) Cd and (○) Si.

3.2. Fluorescence Properties

IVIS images of the colloidal QD/SiO₂ nanoparticle solutions at various QD concentrations are given in Fig. 4. The images of colloidal solutions became bright with increasing QD concentration; the fluorescence

intensity increased with raising QD concentration. Fig. 5 gives the radiant efficiency (RE) versus the QD concentration (black circles). The RE increased steadily from 2.23×10⁹ to 1.01×10¹⁰ p/s/cm²/sr/µW/cm², and a rate of the increase appeared to decrease, with increasing QD concentration from 5.0×10⁻¹⁰ to 8.0×10⁻⁹ M. Conversation of the RE values to values with respect to the QD concentrations was performed in order to correlate the QD/SiO₂ nanoparticles with commercial QDs, or appraise the QD/SiO₂ nanoparticles. Fig. 5 shows the converted RE value versus the QD concentration (the white circles). The converted RE value decreased from 4.46×10¹⁸ to 1.28×10¹⁸ p/s/cm²/sr/µW/cm²/M with raising QD concentration from 5.0×10⁻ ¹⁰ to 8.0×10⁻⁹ M. Concentration quenching might have occurred at the high QD concentrations. In all the concentration range examined, the converted RE values were larger than the value of 2.93×10^{16} $p/s/cm^2/sr/\mu W/cm^2/M$ obtained for the commercial QDs in our previous work [11]. With no shells, the QD nanoparticles are prone to aggregate for the sake of features of nanoparticles. Such aggregation presumably lowered fluorescence intensity of the QD nanoparticles. Contrastively, core-shell structure formation restricted the QD nanoparticles to aggregate by dint of the power of shells as a physical barrier, which retained their fluorescence intensity. Hence, it is noteworthy that the silica-coating functioned as promotion to make QD emit fluorescence efficiently. This result on the larger converted RE for QD/SiO₂ corresponded to our previous work [11] on QD/SiO₂ fabricated by silica-coating using silicon alkoxide.



Fig. 4. In vivo imaging system (IVIS) images of the QD/SiO₂ nanoparticle colloid solutions with QD concentrations of (a) 5.0×10⁻¹⁰, (b) 1.0×10⁻⁹, (c) 2.0×10⁻⁹, (d) 4.0×10⁻⁹, and (e) 8.0×10⁻⁹ M.



Fig. 5. Radiant efficiency (RE) and converted RE for the QD/SiO₂ nanoparticle colloid solutions as a function of the QD concentration.

Fig. 6 show fluorescence spectra of the QD colloid solution and QR/SiO₂ nanoparticle colloid solution after aging, respectively. Prior to aging (at an aging time of 0 day), the QD colloid solution emitted fluorescence with a main peak at 800 nm. Fluorescence was also emitted for the QD/SiO₂ nanoparticle colloid solution, and its main fluorescence was detected as a peak at 800 nm, which was the same as that for the QD. The fluorescence intensity recorded at the peak position for the QD/SiO₂ was 54.7 % of that for the QDs. Although the fluorescence was detected even after the silica-coating, the silica-coating halved the fluorescence intensity.

According to the IVIS (Fig. 5), the converted RE of QD/SiO₂ was larger than that of QDs. In the IVIS, the QD/SiO₂ nanoparticles were irradiated by laser light, and fluorescence emitted in a direction substantially opposite to the laser light was detected directly. Therefore, there was less effect of other QD/SiO₂ nanoparticles on fluorescence intensity. In contrary, in the measurement using the conventional fluoremeter, the QD/SiO₂ nanoparticles in the 1 cm square cuvette were irradiated by a Xenon lamp, and fluorescence emitted in a direction perpendicular to the laser light was detected. Therefore, the emitted fluorescence might have been diminished with absorption and scattering by the QD/SiO₂ nanoparticles. Accordingly, it could be hard to compare both fluorescence intensity values obtained by the IVIS and the conventional fluorescence spectroscopy because of the difference in measuring method.



Fig. 6. Fluorescence spectra of (A) QD nanoparticle colloid solutions and (B) QD/SiO₂ nanoparticle colloid solutions. The measurements were performed with an excitation wavelength of 405 nm at 0 (black), 5 (red), 15 (blue), 20 (green), 30 (orange), 40 (purple), and 52 (brown) days after the preparation of QD nanoparticle colloid solution with QD concentration of 3.2×10^{-9} M.



Fig. 7. Intensities of fluorescence peaks as a function of time after the preparation. ●: QD, ○: QD/SiO₂.

Fig. 7 gives fluorescence intensities of the colloid solutions versus aging time. The fluorescence intensity of the QD colloid solution decreased almost proportionally from 913 to 167 with extending aging time from 0 to 52 days. In semiconductor nanoparticles of cadmium compounds represented by CdSe and CdTe composed of Cd²⁺ and Se²⁻ or Te²⁻, photo-oxidation is induced at their surface by the action of oxygen present around the nanoparticles and of the light irradiated to the nanoparticles [1-3]. The photo-oxidation should replace Se²⁻ or Te²⁻ of the cadmium compound semiconductor with O²⁻, which results in production of cadmium oxide that does not give emission of fluorescence. Oxygen molecules contained in air were dissolved in the solvent, which resulted in such photo-oxidation for the CRs in the present work. For the QD/SiO₂ nanoparticle

colloid solution, its fluorescence intensity almost proportionally decreased from 499 to 151 with an increase in aging time from 0 to 20 days. Photo-oxidation similar to that for the QDs probably takes place for the QD/SiO₂. It should be noted that a rate of the decrease was larger than that of the uncoated QDs. For some of the QD/SiO₂, the SiO₂ shells surrounding the QDs remarkably promoted the photo-oxidation compared to the uncoated QDs, because the SiO₂ has an affinity with oxygen. After 20 days, the fluorescence intensity became almost constant, *or* the fluorescence property was roughly stable, although the intensity still decreased with an increase in aging time. For the QD/SiO₂ other than the photo-oxidized QD/SiO₂, this property in stability of fluorescence was likely related to the limited diffusion of the oxygen molecules in the silica shells, which controlled the oxygen molecules to reach the QDs.

4. Conclusion

The method for synthesizing QD/SiO₂ nanoparticles was developed to stabilize the fluorescence of QDs. The method was on a basis of the formation of silica shells on the QDs. The performance of silica-coating was made by the method using the sodium silicate solution in water containing the QDs. The silica shells formed on the QDs, which resulted in production of the QD/SiO₂ nanoparticles, *or* the core-shell-type nanoparticles comprising of the QD core and the silica shells. The clear images were taken with the IVIS, and the IVIS intensities for the QD/SiO₂ were larger than those of uncoated QDs. The aging in atmosphere at room temperature diminished the fluorescence of QD/SiO₂ nanoparticle colloid solution. However, after the remarkable diminishment, the QD/SiO₂ nanoparticle colloid solution emitted fluorescence more stable than the uncoated QDs.

In this study, we developed a simple, safe, and environmentally friendly silica-coating method for QDs, and found that the silica-coating has the ability to stabilize the fluorescence intensity of QDs. Therefore, the developed particles are expected to be used as a fluorescent marker in a medical field, and studies are awaited for their practical application.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

AT synthesized the samples, performed the characterizations, and drafted the manuscript, under TK, KG, and YK's supervision. TI, MT, CK, and KH also performed the characterizations. NY, KN, KG, and YK modified and finished the manuscript. All authors had approved the final version.

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