

Improvement of emission intensity of PbS quantum dots in thick silica shell by initial coating in organic solvent

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Abstract

Positioning of colloidal quantum dots (QDs) by nanoholes is applicable to fabricating quantum devices such as quantum circuits. A silica coating technique that facilitates the positioning manages the effective size of QDs while preserving the quantum state inside. In the reverse micelle method, which is commonly used for the silica coating, optical properties deteriorate due to the exposure of QD surface to moisture within the reverse micelle. We studied a thin silica coating on the surface of PbS QDs by pyrolyzing tetraethyl orthosilicate in an organic solvent before forming a thick silica shell by the reverse micelle method. As a result, highly luminous silica-coated PbS QDs with a diameter of about 110 nm were realized.

Chemically synthesized quantum dots (QDs) are promising as nanomaterials that are used in next-generation quantum electronics technology. We have realized positional control of single PbS QDs by trapping them into nanoholes on a silicon substrate fabricated by scanning probe microscopy (SPM) [1, 2]. This technique is useful to fabricate devices using only one QD, such as single-photon emitters [3-11]. However, it is difficult to use it in the fabrication of devices such as quantum circuits, which require QDs of different sizes to be arranged at arbitrary positions, because QDs cannot be selectively distributed to nanoholes. The size sensitivity of energy state in QDs greatly exceeds the nanohole processing accuracy by SPM. Silica coating on QDs is a technique that can solve this problem because it can arbitrarily enlarge the effective size of QDs with little change in energy states [12-18]. By preparing nanoholes with distinctly different sizes and QDs in silica shells with matching sizes, QDs with desired energy states can be placed at desired positions. The trapping of small silica shell in large nanoholes can be prevented by trapping the shell in order from the larger size [18].

Silica coating of QDs is generally performed by the reverse micelle method. We have fabricated highly monodisperse silica-coated QDs with an average particle diameter exceeding 100 nm, using PbS QDs with oleic acid (OA) and oleylamine (OLA) as ligands [18, 19]. However, when the silica shell became thicker, the emission intensity of the QDs decreased and the monodispersity also deteriorated. During the coating process, the emission efficiency drops sharply at the beginning of the reaction and then recovers gradually, but the recovery is weak as the amount of tetraethylorthosilicate (TEOS), the raw material of silica, is small [19]. Exposure of the QD surface to moisture in the reverse micelle is believed to be also responsible for the degradation of emission efficiency. It has been reported that the degradation can be suppressed by pyrolyzing TEOS in an organic solvent to coat CdSe/CdS QDs with thin silica without using the reverse micelle method [20].

In this paper, we report a method for fabricating silica-coated PbS QDs with large size, high luminous efficiency and good monodispersity. After the initial silica coating of PbS QDs by pyrolyzing TEOS in an organic solvent, the silica shell thickness was increased by performing the reverse micelle method in combination with 3-aminopropyl triethoxysilane (APTES). It has been reported that adding APTES to TEOS increased the silica shell size of InP/ZnS QDs to about 450 nm [21]. By this method, we were able to

fabricate thick silica-coated PbS QDs with good emission intensity and monodispersity.

PbS QDs were synthesized by the hot injection method as in our previous reports [22, 23]. In a four-necked flask, 0.4233 g of lead oxide, 8.5 mL of oleic acid and 12 mL of octadecene are stirred at 130°C for 1 hour. A well-mixed solution of 4.7 mL of octadecene and 200 μ L of (TEM)₂S is injected with a syringe into above solution at 110°C and stirred for 50 seconds. The reaction is terminated by quenching with ethanol previously chilled in a refrigerator. The synthesized QDs are washed three times with ethanol and toluene using centrifugation and finally dispersed in toluene.

Initial silica coating was applied to the surface of PbS QDs in toluene by pyrolysis method. The procedure is as follows. After 80 μ L of TEOS was added dropwise to 2 mL of PbS QD solution containing 20 μ L of oleylamine over 2 minutes, the solution was heated and stirred at 110°C for 1 hour under a nitrogen atmosphere. As a control sample, silanization was performed instead of the initial silica coating on the QD surface [19, 24]. Silanization is performed by adding 2-8 μ L of TEOS to 1 mL of PbS QD solution and stirring for 24 h at room temperature.

The procedure of the reverse micelle method for thickening the silica shell is as follows. After stirring 6 mL of cyclohexane and 0.35 g of IGEPAL CO-520 for about 10 seconds, 200 μ L of aqueous ammonia was added and stirred for 15 minutes. After adding 600 μ L of a toluene solution of PbS QDs and stirring for 30 minutes, 350 μ L of TEOS was added dropwise and stirred for 24 hours. The same amount of acetone was added to the resulting solution, centrifuged at 14500 rpm for 30 seconds, and the supernatant was discarded. The remaining precipitate was washed alternately with ethanol and ion-exchanged water, and finally dispersed in ion-exchanged water. These samples are called "two-step silica coated sample" in this paper. A sample with a thicker silica shell was also prepared by the following procedure. 350 μ L of TEOS and 350 μ L of APTES were dropped into the solution in which the initial silica coating was applied to the PbS QD surface, and after stirring for 24 hours, 350 μ L of TEOS, 350 μ L of APTES, and 600 μ L of toluene were added and stirred again for 24 hours. The resulting samples were washed in the same manner as the samples described above. These samples are called "three-step silica coated sample" in this paper. We experimentally confirmed that the mixing of toluene in the final step suppressed size variation and adhesion of silica-coated QDs. The toluene mixing probably adjusts the size of the reverse micelles to the size suitable for

the silica shells that have already grown to some extent.

The shape and size QDs were evaluated using a transmission electron microscope (TEM; JEOL, JEM-2100F) and a scanning electron microscope (SEM; Hitachi High Technology, SU8010). Photoluminescence (PL) measurements were performed with a multichannel spectroscopy (OtO, RS1680-NIRA) using a semiconductor laser with a wavelength of 633 nm as excitation light.

We confirmed the change in the appearance of QDs before and after the initial silica coating by the pyrolysis method. Fig. 1(a) shows a TEM image of the QDs as synthesized. The average diameter of the QDs was 5.6 nm with a standard deviation of 0.5. The QD shape was symmetrical, and the QDs were closely packed. A TEM image of the QDs after initial silica coating is shown in Fig. 1(b). The change in QD appearance due to the initial silica coating was obvious. The average diameter was 6.3 nm with a standard deviation of 0.7, i.e., the initial silica coating deteriorated size uniformity with a 11% increase in diameter. Also, after the initial coating, the interdot spacing was expanded randomly and the closest packing did not occur. The contours of QDs were blurred compared to QDs as synthesized. These apparent changes confirm that the QDs were silica-coated and altered in properties, whereas the reduced size uniformity suggests that the coating was not uniform.

After the initial silica coating by the pyrolysis method, the silica coating thickness was increased by the reverse micelle method. Silica-coated QDs with a diameter of up to 60 nm were obtained by two-step silica coating, and silica-coated QDs with a diameter of up to 150 nm were obtained by three-step silica coating. Fig. 2(a) is an example of a SEM image of a three-step silica-coated sample. The average diameter was 105.7 nm with a standard deviation of 9.7. In another three-step silica-coated sample, the standard deviation was 10.9 with an average diameter of 148.7 nm. On the other hand, in the control sample, the standard deviation was 23.7 when the average diameter was 150.2 nm. The initial silica coating improved the monodispersity by about two times.

Fig. 2(b) compares the PL spectra of the initial silica-coated QDs at each fabrication step. The initial silica coating reduced the emission intensity by about 20%. The PL intensity decreased with increasing silica shell thickness. In the sample with an average diameter of 96.1 nm shown in Fig. 2(b), the decrease in peak intensity was only about 25% of the initial value, which was very small. A red shift of the peak wavelength was

observed here. Energy shifts during silica coating have been previously reported in literature, with both blue shift and red shift depending on the differences in material combinations [12, 15-17]. The same red shift as in this figure was not always observed in our experiments, so we don't have enough data at this time to discuss the causes of the red shift. Possibilities include some interaction between shells and QD cores such as QD surface state formation and heterogeneity of the QD solution. On the other hand, in the control sample, almost no luminescence was observed even in samples with a smaller particle size. It is clear that the initial silica coating in the organic solvent suppressed the deterioration of the emission intensity due to the increase in silica shell thickness.

We performed PL measurements of silica-coated QDs with various sizes. Fig. 3 shows the relationship between particle diameter and PL intensity. By changing the concentration of the mixed QD solution, silica shells with different thicknesses were obtained under the same silica coating conditions. Samples with a particle size of 90 nm or more are three-step silica coated samples. When the initial silica coating was applied, the PL intensity decreased as the particle size increased, and decreased more sharply when the size exceeded 110 nm. A sample with a diameter of about 150 nm hardly emitted light. On the other hand, in the control sample, almost no PL emission was observed even with a particle size of about 20 nm. Silanization of the QD surface should suppress the decrease in emission intensity, but the effect was not observed under the conditions in this study because the amount of TEOS added was large. This figure clearly shows the strong effect of the initial silica coating.

As described above, we succeeded in fabricating highly luminous silica-coated PbS QDs with a diameter of about 110 nm. It was effective to pyrolyzing TEOS in an organic solvent to coat the QD surface with silica before forming a thick silica shell by the reverse micelle method. Even when this process was used, luminescence was not observed well when the silica shell was 150 nm or more. Future detailed studies on this process are needed to further increase the size without degrading the emission properties. The first priority should be the optimization of the initial silica coating conditions. As shown in Fig. 1, the initial coating layer was not uniform. If the initial silica coating is incomplete, the coating layer is not sufficiently protective, and some of the QD surface will be exposed to water during the subsequent reaction in the reverse micelle. The phenomenon that PL intensity decreased with increasing shell thickness also suggests that the coating layer

was not completely protective. Improving the quality and thickness of the initial silica coating layer may further enhance the protective ability of the QD surface. In addition, it is important to combine the initial silica coating process with other innovative techniques. For example, silanization of the QD surface alone did not show a sufficient protective effect in this study, but it may improve the initial silica coating layer to enhance its protective function. It has been demonstrated that the highly luminescent large silica-coated QDs needed in the future can be fabricated based on initial silica coating techniques.

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Figure captions

Fig. 1 TEM images of (a) QDs as synthesized and (b) QDs after the initial silica coating in organic solvent.

Fig. 2 (a) SEM image and (b) PL spectra of silica-coated PbS QDs.

Fig. 3 Relationship between diameter of silica-coated QDs and PL intensity. The intensity is normalized by that of QDs as synthesized. Red squares show data with initial coating, and blue circles show data without initial coating.

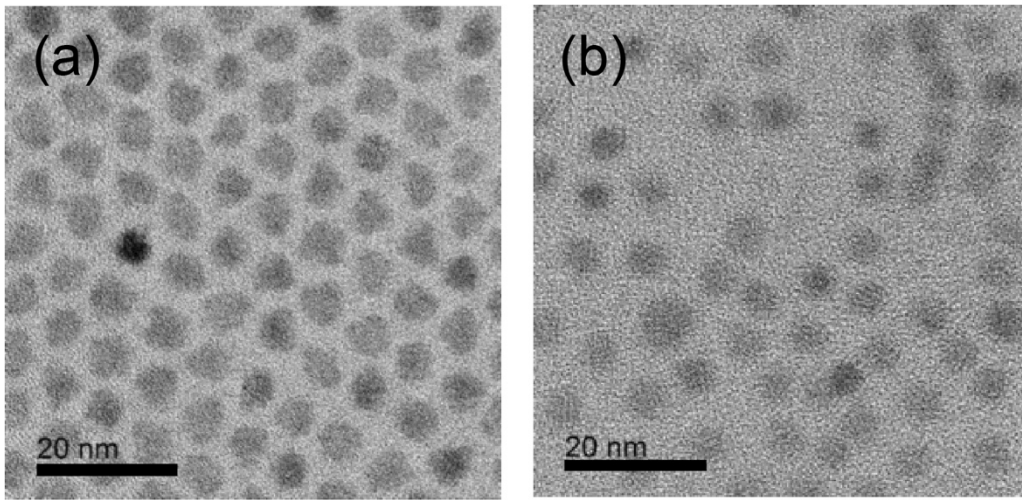


Fig. 1

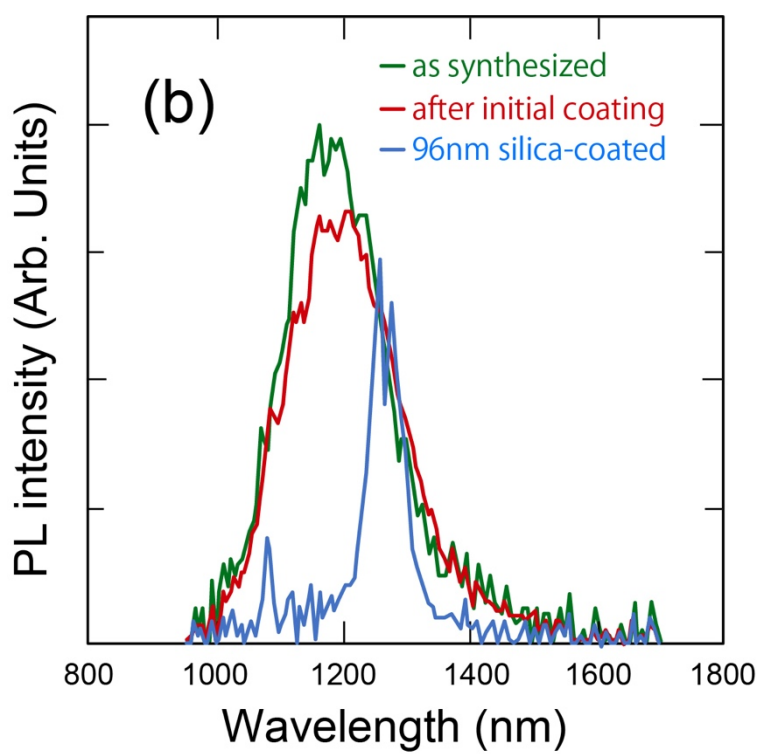
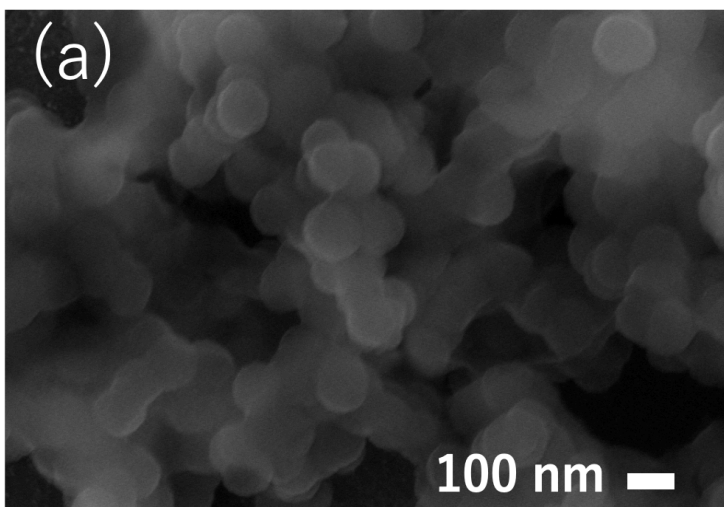


Fig. 2

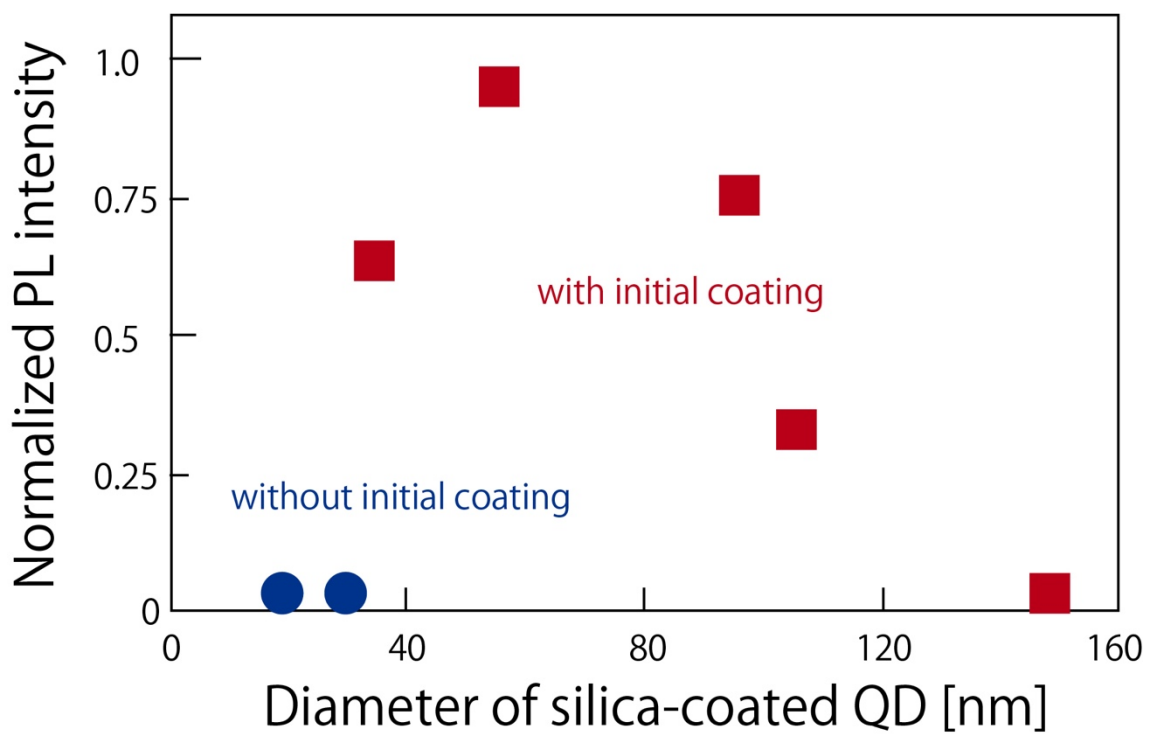


Fig. 3