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# Size Expansion of PbS Quantum Dots by Silica Coating for Position Control with Si Template Fabricated by SPM Lithography

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**Abstract**

**We succeeded in controlling the apparent size of colloidal PbS QD in the range of 20 to 140 nm by silica coating and trapping the coated QD by a nano hole prepared by scanning prove microscope lithography. This technique will aid in the fabrication of nano-size solid devices such as quantum information circuit.**

## 1. Introduction

Quantum information technology, that transmits and processes information by using electrons or photons quantum mechanically, has attracted much attention. Quantum Dot (QD) is one promising material necessary for its realization. If a single QD of various sizes is controlled to an arbitrary position, the technology can be applied to the fabrication of nano-size solid devices such as quantum information circuit. We have successfully controlled the position of one chemically synthesized QD, so-called 'colloidal QD', by a nano hole on silicon substrate [1]. However, it is very difficult to control nano-hole size around QD diameter (about 5 nm), so positioning of QD according to the delicate difference in emission wavelength is impossible. In this work, we developed a technique to prepare PbS QD coated with silica glass of various thickness of about 100 nm, and to trap it on a template with nano holes formed by scanning probe microscope (SPM) lithography.

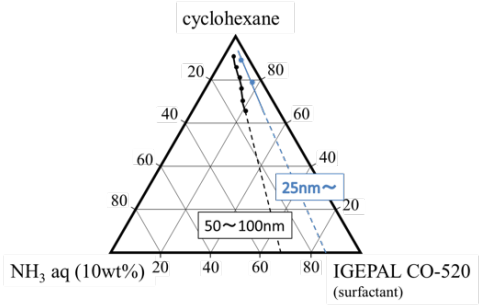


Fig. 1 Relationship of solution mixing ratio and micro emulsion size.

## 2. Experimental

A silica shell was formed by reverse micelle method. First, a reverse micelle solution is prepared with a surfactant (IGEPAL CO-520) and $NH_3$(aq). By adding tetraethoxysilane (TEOS) and PbS QDs to the solution, QD enters the reverse micelle water droplet, and the silica shell is produced by the progress of TEOS reaction. We investigated the influence of reaction condition, i.e., the size of the reverse micelle water droplet, the amount and the number of additions of TEOS, and the amount of $NH_3$(aq), on the shell size. The relationship between the solution composition and the approximate size of reverse micelle water droplet was estimated by light scattering characteristics (Fig.1) [2]. The actual particle size and shape of the silica shell were evaluated by field-emission scanning electron microscopy (FE-SEM), and the emission characteristics of QD were evaluated by photoluminescence (PL) measurement.

Figure 2 shows the procedure for position control of QDs. A mask pattern having various hole sizes was prepared by anodic oxidation of a Si substrate using SPM, and nano holes were formed by wet etching and dry etching. SiOx mask was finally removed by HF treatment. At QD positioning, large silica-coated QDs were first trapped by large holes and then small ones were trapped by small holes. This order prevents small QDs from being trapped in large holes.

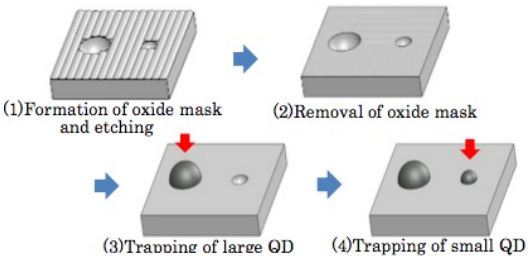


Fig. 2 QD positioning procedure using nano-hole template.

## 3. Results and discussion

The influence of the amount of TEOS was investigated. By increasing TEOS amount from 20 μL to 400 μL, diameter of silica shell was increased from 40 nm to 70 nm. When the silica precipitates not contributing to the silica shell during the synthesis, the amount of TEOS per reverse micelle water droplet changes. At the case, the silica shell diameter was different even if the size of the micelle droplet estimated from the ratio of raw materials was the same. We then attempted the method of adding TEOS several times while removing the precipitate of silica not contributing to the coating. By adding 50 μL of TEOS up to 8 times, the diameter of silica shell was controlled in the range of 30 - 50 nm by 4 nm. We also found that the silica shell was

connected when the amount of the surfactant was too small. This can be understood as the result of coalescence of the micelle droplets after the density of the surfactant at micelle surface decreased too much according to the size of the micelle droplet increased during the growth of the silica shell. Paying attention to the above, spherical silica shell having a maximum diameter of 140 nm could be produced by adding 400 μL of TEOS multiple times. This is the largest silica shell of PbS QD to our knowledge. SEM images of representative silica coated QDs are shown in Fig. 3. Finally, we succeeded in controlling the silica-coated QD in the diameter of 20 - 140 nm by investigating the preparation conditions for reverse micelle water droplets and the addition condition of TEOS.

PL measurement of silica-coated QDs showed that the emission wavelength of QD changed only slightly even after silica coating with sufficient emission intensity.

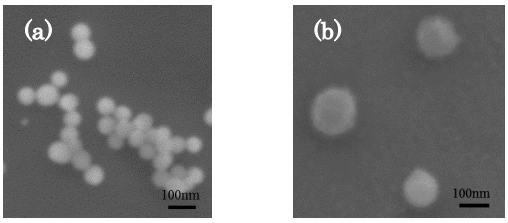


Fig. 3 SEM images of silica-coated QDs, the diameter of which is (a) 70 nm, and (b) 140 nm.

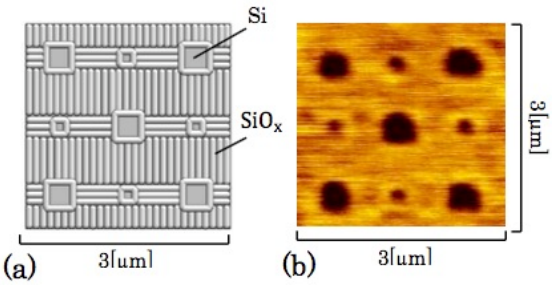


Fig. 4 (a) SiOx mask pattern and (b) plan-view SPM image of nano holes on Si substrate.

Next, a template corresponding to silica-coated QDs was fabricated by SPM lithography using SiOx mask pattern as shown in Fig. 4(a). After removing the thin oxide layer at the hole portion by dry etching using $SF_6$ gas, deep nanoholes were formed by wet etching using a mixed solution of KOH and isopropyl alcohol (IPA) (Fig. 4(b)). IPA suppresses bubble formation which hinders hole etching [3]. Figure 5 shows cross-sectional view of two nanoholes fabricated on one substrate. Nano holes corresponding to the silica-coated QDs with diameter of 100 and 200 nm with the depth of about half of the diameter were fabricated.

A silica coated QD having a diameter of 140 nm was trapped in the nano-hole template, i.e., we tried trapping with single size QDs. The trap procedure is shown in Fig. 6. QDs were hardly trapped in the nano holes by dropping the QD solution and wiping the surface with an industrial swab after drying. We found that QDs can be pushed into the nano holes by tapping lightly in the vertical direction with the swab before wiping the surface. As a result, as shown in Fig. 7, we succeeded in trapping one QD or 10-15 QDs in a nano hole with depth of 120 mm and 180 nm, respectively.

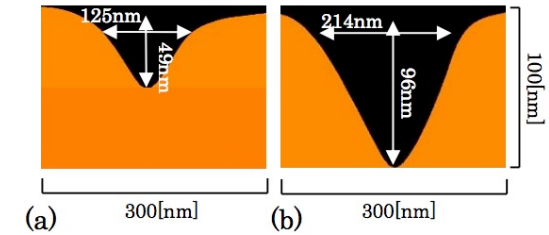


Fig. 5 Cross-sectional SPM images of two nano holes.

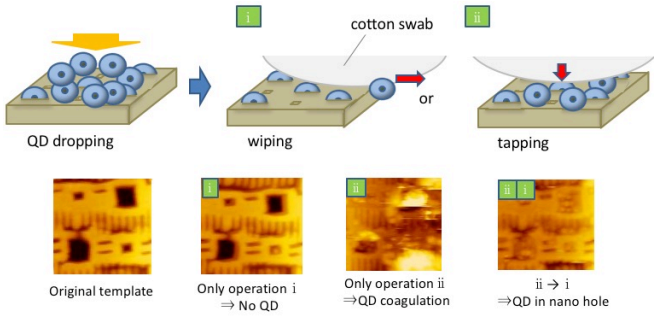


Fig. 6 QD trap procedure and plan-view SPM images.

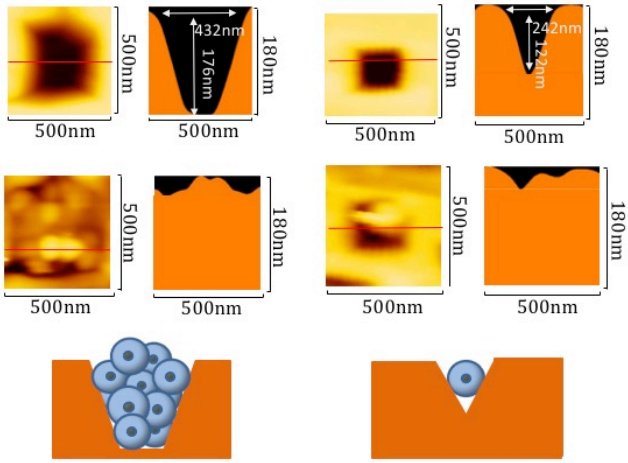


Fig. 7 Plan-view and cross-sectional SPM images before and after QD trapping using a nano hole and their speculative drawing.

## 4. Conclusions

We succeeded in controlling the apparent size of colloidal PbS QDs in the range of 20 to 140 nm by silica coating. We successfully trapped a silica-coated QD in a nano hole fabricated by SPM lithography.


## Acknowledgements

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