Supporting Information

Synthesis of Styryl-Terminated Silicon Quantum Dots: Reconsidering the Use of Methanol

Mai Xuan Dung and Huyn-Dam Jeong*

*Department of Chemistry, Chonnam National University, Gwangju 500-757, Korea. *E-mail: hdjeong@chonnam.ac.kr*
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Meterials

Tetrachlorosilane ($SiCl_4$, 99.998%), lithium aluminum hydride (1 M in THF), tetraoctylammonium bromide (TOAB, 98%), cupper chloride ($CuCl_2$, 97%), phenylacetyelene (PheAc, 98%), chloroplatinic acid ($H_2PtCl_6.xH_2O$, 99.9%), anhydrous toluene, anhydrous methanol, and *N*-methylformamide (NMF, 97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without any further purification. Hexane solvent was dried by refluxing in sodium-benzophenone before use.

The Miniemulsion Approach for the Generation of Silicon Quantum Dot.[1] The synthesis was preceded in oxygen and water free environment using typical Shrink line technique. 0.3 mL of $SiCl_4$ (2.6 mmol) was added into a 500 mL, 2-neck flask containing 300 mL of anhydrous toluene and 4.5 g TOAB. The mixture was then sonicated for 90 minutes for the dispersion of $SiCl_4$ into the core of TOAB inverse micelles. 9 mL of $LiAlH_4$ solution (9 mmol) was then added drop wise over 15 minutes, followed by 90 minutes of sonication to reduce the $SiCl_4$ to hydrogen terminated silicon quantum dots (H- Si QDs). After the reducing reaction, the reaction mixture contained the H-Si QDs, which are still surrounded by TOAB molecules and the remaining $LiAlH_4$ needed to be quenched before doing post-functionalization the H-Si QDs.

Quenching the Remaining $LiAlH_4$ by Methanol. To the above solution mixture, 90 mL of anhydrous methanol was added though a needle and a transparent solution was obtained. After 30 minutes of continuous sonication, 0.3 mL of Pt catalyst solution (0.05M of H_2PtCl_6 in methanol) and 5 mL (45.5 mmol) were subsequently added to start the hydrosilylation reaction. The functionalization reaction was kept for 5 h under sonication and overnight stirring.

Quenching the Remaining $LiAlH_4$ by *tert*-butanol. To the solution of H-Si QDs, 20 mL of anhydrous tert-butanol was added to quench completely the remaining $LiAlH_4$. Though a transparent solution was not obtained, as the case when MeOH was used, the post-functionalization reaction was still working. The capping reaction was done as same as in the case of using MeOH, as mentioned above.

Quenching the Remaining $LiAlH_4$ by Cupper Chloride. Instead of using methanol, 7 g of $CuCl_2$ dispersed in 30 mL of anhydrous toluene was added to the solution of H-Si QDs *via* a cannula to quench the remaining $LiAlH_4$. The quenching reaction was lengthened for 1 hour under sonication. The mixture was then left fore free for the sedimentation of the remaining $CuCl_2$ and resultant Cu metal. The upper part of the mixture was then transferred to a new flask *via* a cannula with a tuft of cotton at one end. To this solution mixture, Pt catalyst solution and capping molecule were added to implement the hydrosilylation reaction as the same as the cases when alcohols were used.

Preparation of a Control Si QD Sample. The control sample was prepared using the same procedure as mentioned above when MeOH was used as quenching agent with an exception that the post functionalization step was not conducted.

Purification of Silicon Quantum Dots. After the hydrosilylation reaction, all solvents were removed at 40 °C under reduced pressure by using rotary evaporator. 100 mL of hexane was added to the solids and the Si QDs were dispersed in hexane by sonication. The suspension solids were removed by centrifugation at 7000 rotation per minute for 10 minutes followed by filtration through a PTFE filter with pore size of 0.2μ. The remaining PheAc and TOAB were successfully removed by extraction the hexane solution with *N*-methylformamide (50 mL × 5 times). The *N*-methylformamide in hexane was then removed by extraction with DI water (100 mL × 4 times). The resultant hexane solution of Si QD was finally dried with brine (100 mL × 2 time) and 2 g of anhydrous magnesium sulfate.

Preparation of Silicon Quantum Dot Samples Without Using TOAB. As mentioned in the main communication, IR spectra of the resultant quantum dot samples show very intense peaks in the 2800-3000 cm^{-1} originated from aliphatic C-H stretching. Though the TOAB is very less soluble in hexane it could be absorbed on the surface of Si QDs, hence remaining in the Si QD samples. In addition, since the TOAB molecules are surrounding the H-Si QDs they could also kinetically hinder the H-Si QDs from hydrosilylation. Therefore, in order to have unambiguous spectroscopic interpretations, hence clear understanding the effect of quenching agents on the capping step, various Si QD samples

were also prepared using the same procedure as mentioned above with an exception that TOAB was not used. With respect to the important role of TOAB in the formation of micellar system, we believed that hydrogen terminated Si QDs were still formed under the sonication conditions used in our experiments.[2] The surface chemistry between samples obtained with or without using TOAB was the same.

Characterization. Fourier transform infrared (FT-IR) was conducted to investigated the chemical structure of the resultant Si QD samples. Samples were carefully dried at 100 ^{o}C in a vacuum oven for overnight. FT-IR spectra were performed on a PerkinElmer spectrometer (Waltham, Massachusetts, U.S.A) from 4000 to 400 cm^{-1} in transmittance mode with a resolution of 8 cm^{-1} and the results were accumulated from 8 scans.

The surface chemistry of Si QD samples were further characterized by ^{1}H-, and ^{13}C- nuclear magnetic resonance (NMR) spectroscopies, which were implemented on a superconducting FT-NMR 300 MHz (Varian, Inc, Paolo Alto, California, U.S.A).

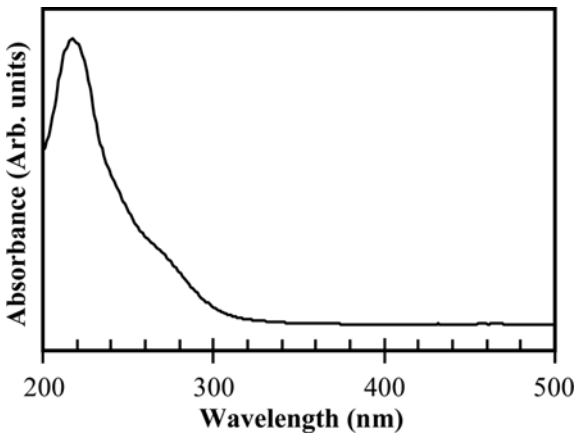

Figure S1. UV absorbance spectrum of styryl terminated silicon quanum dot in hexane solution. The Si QD was obtained when $CuCl_2$ was used to quench the excess $LiAlH_4$.

References

1. Tilley, R. D.; Warner, J. H.; Yamamoto, K.; Matsui, I.; Fujimori, H. *Chem. Commun.* **2005**, 1833.
2. Wang, J.; Sun, S.; Peng, F.; Cao, L.; Sun, L. *Chem. Commun.* **2011**, *47*, 4941.