

Notes

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

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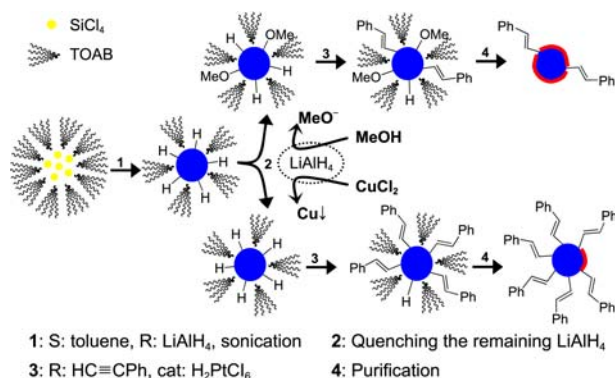
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Quantum dot solids, in which individual quantum dots (QDs) such as CdSe, PbSe, and InP QDs are assembled into 3 dimensions, have been paid much research interest due to their potential applicability to diverse optoelectronic fields.^{1,2} Silicon QDs whose electric transitions are direct-like due to the relaxation of k conservation rule³ are hopeful to replace these QDs owing to its non-toxicity, abundance, and easy integrating into the widely developed silicon industries. Solution processes are preferred for the generation of these solids due to the low cost and large area capability. A post ligand exchange and/or thermal annealing is necessary to enhance physical interactions and electronic communications among the individual QDs.² However, in the cases of Si QDs, the post ligand exchange is inapplicable due to the strong covalent bonds between the dot and the capping molecules. Therefore, capping Si QDs with organic molecules has to be logically designed during the synthetic course not only to prevent the Si QDs from unexpected oxidation and give high solubility but also to ensure sufficient QD-QD physical interactions for the solid assemblies.

Recently, Tilley group has reported the use of miniemulsion approach for the generation of hydrogen-terminated Si QDs (H-Si QDs), which are easily post-functionalized with

1-alkene using Pt catalyzed hydrosilylation.^{4,5} We initially adopted this process to synthesize styryl-terminated Si QDs (PheAc-Si QDs), as illustrated in Scheme 1. In the first step, SiCl₄ confined inside the inverse micelles of TOAB (tetra-*o*-tetylammonium bromide) was reduced by LiAlH₄ (3 molar equivalent) to generate H-Si QDs. The remaining LiAlH₄ was quenched by methanol (MeOH) before phenylacetylene (PheAc) and H₂PtCl₆ catalyst were added to start the hydrosilylation reaction in the capping step. Finally, multiple-step purification was carried out to obtain TOAB-free Si QD solution in hexane. However, the resultant Si QD contains very few styryl groups as confirmed by low intensity of aromatic C-H stretching peaking in the 3000-3200 cm⁻¹ range in its IR spectrum, curve (c) in Figure 1. At the same time, a broad band from 1000 to 1100 cm⁻¹ originated from oxidized components, such as Si-O-Si or Si-O-R is intensive. Its intensity is about 60% when compared with oxidized components of a control Si QD sample, which was obtained without capping step, curve (d) of Figure 1.



Scheme 1. Synthetic generation of styryl-terminated Si QDs and the effect of using MeOH or CuCl₂ on the surface chemistry of resultant Si QDs. The red parts on the Si QD surface represents oxidized components.

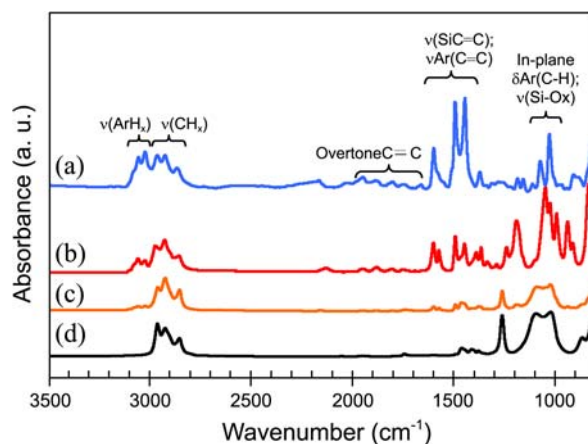


Figure 1. FT-IR spectra of resultant Si QDs when CuCl₂ (a), *tert*-butanol (b), methanol (c) were used to quench the remaining LiAlH₄. (d) FT-IR spectra of a control sample generated as (c) without capping step. The spectra were normalized to the intensity of aliphatic C-H stretching at 2862 cm⁻¹ and vertically shifted for clarity.

In the Figure 1, three intense peaks in the 2800-3000 cm^{-1} range, which are fingerprint of aliphatic C-H stretching, are visible even in the control Si QD sample (curve (d)). We tentatively assigned these peaks to trapped hexane solvent and/or aliphatic groups (methylene and methine) resulted from branching process between the surface Si-CH=CH-groups during drying the samples.⁶ Without any *in situ* evidences, we assumed that the methoxy ions generated from the reaction between MeOH and LiAlH_4 in the quenching step, step 2 in Scheme 1, could react with H-Si QDs to form partial Si-OMe termination, which was further converted into oxidized components during the purification steps. The oxidation of H-Si QD surface by alkoxy has been reported previously in the microplasma reaction, where ethanol solvent was dissociated into ethoxy ions by reacting with plasma electron.⁷ The formation of Si-OMe termination also hindered the hydrosilylation reaction, resulting in Si QDs with very few styryl functional groups, as discussed above from FT-IR spectrum, curve (c) of Figure 1. The effect of using MeOH as quenching agent on the oxidation and capping efficiency is tentatively illustrated in Scheme 1.

The above assumption that H-Si QDs were degraded by methoxy ions was further supported by an observation that the capping efficiency was increased when methanol was replaced by a more bulky alcohol such as *tert*-butanol, or inorganic salts. As could be seen from curve (b) of Figure 1, the peaks of aromatic C-H stretching are more intense in comparison with that in curve (c). Finally, the best sample of PheAc-Si QDs was obtained when CuCl_2 was used as quenching agent. The FT-IR spectrum of this Si QD sample is shown in Figure 1, curve (a). In addition to the increase of aromatic C-H stretching intensity, the overtone or combination bands peaking in the 1600-2000 cm^{-1} range are also clearly visible. Importantly, the peak of C=C stretching in Si-C=C group has been red-shifted about 40 cm^{-1} from 1640 cm^{-1} of typical alkenes to about 1600 cm^{-1} due to the σ - π conjugation between Si and vinyl group.⁸ This peak is overlapping with C=C stretching of the phenyl ring whose additional two peaks locate at 1442 cm^{-1} and 1492 cm^{-1} . There are two sharp peaks in the range from 1000 to 1100 cm^{-1} , curve (a) of Figure 1, originated from out-of-plane C-H bending of phenyl ring, with very less background broadness, indicating that the resultant Si QD is less oxidized when compared with other samples (curves (b) and (c)), as tentatively drawn in Scheme 1.

The structure of PheAc-Si QD, as drawn in Scheme 1, was further confirmed by NMR spectroscopies, as shown in Figure 2. In the ^1H -NMR spectra, Figure 2 (a), two protons, Si-CH=C and Ph-CH=C, are peaking distinguishably at ~ 5.8 and 6.2 ppm, respectively. Chemical shifts of protons in the phenyl ring are in the range from 6.6 to 7.5 ppm.⁶ Three peaks, marked by "*" in Figure 2(a), whose chemical shifts are 0.88, 1.25, and 1.54 ppm may be arisen from trapped solvents (hexane and water) or from methylene and methine fragments, probably formed due to branching process between the Si-CH=CH- groups during drying the sample. These groups and/or trapped hexane give the IR peaks in the

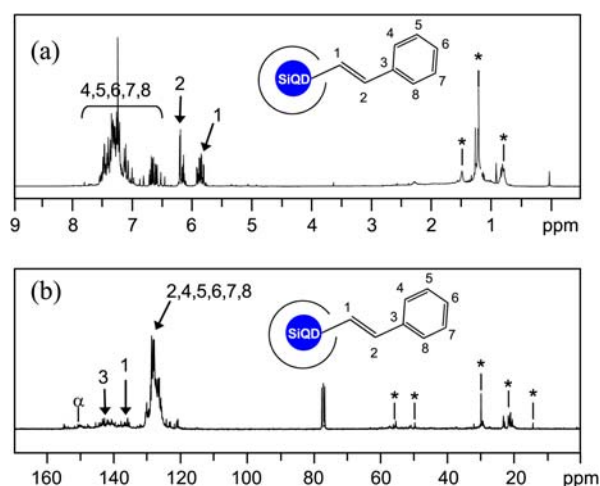


Figure 2. (a) ^1H -NMR (300 MHz, CDCl_3) and (b) ^{13}C -NMR (300 MHz, CD_2Cl_2) spectra of PheAc-Si QD when CuCl_2 was used as quenching agent. The (α) is likely carbon peak of methylene group ($=\text{CH}_2$) in the α -hydrosilylation product. The "*" notes indicate peaks arisen from trapped solvents (hexane and water) or branching products of the Si-CH=CH- groups.

2800-3000 cm^{-1} range, as seen in curve (a) of Figure 1. These aliphatic groups could also response for carbon peaks at about 21, 29, 49, and 56 ppm in the ^{13}C -NMR spectrum, Figure 2(b). Three clearly visible peaks with chemical shifts at ~ 128 , 137, and 142 are well matched with the structure: styryl-terminated Si QD.⁹ The above assignments for protons and carbons are fairly cartooned in Figure 2. A carbon peak located at ~ 152 ppm, marked as " α " in Figure 2(b), is probably arisen from the ($\text{CH}_2=$) group in α -hydrosilylation product.

In summary, the synthesis of styryl-terminated Si QDs were not successful by adopting the miniemulsion approach in which MeOH was used to quench the remaining LiAlH_4 , probably due to the attachment of methoxy ions to the hydrogen-terminated Si QDs. A minor modification, replacing MeOH by CuCl_2 , was found to be very efficient from which styryl-terminated silicon quantum dots were obtained, as confirmed by FT-IR and NMR spectroscopies.

Experimental

All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without any further purification. All synthesis procedures were conducted under oxygen and moisture free, positive pressured argon environment using typical Schlenk line technique.

Synthesis of Styryl-Terminated Si QDs Using Different Quenching Agents. Within an argon filled glove box, 4.5 g of TOAB (tetraoctylammonium bromide) was weighted into a 500 mL 2-neck flask, which was then taken out and connected to a Schlenk line through a connector. 300 mL of anhydrous toluene was added through a needle and the mixture was degassed and refilled with argon gas for 3 times. The flask was then sonicated continuously at constant temperature using a bath-type sonicator. 0.3 mL of SiCl_4 (2.6

mmol) was added to the surfactant solution. After 90 minutes, 9 mL of LiAlH₄ solution (1 M in THF, 9 mmol) was then added dropwise over 15 minutes and the reaction was carried out for 180 minutes to perform hydrogen-terminated silicon quantum dots (H-Si QDs). At this time, solution contained H-Si QDs surrounded by TOAB molecules and remaining LiAlH₄, which needed quenching prior to capping the H-Si QDs with target molecules. According to the report by Tilley,⁴ the remaining LiAlH₄ was quenched by 90 mL of anhydrous methanol for 90 minutes. In other baths, the H-Si QDs solutions were prepared by the same procedure as mentioned above, but 20 mL of anhydrous *tert*-butanol or 7 g of CuCl₂ were used instead of methanol to quench the remaining LiAlH₄. In the case of using CuCl₂, remaining CuCl₂ and the resultant Cu metal were removed by centrifugation prior to the capping step. To cap the Si QDs with styryl groups, 5 mL of phenylacetylene (45.5 mmol) and 0.3 mL of H₂PtCl₆ solution (0.05 M in methanol) were sequentially added to start the hydrosilylation reaction, which was then proceeded under sonication for 5 hours and overnight stirring.

Purification: All solvents were removed under reduced pressure at 40 °C using a rotary evaporator. Hexane (100 mL × 2 times) was added to extract the Si QDs. The combined hexane solution of Si QDs was then extracted with *N*-methylformamide (NMF: 100 mL × 3 times) to remove a small amount of TOAB and unreacted phenylacetylene. The dissolved NMF was removed by extraction with DI water (100 mL × 3 times). Finally, the hexane solution was sequentially dried with brine (100 mL × 2 times) and 2 g of anhydrous MgSO₄ followed by filtration to perform Si QD solution. A control Si QD sample was also prepared using the procedure above with an exception that capping step was not conducted.

Characterizations. The hexane solvent was removed and the Si QD samples were dried overnight in a vacuum oven at

100 °C for Fourier transform infrared (FT-IR) and nuclear magnetic resonance spectroscopic characterizations. The FT-IR spectra were obtained on a PerkinElmer (Waltham, Massachusetts, U.S.A) spectrometer in the range from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 8 cm⁻¹. The ¹H-NMR and ¹³C-NMR spectra were performed on a superconducting FT-NMR 300 MHz (Varian, Inc, Paolo Alto, California, U.S.A).

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Supporting Information. Additional UV absorption spectrum of the styryl-terminated Si QD in hexane solution.

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