Synthesis and Electrochemical Performance of 7-Conjugated Molecule Bridged Silicon Quantum Dot Cluster as Anode Material for Lithium-Ion Batteries

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INTRODUCTION

Lithium-ion batteries (LIBs) with improved performance should be developed to fulfill the increased demand for consumer electronics, renewable energy storage, and electric vehicles.1–3 Currently, commercialized graphite anode cannot meet the criteria for application due to its low theoretical capacity (372 mAh/g).4 Silicon-based electrodes are considered as one of the most promising candidates for use in the next-generation LIBs because of their environmental friendliness, natural abundance, nontoxicity, low cost, low discharge potential plateau (−0.37 V versus Li/Li+), and high theoretical specific capacity (∼4200 mAh/g).5,6 The high theoretical capacity, corresponding to the maximum lithiation state of Li22Si5, is an order of magnitude compared with commercial graphite.7 However, the practical use of Si anodes is hampered primarily by the fact that Si experiences huge volume changes up to 400% during the lithiation/delithiation process.8 The mechanical stress occurring over extended cycles inevitably leads to degradation, electrode pulverization, subsequent loss of electrical contact between active materials and the current collector, and formation of unstable solid electrolyte interface (SEI), resulting in rapid capacity fading.9 Significant efforts have been devoted to overcoming the aforementioned challenges of Si-based electrodes. The strategies investigated include modification of electrolyte additive,10 construction of artificial coatings,11 development of novel binder systems,12 and nanoscale engineering of Si-based electrode materials with various structures such as nanoparticles,13–15 nanowires,16 nanotubes, and nanoporous silicon.16,17 Nanoscale materials can efficiently accommodate the large mechanical stresses that result from the alloying reaction of Si with lithium, leading to stable cycling performance. Recently, reducing the size of Si electrode materials further to quantum dot (QD) scale has been proven to improve the electrochemical performance significantly. Aghajamali et al. investigated the electrochemical properties of nanocomposites with 3, 5, 8, and 15 nm Si nanocrystals in conductive mesoporous graphene aerogels for LIBs and found that when the size of the nanocrystals decreased from 15 to 3 nm, the cycling stability of annealed Si nanocrystals nanocomposite was improved significantly, owing to its high stress/strain tolerance.20 However, a reduction in the size of Si material...
to the QD scale leads to inferior electronic conduction due to numerous interfacial contacts between QDs and extreme SEI formation due to the relatively larger surface area. In addition, these QDs are likely to aggregate into larger particles, which severely reduces the active sites during extended cycles, leading to rapid capacity fading. To address these limitations, assembling the QDs into clusters might be an efficient approach. Assembling the QDs into a cluster not only provides free space that can accommodate volume expansion and maintain its structure during cycles but also facilitate the formation of SEI on the outer surface.22 Herein, we report the successful preparation of Si QD cluster with π-conjugated molecular bridges using Sonogashira C–C cross-coupling reaction between 4-Bs/Oct Si QDs and 1,4-diethynylbenzene. Compared with the 4-Bs/Oct Si QD electrode, the Si QD cluster exhibited improved electrochemical performances due to the π-conjugated molecules between QDs and on the surface of the Si QD cluster, which facilitate and enhance the electrical contact with the current collector and accommodates volumetric expansion occurring over extended cycles. The cluster synthesis strategy can be an attractive approach to boost the electrochemical performances of the QD cluster by modifying the organic structures and introducing different functional groups.

**RESULTS AND DISCUSSION**

The π-conjugated molecule bridged Si QD cluster was prepared via a Sonogashira cross-coupling reaction between the 4-Bs/Oct Si QDs and 1,4-diethynylbenzene, as shown in Scheme 1b, where Si QDs are covalently connected with vinylene-(phenylene-ethynylene)$_2$-phenylene-vinylene (−≡≡ϕ−≡≡ϕ−≡≡ϕ−≡≡ϕ−). The surface chemical structures of the 4-Bs/Oct Si QD and Si QD clusters were characterized by Fourier transform infrared (FT-IR) spectroscopy compared with those of surface capping and bridging molecules including 1-bromo-4-ethynylbenzene and 1,4-diethynylbenzene, respectively (Figure 1a). The FT-IR spectrum of 4-Bs/Oct Si QD and Si QD clusters were characterized by FT-IR and 1H NMR results, we conclude that the 4-Bs/Oct Si QDs and 1,4-diethynylbenzene were C–C cross-coupled together in the Si QD cluster.

### Scheme 1.

(a) Hydrosilylation Reaction between Hydride-Terminated Si QD and 1-Bromo-4-ethynylbenzene/1-Octene. (b) Sonogashira C–C Cross-Coupling Reaction between 4-Bs/Oct Si QDs and 1,4-Diethynylbenzene

![Scheme 1](https://pubs.acs.org/acsomega/article-structure-v1.0/2020/5/8629-8637/acsomega.2000019.s001.png)

Comparing with the 4-Bs/Oct Si QDs, the peaks are clearly assigned, as shown schematically in the inset: 7.5–7 ppm (aromatic, c, d), and 3.0 ppm (ethyl CH, e). Compared with 1-bromo-4-ethynylbenzene, the spectrum of 4-Bs/Oct Si QD revealed additional peaks at 3.6 and 5.3 ppm, which could be assigned to protons in the vinyl group bonded Si atom. Therefore, based on the FT-IR and 1H NMR results, we conclude that the formation of Si QDs is well functionalized by 1-octene and 1-bromo-4-ethynylbenzene via the Si–C chemical covalent bond. Meanwhile, as seen in Figure 1a, the Si QD cluster exhibits features that are mostly identical to 4-Bs/Oct Si QDs in the FT-IR spectra. In addition, the peak at 2240 cm$^{-1}$ corresponding to C≡C stretching of Si QD cluster shifted to a higher frequency compared with that of 1,4-diethynylbenzene (2110 cm$^{-1}$). It is known that the polycapsulation of polyarylene ethynylene shifts the C≡C stretching peak of the original HC≡C–Ar–C≡CCH to a higher frequency.27 Therefore, these FT-IR results indicate that 4-Bs/Oct Si QDs and 1,4-diethynylbenzene were C–C cross-coupled together in the Si QD cluster.

The morphologies of the Si QD cluster were confirmed using field-emission transmission electron microscopy (FE-TEM). As seen in the low-magnitude TEM images (Figure 2a), the Si QD cluster are approximately 1 μm agglomerates, with a secondary structure consisting of relatively small clusters measuring 80–100 nm in diameter. The high-magnitude TEM image (Figure 2d–f) reveals that the Si QDs with an average diameter of 2.7 ± 0.4 nm were clearly distinguishable from the π-conjugated organic molecule matrix in the Si QD cluster with high crystallinity, and its interplanar distance of 0.19 nm corresponded to the (220) crystal plane of the diamond cubic
Si. Importantly, the Si QDs were uniformly distributed over the QD cluster without aggregation, which could be attributed to the presence of π-conjugated bridging molecules between Si QDs and dense functional groups on the surface of Si QDs. To further identify the distribution of QDs in the Si QD cluster, elemental mapping images shown in Figure 3, it was confirmed that the species of C, O, and Si were uniformly distributed in the Si QD cluster without aggregation, which could be attributed to the presence of π-conjugated molecules between Si QDs and dense functional groups on the surface of Si QDs.

The porous structure of the 4-Bs/Oct Si QD and Si QD clusters was investigated using the nitrogen adsorption–desorption isotherm and the Barrett–Joyner–Halenda (BJH) pore diameter distributions (Figure 4). The isotherm of the Si QD cluster showed a typical type IV isotherm, indicating their mesoporous structure, while the isotherm for 4-Bs/Oct Si QDs had no characteristics of a porous structure. From the nitrogen adsorption–desorption isotherm, the specific surface area, pore volume, and average pore size were evaluated to be ~31.53 m²/g, 0.18 cm³/g, and 22.02 nm, respectively. This mesoporous architecture of the Si QD cluster may facilitate the transportation of lithium ions into the structure and accommodate the extreme volume expansion/contraction during the repeated lithiation/delithiation process. Therefore, the Si QD cluster is expected to exhibit promising electrochemical performance as anode materials for lithium-ion batteries.

The electrochemical performance of the 4-Bs/Oct-Si QDs and Si QD clusters as anode active materials was evaluated using a CR 2032 coin-type cells with lithium metal as the counter electrode. All of the specific capacities were calculated based on the silicon content obtained from the elemental analyses (Table 1). Figure 5a–d shows the galvanostatic charge–discharge curves and the corresponding differential capacity plots (dQ/dV) for the 4-Bs/Oct-Si QDs and the Si QDs clusters at a current density of 200 mA/g in the potential window of 0.01–2.5 V versus Li/Li⁺. In the first cycle for the 4-Bs/Oct Si QDs, the specific charge and discharge capacities were 17 and 10 mAh/g, respectively, with 59% initial Coulombic efficiency (CE). Considering that carbon black has lithium ion uptake ability, these specific capacities can be regarded as essentially zero. No characteristic delithiation plateaus and peaks of amorphous Si at ~0.30 and ~0.47 V versus Li/Li⁺ were observed in the potential profile (Figure 5c) and dQ/dV plot (Figure 5d), respectively, indicating that the 4-Bs/Oct Si QDs did not participate in delithiation process. This result is in good agreement with the report by Aghajamali et al., who observed an extremely low specific capacity of undecanoic acid-functionalized silicon nanocrystals with an average diameter of 3.2 nm. The failure of the 4-Bs/Oct-Si QDs electrode could be ascribed to the loss of electrical contact with the current collector due to a much smaller average Si QD size (2.7 ± 0.4 nm) compared with that of carbon black (46.5 ± 13.5 nm, Figure S1). Further, the dissolution problems generally encountered in organic molecule-based electrodes may induce extremely low capacities in the 4-Bs/Oct Si QDs. From the fact that the surface-functionalized Si QDs can be soluble in a common solvent, it is possible that the 4-Bs/Oct-Si QDs were dissolved in the electrolyte away from the current collector before or immediately after the lithiation reaction. In contrast, the Si QD cluster exhibits an improved electrochemical performance with the initial specific charge and discharge capacities of 8151 and 1957 mAh/g, respectively. This result could be attributed to the increase in the overall size of Si anode by clustering and the presence of π-conjugated molecules between Si QDs and on the surface of the Si QD cluster, which facilitates the electrical contact between the anode active material and the conductive carbon black. As shown in Figure 5b, the differential capacity plots of the Si QD cluster in delithiation reaction showed peaks at ~0.37 and ~0.53 V versus Li/Li⁺.
which indicates the participation of Si QDs in the electrochemical reaction. In addition, another broad peak was observed at around 1.0 V versus Li/Li+. This can be attributed to the deinsertion reaction of lithium ions in the unsaturated π-conjugated molecules of the Si QD cluster during the first lithiation cycle. Even though it is difficult to form Li/C

Table 1. Elemental Analyses of the 4-Bs/Oct Si QD and Si QD Clusters

|                  | % C | % N | % H | % S | % O | % Si (remaining) |
|------------------|-----|-----|-----|-----|-----|-----------------|
| 4-Bs/Oct Si QD   | 49.80 | 0.09 | 7.01 | 0.47 | 1.48 | 41.15           |
| cluster          |      |     |     |     |     |                 |
| Si QD cluster    | 72.87 | 0.27 | 4.86 | 0.08 | 6.78 | 15.14           |

Figure 2. TEM images (a, b, d–f) of the Si QD cluster. Size distribution (c) of Si QDs in the Si QD cluster.

Figure 3. TEM image (a), corresponding secondary electron TEM image (b), EDX mapping (c–e), and EDX spectrum (f) of the Si QD cluster.

Figure 4. Nitrogen adsorption–desorption isotherms (a) and the corresponding Barrett–Joyner–Halenda (BJH) pore diameter distribution (b) of the 4-Bs/Oct Si QD and Si QD clusters.
complexes from unsubstituted aromatics, such as pyrene and naphthalene, it seems that the abundant number of ethynyl groups in the Si QD cluster is capable of providing excellent electron-donating properties, leading to the insertion of lithium ions. The lithium-ion insertion into the π-conjugated bridged molecules may explain why the specific charge capacity (8151 mAh/g) of the Si QD cluster is much larger than the theoretical capacity of Si (4200 mAh/g) for the most saturated lithium silicide phase L22Si5. The intensity of the broad peak at around 1.0 V versus Li/Li+ was drastically decreased in the second cycle compared with the peaks at ∼0.37 and ∼0.53 V, which suggests an irreversible reaction of the π-conjugated molecules composed of phenyl and ethynyl groups. Therefore, it can be considered that the specific capacities of the Si QD cluster upon the following cycles were mainly provided by Si QDs. In the galvanostatic charge–discharge curves and the corresponding differential capacity plots of lithiation reaction, the long, flat plateau and high-intensity peak were observed below 0.3 V versus Li/Li+. The characteristics of crystalline Si at around 0.11 V were not clearly distinguished because of the π-conjugated molecules. Additionally, at around 1.5 V versus Li/Li+, the peaks associated with the side reaction of the Si electrode, including the SEI formation and reduction of SiOx on the surface of the Si QDs were observed. As a result of the SEI formation, reduction of SiOx on the surface of the Si QDs, and the irreversible reaction of π-conjugated molecules in the Si QD cluster, the initial CE of the Si QD cluster was only 24%.

Figure 5e shows the cycling performance of the 4-Bs/Oct-Si QDs and Si QD clusters at a current density of 200 mA/g. As mentioned above, the 4-Bs/Oct Si QDs showed low specific capacities close to zero. The reversible capacity of the Si QD cluster was estimated around 1957 mAh/g in the first cycle, which decayed during the fifth cycling process while still retaining ∼63% (1232 mAh/g) of its initial capacity after charge/discharge over 100 cycles. The good cycling stability of the Si QD cluster is attributed to the π-conjugated molecules between Si QDs and on the surface of the Si QD cluster, which
was proved by examining the morphologies of the cycled electrode using scanning electron microscopy (SEM) (Figure S3). The π-conjugated molecules between Si QDs and on the surface of the Si QD cluster acts as a buffer layer to mitigate the mechanical stresses arising from the alloying reaction of Si with lithium during the extended cycles. Furthermore, the ability to enable electron/Li+ ion transport of the π-π network in π-conjugated molecules would also have contributed to the cycling stability.32 The CE of Si QD cluster at the current rate of 200 mAh/g reached 80% after the second cycle, with an average of 97% during the 10th–100th cycles. Furthermore, the rate capability of the 4-Bs/Oct Si QD and Si QD clusters was evaluated under various current rates ranging from 200 to 8000 mAh/g, as shown in Figure 5f. At a high current density of 2000 mA/g, the Si QD cluster retained only ∼3% of its average specific capacity at 200 mA/g. As can be seen from the pore distribution of the Si QD cluster (Figure 4), due to the macropores in the Si QD cluster, the SEI formation could not be completely confined to the surface. As a result, a thick SEI layer was formed on both the inside and the outside of the Si QD cluster, which inhibited the diffusion of lithium ions, leading to low capacities at a high current rate. Nevertheless, the reversible capacity was recovered up to 87% (1545 mAh/g) of its average specific capacity when measured again at 200 mA/g, which indicates the structural stability of the π-conjugated molecule bridged Si QD cluster during repeated charge/discharge cycles.

To further elucidate the failure of the 4-Bs/Oct Si QD cluster and the improvement of the Si QD cluster in the electrochemical performance, electrochemical impedance spectroscopy (EIS) measurements were conducted under the full delithiation state after 100 cycles at a current rate of 200 mA/g. The fitted impedance plots indicated by solid lines are in good agreement with the experimental EIS plot and the fitted parameters are summarized in Table 2. Apparently, the SEI film resistance ($R_{\text{ct}}$) of the Si QD cluster (271.30 Ω) is lower than that of the 4-Bs/Oct Si QDs (667.20 Ω), indicating that the QD clustering can inhibit the growth of the SEI layer. Notably, the charge-transfer resistance at the electrolyte/active material and active material/current collector interface ($R_{\text{ct}}$) of 4-Bs/Oct Si QDs (147 620 Ω) is substantially greater than that of the Si QD cluster (845 Ω), which may be attributed to the poor contact with the current collector (Figure 7a). This finding confirms that the increase in the overall size of Si anode by clustering and the presence of π-conjugated molecule between Si QDs and on the surface of the Si QD cluster facilitates electrical contact with the current collector, resulting in improved electrochemical performance (Figure 7b).

## CONCLUSIONS

A π-conjugated molecule bridged Si QD cluster was successfully prepared via Sonogashira C–C cross-coupling reaction between 4-Bs/Oct Si QDs and 1,4-diethynylbenzene. Compared with the 4-Bs/Oct Si QD electrode, the Si QD cluster electrode exhibits improved electrochemical performance, such as a high initial reversible capacity of ∼1957 mAh/g and good cycling stability with ∼63% capacity retention following 100 cycles at a current rate of 200 mA/g. The improved electrochemical performance of the Si QD cluster is attributed to the π-conjugated molecules between QDs and on the surface of the Si QD cluster, which acts as a buffer layer to alleviate mechanical stresses arising from the alloying reaction of Si with lithium, and maintains the electrical conduits in the anode system. This cluster synthesis strategy can be an attractive approach because the electrochemical performance of the QD cluster can be further enhanced by modifying the organic structures and introducing different functional groups.

## EXPERIMENTAL SECTION

### Chemicals and Materials

All chemical reagents were used as received without further purification. Toluene (anhydrous, 99.8%), borane–tetrahydrofuran complex solution (BH₄·OC₆H₆, 1.0 M in THF), 1,4-diethynylbenzene (C₁₀H₈, 96%), 1-octene (C₁₀H₁₆, 98%), bis-(triphenylphosphine)palladium(II) dichloride (Pd-(PPh₃)₂Cl₂, 98%), copper(I) iodide (CuI, >98.0%), triethylamine (TEA) (N(CH₃)₃, 99.0%), vinylene carbonate (VC) (99%), sodium chloride (NaCl) (≥98.0%), and poly(acrylic acid) (PAA) (average $M_n$ ∼ 450 000) were purchased from Sigma-Aldrich. Hydrofluoric acid (HF, 48–51%) and ammonium hydroxide solution (NH₄OH, 25%) were purchased from J.T. Baker and Acros Organic, respectively. Super P carbon black, n-methyl-2-pyrrolidone (NMP), Cu-foil, and Li-metal were obtained from Wellcos Corporation (South...
Figure 7. Difference in the charge-transfer reaction from the current collector to the 4-Bs/Oct Si QD (a) and Si QD clusters (b).

Korea). Ethanol (EtOH) (C₂H₅OH, 99.5%) and methanol (MeOH) (CH₃OH, 99.5%) were purchased from Dae-Jung (South Korea). 1-Bromo-4-ethynylbenzene (C₈H₅Br, >98.0%) was purchased from TCI. One molar lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:1 v/v) was obtained from Soul-Brain (South Korea).

Synthesis of 4-Bromostyrlyl and Octyl Co-Capped Si QDs. The synthetic procedures of silica nanoparticles (SiO₂ NPs) and oxide-coated silicon nanocrystals (Si NCs@SiO₂) are described in the Supporting Information. Freestanding 4-bromostyrlyl and octyl co-capped Si QDs (4-Bs/Oct Si QDs) were prepared using borane-catalyzed hydrosilylation reaction between 1-bromo-4-ethynylbenzene/1-octene and hydride-terminated Si QDs (H-Si QDs). The H-Si QDs were synthesized only from Si NCs@SiO₂ NPs) and oxide-coated silicon nanocrystals (Si NCs@SiO₂). Finally, the 4-Bs/Oct Si QDs were obtained as bright yellow solids after drying with a rotary evaporator.

Synthesis of π-Conjugated Molecule Bridged Si QD Cluster. The π-conjugated molecule bridged Si QD cluster was prepared via Sonogashira cross-coupling reaction following our previous report, with some modifications. The C–C cross-coupling reaction between 4-Bs/Oct Si QDs and 1,4-diethynylbenzene was carried out in an argon atmosphere using the standard Schlenk line technique. The 4-Bs/Oct Si QDs (50 mg), 1,4-diethynylbenzene (63 mg), Pd(PPh₃)₂Cl₂ (20 mg), and CuI (8 mg) were dissolved into anhydrous toluene (30 mL) and the reaction mixture was transferred to a 100 mL two-neck flask equipped with a condenser that was connected to an argon-filled Schlenk line. After the addition of TEA (3 mL) to the flask, the reaction mixture was stirred at 110 °C for 2 h to obtain a dark-brown solution. After cooling the reaction mixture, methanol (MeOH) was added to precipitate the Si QD cluster. The Si QD cluster was centrifuged at 12 000 rpm for 10 min and washed three times with MeOH (100 mL) to remove the catalyst. Finally, the Si QD cluster was obtained as a dark-brown powder after drying with a rotary evaporator.

Material Characterization. Field-emission transmission electron microscopy (FE-TEM) was performed using a JEM-2100F electron microscope (JEOL, Japan) with an accelerating voltage of 400 kV. For TEM sampling, 0.1 wt% solution of the Si QD cluster in toluene was drop-cast onto a lacy carbon-coated copper grid, and the solvent was evaporated in vacuum. Proton nuclear magnetic resonance (H NMR) data were collected with the superconducting FT-NMR at 300 MHz (Varian Inc., Palo Alto, California). Chemical shifts were reported in parts per million (ppm) in a solvent of chloroform-δ (99.8 atom % D). Fourier-transform infrared (FT-IR) spectroscopy was performed using a Nicolet 380 spectrometry system (Waltham, MA) operated in the mid-IR range of (4000–400) cm⁻¹, with the spectra obtained at a spectral resolution of 2 cm⁻¹ in the transmittance mode. Carbon, hydrogen, nitrogen, sulfur, and oxygen contents were measured using a Thermo Scientific Flash 2000 organic elemental analyzer and vario MICRO cube elemental analyzer. Nitrogen adsorption–desorption isotherms were recorded using Belsorp mini II surface area and porosimetry analyzer. Prior to the measurements, the Si QD cluster was degassed under vacuum at 70 °C for 6 h.

Electrochemical Characterization. The electrochemical performance of the 4-Bs/Oct Si QD and Si QD clusters was evaluated using a CR 2032 coin-type cell with Li metal as the counter/reference electrode. The working electrodes were prepared by casting a mixture of the test materials, super P carbon, and poly(acrylic acid) in a weight ratio of 70:15:15 onto a copper foil, which serves as a current collector. The copper foils were dried at 60 °C for 5 h in a vacuum oven to remove the solvent used for slurry preparation. The mass loading of all the electrodes was ~1.0 mg/cm². The coin cells were assembled in an argon-filled glovebox using lithium metal...
and glass fiber (GF/F, Whatman) as a separator. One molar LiPF\textsubscript{6} in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (1:1 v/v) containing 5 wt % vinylene carbonate (VC) was used as an electrolyte. Galvanostatic charge-discharge and cycling performance measurements were conducted in the potential range of 0.01–2.5 V versus Li/Li\textsuperscript{+} at room temperature using a battery cycling system (WonATech-WBCS 3000L). The AC impedance was also measured by CompactStat (IVIUM TECHNOLOGIES), with a frequency range of 100 kHz to 0.01 Hz and a voltage amplitude set to 10 mV. Cyclic voltammetry scans were performed with a potential range of 0.01–2.5 V (versus Li/Li\textsuperscript{+}) at the scan rate of 0.01 mV/s.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00019.

Synthetic procedures of SiO\textsubscript{2} NPs and Si NC@SiO\textsubscript{2}; scanning electron microscopy (SEM) image and size distribution of the conductive carbon black; cycle performance of hydride-terminated Si QDs (H-Si QDs); top-view SEM images of H-Si QDs (a, b), 4-BS/Oct Si QD cluster (c, d), and Si QD cluster (e, f) electrodes after 100 charge/discharge cycles; cyclic voltammograms of H-Si QDs, 4-BS/Oct Si QD cluster, and Si QD cluster electrodes at a scan rate of 0.01 mV/s between 0.01 and 2.5 V for the first and second cycles (PDF)

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