Supporting Information for the manuscript "Emerging Atomic Energy Levels in Zero-Dimensional Silicon Quantum Dots"

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SI 1. Materials and Methods

SI 1.1 Reagents

All chemicals were used as received, without further purification. Triethoxysilane (TES; 97%) was obtained from Tokyo Chemical Industry (TCI) Co., LTD. Hydrofluoric acid (HF; 46–51% aqueous solution, metal impurity <100 ppm) was obtained from Kanto Rea-gents. Milli-Q Water (18.2 M Ω ·cm of resistivity) was obtained by a Sartorius (Arium 611UV) water purification system.

SI 1.2 Synthesis of hydrogen-terminated silicon quantum dots (Si QDs)



Figure S1. Schematic illustration of the preparation of Si QDs.

Figure S1 shows a scheme of preparing of Si QDs. In a typical, 16 mL of TES was placed to 2neck round-bottom flask, kept in ice bath and stirred in Ar atmosphere. 32 mL of hydrochloric acid solution of pH 3 was added dropwise to the TES with vigorous stirring under a flow of Ar gas. The transparent, colorless TES solution obtained was stirred for another 30 min. Then, by removing the ice bath, we brought the solution back to the room temperature while stirring (60~90 min was taken). Then, the solution was subjected to the filtration under reduced pressure. The resultant white powder was washed with Milli-Q water until it becomes pH 7, followed by drying overnight under a vacuum. The average weight of the dried powder was approximately 4.3g. The dried powder was characterized for clarification of its structure. A narrow scan of X-ray photoelectron spectroscopy (XPS) showed the appearance of a single peak at 102.3 eV in the Si2p region which indicates the formation of three-valence of oxidation state of Si according to equation (1). ATR-FTIR study indicated that the product is composed of the amorphous structure of hydrogen silsesquioxane, referred as (HSiO_{1.5})_n, as a result of hydrolysis of TES.

 $4HSi(OCH_2CH_3)_3 + 6H_2O \rightarrow 4HSiO_{1.5} + 12CH_3CH_2OH$ (1)

The dried powder of 2.0 g was placed in a tiny quartz crucible, and transferred to a vacuum furnace. Prior to start heating for thermal disproportination of $(HSiO_{1.5})_n$, the atmosphere in the vacuum furnace was displaced with 5%-H₂/95%-Ar gas. The internal temperature of the furnace was raised and the rate of temperature increase was 200°C/min from room temperature to 400°C. The temperature was kept for 30 min at 400°C. Then, the temperature was raised to 600°C from 400°C with the rate of 100°C/min, followed by degassing for 30 min at 600°C. Finally, the temperature was raised to the predefined temperature for the reaction with the rate of 250°C/min. The reaction temperature were controlled between 900°C and 1100°C at which the dried powder, i.e., $(HSiO_{1.5})_n$, is disproportionated into two different oxidation states such as Si⁰ and Si⁴⁺ according to equation (2). After the predefined time passing, the internal temperature of the furnace was cooled down to the room temperature by the flow gas cooling.

 $4\text{HSiO}_{1.5} \rightarrow \text{Si} + 3\text{SiO}_2 + 2\text{H}_2 \quad (2)$

A color of the powder turned brown from white by the heating, and became darker with increase of the reaction temperature due to increasing size of SiQDs. Since the products annealed at 925°C or less suffered from a low crystallinity of Si, we chose the range of temperature between 1000 and 1100°C for the disproportionation reaction.

Prior to hydrogenation of Si QD, the grinding of the brown powder (300 mg) in a mortar and pestle was performed to prepare the fine powder. Next, the fine powder placed in a Teflon container containing 24 mL of etching solution of HF/ethanol with a 2:1 volumetric ratio was stirred for the predetermined time to remove a matrix of SiO₂, along with the size reduction of silicon nanocrystals by HF etching, followed by surface termination of the nanocrytals with hydrogen atoms to yield Si QDs. The resulting etching solution was centrifuged at 15,000 rpm for 5 min. A simple hydrofluoric etching, by employing HF of 48–51% conc., allowed the preparation Si QD specimens that exhibit red-, orange- and yellow PL spectral features. On the other hand, the use of a stepwise etching, by employing different HF concentrations, were required to prepare green and green-yellow luminescent Si QD specimens for fine tuning of QD size as a result of hydrofluoric etching at a slow rate. The hydrofluoric supernatant was subsequently decanted, leaving a precipitate of Si QD specimens. Next, the specimens were washed with ethanol, acetonitrile and dichloromethane, in this order, by centrifugation. After being washed, the specimens were dried in a glove-box filled with Ar gas until the spectroscopic measurement. The synthetic conditions adapted for tuning of PL spectra are summarized in Table S1. The estimated production yields by weight were $\sim 2\%$, $\sim 0.7\%$ and $\sim 0.3\%$ for the red, yellow and green fluorescent Si QD specimens, respectively.

| | Reaction temperature and time | Etching Time (min) | Diameter (nm) | | | |
|---------|-------------------------------|-----------------------|---------------|-------|-------|------|
| Samples | | | | XRD | | SAXS |
| | | | (111) | (220) | (311) | |
| А | 1000°C, 1.5hrs | 175 | 1.16 | 1.24 | 1.21 | 1.23 |
| В | 1000°C, 1.5hrs | 165 | 1.16 | 1.26 | 1.25 | |
| С | 1000°C, 1.5hrs | 150 | 1.18 | 1.29 | 1.24 | |
| D | 1000°C, 1.5hrs | 100 | 1.38 | 1.46 | 1.34 | 1.44 |
| Е | 1000°C, 2.0hrs | 65 | 1.52 | 1.54 | 1.61 | 1.67 |
| F | 1100°C, 1.5hrs | 20 | 1.98 | 1.88 | 1.83 | |
| G | 1100°C, 2.0hrs | 15 | 2.05 | 1.91 | 1.86 | 1.88 |
| н | 1100°C, 2.0hrs | 35 | 2.11 | 1.97 | 1.92 | 2.04 |

Table S1. Summary of the diameters estimated from SAXS and Scherrer analysis of XRD line broadening for the Si QD specimens prepared at typical conditions.

SI 1.3 Characterization

The Si QD of film forms deposited onto predefined sample holders were characterized by X-ray powder diffraction (XRD, the Rigaku SmartLab), small-angle X-ray scattering (SAXS), and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy using a germanium prism on a JASCO FTIR 4100 spectrometer. For SAXS measurements, the samples were measured in ambient conditions by transmission method on a Nano-Viewer of Rigaku system using a rotating copper anode X-ray source ($\lambda = 0.15418$ nm) operating at 40 kV and 30 mA with a PILATUS detector. Two-dimensional SAXS measurements were performed in the $0.22^{\circ} \le 2\theta \le 5.0^{\circ}$ range. A 3.0 mm of Beam stopper and 341.52 mm of camera length were employed. The resulting profiles were analyzed using a NANO-solver software (for details of the NANO-Solver

on the website http://www.rigaku.com/software/nanosolver.html.), to estimate the average particle size distributions of the specimens.

Raman spectra at a single excitation wavelength (532 nm) were acquired on the Si QD film on a slit-scanning Raman microscope (RAMAN-11; Nanophoton, Japan). The samples were observed on the JEOL JEM-ARM200F with STEM mode operating at 200 kV. The observation with the STEM offers an unprecedented opportunity to probe structures with sub-Angström resolution. The bright-field and the dark-field images were acquired with in-line and HAADF detectors, respectively. A low-pass filter was applied to the image for noise reduction. To avoid the solvent effect on PL QYs, all the optical properties were measured using the QD films deposited onto quartz glass substrates. PL and PLE measurements were carried out using a modular double grating Czerny-Turner monochromator and an iHR 320 emission monochromator (1200 lines/mm of gratings) coupled to a photomultiplier tube (PMT) on a NanoLog Horiba Jovin Yvon spectrofluorometer with 450W xenon arc lamp. The spectral resolution of the system is around 0.3 nm. The time-resolved PL decay curves were acquired at room temperature in air for the solidstate Si QD powders sandwiched between quarts glass plate. The same NanoLog Horiba Jovin Yvon spectrofluorometer was used for the analysis. A longer decay time on usec-scale was measured by a multi-channel scaling (MCS) mode using a pulsed spectral LED of 370 nm emission. A shorter decay time on subnanosecond-scale was measured by time-correlated single photon counting (TCSPC) mode using a laser diode (NanoLED-375LS; λ_{em} = 370±10 nm, pulse width < 200psec., average power 100 mW, Frequency 100 MHz). To avoid scattered excitation lights, cut filters for 495-nm-light was placed in the front of monochrometer-PMT setup. The absolute PL quantum yields (PL QYs) were measured at room temperature using the QY measurement system C9920-02 from Hamamatsu Photonics Co. Ltd with a 150 W xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as a sample chamber, and a multichannel analyzer for signal detection. The film form specimens of Si QD were used for the estimation of PL QYs. For the temperature-dependent PL measurements, the samples were placed into an Opticool Stage cryostat connected to GM cooler and controlled by Mercury-iTC temperature controller, which allowed tuning the sample temperature in the range from 2 to 298 K. The samples for temperature-dependent fluorescence study were prepared by casting a non-luminescent dichloromethane solution of the QDs over the surface of quartz glass substrate followed by drying under vacuum conditions.

SI 2. Structural Analysis of Si QD specimens

SI 2.1 XRD study

Figure 1(b) shows XRD patterns of the specimens A-H and R. Diffraction peaks of the specimen R were obtained for the 3.6-nm Si QD specimen, and are positioned at 28.4°, 47.3°, and 56.1°. These values agree well with diffraction angles for diamond cubic lattice of bulk Si (Figure S2b). So, the specimen R serves as a standard. All the XRD patterns in Figure 1(b) demonstrate the peak characteristics of diamond cubic Si, and are totally different from that of amorphous Si. Because amorphous Si is comprised of two broad diffraction peaks at $2\theta = \sim 28^{\circ}$ and $\sim 52^{\circ}$ (1).

Interestingly we see that the specimen H has pronounced shifts for the 111, 220 and 311 diffraction peaks to lower angles than that of the standard positions of the bulk, as guided by greenlines. For accuracy, we also measured a similar specimen with Synchrotron XRD (Figure S2a). The strong XRD pattern shows that the diffraction lines shift to a lower diffraction angle side, consistent with the result of Figure 1(b). Worth mention, this suggests that the resolution of the diffraction lines in Figure 1(b) measured by the conventional XRD (Rigaku SmartLab) is as high as that of the diffraction lines measured by the synchrotron XRD (Figure S2a). The shift of XRD lines appears due to the expanding *d*-spacing of the crystallographic plane, causing the local–crystal–lattice distortion (2) Comparing it with other patterns in Figure 1(b), the diffraction-line shift seems to be enhanced as the size decreases.

XRD linewidth is generally determined by the combination of crystalline size and lattice strain. Williamson-Hall method was a conventionally used to estimate the both parameters from the diffraction linewidths for all the specimens. In Figure 1(b), the diameters are somewhat smaller than the values measured by SAXS due to anisotropic peak broadening, which also reflects crystallographic strain (see Figure S2c). The presence of the lattice distortion will be discussed based on the STEM and Raman spectroscopic studies for more details.



Figure S2. (a) High-resolution synchrotron XRD pattern of the specimen H measured using a Debye-Scherrer camera installed on BL15XU at SPring-8 at a wavelength of 0.65298Å. The sample for synchrotron XRD was sealed into Lindemann glass capillaries with an inner diameter of 0.3 mm. The capillary was rotated during the measurement to reduce the preferred orientation effect and to average the intensity. (b) Conventional XRD pattern of a commercial powder of crystalline Si particle of 120 nm average-diameter which works as a standard. From the pattern (b), we see the *d*-spacing values of the Bragg angles for reflection from the (111), (220) and (311) planes of crystalline Si (lattice parameter = 5.42 Å) at the Cu K α radiation of wavelength λ =1.5418 Å are 28.4°, 47.3° and 56.1°. The dotted lines in the (a) position at the diffraction angles of bulk Si (b). (c) A relationship between lattice strain and diameters of the QDs. Both parameters were calculated from the XRD patterns using Williams-Hall method.

SI 2.2 STEM study

STEM allows the direct observation of a real crystallographic structure of individual QDs. Unlike QDs in heavy-metal semiconductors, the low atomic number contrast between Si and the

underlying carbon of the STEM mesh obscures the lattice fringes. Furthermore, the electron-beam damage of Si QD become too large to ignore at a high magnification. In practice, we often observe the disappearance of small QDs (d = -1 nm) at a high magnification due to the possible disruption caused by electron-beam damage. Wilcoxon et al. feared a difficulty of statistically embodying a broad distribution of sizes for Si QDs by TEM (3). Thus, it makes sense that successful observation of lattice fringes has been limited to the QDs with diameters of 3 nm or larger in other literatures (4,5). In our study, we observed for the first time the lattice fringes of QDs with diameters smaller than 2 nm through careful and tenacious efforts on operation of STEM. Figure 1c shows the representative bright-field (BF) STEM images of 1.45 nm and 1.82 nm QDs which were found in the specimens D and F, respectively. Figures S3-S5 show BF STEM images that were simultaneously recorded with a high-angle annular dark-field (HAADF) images for the specimens C, E and G, in which we see 1.28 nm, 1.67 nm and 1.91 nm QDs. In this work, we used inverse fast Fourier transform (IFFT) analysis to examine the crystallographic subtleties in the smallest size regime (d < 2 nm diameter). As indicated by the two open rectangles in Figure S4, the IFFT of the 1.67 nm Si QD viewed along the [111] zone axis illustrates direct experimental evidence of crystallographic distortions that may appear due to spontaneous angular distortion and concurrent displacement of the crystalline Si lattice. A similar loss of the structural coherence that breaks the translational symmetry is observed in different sizes of Si QD (see Figures. 1c, S3 and S5). Although the observation area is limited, the local-lattice distortion is apparently enhanced for the 1.28 nm Si QD (Figure S3). As expected, such a structural incoherency is not observed for the 6.8 nm or larger Si QD. From the line profiles of the STEM images, the inhomogeneously-strained configurations are concentrated in the area nearest to the surface rather than at the centers of ODs, which is consistent with our previous study (2). An enhanced distortion of lattice has been also suggested for QDs by Pi's and by Korgel's groups recently, but the structural origin was unknown (5,6). Our STEM confirms that the local-lattice distortion causes the structural incoherency, and is dependent of OD size, consistent with the results of XRD.



Figure S3. (a) BF- and (b) HAADF-STEM images of the specimen C. The (200), (220) and (111) lattice spacing in bulk crystalline Si are 2.7Å, 1.9Å and 3.1Å, respectively. Both (c) and (d) display the magnified images of the same QD pointed by an arrow in the image (a). (e) The intensity profile is plotted, showing the intensity variation along the [220] zone axis marked by the yellow line. The profile was acquired by a free-software "Digital Micrograph, GATAN, Inc.".



Figure S4. (a) BF- and (b) HAADF-STEM images of the specimen E. The (200), (220) and (111) lattice spacing in bulk crystalline Si are 2.7Å, 1.9Å and 3.1Å, respectively. (c) A magnified image of a Si QD pointed by an arrow in the image (a). (d) (e) Corresponding intensity profiles for yellow and violet line traces in the image (c), showing the intensity variation along the [220] zone axis. The profiles are acquired by a commercial software "Digital Micrograph, GATAN, Inc."



Figure S5. (a) BF- and (b) HAADF-STEM images of the specimen G. The (200), (220) and (111) lattice spacing in bulk crystalline Si are 2.7Å, 1.9 Å and 3.1Å, respectively. Both (c) and (d) display the magnified images of the same QD pointed by an arrow in the image (a). (e) The intensity profile is plotted, showing the intensity variation along the [111] zone axis marked by the yellow rectangle. The profile was acquired by a free-software "Digital Micrograph, GATAN, Inc.".



Figure S6. (a) Representative Raman spectra of the Si QD specimens with different diameters. (b) Calculated Raman shift with bond-polarizability model (open circles) and the correlation length model (open triangles), respectively. The closed circles are the Raman shift of our experimental results.

Figure S6 shows a summary of Raman study for Si QD specimens with different size. The panel (a) shows the Raman spectra for the specimens with representative visible-PL colors. The spectra were recorded in the $\Phi 10$ -µm focused area of a 532-nm laser with a power density of 9 kW/cm². This power density is too low to influence on the spectral shape and position, which are due to local thermal heating (7,8). For bulky Si, the optical phonon, which is the Raman active mode due to its zero momentum, occurs at the center of the Brillouin zone (q = 0) to give a sharp peak at a Raman shift of 520 cm⁻¹. According to the previous studies, the frequency downshift and the spectral broadening occur for QDs that are miniaturized to a diameter of ~20 nm because the selection rule with k = 0 for the first-order Raman scattering is relaxed and phonon scattering is no longer limited to the center of the Brillouin zone (9,10). The spectral redshift and broadening are enhanced upon further reduction of the QD size as shown in the Panel (b). It has been widely recognized that the size-dependence of the Raman spectra is described by a theoretical model that quantizes the phonon confinement (11). There are two representative models expressed by:

$$\Delta \varpi (\mathbf{D}) = -A[\frac{a}{D}]^{\gamma} \qquad (3)$$

where $\Delta \varpi$ (D) is the Raman shift as a function of the diameter (D), "*a*" is the lattice constant of diamond cubic Si (5.43 Å), and A and γ are the fitting parameters. For example, A = -47.41 cm⁻¹ and γ = 1.44 for the bond-polarizability model, and A = -97.462 cm⁻¹ and γ = 1.39 for the correlation length model (*12,13*). As shown in the Panel (c), the experimental plots for two specimens (*d* = 5 nm and 7 nm), which serve as the standard, can be reproduced by the correlation length model, whereas those for specimens A–H deviate from the predictions based on the models. Instead, the downshifting behavior, which is more noticeable for a diameter smaller than 1.7 nm, depicts another curve as a function of size. Raman spectra of the specimens A–H are centered at 489–495 cm⁻¹ as seen in the Panel (a), and are sufficiently broad to cover the Raman bands that are attributed to the amorphous (~480 cm⁻¹) and crystalline structures.

The Raman study suggests that small Si QD (d < 2 nm) adopts a local-lattice-symmetry unlike larger Si nanocrystals (d > -5 nm) where a long-range order of the diamond cubic crystalline state is maintained across the entire particle, consistent with the previous study (2). Interestingly, we see a size-dependent shift of the Raman peaks to the lower frequency side as the size decreases even in the 1.1–1.7 nm regime. This is possibly explained by the force constant, which is regarded as the strength of the spring in a ball-spring model for molecular vibration, for the amorphous-like structure, which is smaller than that for the crystalline structure. Since the surface of Si QD is highly distorted (as confirmed by the HR-TEM observation), the ratio of the amorphous-like (surface) to the crystalline (core) configuration increases with the reduction in diameter. Consequently, we see the decreasing trend might be observed for the force constant with a size reduction, which is proportional to the Raman shift. The results obtained from Raman study is also consistent with those of XRD and STEM studies.

SI 2.4 SAXS study

XRD linewidth is generally determined by the combination of crystalline size and lattice strain. Williamson-Hall method is a conventionally used to estimate the both parameters from the diffraction linewidths. Using this method, the estimated diameters are given in the inset of Figure S2c for each specimen. The diameters are somewhat smaller than the values measured by SAXS due to anisotropic peak broadening, which also reflects crystallographic strain. Figure 1(d) shows the size distribution profiles obtained by SAXS for the specimens with typical PL colors. The SAXS profiles of specimens G and H have tails indicating the presence of 2–4 nm of QDs for





Figure S7. (a) Size-distribution patterns of the Si QD specimens A, D, E, G and H estimated by SAXS measurement. (b) The SAXS profiles of the experimental plots (red curves) could be reproduced by the calculated curves (blue) that consist of three components (aqua, orange and green curves), respectively.

The two-dimensional SAXS patterns recorded at room temperature were analyzed by a NANO solver software of Rigaku. We chose a sphere model of the software. The simulated profiles (shown by blue curves) are generated by the equations (3) and (4) according to the literature.³⁸

 $I(q) = |F(q)|^2 S(q)$ (3) where q is the scattering vector, I(q) is scattering intensity, and F(q) is the form factor and S(q) is the structure factor. In our case, the S(q) could be close to $S(q) = 1.^{39}$

For spherical particles with a radius of R of the QD, the form factor is expressed as $[F(q, R)] = \Delta \rho \frac{4\pi \{\sin (qR) - qR \cos(qR)\}}{a^3}$ (4)

The best profiles indicated by blue-curves were obtained for the case that the residual between the raw (red-curve) and simulated profiles are the lowest. The best simulations compose of three components described with aqua, orange and green curves in each graph.



Figure S8. Normalized PL spectra at different excitation ranging between 390 nm and 435 nm at 15 nm interval. This figure demonstrate that PL spectral shape and peak position are independent of excitation wavelength, and remains unchanged. **NOTE**:

The size dispersity of QDs was examined by measuring the PL spectra at different excitations. For this purpose, we prepared another specimen of Si QD that exhibits a green emission. The observed PL spectra, which were collected with different excitation wavelengths from 390 to 435 nm in 15-nm increments, seem to duplicate each other in terms of shape, fwhm, and peak position. Therefore, we confirmed that the green emission originating from the same upper energy level of the optical gap has a very narrow size distribution, suggesting a same PL origin for specimens A-E also (14).

SI 2.5 FTIR study

The specimens A-H were characterized by Attenuated Total Reflection Fourier transform infrared (ATR–FTIR) spectroscopy. The spectra exhibit prominent features centered at ca. 2098 cm⁻¹, and a doublet in the range 910–845 cm⁻¹. The peak near 2098 cm⁻¹ is attributed to the SiH_x stretching mode (*15*). The doublet is comprised of two sets of absorption peaks. The first set, which is centered at 895 cm⁻¹, is attributed to the SiH₃ degenerate deformation and the SiH₂ scissoring modes. The second set, which is centered at 859 cm⁻¹, is assigned to the SiH₃ symmetric deformation and the SiH₂ wagging modes (*16*). The O–Si–O stretching band at 1050 cm⁻¹ implies the presence of surface oxide species. The ratio of the integrated absorption intensity of the Si–H vibration divided by that of the O–Si–O vibration falls within the range of 1.5–3.0 and is independent of the Si QD size, suggesting that most of the surface Si atoms are terminated with hydrogen atoms.



Figure S9. ATR-FTIR spectra for the Si QD specimens A-H.



Figure S10. Plots of $F(R_{\infty})^2$ versus photon energy for the ncSi:H specimens A, B, C and D. Optical absorption peak relatively shifts to high photon energy with reduction in size of QD.



Figure S11. PL bands fitted by a single Gaussian for the specimens A-H. The estimated values of PL FWHM are obtained from the result of the fitting.

SI 3. Room-temperature optical properties of Si QD specimens

SI 3.1 Stability of PL properties in different environments



Figure S12. Time-dependent PL spectra of specimens of Si QD peaking at (a) 555 nm and (b) 576 nm. We used two mother samples emitting PL spectra peaking at 555 nm and 576 nm. Each was divided into six specimens. One was used for PL measurement for 0 day, but the rest were move into the Ar-filled glove box of $O_2 < 1$ ppm and $H_2O < 1$ ppm, and stored there prior to the PL measurement. Surprisingly, the PL QYs were unchanged even after one year.



Figure S13. PL spectra of the specimen C ($\lambda_{em} = 551$ nm) that is exposed to ambient air for 0, 9 and 21 days.

NOTE:

Oxidation of QD surface results in not only a reduction of PLQY but also a broadened spectrum, spectral tailing on the lower energy side, and a small PL peak shift to blue because of size reduction of crystalline Si.

SI 3.2 Increasing PLQYs as QD diameters decrease



Figure S14. (a) Changes of absolute PLQYs as a function of excitation wavelength for the specimens A-H. (b) PLQYs versus PL peak in the range between 500 and 1100 nm for Si QD samples prepared in the present study and literatures. The increasing trend of PLQY is explained as a result of the quantum confinement effect that is strengthened with decreasing diameter of QD. The PLQYs of our specimens A-H are high enough to match the prediction from the PLQYs of NIR emitting Si QD specimens. Refs. (Blue circle) Hessel, et al., Chem. Mater. 2012, 24, 393. (Green circle) Ghosh et al., J. Phys. Chem. C 2018, 122, 6422. **NOTE**:

In this study, the specimens A–H in the solid form, which were powders placed in short columnshaped cuvettes (Φ 20 mm) of quartz glass, were measured by the standardized integrating-sphere method for accuracy of the measured values and to avoid the solvent effect on the PLQY (17,18). The QC effect is strengthened as the crystalline size of the semiconductors is reduced. Similarly, the PL peak shifts on the higher energy side and PLQY increases. Panel (a) plots the PLQYs of specimens A–H measured against different excitation wavelengths. The observation of PLQYs of 10% or higher is consistent with the reported size-dependent trends measured for the red–NIR emitting Si QD specimens (Figure S14b).



Figure S15 (a) ATR-FTIR spectra and (b) PLQYs of the specimen C (λ_{em} =551 nm) with different amount of surface oxide. For oxidation, the specimen C was divided two samples. Each sample mounted on the ATR-FTIR holder and in the cuvettes of quartz glass was placed at ambient conditions. Then, the samples were subjected to the estimation of PLQYs and the ATR-FTIR analysis at a regular interval. (a) The ratio of integrated absorption intensity of Si-H vibration

divided by that of O-Si-O vibration increases with time for duration the specimen was left in air, leading to the decline of PLQY. (b) The variation in the absolute PLQYs versus the ratio of Si-H_x to O-Si-O content of the sample C (λ_{em} =551 nm) measured using ATR-FTIR spectrometer. The intensity and total area of the absorption peak assigned as O-Si-O bonds increased as a function of time. (b) The variation in the absolute PLQYs versus the ratio of Si-H_x to O-Si-O content of the sample C measured using ATR-FTIR spectrometer. The intensity and total area of the absorption peak assigned as O-Si-O bonds increased as a function of the sample C measured using ATR-FTIR spectrometer. The intensity and total area of the absorption peak assigned as O-Si-O bonds increased as a function of time.

NOTE:

The change in the bonding-state of the QD surface as the oxidation time increases was measured in regular intervals on ATR-FTIR and the PLQY was estimated. According to the ATR-FTIR spectra in the Panel (a), the intensity of the absorption peak assigned to the Si–O–Si vibration increases with time while the absorption intensity of the Si–H vibration decreases, indicating a monotonically increase in shell thickness of SiO_x. The Panel (b) shows a typical result of the declining QY of the PL band peaking at 551 nm as the oxidation of the QD surface increases. A strong dependence of PLQY on the ratio of the integrated absorption intensity of Si–H vibration divided by that of O–Si–O vibration is observed. The surface oxide probably works as a nonradiative channel for photoexcited carriers, resulting in a decrease in PLQY. Oxidation results in not only a reduction of PLQY but also a broadened spectrum, spectral tailing on the lower energy side, and a small PL peak shift to blue (Figure S13). In contrast, such a change of PL properties has never happened for Si QD specimens when they stored in argon-filled glove box (Figure S12).

SI 3.3 Effective mass approximation (EMA)

The effective mass approximation (EMA) is expressed by (19):

$$E(d) = E_g + \frac{h^2 \pi^2}{2d^2} \left[\frac{1}{m_{e^*}} + \frac{1}{m_{h^*}} \right] - \frac{1.786e^2}{\epsilon_r d} \quad (5)$$

where *d* is the QD diameter, e is the electron charge, and ε_r is the relative permittivity of Si (11.68). m_e^* , m_h^* , and m_0 are the effective masses of an electron (0.19 m_0), hole (0.286 m_0 , 0.49 m_0 or 0.57 m_0), and the free-electron mass (19-21), respectively.

The experimental plots of E(d) for the specimens of QDs with diameters more than 1.7 nm was reproduced by theoretical curved of EMA while the plots of E(d) for the specimens of QDs with diameters smaller than 1.7 nm could not be reproduced with the theoretical curve. Furthermore, the increasing trend of PL peak energy for the Si QD (d < 1.7 nm) does not overestimated EMA. In a situation where EMA is more than the experimental curve, the role of surface oxide on the PL peak energy has been extracted to bridge the differences in the previous literatures (3,22). A classic case of the oxide at work is reported by Wolkin *et al.* They postulate a case where the Si=O related radiative recombination center dominates the PL origin (22). Slowly increasing trends in a monotone are commonly reported for various forms of fluorescent Si with oxide (3). However, our experimental plot does not depict a monotonous increasing trend. Therefore, it makes sense to discuss that our experimental plots of E(d) has two different trends of E(d) that are dependent of QD size.

SI 3.4 Time-resolved PL spectroscopic study

The slow decay profiles, I(t), are approximately fitted by a biexponential function with time constants of 5.3 and 19 μ sec for the orange PL and 9.9 and 30 μ sec for the red PL. In contrast, we have not observed any measurable long-lived PL signal on the μ sec-msec time-scale for specimens A, D, and E. Instead, the specimens A-E exhibit lifetimes that are five orders of magnitude smaller than those in orange- and red-emitting QDs as evidenced in Figure S16 (see also Figure 3 and Table 1).



Figure S16. PL decay curves of the representative Si QD specimens. The inset shows the enlarged time range of 1-40 nsec for the decay curves of the specimens A, D and E. The excitation wavelength is 368 nm, and detection wavelengths are 535 nm (A), 566 nm (D), 574 nm (E), 603 nm (F) and 701 nm (H).

SI 4. Low-temperature PL spectroscopic analysis of the Si QD specimens

We prepared four additional specimens with different PL colors. Next, their PL spectra were measured as a function of temperature from cryogenic to 300 K while strictly controlling temperatures fluctuations within ± 0.1 K. The specimens were cooled to 2 K and then heated back to 298 K without any apparent damage to the PL properties, including the spectral shape, intensity, position and QY (see Figure S17).



Figure S17. PL spectra peaked at 556 nm for the Si QD specimen before and after temperaturedependent PL spectroscopic measurement. No change in spectral features including shape, PLQY and peak position indicates no change of electronic structure that determines the optical transition for light emission before and after rising and falling temperature. Therefore, we discussed the photophysical meaning of PL properties as a function of temperature.

SI 4.1 Decreasing behavior of PL intensity as a function of temperature

Figure 4e exhibits the integrated values of the PL intensity at each temperature, which are normalized with respect to a value at 300 K. The plots of the PL intensity exhibit a monotonically decreasing function for each specimen. It is well known that possible processes resulting in carrier relaxation in QDs include radiative relaxation, Auger nonradiative scattering, and thermally activated trapping in the surface and/or defect/impurity states. In our experiments, Auger scattering is ruled out due to the very low excitation density. Therefore, the nonradiative relaxation is most likely the contributing factor. On the assumption that the decreasing trends appear due to thermal activation of nonradiative trapping channels, the red-luminescent specimen with a more rapid decline in the PL intensity possesses more nonradiative channels, consistent with the result that the peak PLQY of the specimen H is the lowest. In general, the study of the evolution of the PL intensity with the temperature gives an indication to know whether further increase of PLQY will be expected or not. Jing et al. investigated the relationship between PLQYs and temperaturedependent nonradiative relaxation processes in the CdSe-based core/shell QDs with changing the shell structures (23). In their work, the highest PLQY is obtained from the QD with a character of PL intensity that remains constant between cryogenic and room temperatures because of suppressed nonradiative recombination even at room temperature. According to this scenario, the decreasing trends of the PL intensity observed for all the specimens in Figure 4e presents hope for further increasing the PLQY due to pathway inhibition of nonradiative relaxation and recombination.



Figure S18. Arrhenius plot of the PL intensity for the 550-nm band, 567-nm band and 733-nm band and the fitted curves.

SI 4.2 Temperature-dependent PL peak energy

Studies on the temperature-dependent PL peak energy offer creditable advice to discuss whether the recombination for the emission is dominated by the QC effect (2,24-26). For QDs of semiconductors, the temperature dependence of the PL peak energy empirically follows Varshni's law, which considers the cumulative effect of the mechanisms for lattice expansion/shrinkage and electron-phonon coupling. This law is also valid and fits the decreasing trend of the PL peak energy as a function of temperature for not only Si QD but also the SiQD/SiO₂ core/shell structure (2,26). Varshini's relation modified with an extra corrected term for the QC energy, as expressed by:

$$E_g^{nc}(T) = [E_g^{bulk}(0) + E_g^{conf}] - \frac{\alpha T^2}{\beta + T} \quad (6)$$

where α is the temperature coefficient (i.e., dE_g/dT), β is close to the Debye temperature, E_g^{bulk}(0) represents the bulk bandgap of Si obtained at 0 K (=1.17 eV), and E_g^{conf} is the value of the QC energy corresponding to the difference in energy between the PL peak and the bulk bandgap at 298 K (see Table S2 for the estimated values of α , β and E_g^{conf}). In Table S2, we see an increasing trend of α with size reduction, possibly due to the confinement of carriers which is strengthened more and more with size reduction.

| PL peak Parameter | 550 (nm) | 567 (nm) | 585 (nm) | 733 (nm) |
|----------------------|--------------------------------|--------------------------------|--------------------------------|------------------------------|
| E ₀ [eV] | 1.17 | 1.17 | 1.17 | 1.17 |
| α [eV/K] | 8.0±0.09 × 10 ⁻⁴ | $7.6 \pm 0.08 \ 	imes 10^{-4}$ | $7.1 \pm 0.09 \ 	imes 10^{-4}$ | $6.9{\pm}0.08 otin 10^{-4}$ |
| β [K] | 620±8 | 622±7 | 624±8 | 630±7 |
| E _c [eV] | 1.20±0.002 | 1.13±0.002 | 1.05±0.002 | 0.595±0.002 |

Table S2. Fitting parameters of the PL peak energy as a function of temperature (Figure 4f) based on Eq. (6).

SI 4.3 Other Si QDs that exhibit the PL peaking in the shorter-visible wavelength range

A few papers have reported fluorescence colors in the short-wavelength visible region. Korgel *et al.* used a single-dot spectroscopic technique to capture a very narrow PL spectrum peaking at \sim 566 nm (*14*). Veinot *et al.* reported that prolonged hydrofluoric-etching of freestanding SiO₂/Si

composites results in green and yellow fluorescent solution specimens (27) Gregorkiewicz and coworkers reported a short-living visible and weak PL band (i.e., F-band) in the green-yellow wavelength range, which appears together with a longer-living and strong red-NIR PL band (28). Blue-aqua emitting specimens can be prepared via the electronic reduction of silicon tetrahalide (29-32), but these PL emissions exhibit a nanosecond PL lifetime but their crystallographic structures are unknown. Furthermore, they are oily product, which do not permit to be mounted as an optically active layer for device fabrication (29,30).

Other efforts on tunability of the PL spectra in the 530-580 nm region involves surface engineering that takes advantage of the surface state or energy transfer for light emission (33-37)

Movie S1.

Typical movie for the green emitting Si QD specimen.

Movie S2.

Typical movie for the green-yellow emitting Si QD specimen

Movie S3.

Typical movie for the yellow emitting Si QD specimen

Movie S4.

Typical movie for the red emitting Si QD specimen

References

1. J. T. Harris, J. L. Hueso, B. A. Korgel, Hydrogenated amorphous silicon (a-Si:H) colloids. *Chem. Mater.* **22**, 6378-6383 (2010).

2. B. Ghosh, *et al.*, Origin of the photoluminescence quantum yields enhanced by alkanetermination of freestanding silicon nanocrystals: temperature-dependence of optical properties. *Sci. Rep.* **6**, 36951 (2016).

3. J. P. Wilcoxon, G. A. Samara, P, N. Provencio, Optical and electronic properties of Si nanoclusters synthesized in inverse micelles. *Phys. Rev. B* **60**, 2704 (1999).

4. B. Lee, *et al.*, Quasi-direct optical transitions in silicon nanocrystals with intensity exceeding the bulk. *Nano Lett.* **16**, 1583-1589 (2016).

5. M. G. Panthani, *et al.*, Graphene-supported high-resolution TEM and STEM imaging of silicon nanocrystals and their capping ligands. *J. Phys. Chem. C* **116**, 22463-22468 (2012).

6. Z. Ni, *et al.*, Size - Dependent structures and optical absorption of boron - hyperdoped silicon nanocrystals. *Adv. Opt. Mater.* **4**, 700-707 (2016).

7. Y. Duan, J. F. Kong, W. Z. Shen, Raman investigation of silicon nanocrystals: quantum confinement and laser - induced thermal effects. *J. Raman Spect.* **43**, 756–760 (2012).

8. D. M. Sagar, Quantum confined electron–phonon interaction in slicon nanocrystals. *Nano Lett.* **15**, 1511-1516 (2015).

9. C. M. Hessel, Raman spectroscopy of oxide-embedded and ligand-stabilized silicon nanocrystals. *J. Phys. Chem. Lett.* **3**, 1089-1093 (2012).

10. I. Doan, I., M.C. M. Sanden, Direct characterization of nanocrystal size distribution using Raman spectroscopy. *J. Appl. Phys.* **114**, 134310 (2013).

11. W. Ke, X. Feng, Y. Huang, The effect of Si-nanocrystal size distribution on Raman spectrum. *J. Appl. Phys.* **109**, 083526 (2011).

12. P. M. Fauchet, I. H. Campbell, *Crit. Rev. Solid State Mater. Sci.* Raman spectroscopy of low-dimensional semiconductors. **14**, S79 (1988).

13. J. Zi, et al., X., Raman shifts in Si nanocrystals. Appl. Phys. Lett. 69, 200 (1996).

14. D. S. English, *et al.*, Size tunable visible luminescence from individual organic monolayer stabilized silicon nanocrystal quantum dots. *Nano Lett.* **2**, 681-685 (2002).

15. D. J. Michalak, *et al.*, Nanopatterning Si(111) surfaces as a selective surface-chemistry route. *Nat. Mater.* **9**, 266-271 (2010).

16. J. Holm, J. B. Roberts, Surface chemistry of aerosolized silicon nanoparticles: evolution and desorption of hydrogen from 6-nm diameter particles. *J. Am. Chem. Soc.* **129**, 2496-2503 (2007).

17. A. M. Rossi, T. E. Murphy, V. Reipa, Ultraviolet photoluminescence from 6H silicon carbide nanoparticles. *Appl. Phys. Lett.* **92**, 253112 (2008).

18. M. Jones, *et al.*, Photoenhancement of luminescence in colloidal CdSe quantum dot solutions. *J. Phys. Chem. B* **107**, 11346-11352 (2003).

19. C. M. Hessel, *et al.*, Synthesis of ligand-stabilized silicon nanocrystals with size-dependent photoluminescence spanning visible to near-infrared wavelengths. *Chem. Mater.* **24**, 393-401 (2012).

20. M. S. Hybertsen, Absorption and emission of light in nanoscale silicon structures. *Phys. Rev. Lett.* **72**, 1514 (1994).

21. S. Ossicini, L. Pavesi, F. Priolo, "Light emitting silicon for microphotonics", Springer Verlag Berlin Heisenberg (2003).

22. M. V. Wolkin, *et al.*, Electronic states and luminescence in porous silicon quantum dots: the role of oxygen. *Phys. Rev. Lett.* **82**, 197-200 (1999).

23. P. Jing, *et al.*, Temperature-dependent photoluminescence of CdSe-Core CdS/CdZnS/ZnSmultishell quantum dots. *J. Phys. Chem. C* **113**, 13545–13550 (2009).

24. C. Ji, *et al.*, Temperature-dependent photoluminescence of Ag₂Se quantum dots. *J. Phys. Chem. C* **119**, 13841-13846 (2015).

25. P. Yu, X. Wen, Y. Toh, J. Tang, Temperature-dependent fluorescence in carbon dots. *J. Phys. Chem. C* **116**, 25552-25557 (2012).

26. H. Rinnert, O. Jambois, M. Vergnat, Photoluminescence properties of size-controlled silicon nanocrystals at low temperatures. *Appl. Phys. Lett.* **106**, 023501 (2009).

27. C. M. Hessel, E. J. Henderson, J. G. C. Veinot, Hydrogen silsesquioxane: a molecular precursor for nanocrystalline Si–SiO₂ composites and freestanding hydride-surface-terminated silicon nanoparticles. *Chem. Mater.* **18**, 6139-6146 (2006).

28. J. Valenta, *et al.*, On the origin of the fast photoluminescence band in small silicon nanoparticles. *New J. Phys.* **10**, 073022 (2008).

29. N. Shirahata, S. Furumi, Y. Sakka Micro-emulsion synthesis of blue-luminescent silicon nanoparticles stabilized with alkoxy monolayers. *J. Cryst. Grow.* **311**, 634-637 (2009).

30. J. Zou, R. K. Baldwin, K. A. Pettigrew, S. M. Kauzlarich, Solution synthesis of ultrastable luminescent siloxane-coated silicon nanoparticles. *Nano Lett.* **4**, 1181-186 (2004).

31. A. Shiohara, *et al.*, Chemical reactions on surface molecules attached to silicon quantum dots. *J. Am. Chem. Soc.* **132**, 248–253 (2010).

32. Y. Su, X. Ji, Y. He, Water-dispersible fluorescent silicon nanoparticles and their optical applications. *Adv. Mater.* **28**, 10567–10574 (2016).

33. Q. Li, *et al.*, Silicon nanoparticles with surface nitrogen: 90% quantum yield with narrow luminescence bandwidth and the ligand structure based energy law. *ACS Nano* **10**, 8385–8393 (2016).

34. L. Wang, *et al.*, Ultrafast optical spectroscopy of surface-modified silicon quantum dots: unraveling the underlying mechanism of the ultrabright and color-tunable photoluminescence. *Light: Sci. Appl.* **4**, e245 (2015).

35. M. Dasog, *et al.*, Size vs surface: tuning the photoluminescence of freestanding silicon nanocrystals across the visible spectrum via surface groups. *ACS Nano* **8**, 9636-9648 (2014). 36. Q. Li, *et al.*, *J. Am. Chem. Soc.* **135**, 14924-14927 (2013).

37. L. M. Wheeler, N. R. Neale, T. Chen, U. R. Kortshagen, Hypervalent surface interactions for colloidal stability and doping of silicon nanocrystals. *Nat. Commun.* **4**, 2197 (2013).

38. A. Baksi, *et al.*, Size evolution of protein-protected gold clusters in solution: a combined SAXS–MS investigation. *J. Phys. Chem. C* **119**, 2148–2157 (2015).

39. S. Manet, Structure of micelles of a nonionic block copolymer determined by SANS and SAXS. J. Phys. Chem. B 115, 11318–11329 (2011).