Electronic Supplementary Information (ESI)

Deep-Blue Amplified Spontaneous Emission and Lasing in Colloidal Silicon Nanoclusters

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Experimental Procedures

Synthesis of decane-terminated silicon nanoclusters

2.0 mL of 1-decene was treated with sodium sulfate and collected in a Schlenk flask. The Schlenk flask was then subjected to a freeze-pump-thaw (FPT) cycle on a grease-free vacuum line for at least 30 min using a Dewar flask filled with liquid nitrogen to remove dissolved oxygen. Finally, they were stored under an Ar atmosphere. These procedures were performed at room temperature and atmospheric pressure on a grease-free glass vacuum line.

The hydrogen-terminated silicon wafer was placed in a quartz cell and purged several times with Ar gas. The quartz cell was then filled with the FPT-treated 1-decene and laser ablation was performed in a liquid environment. In the cell, the target silicon was ablated with an Nd:YAG pulsed laser for 30 min (λ= 355 nm, power density: 1.0 J/cm^2, pulse width: 4-6 ns, repetition rate: 10 Hz). After 30 min, unreacted 1-decene was removed by rotary evaporation. Afterwards, the decane-terminated silicon nanoclusters were purified by high-performance liquid chromatography (HPLC, Japan Analytical Industry, Japan). The unreacted 1-decene was completely separated from the nanocluster sample. and the purified nanoclusters were redispersed in dichloromethane.

Characterization

High-resolution transmission electron microscopic (HR-TEM, JEOL-JEM 2100) was operated at 200 V to obtain the nanostructure images. The Scanning TEM (STEM) mode of the JEOL JEM-ARM200F was operated at 200 kV. The STEM observations could reveal nanostructures with sub-angstrom resolution. Dark-field images were acquired using a high-angle annular dark-field (HAADF) detector. A low-pass filter was applied to the images for noise removal. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were acquired using an FTIR-4100 (JASCO, Japan). Optical absorption and photoluminescence (PL) properties of the nanoclusters were measured with dichloromethane solution of the nanoclusters.

Optical absorption spectra were recorded using a UV-vis spectrophotometer (JASCO V-650, Japan). PL measurement was carried out using a modular double grating Czerny–Turner monochromator and an iHR 320 emission monochromator (1200 lines per mm of gratings) coupled to a photomultiplier tube (PMT) on a NanoLog Horiba Jovin Yvon spectrofluorometer with a 450 W xenon arc lamp. The spectral resolution of the system is around 0.3 nm. To avoid scattered excitation lights, a cut filter for 395 nm-light was placed in front of the monochromator-PMT setup. The absolute PL quantum yield (QY) was 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. Time-resolved fluorescence decay profiles were obtained with a time-correlated single photon counting (TCSPC) lifetime spectroscopy system (NanoLog, Horiba Jovin Ybon, Japan), equipped with pulsed laser diodes (λ_{em}= 375 nm, average pulse width of 200 ps or less, frequency of 1 MHz) as an excitation light-source. The quality of the fit was assessed based on the R^2 value and visual inspection of the residuals. Specifically, the decay curve plotted with open circles in Fig. 1f could be fitted with biexponential function given by:

$$I(t) \approx B_1 exp\left[-\frac{t}{\tau_1}\right] + B_2 exp\left[-\frac{t}{\tau_2}\right]$$

where τ_1, and τ_2, and are the first and second components of the decay time, and B_1, and B_2 are the amplitudes of each component. The parameters obtained from the best-fit curves (statistical deviation, χ^2= 1.14) are summarized in the inset of Fig. 1g. The fit gave effective values in PL decay time of $\tau_1 =$ 10.5 and $\tau_2 =$ 4.2 nsec.

The average PL lifetime was calculated using the following equation:[1,2]

$$\tau_{avg} = \sum_{i=1}^{n} B_i \tau_i$$

In this calculation, the coefficients $B_1 = 0.52$ and $B_2 = 0.48$ were used, resulting in an average PL lifetime of 7.5 nsec.

References

1. Y. Altıntas, M. Y. Talpur, M. Ünlü and E. Mutlugün, J. Phys. Chem. C, 2016, 120, 7885–7892.

2. J. R. Lakowicz, Principles of fluorescence spectroscopy, Springer, New York, 3rd ed., 2006.

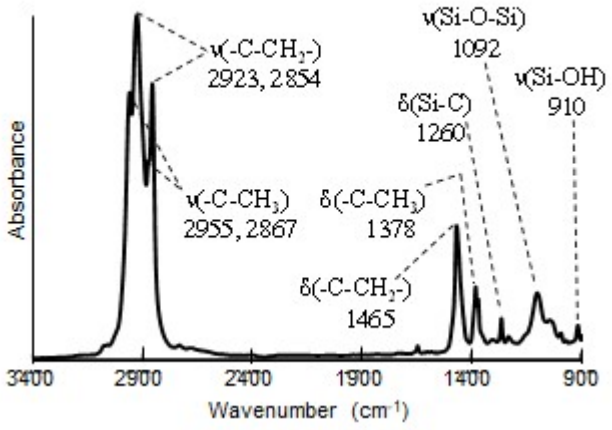

Fig. S1 ATR-FT-IR spectrum of the decane-terminated silicon nanoclusters.

NOTE: The observation of absorbances in the aliphatic C-H stretching region between 2850 and 2960 cm^{-1}, and the bending/scissoring region between 1350 and 1500 cm^{-1} indicates the presence of hydrocarbon chains.[3] The observation of a small peak appearing as a shoulder at 1260 cm^{-1} is attributed to the bending mode of the interfacial C-Si covalent linkage.[3] An absorbance peaking at 1092 cm^{-1} is attributed to O-Si-O linkages, suggesting the partial oxidation of nanocluster surface.

Reference

3. C.S. Yang, R. A. Bley, S. M. Kauzlarich. H. W. Lee and G. R. Delgado, J. Am. Chem. Soc. 1999, 121, 5191-5195.

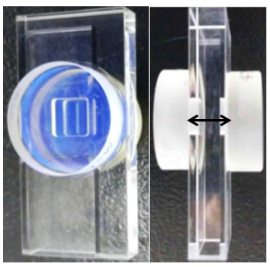

Fig. S2 A photograph of optical cavity of quartz glass cuvette with dielectric multilayer-coated mirrors on both sides. The double-ended arrows in the right photograph corresponds to 10 mm. This width works as an optical cavity length.

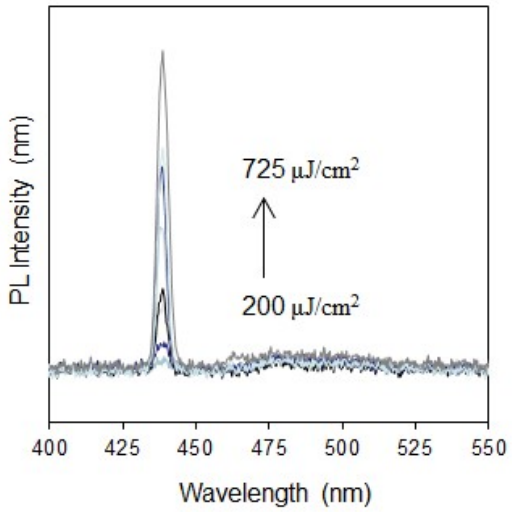

Fig. S3 Evolution of the PL spectra of silicon nanoclusters upon increasing the pumping density. The value of PL intensity.