Supporting Information for

Solid-State Synthesis of Colloidal Tin-Incorporated Silicon Nanocrystals

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Experimental Section

Materials. All chemicals were obtained commercially and used without further purification. Trimethoxysilane (TMOS, 95%), tin tetrachloride ($SnCl_4$, 99.9%), 1-dodecane (95%), and toluene (99%) were purchased from Aladdin Inc. Ethanol (EtOH, 99.7%) was purchased from Energy chemical Inc. Methanol (MeOH, ≥98%) and hydrogen nitrate (HNO_3, ≥98%) solution were purchased from Guangzhou Sci-Tech Co. Hydrofluoric acid (HF, 49% aqueous solution, electronic grade) was purchased from Macklin Inc.

Solid-state synthesis of tin-doped and tin-free silicon nanocrystals (Sn@Si and Ctrl NCs). 2.9 mL of TMOS (23 mmol) was weighed out in a nitrogen filled glovebox and transferred immediately into a 100 -mL Schlenk flask equipped with magnetic stirring under a nitrogen atmosphere. A predesigned amount of $SnCl_4$ was added to the flask to prepare Sn-doped precursor solution. For the preparation of the Sn/Si = 1:40 sample (atomic ratio), 67 µL (0.575 mmol) of $SnCl_4$ and 5 mL of methanol was added into the flask and mixed for 30 min under a continuous flow of nitrogen. After that, 5 mL of a diluted HNO_3 solution (0.05 mol/L) was added dropwise to initiate the hydrolysis. Within ~5 min, white flocculent precipitation was generated in the flask. The product was set still without mechanical stirring under a nitrogen atmosphere for 24 h. After the aging process, the product was first isolated from the residual liquid by vacuum filtration and subsequently transferred to a vacuum oven and dried for 24 h. ~2 g of the powder was then placed in a quartz reaction boat and moved to a high-temperature tube furnace (Lindberg, TF55035KC-1). The sample was heated from ambient to the predesigned peak temperature (e.g., 900°C) at 18°C/min in a slightly reducing atmosphere (5%

H_2 + 95% Ar). The sample was maintained at the processing temperature for 1h and then naturally cooled down to room temperature. The resulting black-brown powdery product was ground to fine powders and stored in a 20-mL vial in ambient condition for further use.

The control sample (Ctrl-SiNCs) is prepared following the same conditions without adding Sn species during the preparation of sol-gel product.

Liberation of Sn@Si NCs. ~0.2 g of the abovementioned finely ground product was placed in a polyethylene terephthalate beaker equipped with a Teflon-coated stir bar. 3 mL deionized water and 3 mL ethanol were added to the beaker and mixed under mechanical stirring to form a black brown suspension. Subsequently, 3 mL of a 49%-51% HF aqueous solution was added into the mixture under ambient conditions to initiate the etching process (**Caution! HF is highly hazardous and must be handled with extreme care**). The reaction was stirred at room temperature for 1 h. After that, 3*10 mL of toluene was added to the beaker to extract the hydride-terminated SiNCs (H-Sn@Si NCs), and the upper solution was transferred via a ~3-mL plastic pipette. After the extraction, ~100 mL of saturated $CaCl_2$ aqueous solution was added to the PVC beaker to neutralize the residual HF. The extracted solution was centrifuged at 7830 rpm for 10 minutes. After that, the solution was decanted, and the precipitant was redispersed in 1-dodecene (C12) for the next step.

Surface functionalization. 5 mL of C12 was transferred to a 100-mL Schlenk flask which was purged with nitrogen gas. Under a constant flow of nitrogen, 5 mL of the abovementioned freshly etched particle C12 solution was transferred to the flask. The reaction process was carried out at 190^{o}C for 12 h under a nitrogen atmosphere, yielding of a transparent orange solution. After cooling to room temperature naturally, 10 mL of the C12-functionalized Sn@Si

NCs (C12-Sn@Si NCs) solution was equally dispensed into two 50-mL centrifuge tubes. 30 mL of methanol was added to each centrifuge tube, yielding~40mL of cloudy light-yellow dispersion. The tubes were then centrifuged at 7800 rpm for 10 min. The supernatant was decanted, and the precipitate was redispersed in a minimal amount of toluene (~2 mL) and reprecipitated upon the addition of methanol. The redispersion/centrifugation/supernatant-removal procedure was repeated twice. Finally, the precipitate was redispersed in toluene for further use.

Transmission electron microscopy (TEM) characterizations. TEM imaging was performed using a FEI Talos F200s electron microscope operated at an accelerating voltage of 200 kV. The functionalized NCs were redispersed in toluene and drop-cast onto a 200-mesh carbon-coated copper TEM grid. The grid was dried in a vacuum oven at 25°C for 16 h to remove the residual solvent prior to imaging. All images were processed using ImageJ (software version: 1.52a).

Static-state photoluminescent properties of Sn@Si NCs. Excitation-emission matrix (EEM) and photoluminescence (PL) measurements were conducted using an FLS980 fluorescence spectrometer equipped with a Xenon lamp and monochromator (Edinburgh Instruments Ltd.). PL lifetime decay was measured using a 365 nm pulse diode laser excitation from a picosecond pulsed diode laser station (Edinburgh Instruments Ltd., EPL 365 nm). Absorption spectra were recorded using a UV3600 fluorometer (Shimadzu Inc.).

Powdery X-ray diffraction (PXRD) and X-ray photoelectron spectroscopic (XPS) measurements. PXRD patterns were measured using a Rigaku Miniflex 600 diffractometer

(Cu-Kα, λ = 1.5406 Å) operated at 45 kV and 15 mA. XPS analysis was performed using a Thermo Scientific K-Alpha XPS system with a monochromatic Al Kα X-ray source (1486.7 eV). Elemental spectra were acquired in constant analyzer energy mode at 100 eV. All spectra were internally calibrated using the C 1s peak at 284.8 eV. Data analysis was conducted using Casa XPS software (version V2.3.16.PR1.6, VAMAS).

Fourier transform infrared (FT-IR) and Raman spectroscopic measurements. FT-IR spectra were obtained using a Nicolet/Nexus-670 FT-IR spectrometer in ATR mode. As for Raman measurement, freshly etched H-Sn@Si NCs were isolated from the solution by centrifugation and then dried in a vacuum oven at 40 ℃ overnight, and transferred onto a sample window for Raman measurements using a PI TriVista CRS TR557 spectrometer. The samples were excited by a laser with wavelength of 532 nm and the laser power was intentionally maintained below 1 mW to minimize heating effects on the samples. The slit width was set at 50 μm, and a X50 objective with a numerical aperture (N.A.) of 0.9 was employed, resulting in a spectral resolution of ~1 cm^{-1}. Th spectra were calibrated using the Rayleigh scattering line for accuracy.

Inductively coupled plasma atomic emission spectroscopic (ICP-AES) measurements. ICP-AES measurements were performed using a PerkinElmer Optima 8300 ICP-AES spectrometer. 5 mg of the powder sample was dissolved in a mixed solution comprising 0.5 mL of HF solution (49%) and 0.75 mL of HNO_3 solution (98%), then diluted with deionized water to final volume of 25 mL. A 10 mL aliquot of the diluted solution was used for ICP-AES analysis.

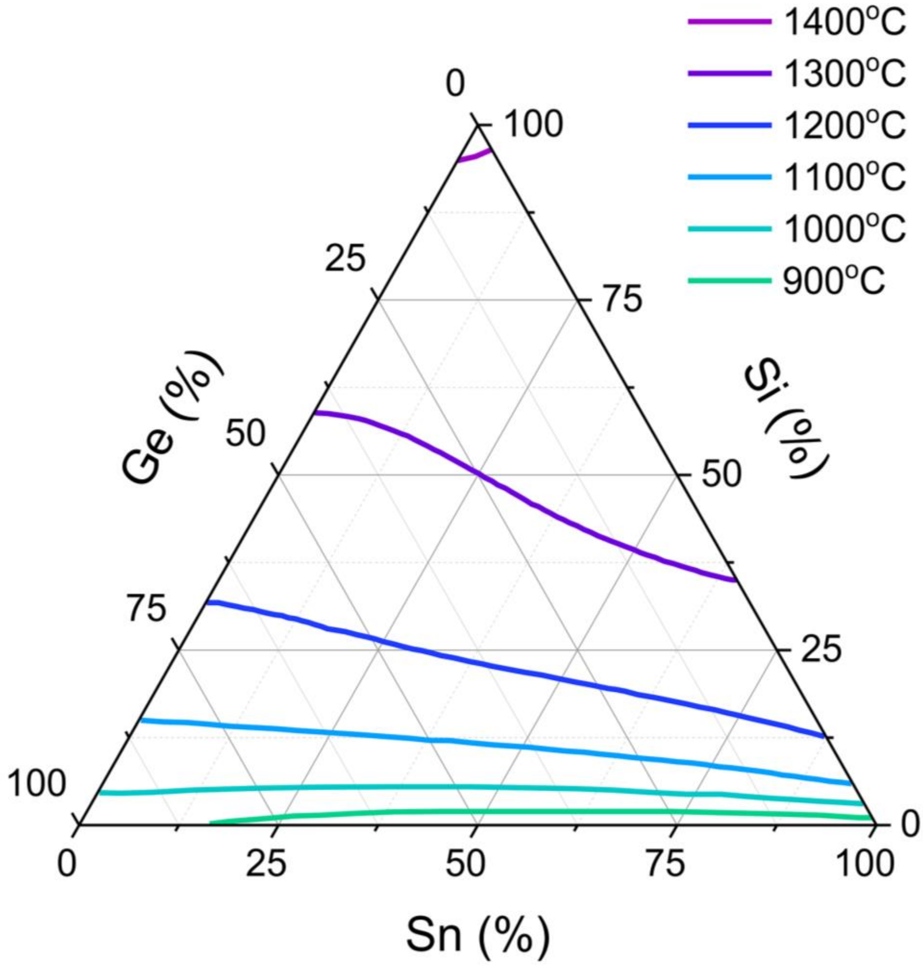

Figure S1. Calculated phase diagram of Si-Ge-Sn ternary system. The figure was adapted from the results reported by Fleurial and Borshchevsky. [1]

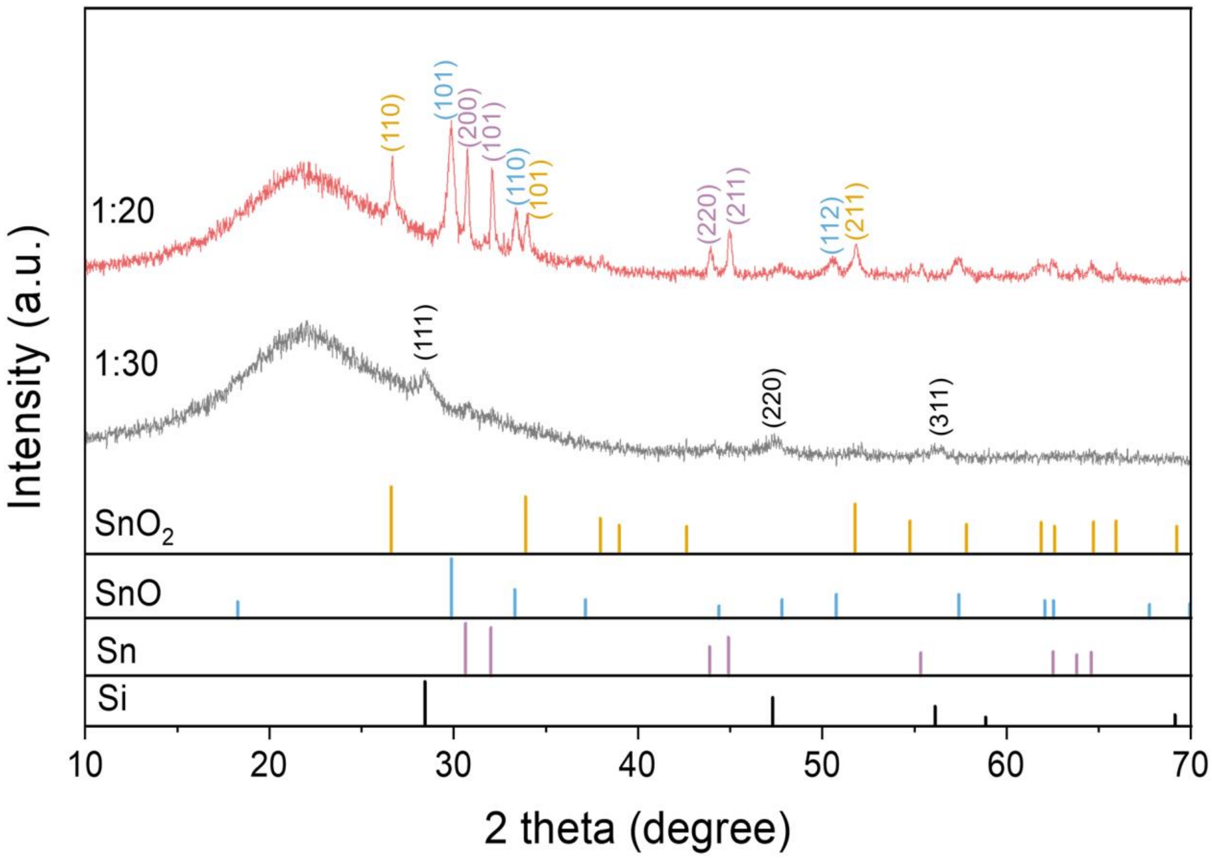

Figure S2. XRD results of Sn@Si NCs at higher Sn:Si ratios. JCDPS References: (Si) #27-1402, (Sn) #04-0673, (SnO) #06-0395, and (SnO_2) #41-1445.

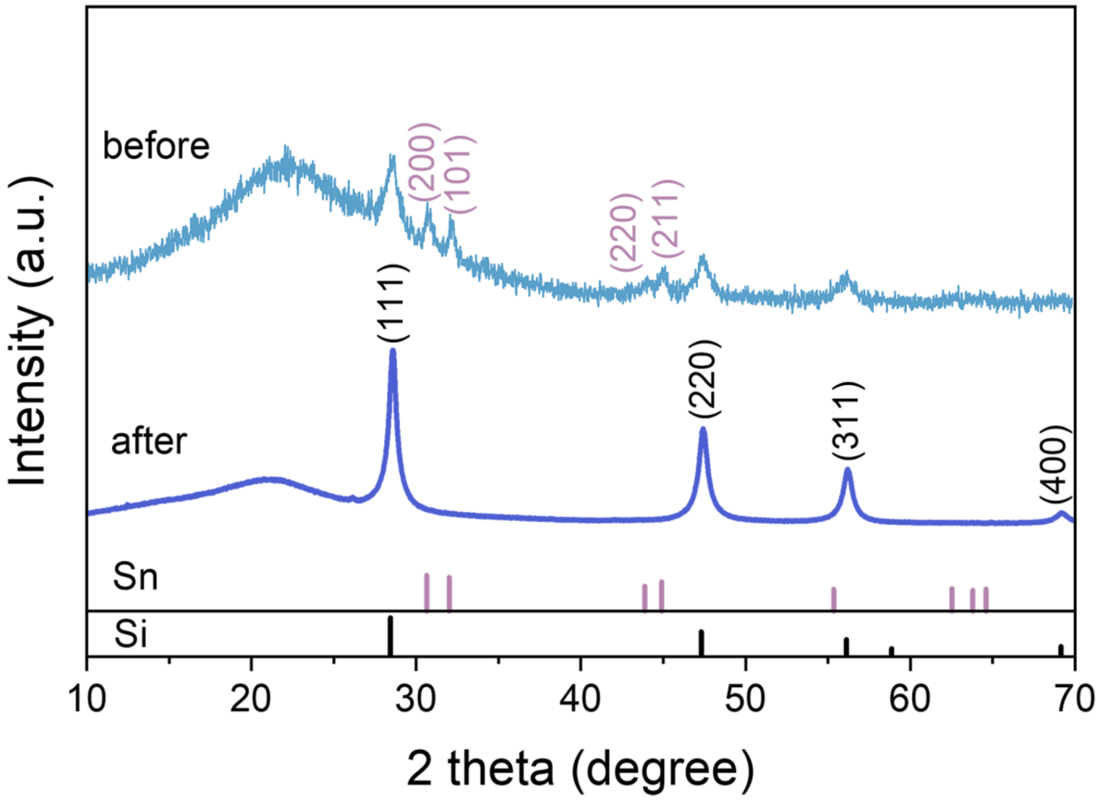

Figure S3. Comparison of XRD patterns of Sn@Si NC samples before and after HF-etching. JCDPS References: (Si) #27-1402 and (Sn) #04-0673.

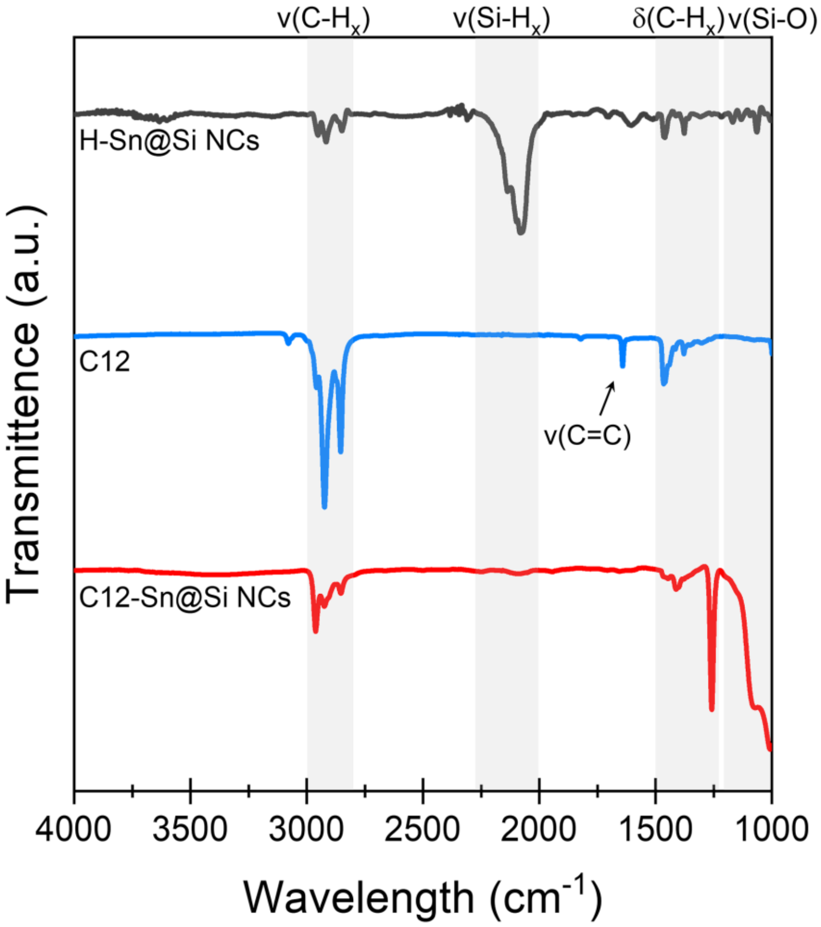

Figure S4. FT-IR spectra of hydride-terminated Sn@Si (H-Sn@Si) NCs, freestanding dodecene molecule (C12), and dodecyl-functionalized Sn@Si (C12-Sn@Si) NCs.

Table S1. ICP-AES results of the precursor, annealed Sn@Si NC, and HF-etched Sn@Si NCs (unit: mg/L).

Sample \ Element	Si	Sn
Blank	30.5	-
Sol-gel precursor	96.7	5.78
Annealed@900ºC	141	6.02
HF-etched	97.4	0.507

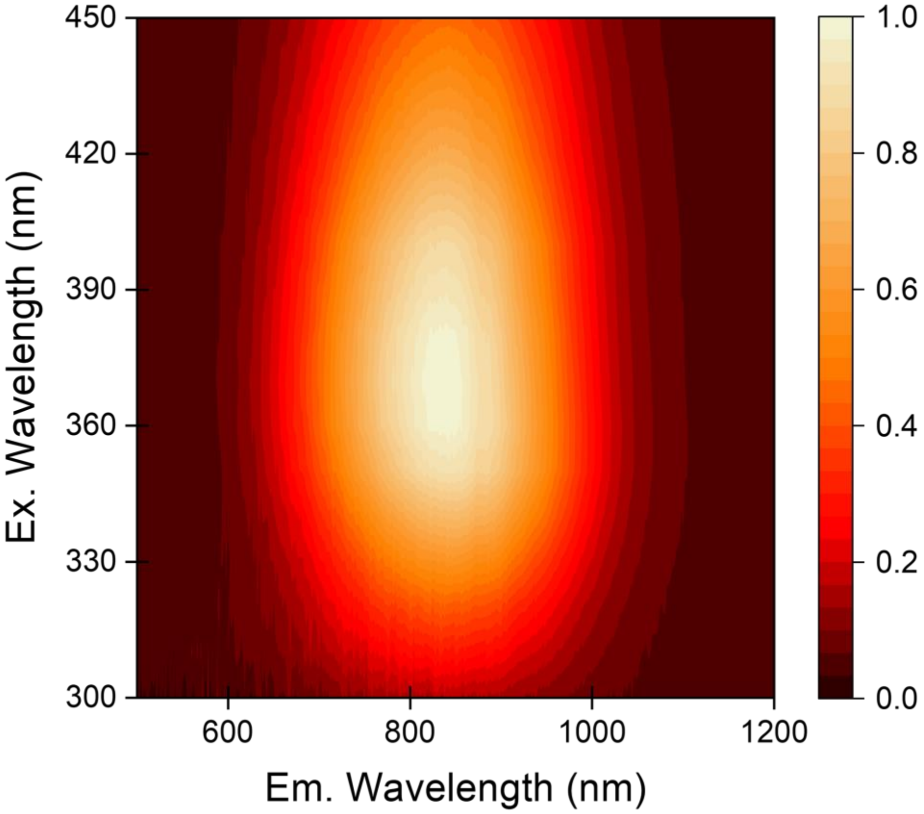

Figure S5. EEM spectra of the C12-functionalized Ctrl-Si NCs toluene solution.

Note S1. Details of the data analysis of PL lifetime decay fitting curves in Figure 4.

All time-resolved PL decay results were fitted using the following equation:

$$y(t)=y_0+A_1e^{-(x-x_0)/\tau_1}+A_2e^{-(x-x_0)/\tau_2}+\cdots+A_ne^{-(x-x_0)/\tau_n} \quad \text{(Equation 1)}$$

The average lifetime results were calculated using the intensity-weighted model as:

$$\tau_{ave}=\frac{A_1\tau_1^{2}+A_2\tau_2^{2}+A_3\tau_3^{2}+\cdots+A_n\tau_n^{2}}{A_1\tau_1+A_2\tau_2+A_3\tau_3+\cdots+A_n\tau_n} \quad \text{(Equation 2)}$$

The results of the data fitting are summarized in Tables S2 to S4 (see below).

Table S2. Summary of the fitting results of the PL lifetime decay values of the Sn@Si NC toluene solution shown in Figure 4d.

Sample	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ_{ave} (μs)
Sn@Si	62.5 (1.5%)	271.5 (39.8%)	641.7 (58.7%)	485.7
Ctrl	60.5 (9.4%)	185.1 (63.4%)	347.3 (27.2%)	217.5

Table S3. **Summary of the fitting results of the PL lifetime decay values of the Sn@Si NC toluene solution shown in Figure 4f.**

Temperature (K)	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ_{ave} (μs)
77	79.5 (0.8%)	614.9 (50.4%)	1222.1 (48.8%)	906.5
100	89.4 (0.9%)	511.3 (34.9%)	1045.7 (64.2%)	850.6
120	104.7 (1.6%)	573.7 (49.8%)	1124.6 (48.6%)	834.2
160	20.6 (0.2%)	361.0 (24.1%)	846.8 (75.8%)	728.6
180	143.5 (2.3%)	520.0 (60.6%)	1084.6 (37.1%)	720.8
200	118.2 (2.2%)	457.7 (49.4%)	916.3 (48.5%)	672.7
220	66.5 (1.2%)	412.4 (48.3%)	892.0 (50.5%)	650.7
240	120.3 (3.1%)	418.0 (53.8%)	915.5 (43.1%)	623.4
260	80.6 (2.2%)	372.4 (51.4%)	824.3 (46.4%)	575.9
280	85.1 (2.8%)	337.4 (49.6%)	739.5 (47.7%)	522.0
300	62.5 (1.5%)	271.5 (39.8%)	641.7 (58.7%)	485.7

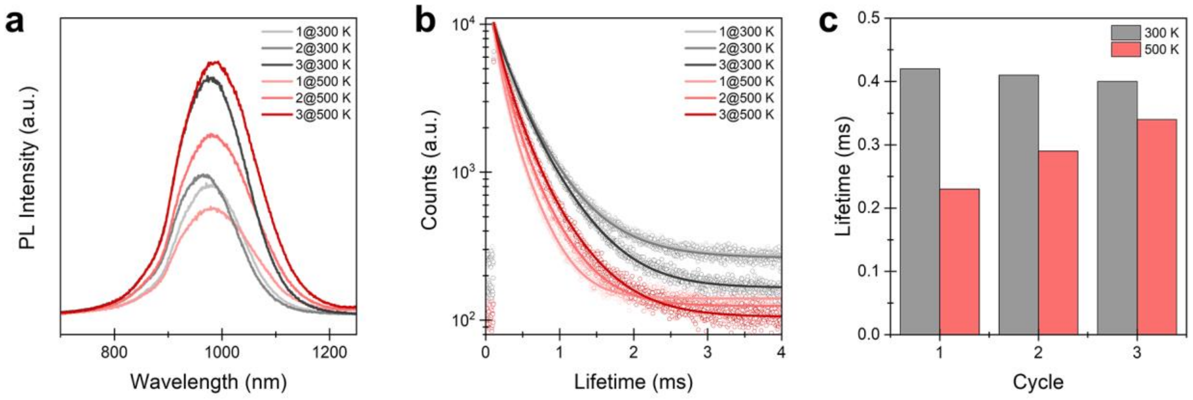

Figure S6. (a) PL spectra, (b) fitting curves and (c) the corresponding lifetime decay results of Sn@Si NC solutions for the stability tests. Detailed fitting parameters are listed in Table S4.

Table S4. **Summary of the fitting results of the PL lifetime decay values of the cycles of Sn@Si NCs shown in Figure S6.**

Cycle@Temperature	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ_{ave} (μs)
Cycle 1@300K	31.8 (0.8%)	239.1 (35.8%)	556.4 (63.5%)	438.8
Cycle 1@500K	70.2 (11.4%)	201.9 (60.3%)	448.6 (28.3%)	256.7
Cycle 2@300K	66.1 (1.5%)	305.7 (61.9%)	646.4 (36.6%)	426.7
Cycle 2@500K	74.6 (8.5%)	204.8 (55.1%)	482.2 (36.4%)	294.7
Cycle 3@300K	176.7 (17.5%)	384.4 (65.4%)	803.2 (17.1%)	419.9
Cycle 3@500K	79.6 (5.4%)	243.8 (58.2%)	584.6 (36.4%)	359.1

References

1. J. P. Fleurial and A. Borshchevsky, *J. Electrochem. Soc.*, 1990, **137**, 2928.