

Supporting Information

Transition-Metal-Doped NIR-Emitting Silicon Nanocrystals

Sourov Chandra, Yoshitake Masuda, Naoto Shirahata, and Françoise M. Winnik**

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Author Contributions

S.C. Conceptualization: Equal; Methodology: Lead; Writing—original draft: Equal

Y.M. Investigation: Supporting; Methodology: Supporting

N.S. Conceptualization: Supporting; Funding acquisition: Equal; Methodology: Supporting; Writing—review & editing: Supporting

F.W. Funding acquisition: Equal; Investigation: Supporting; Methodology: Supporting; Validation: Supporting; Visualization: Supporting; Writing—review & editing: Lead.

Supporting Information

Experimental

Materials

Water was purified and deionized using a Sartorius (arium 611 UV) water purification system. Triethoxysilane (TES), MnCl_2 , NiCl_2 , CoCl_2 , CuCl_2 , 1-octadecene and mesitylene were purchased from Sigma Aldrich and used as received. All other chemicals were purchased from Wako Pure Chemical Industries Ltd. (Japan) and used as received.

Synthesis of doped and undoped Si-SiO₂ composites

TES (10 mL, 90 mM) was placed to a 2-neck round-bottom flask, kept in an ice bath and stirred in an argon atmosphere. To prepare the undoped silicon nanocrystals (SiNCs), acidic water (10 mL, pH 3 by using HCl) was added dropwise to TES with vigorous stirring under a flow of Ar. A xerosol formed within 15 hr. It was dried in vacuum. The resulting white solid was placed in a quartz crucible, transferred to a high-temperature vacuum furnace, and heated at 1100°C for 2 hr or at 900°C for 6 hr under 10^{-4} Pa pressure. The black solid recovered upon cooling to room temperature was ground mechanically in a mortar to yield $(\text{HSiO}_{1.5})_n$ as a fine, free-flowing dark brown powder. To prepare doped SiNCs, an aqueous solution of the selected metal chloride (pH 3) was added dropwise to TES at 0 °C under argon, instead of aqueous acidic solution.

Synthesis of free standing silicon nanocrystals (SiNCs)

The fine $(\text{HSiO}_{1.5})_n$ powder (150 mg) with or without dopant was placed in a small Teflon container and slurried in a mixture of ethanol (10 mL), HF (48 %, 10 mL) and water (10 mL). The mixture was stirred vigorously for 1 hr, during which time the SiO_x matrix was gradually removed by acidic etching. The resulting hydride-terminated SiNCs were isolated by centrifugation at 15,000 rpm for 5 min, washed twice with ethanol, followed by isolation through centrifugation and decanting. The product was transferred into a Schlenk flask containing mesitylene (15 mL) and 1-octadecene (15 mL). The resulting

slurry was degassed for at least 15 min with Ar and heated at 180°C for 16 hr in an Ar atmosphere. The mixture was cooled to room temperature. The resulting octadecyl coated silicon nanocrystals were slurried in a mixture of toluene/methanol 1/1 v/v, subjected to centrifugation at 15,000 rpm for 40 min. The supernatant was decanted and replaced with a fresh toluene/methanol solution, and subjected to centrifugation several times to remove traces of mesitylene and unreacted 1-octadecene. The final product was dried under vacuum and redispersed in toluene.

Characterizations

UV-visible absorption spectra were recorded on a JASCO V-7200 UV-Vis spectrophotometer. X-ray powder diffraction (XRD) patterns were acquired with a Rigaku Smart lab X-ray diffractometer. High-resolution transmission electron microscopy (HR-TEM) was performed with JEOL JEM 2010, operating at an acceleration voltage of 200 kV. Samples for HR-TEM analyses were drop-casted from dilute dispersions of SiNCs in ultrathin-carbon (<10 nm thickness) coated copper grids. PL and PLE spectra were obtained with a NanoLog Horiba Jovin Yvon spectrofluorometer using an InGaAs detector for NIR (Hamamatsu Photonics Co. Ltd, Japan) at room temperature. Time-resolved fluorescence decay profiles were recorded at room temperature on a time-correlated single photon counting (TCSPC) lifetime system (NanoLog Horiba Jovin Yvon, Japan), equipped with pulse laser diodes ($\lambda_{em} = 370$ nm). The quality of the fit was assessed based on the χ^2 value (~ 1.0) and visual inspection of the residuals. Absolute PL quantum yields were measured using a C9920-03G system equipped with a 150 W xenon lamp (Hamamatsu Photonics Co. Ltd, Japan). Dilute solutions having absorption in between 0.1 to 0.2 were inserted in the instrument sample compartment with 1 cm² quartz cuvettes. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed with an Agilent 720-ES system. Samples for ICP-OES were prepared by decomposition of doped SiNCs with nitric acid and HF. Briefly, 5 mg of sample was transferred into a Teflon beaker and mixed with 5 mL of HNO₃ and 2 mL of HF. After that, they were decomposed by heating. The solutions were evaporated to dryness and dried residues were

dissolved in 5 mL of nitric acid. The solutions were poured into 50 mL volumetric flasks and diluted to the marked line with Milli-Q water. Finally, the concentrations of metal atoms were evaluated by ICP-OES analysis. The Co-doped Si sample was examined by X-ray photoelectron spectroscopy (XPS; JEOL, Ltd., JPS-90MX) using $MgK\alpha$ ($E = 1253.6$ eV) radiation. The binding energy (BE) scale was calibrated to provide $Au4f_{7/2} = 83.9$ eV and $Cu2p_{3/2} = 932.8$ eV. The X-ray source was operated at 15mA and 8 kV with the analyzer's constant pass energy at 20 eV. The pressure in the analysis chamber was about 8×10^{-8} Pa during measurements. The core-level signals were obtained at a photoelectron takeoff angle of 90° (with respect to the sample surface). The BE scale was referenced to 285.0 eV as determined by the location of the maximum peak on the C1s spectra of hydrocarbon, associated with an adventitious contamination. The accuracy of the BE determined with respect to this standard value was within ± 0.3 eV.

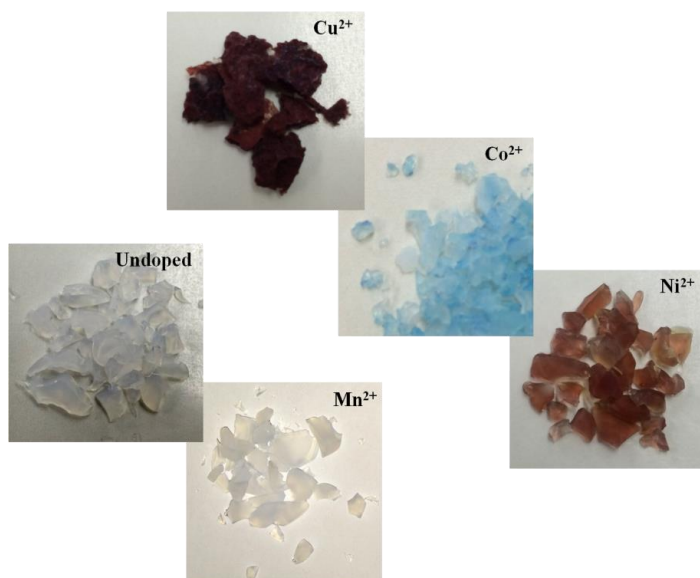


Figure S1 Photographic images of the (HSiO_{1.5})_n samples, produced starting with 12.5 mg of metal chlorides with 10 mL of TES.

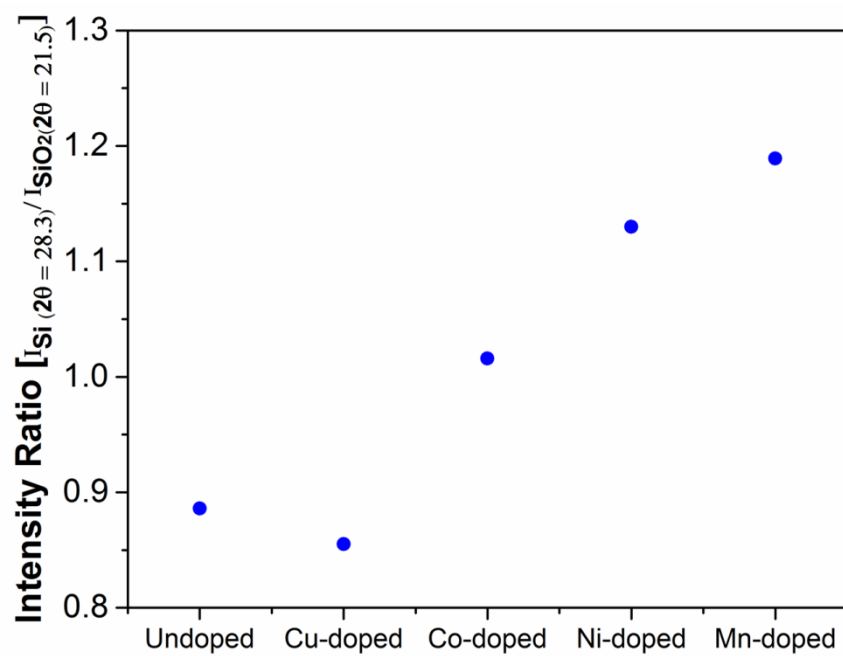


Figure S2 XRD peak intensity ratio of Si:SiO₂ in undoped and doped Si-SiO₂ composites, grown at 1100°C in absence and presence of various metal salts.

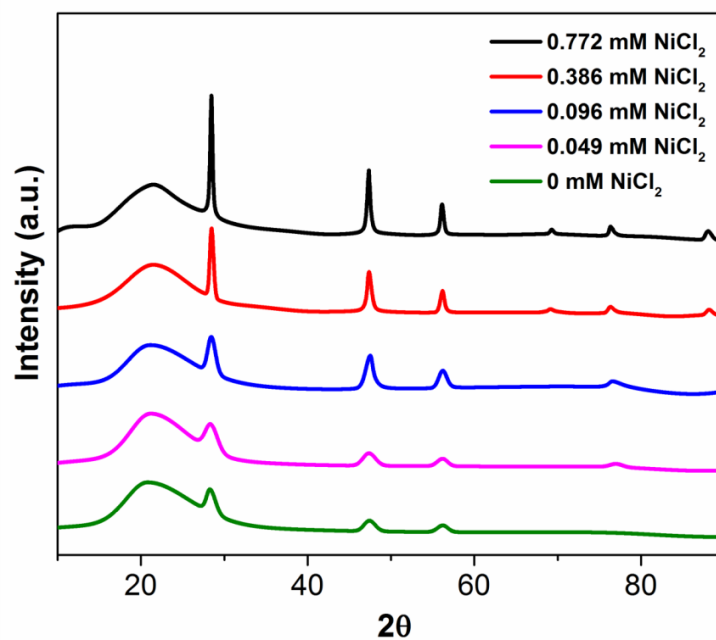


Figure S3 X-ray diffraction patterns of Ni-doped Si-SiO₂ composites, prepared starting with different concentrations of NiCl₂ and heated at 1100°C.

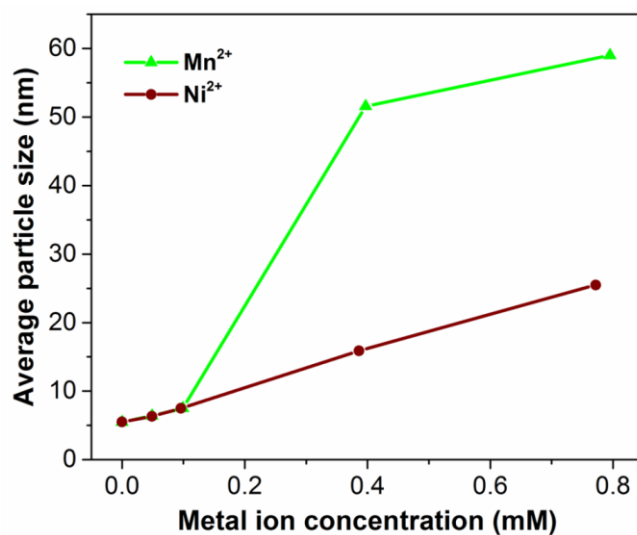


Figure S4 Average particle size, determined by XRD, of the silicon nanocrystals in Si-SiO₂ composites, prepared starting with different concentrations of metal ions.

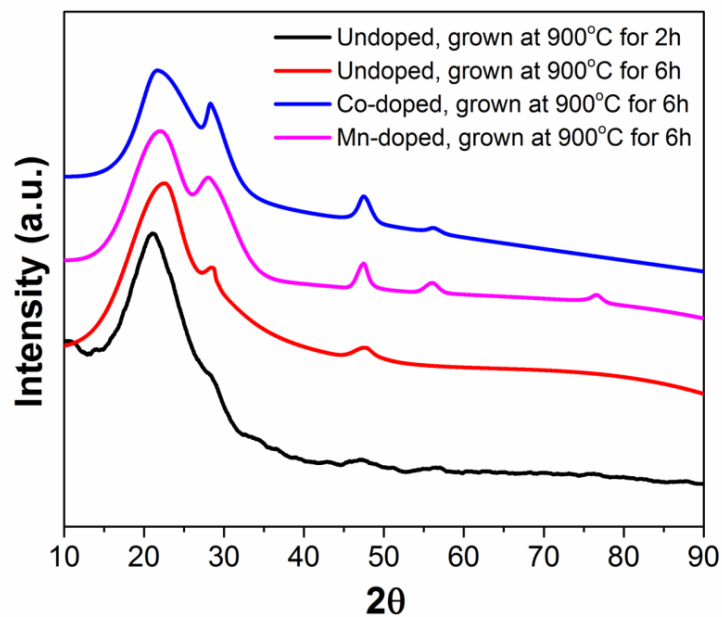


Figure S5 X-ray diffraction patterns of Si-SiO₂ composites, grown at 900°C.

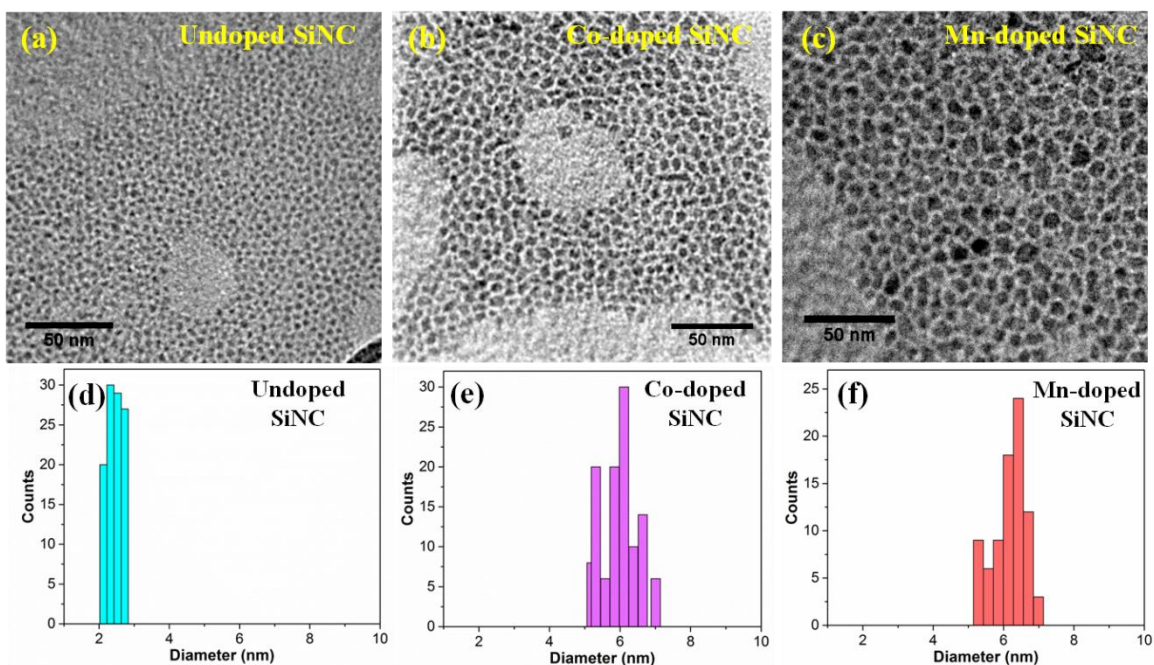


Figure S6 TEM images and size distribution histograms of undoped and undoped SiNCs, grown at 900°C.

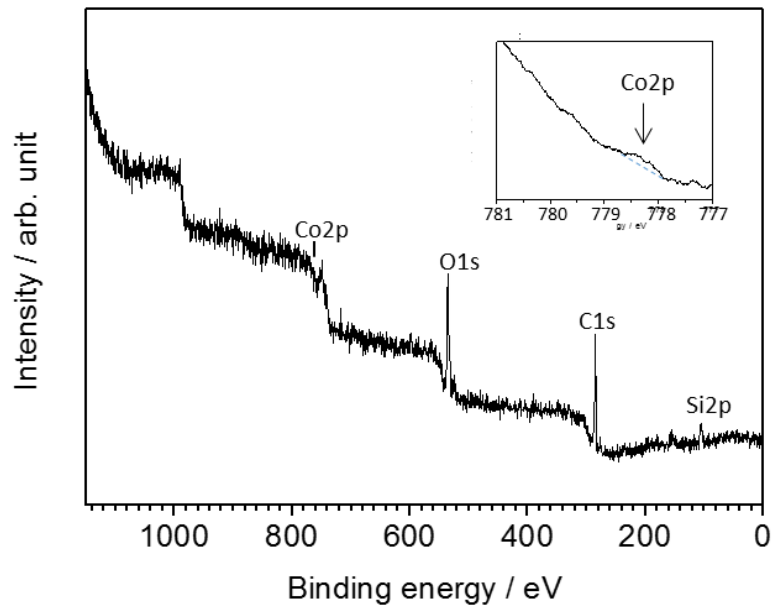


Figure S7 XPS spectra of Co-doped SiNCs. The inset shows the enlarged spectral domain around to the Co2p binding energy.

Table S1 Size and optical properties of SiNCs, grown at 1100°C.

Sample	Particle size	PL Maxima	FWHM	QY ($\lambda_{\text{ex}} = 350 \text{ nm}$)
Undoped	2-8 nm	914 nm	300 meV	30%
Mn-doped	6-9 nm	985 nm	210 meV	8%
Co-doped	6-8.6 nm	1000 nm	200 meV	26%
Ni-doped	5.5-12 nm	982 nm	220 meV	5%

Table S2 Size and optical properties of SiNCs, grown at 900°C.

Sample	Particle size	PL Maximum	FWHM	QY ($\lambda_{\text{ex}} = 350 \text{ nm}$)
Undoped	2.1-2.7 nm	707 nm	324 meV	27%
Mn-doped	5-7 nm	984 nm	186 meV	9%
Co-doped	5-7 nm	971 nm	181 meV	32%

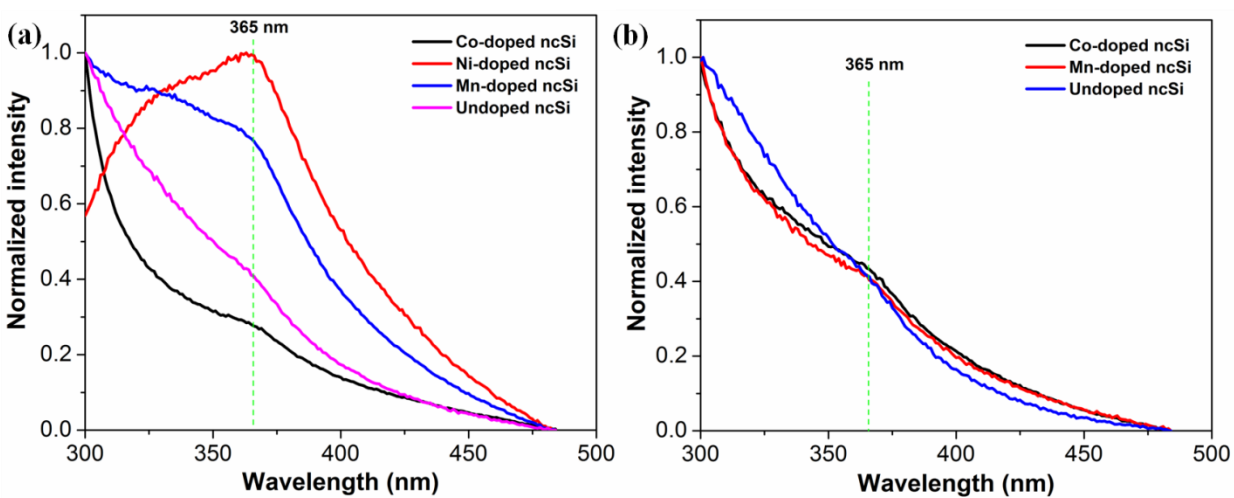


Figure S8 Photoluminescence excitation (PLE) spectra of doped and undoped SiNCs grown at (a) 1100°C and (b) 900°C.

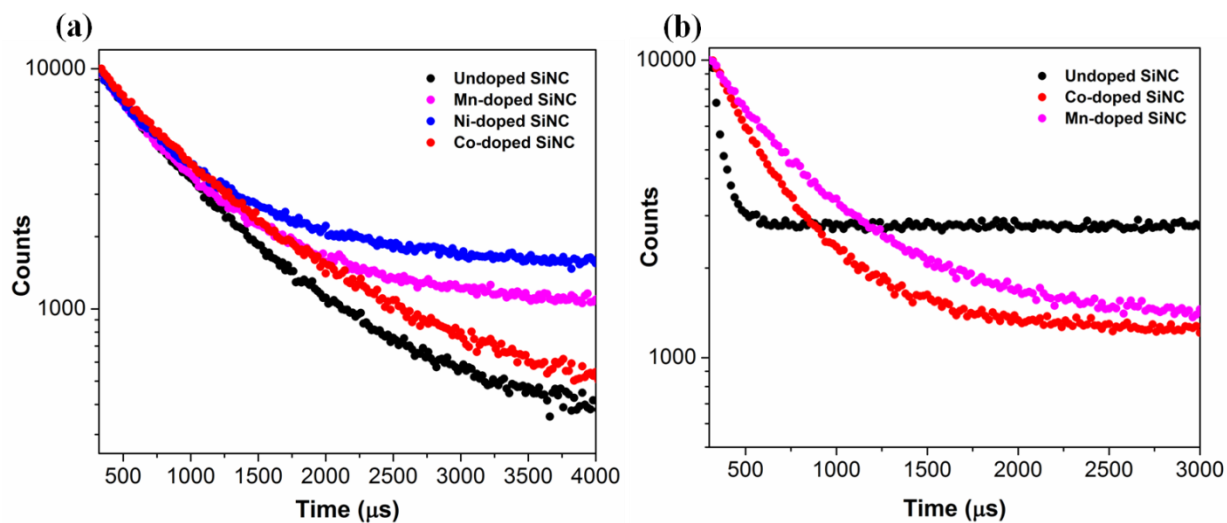


Figure S9 TCSPC lifetime decay profiles of the emission of doped and undoped silicon nanocrystals grown at (a) 1100°C and (b) 900°C.

The time-dependent emission decay profiles, taken at the maxima of their PL emissions, follow bi-exponential decay kinetics. The profiles were fitted by the following equation:

$$F(t) = A + B_1 \exp\left(-\frac{t}{\tau_1}\right) + B_2 \exp\left(-\frac{t}{\tau_2}\right)$$

Where τ_1 and τ_2 are the first and second component of the decay time and B_1 and B_2 are the amplitudes of the two components, respectively. The biexponentially fitted decay for each comprises the fast and slow decay components.

Table S3 PL decay lifetimes of the SiNCs, grown at 1100°C

Sample	B₁	τ₁ [μs]	B₂	τ₂ [μs]	χ²
Undoped	0.671	1.68	0.329	515.43	1.07
Mn-doped	0.599	3.76	0.401	926.07	0.98
Co-doped	0.619	5.16	0.381	1236.62	1.06
Ni-doped	0.591	3.86	0.409	974.26	1.01

Table S4 PL decay lifetimes of the SiNCs, grown at 900°C

Sample	B₁	τ₁ [μs]	B₂	τ₂ [μs]	χ²
Undoped	0.202	2.29	0.798	52.92	1.03
Mn-doped	0.531	3.18	0.469	680.92	1.01
Co-doped	0.542	2.51	0.458	449.63	0.98