Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information For

Silicon Monoxide – A Convenient Precursor for Large Scale Synthesis of Near Infrared Emitting Monodisperse Silicon Nanocrystals

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Experimental section

Synthesis of ncSi in Silicon Oxide Matrix

Solid SiO (purchased from Sigma-Aldrich, -325 mesh powder) was placed in a quartz reaction boat and transferred to a tube furnace. The samples were typically heated at a rate of 18 ℃/min under a flow of 95% Ar/5% H_2 to a peak processing temperature between 850 ℃ and 1100 ℃, then held at that temperature for 1 h before the furnace was allowed to cool to room temperature. For the processing temperature of 920 ℃ and 925 ℃ in the optimum PL study, the holding time were 35 min and 30 min respectively instead of 1 h.

Liberation of ncSi from Silicon Oxide Matrix

For a typical batch synthesis, 0.3 g of thermally treated SiO powder was transferred to a Teflon beaker containing a mixture of 10 ml of 95% ethanol (aq. Sigma Aldrich) and 20 ml of 48% HF (aq. Caledon). ***Personnel should be well trained in the handling of HF***. The mixture was stirred for at least 1 h 30 min to fully etch away the silicon oxide matrix. The hydride-terminated ncSi were then extracted from the aqueous solution into 20 mL 1-decene (Sigma Aldrich, 94%) for surface functionalization by hydrosilylation. The scale of the batch could be enlarged as long as the volume of the beakers and flasks are sufficient for safe handling of chemicals, for example, starting with 2 g of SiO powder instead of 0.3 g.

Surface Functionalization of ncSi

The cloudy orange organic layer (around 20 ml) containing hydride-terminated ncSi and 1-decene was quickly collected and transferred into a 100 ml round bottom flask with a magnetic stir bar and preserved under a flow of N_2 gas. Just before functionalization, the dispersion of ncSi was degassed under vacuum, then purged with nitrogen. The mixture was heated to 170 ℃ for capping with 1-decene and reacted overnight for 20h with stirring to yield a transparent dispersion. The scale of the reaction could be enlarged, for example, using 133 ml solvent and a 250 ml flask if starting with 2g of SiO.

Size-selective Precipitation

The procedure has been described in previous work reported by our group.[1] Briefly, after centrifugation for 10 min to exclude the non-colloidally stable portions, methanol:ethanol 2:3 (v/v) as anti-solvent was added drop-wise into 10 ml clear dispersion until it turned turbid, then the dispersion was centrifuged for 10 min at 6461 g. The solid precipitated was dried in air and re-dispersed in hexane for decyl-capped ncSi, while the precipitation process was repeated with the supernatant. For larger fraction numbers, corresponding to smaller size ncSi, more anti-solvent and longer centrifuge times were required.

Characterization

Attenuated total reflection (ATR)-FTIR spectra were measured on a Perkin Elmer Spectrum One spectrometer with ATR attachment and processed using Perkin Elmer Spectrum software. Raman spectroscopy was performed using a JY Horriba LabRam confocal Raman instrument. The excitation laser had a wavelength of 784.88 nm. The laser power reaching the sample was 0.15 mW. The measurements were carried out using an objective lens with a magnification of 100 x. A grating with 1800 lines/mm was used for high spectra resolution. Each spectrum was a result of 20 averaged measurements, each with an exposure time of 20 seconds. The spectra where then processed, with the background signal removed for accurate line-shape fitting and subsequent analysis. Diffuse reflectance of the samples prepared by drop casting powders from an isopropanol dispersion onto 1”x1” binder free borosilicate glass microfiber filters (Whatman, GF/F, 0.7 µm), was measured using a Lambda 1050 UV/VIS/NIR spectrometer from Perkin Elmer and an integrating sphere with a diameter of 150 mm. Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D2 Phaser with copper Kα radiation source. Solution phase PL measurements and AQY determinations were performed using the same setup as described in our previous work using Friend’s method.[1]

Technicians’ affiliations and instrumental descriptions for STEM imaging

For Fig. S4:

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STEM images were acquired in a probe-corrected JEOL ARM200F operated at 80 kV equipped with a cold field emission gun and a high resolution pole-piece. Middle angle annular dark field (MAADF) images were acquired with 45 and 180 mrad inner and outer collection angles respectively, while BF images used 11 mrad collection angles. Both images were recorded with a dwell time of 38 µs, and convergence semi-angle of 25 mrad resulting in a probe current of 40 pA. Samples were drop-casted onto Graphene-Cu grids (Graphene Supermarket) to ensure an ultra-thin support film of less than 2 nm.

For Fig. 6:

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The samples were characterized by Cs-corrected JEOL JEMARM200F electron microscope operated at 200 kV, equipped with a CEOS Cs corrector on the illumination system. A drop of the suspension was deposited onto a Holey-carbon grid and immediately allowed to dry at room temperature. STEM images were recorded simultaneously in both the HAADF and BF modes. The probe correction was performed with a CEOS corrector, which obtained a 12-fold Ronchigram with a flat area of ~40 mrad. The images were registered with a condenser lens aperture of 40 µm (convergence angle ~34 mrad), the HAADF collection angle ranged from 33 to 125 mrad and the probe current used for acquiring the HAADF-STEM images was (35 pA), the probe size corresponding is ~1 Å.

Raman fitting method

Multiple peak fitting was performed using the peak analyzer in Origin 8.5. A region from ~200 to 600 cm^{-1} was abstracted from the whole spectra, and then the background was subtracted to make the baseline horizontal. A total of 4 peaks were fitted until the result is convergent. The peaks at ~300, ~425, and ~480 cm^{-1} were fitted using Gaussian profiles, while the peak at ~517 cm^{-1} was fitted using Fano profiles. The sample processed at 850 ℃ was not fitted because no crystalline peak could be observed.

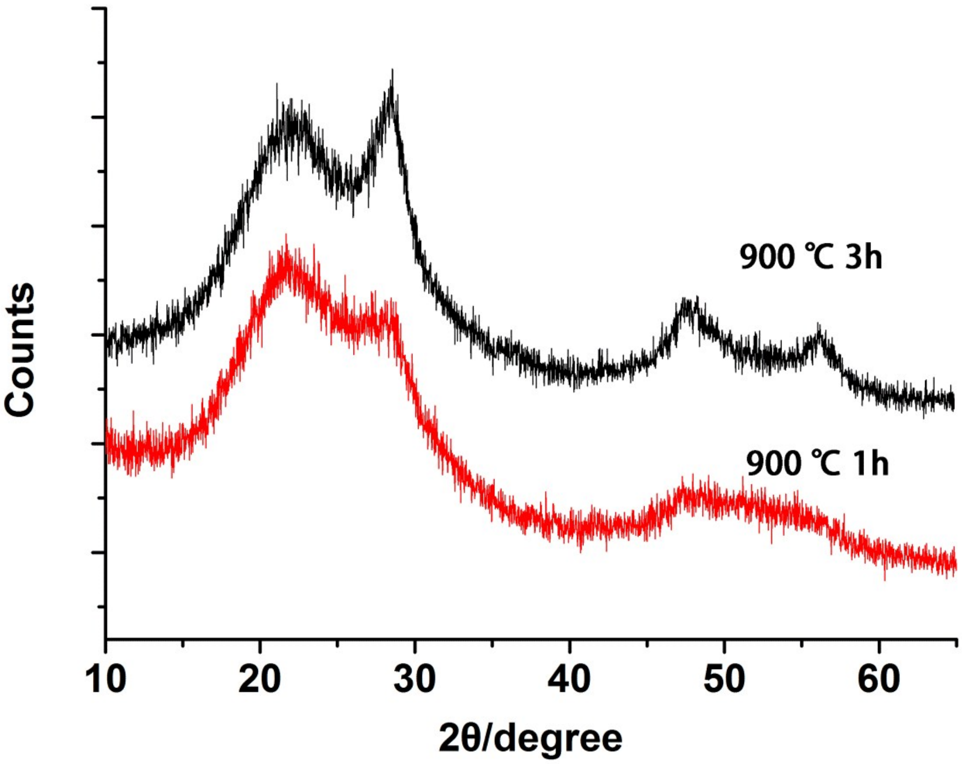

Figure S1. XRD patterns of SiO thermally processed at 900 ℃ for 1h and 3h, indicating more and larger ncSi are produced if the processing time is longer.

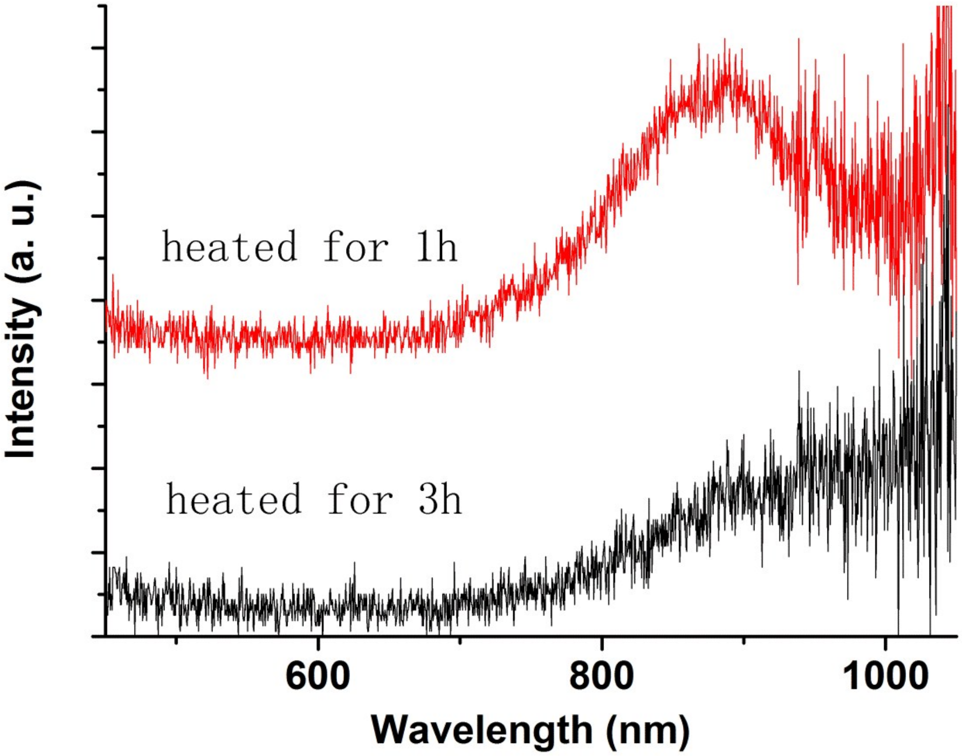

Figure S2. PL spectra of ncSi:H from SiO thermally processed at 900 ℃ for 1h and 3h. 3 h of processing led to weak PL within the detecting range.

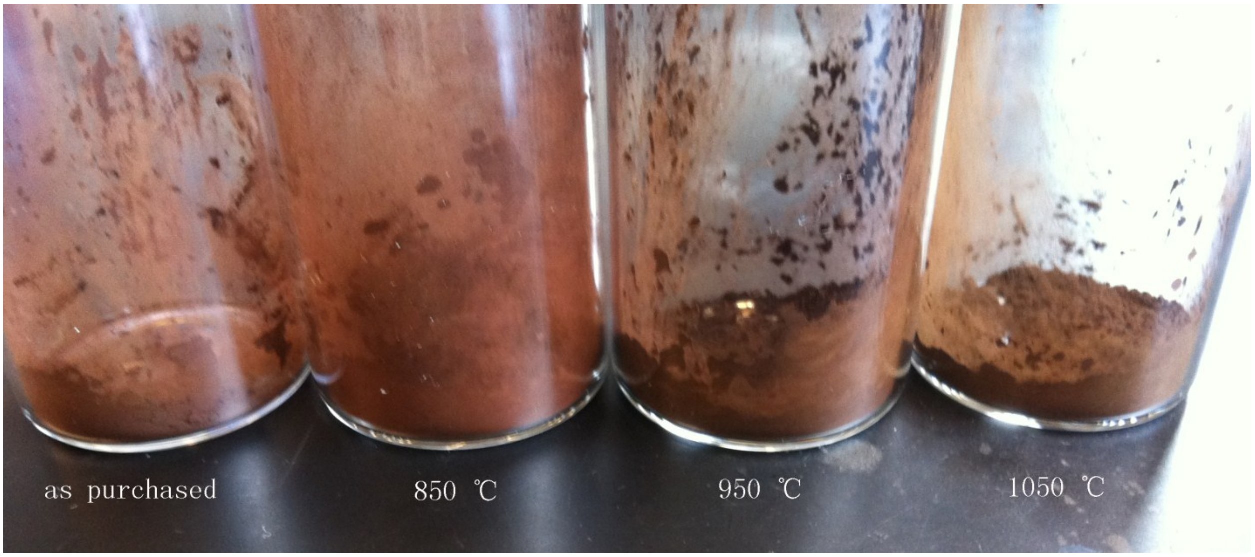

Figure S3. A photo of the SiO powders thermally processed at different temperatures.

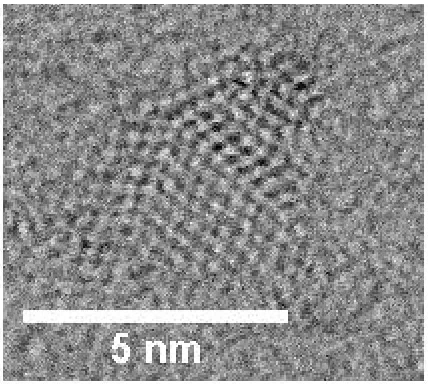

Figure S4. STEM image showing stacking faults in a large ncSi.

References

1. M. L. Mastronardi, F. Maier-Flaig, D. Faulkner, E. J. Henderson, C. Kübel, U. Lemmer and G. A. Ozin, *Nano Letters*, 2011, **12**, 337-342.