Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

The influence of surface functionalization methods on the performance of silicon nanocrystal LEDs

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Content

1 Analytical Data

1.1 Dynamic Light Scattering (DLS)

Table S1. DLS data of SiNCs functionalized with hexyl groups *via* hydrosilylation (HS) and with organolithium reagents (OLR). Mean and standard values calculated over 5 measurements were listed. Every data point was obtained as the mean value of 10 acquisitions. Measurements were performed at room temperature in toluene.

Surface Functionalization	**Organolithium Reagents**		**Hydrosilylation**	
	Hydrodynamic Radius (nm)	Polydispersity (%)	Hydrodynamic Radius (nm)	Polydispersity (%)
1.	2.0	34.8	2.5	37.3
2.	2.4	31.2	2.9	31.1
3.	2.5	31.6	2.6	34.4
4.	2.6	34.9	2.2	31.8
5.	2.5	36.3	2.3	28.2
Average	2.4	33.8	2.5	32.6
Standard deviation	0.2	2.0	0.3	3.1

1.2 TEM Images

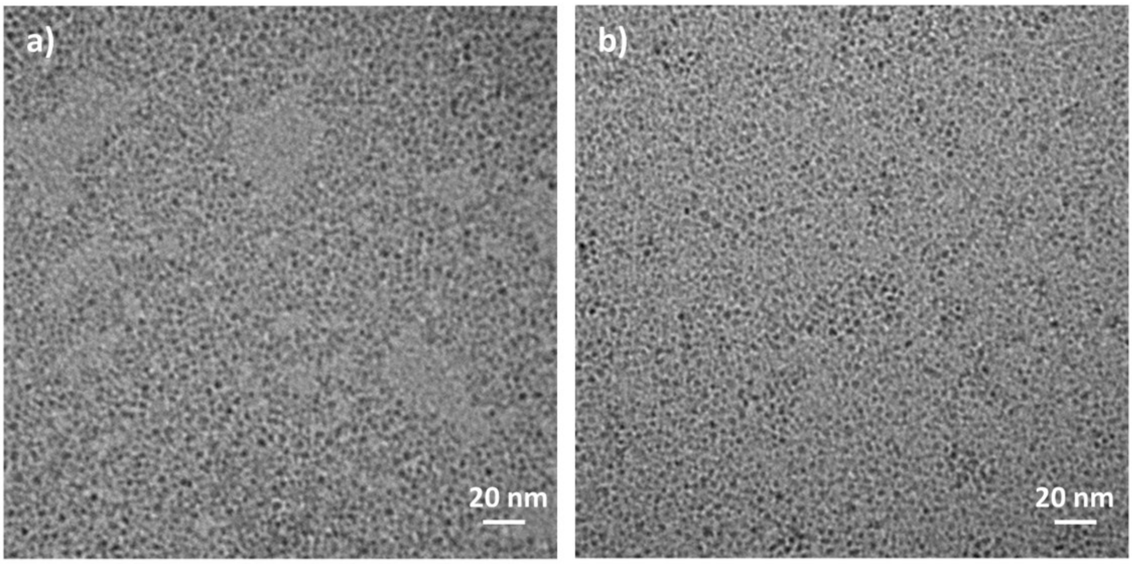


Figure S1. Bright field TEM images of SiNCs functionalized with a) *n*-hexyllithium *via* OLR, b) 1-hexene *via* HS method.

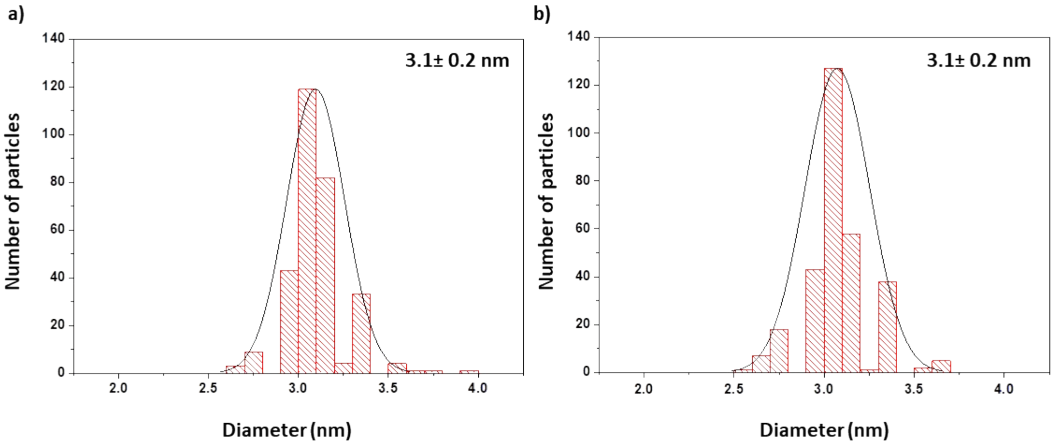


Figure S2. Size distributions of SiNCs functionalized with a) *n*-hexyllithium *via* OLR, b) 1-hexene *via* HS method found by counting 300 SiNCs. Mean and standard deviation of the distributions are given in the inset.

1.3 UV-VIS Spectroscopy

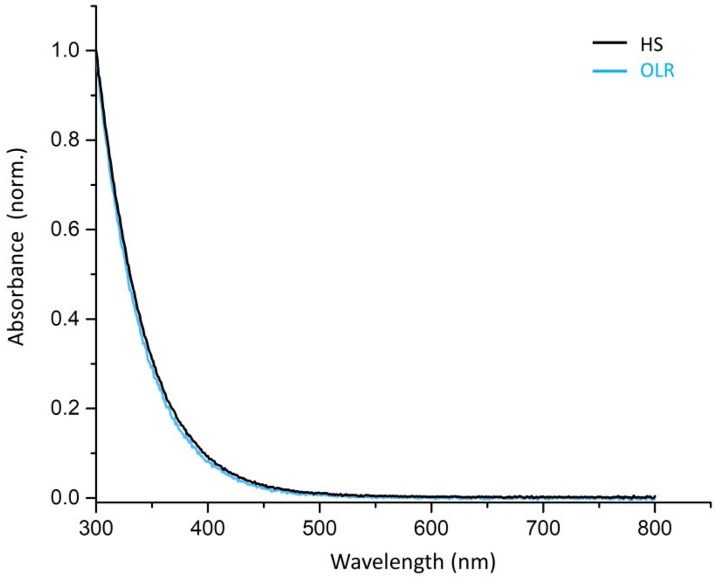
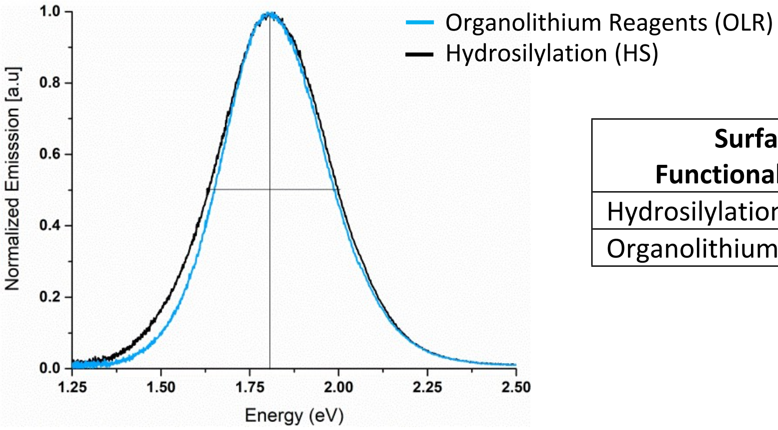


Figure S3. UV-Vis spectroscopy data of SiNCs functionalized with hexyl groups *via* OLR and HS methods. Absorption data is normalized at 300 nm.

1.4 Full Width Half Maximum (FWHM) Analysis



Surface Functionalization	FWHM (eV)
Hydrosilylation	0.36
Organolithium Reagents	0.34

Figure S4. FWHM analysis on PL data obtained for SiNCs functionalized with OLR and HS methods. FWHM values of 0.34 eV and 0.36 eV were found for OLR-SiNCs and HS-SiNCs, respectively.

2 Experimental Details

2.1 Synthetic and Preparative Techniques

General information and materials: Surface functionalization of SiNCs was performed with standard Schlenk and glovebox techniques. All chemicals were used as received, unless stated otherwise. *n*-hexyllithium (2.3 M, in hexane), 1-hexene, 49% HF solution, 1,2-Dichlorobenzene and ZnO nanoparticle solution (Nanograde N-10X) were purchased from Sigma Aldrich. AIBN was bought from Fluka. Dry solvents were obtained from a MBraun SPS 800 solvent purification system with Argon 5.0 as the operating gas. PEDOT:PSS solution was purchased from Heraeus, Germany (Clevios P VP Al 4083), PolyTPD from Solaris Chem Inc., Canada.

Preparation of oxide-embedded SiNCs: Polymeric hydrogen silsesquioxane (HSQ) was synthesized based on a literature known procedure.[1] HSQ (7 g) was weighed in a quartz reaction boat, heated from ambient to a peak processing temperature of 1100 °C at 18 °C/min in a Nabertherm RD 30/200/11 furnace with quartz working tube under an atmosphere consisting 5% H_2 and 95% N_2. The sample was kept at 1100 °C for 1 h. After cooling to room temperature, the resulting solid was ground into a fine brown powder using mortar and pestle. The composite was dispersed in ethanol and further ground in a shaker for 24h with high-purity silica beads using a WAB Turbula mixer. The resulting SiNC/SiO_2 composite was dried *in vacuo.*

Liberation of hydride-terminated SiNCs: 300 mg of the SiNC/SiO_2 composite was transferred to an ethylene-tetrafluoroethylene (ETFE) beaker equipped with a Teflon-coated stir bar. Ethanol (3 mL) and water (3 mL) were then added, and stirred to form a brown suspension, followed by addition of 3 mL of 49% HF aqueous solution. After 30 min of etching, the color of the suspension turned to yellow. Hydride-terminated SiNCs were subsequently extracted from the aqueous layer into *ca.* 30 mL of toluene by multiple (*i.e.,* 3 × 10 mL) extractions. The SiNC toluene suspension was centrifuged in an ETFE-centrifuge tube at 9000 rpm for 4 mins. Extracted particles were re-dispersed in 5 ml dry toluene and centrifuged once more to remove any residual water/ethanol.

Surface functionalization of SiNCs with organolithium reagents: Freshly etched hydride-terminated SiNCs (from 300 mg Si/SiO_2 composite) were dispersed in 2 mL of a dry toluene in a Schlenk flask equipped with a stir bar. The dispersion was degassed *via* three freeze-thaw cycles. *n*-hexyllithium (0.2 mmoles from 2.3 M solution) was then added. Upon addition, the color of the reaction mixture turned dark brown. The reaction was run for 15 hours under an argon atmosphere at room temperature and terminated by precipitation of the functionalized SiNCs from a 5 mL 1:1 ethanol-methanol mixture, acidified with HCl conc. (0.2 mL). Obtained SiNCs were centrifuged at 9000 rpm for 6 minutes and the sediment was re-dispersed in minimum amount of toluene. The precipitation-centrifugation-redispersion cycle was performed two more times from toluene and ethanol-methanol. Finally, functionalized SiNCs were dispersed in toluene and filtered through a 0.45 µm PTFE syringe filter.

Surface functionalization of SiNCs *via* hydrosilylation: Freshly etched hydride-terminated SiNCs (from 300 mg Si/SiO_2 composite) were dispersed in 2 mL of a dry toluene in a Schlenk flask equipped with a stir bar. 10 mg AIBN and 0.4 mL 1-hexene were added and the reaction mixture was degassed *via* three freeze-thaw cycles. This reaction mixture was heated at 70 °C for 15 hours. At the end of the reaction, purification was achieved by precipitating the functionalized SiNCs from a 5 mL 1:1 ethanol-methanol mixture. SiNCs were then centrifuged at 9000 rpm for 6 minutes and the sediment was re-dispersed in a minimum amount of toluene. The precipitation-centrifugation-redispersion cycle was performed two more times from toluene and ethanol-methanol. Finally, functionalized SiNCs were dispersed in toluene and filtered through a 0.45 µm PTFE syringe filter.

Device fabrication: Glass substrates with pre-patterned ITO films (120 nm, 15 Ω/square) were cleaned by successive sonication in lab detergent, acetone, and isopropanol (IPA) and subsequent rinsing with deionized water. PEDOT:PSS solution (Clevios P VP Al 4083, filtered with a 0.45 µm RC filter and diluted with two parts IPA) was spin coated on top at 3000 rpm for 30 sec. Afterwards, the substrates were transferred into a nitrogen-filled glove box and all following steps were done under inert atmosphere. The PEDOT:PSS film was heated on a hot plate at 140°C for 10 minutes to evaporate any remaining solvent before the deposition of subsequent layers. PolyTPD solution was prepared with 5 mg/mL in 1,2-Dichlorobenzene and stirred for 30 minutes at 60°C. It was then spun on top of the PEDOT:PSS layer at 4000 rpm for 30 seconds and dried at 140°C for 10 minutes. SiNC were spun coated from toluene solution with different concentrations and speeds and heated at 140°C for 10 minutes. The ZnO nanoparticle solution was diluted to 1 wt.-% in IPA, spin coated at 3000 rpm for 30 sec and heated at 140°C for 10 minutes. A top electrode consisting of 20 nm calcium and 100 nm aluminum was deposited by thermal resistive evaporation under vacuum (10^{-6} mbar) using a shadow mask. The active area of the devices is determined by the overlap of top and bottom electrodes and amounts to 9 mm^2. Finally, the finished devices were encapsulated using a thin glass sheet and a two component epoxy resin (Araldite 2011).

2.2 Characterization Methods

Characterization of SiNCs: FTIR spectra were collected with a Bruker Vertex 70 FTIR using a Platinum ATR from Bruker. PL spectra were measured with an AVA-Spec 2048 from Avantes using a Prizmatix (LED Current controller) as light source. Samples were excited with a 365 nm source. UV-Vis Spectroscopy was performed with a Varian Cary 50 Scan Spectrometer within the 200-800 nm range. Absolute quantum yield of SiNCs was measured with Hamamatsu Absolute PL Quantum Yield C11347 spectrometer. Every measurement was obtained over ten acquisitions. Mean and standard deviation values were calculated over three measurements. Dynamic light scattering measurements were done with a Dyna Pro NanoStar from Wyatt with toluene as solvent. Every measurement was obtained over ten acquisitions. Mean and standard deviation values were calculated over five measurements. TGA analysis was performed with a Netzsch TG 209 F1 Libramachine at a heating rate of 10 K/min in an argon flow of 20 mL/min (Ar 4.8) in platinum pans. Bright field TEM images were obtained using a JEOL-2012 electron microscope equipped with LaB_6 filament and operated at an accelerating voltage of 200 kV. Particle size distribution was calculated by counting at least 200 particles using ImageJ software (Version 1.49).

Device characterization: Film thickness was measured with a Bruker Dektakt XT profilometer by preparing single films on a glass substrate and scratching it with a scalpel. Scanning electron microscope images were taken with a Carl Zeiss NVision40 field-emission scanning electron microscope. The luminance-current-voltage-characteristics were measured using a Keithley 2602 sourcemeter and a MAVO-SPOT 2 USB luminance meter. The EL spectrum was measured with an AVANTES SenseLine CCD spectrometer with integrated monochromator (ULS2048x64 TEC). EQE was calculated from the luminance data assuming lambertian emission and using a weighted average of the emission spectrum to determine the dominant emission wavelength for conversion with the luminous efficiency function. All characterization steps were performed in ambient conditions.

References

1 H. M. Bank, M. E. Cifuentes, E. M. Theresa, *United States Pat.*, 1991, 5.010.159.