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Size controlled solid state synthesis of luminescent silicon nanocrystals

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Experimental:

1. Materials: Tetraethoxysilane (TEOS, 99%, Sigma-Aldrich), ammonium hydroxide (NH_4OH, 42%, Caledon), magnesium powder (Mg, 99%, BDH), toluene (ACS grade, BDH), ethanol (ACS grade, sigma-aldrich), hydrofluoric acid (HF, 49%, J. T. Baker), trioctylphosphine oxide (TOPO, 97%, Sigma-Aldrich) were used as received.

2. Synthesis of Stöber silica particles: Stöber silica particles were synthesized via base catalyzed sol-gel method. Briefly, TEOS (10 mL, 45 mmol) was stirred with ethanol (10 mL), deionized water (20 mL) and NH_4OH solution (42 %, 5 mL) for varying times (tabulated below) to yield different size particles. The white precipitate was collected by vacuum filtration and washed with deionized water multiple times (4 × 25 mL). The solid was transferred to an oven and was kept there for 24 hours at 100^{o}C to drive off any residual water and ethanol.

Table 1: Varying stöber silica particle sizes with the reaction time and respective reaction yields.

Reaction time (hour)	Particle size (nm)	Reaction yield (%)
0.5	6.0 ± 0.5	72
1	15 ± 1	77
2	25 ± 3	74
5	40 ± 5	80
10	52 ± 5	74
24	75 ± 8	85
36	83 ± 10	82

48	95 ± 8	85
60	120 ± 10	88
72	145 ± 8	94
84	170 ± 10	90
100	200 ± 18	92

3. Synthesis of silicon nanocrystals (Si-NCs): Silica particles (1.00 g, 17 mmol w.r.t Si content) and magnesium powder (0.87 g, 36 mmol) were mixed together manually and thermally processed at 500^{o}C for 15 hours under argon atmosphere. The resulting greyish brown powder was treated with concentrated hydrochloric acid (5 mL) for 30 min to remove magnesium oxide (MgO). The brown precipitate was obtained by vacuum filtration. The solid was washed with deionized water until the washings had a neutral pH (ca. 7). This was followed by washing with ethanol (20 mL) and acetone (3 × 20 mL) and was air dried to yield oxide coated Si-NCs.

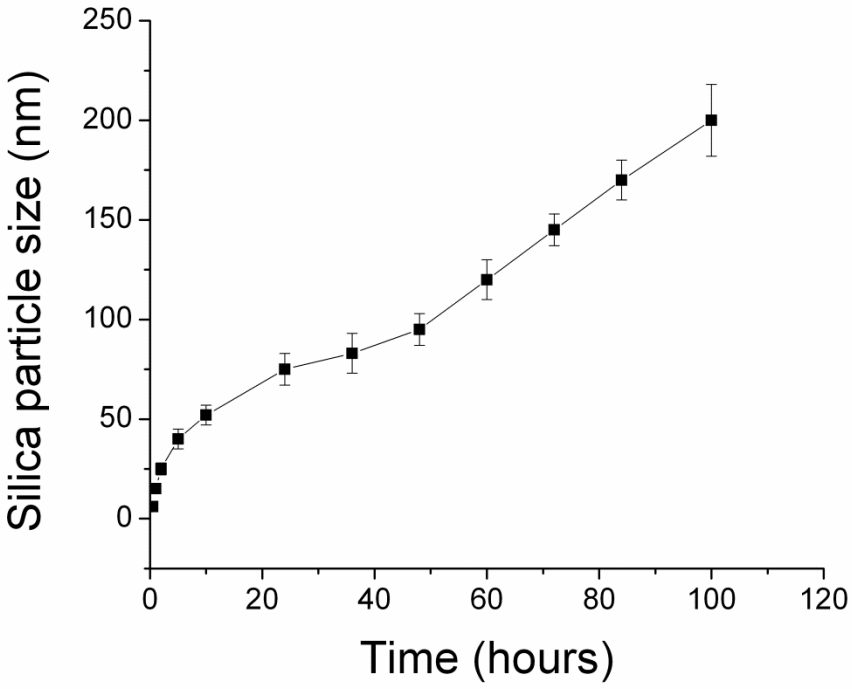
4. Synthesis of hydride terminated Si-NCs: The composite obtained by the procedure above was treated with hydrofluoric acid to remove the protective SiO_2 layer. In a typical etching procedure, 0.5 g of the sample was transferred to a Teflon test tube and 1:1:1 solution of 49% $HF_{(aq)}$: H_2O : ethanol (10 mL) was added. The mixture was stirred for 60 min followed by extraction into 10 mL toluene. The free standing nanocrystals were washed multiple times with toluene by centrifugation at 32000 rpm.

5. Functionalization of Si-NCs with TOPO: Hydride terminated Si-NCs (100 mg) were stirred together with TOPO (13.8 g, 36 mmol) in toluene (20 mL) for 12 hours under ambient conditions. After the completion of the reaction the solution turns clear light yellow color from a

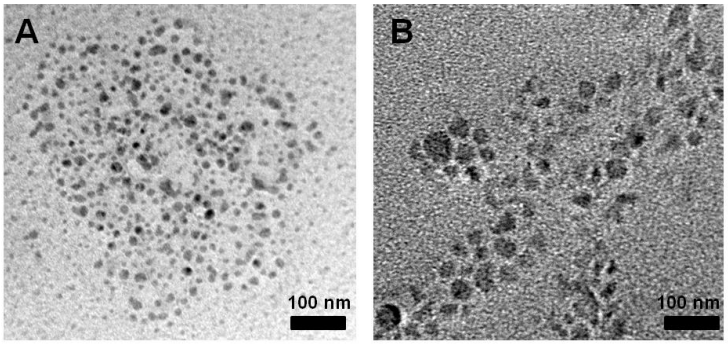
cloudy orange dispersion. The attempts to remove excess TOPO led to precipitation of the NCs from the solution. We believe excess TOPO is required to encapsulate hydroxyl Si-NCs within TOPO micelle to render them solution dispersible.

6. Characterization: Fourier Transformation Infrared Spectroscopy (FTIR) was performed on Nicolet Magna 750 IR spectrometer. X-ray powder diffraction (XRD) patterns were collected using an INEL XRG 3000 X-Ray diffractometer with CuK_{α} radiation (λ = 1.54 Å). Photoluminescence spectra for the solution phase samples were acquired using a Varian Cary Eclipse Fluorescence Spectrometer. Transmission electron microscopy (TEM) analyses were performed using a JOEL-2010 (LaB_6 filament) with an accelerating voltage of 200 keV. The samples were prepared by drop coating solutions of composite or free standing NCs dispersed in ethanol and toluene, respectively onto a carbon coated copper grid (400 mesh) and allowing the solvent to evaporate in air. The particle sizes were measured using Image J software. Scanning electron microscopy (SEM) was performed on JSM- 6010LA In TouchScope instrument. The powder sample was mounted on carbon tape for imaging.

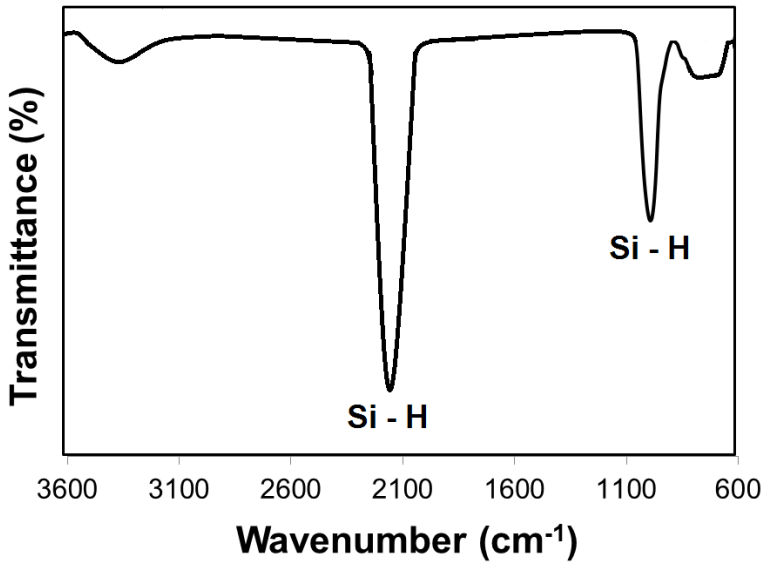
ESI Fig. 1: Evolution of Stöber silica particle size as a function of reaction time.



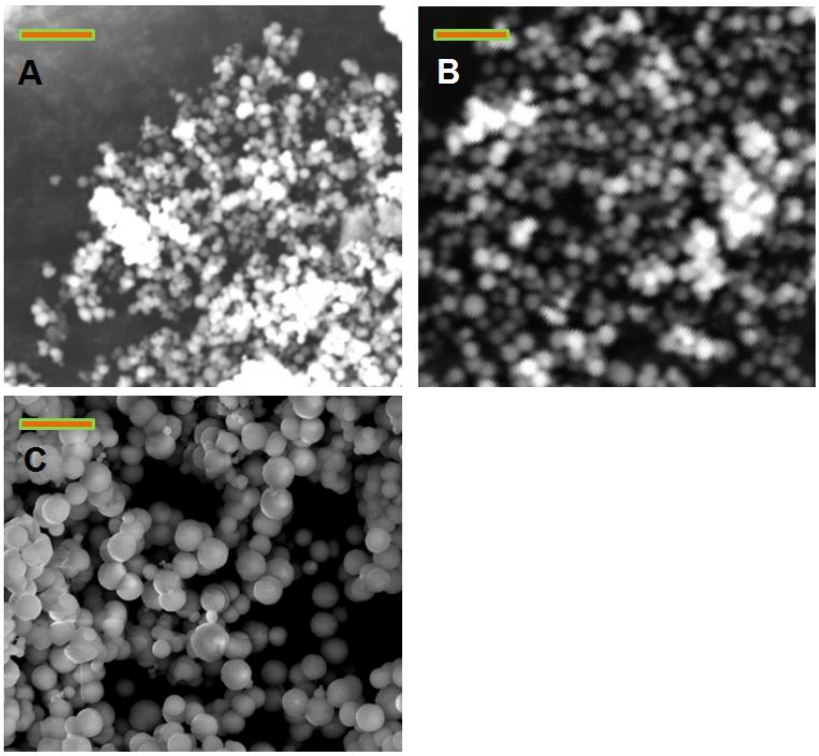
ESI Fig. 2: Transmission electron microscope (TEM) images of (A) 15 and (B) 40 nm stöber silica particles.



ESI Fig. 3: FTIR spectrum of hydride terminated Si-NCs.



ESI Fig. 4: SEM images of (A) 75 nm (B) 110 nm and (C) 177 nm silicon nanocrystals. The scale bar is 1 µm.



ESI Fig. 5: FTIR spectrum of hydroxyl terminated Si-NCs.