Electronic Supplementary Material (ESI) for Chemical Communications

Solid-State Synthesis of Luminescent Silicon Nitride Nanocrystals

Mita Dasog and Jonathan G. C. Veinot

Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G2G2, Canada

Experimental

1. Materials: Tetraethoxysilane (TEOS, 99%, Sigma-Aldrich), urea ($CO(NH_2)_2$, 98%, Fisher), sodium hydroxide (NaOH, 97%, Caledon), magnesium powder (Mg, 99%, BDH), toluene (ACS grade, BDH), ethanol (ACS grade, Sigma-Aldrich), hydrofluoric acid (HF, 49%, J. T. Baker) were used as received.

2. Synthesis of the $(SiO_2)_n$ sol-gel polymer: The silica sol-gel was synthesized via a base catalyzed method. Briefly, TEOS (5 mL, 22.5 mmol) was stirred with ethanol (10 mL), deionized water (20 mL) and NaOH solution (10 M, 0.5 mL) for 3 days. 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 (yield 92%)

3. Synthesis, Purification and Isolation of Freestanding Si_3N_4 NCs: Silica sol-gel polymer (1.00 g, 17 mmol w.r.t Si content), urea (0.90 g, 15 mmol) and magnesium powder (0.82 g, 34 mmol) were mixed manually with a mortar and pestle and thermally processed at $500^{o}C$ for 3 hours under 5% H_2/95% Ar atmosphere. The resulting grey/black powder (1.62 g) was treated with concentrated hydrochloric acid (5 mL) for 30 min to remove reaction byproducts. The grey/white precipitate (0.65 g) was isolated 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 crude, silica contaminated Si_3N_4 nanocrystals.

The solid obtained from the HCl extraction was treated with hydrofluoric acid to remove SiO_2 impurities. In a typical etching procedure, 100 mg 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 freestanding nanocrystals were washed multiple times with toluene by centrifugation at 32000 rpm.

5. 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). Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris 1 using a platinum sample pan at a heating rate of 18^oC/min in air. XPS analysis was performed using a Kratos Axis Ultra instrument operating in energy spectrum mode at 210 W. The base pressure and operating chamber pressure were maintained at 10^{-7} Pa. A monochromatic Al K_α source (λ = 8.34 Å) was used to irradiate the samples, and the spectra were obtained with an electron takeoff angle of 90°. To minimize sample charging, the charge neutralizer filament was used when required. Survey spectra were collected using an elliptical spot with major and minor axis lengths of 2 and 1 mm, respectively, and 160 eV pass energy with a step of 0.33 eV. CasaXPS software (Vamas) was used to interpret high-resolution (HR) spectra. All of the spectra were internally calibrated to the C 1s emission (284.8 eV). After calibration, the background was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. The full width half maxima (fwhm) were maintained below 1.2 eV.

UV-Visible spectra were recorded on Cary 400 UV-Vis Spectrometer. Photoluminescence spectra for the solution phase samples were acquired using a Varian Cary Eclipse Fluorescence Spectrometer. Quantum yields were determined using methods adapted from the work of

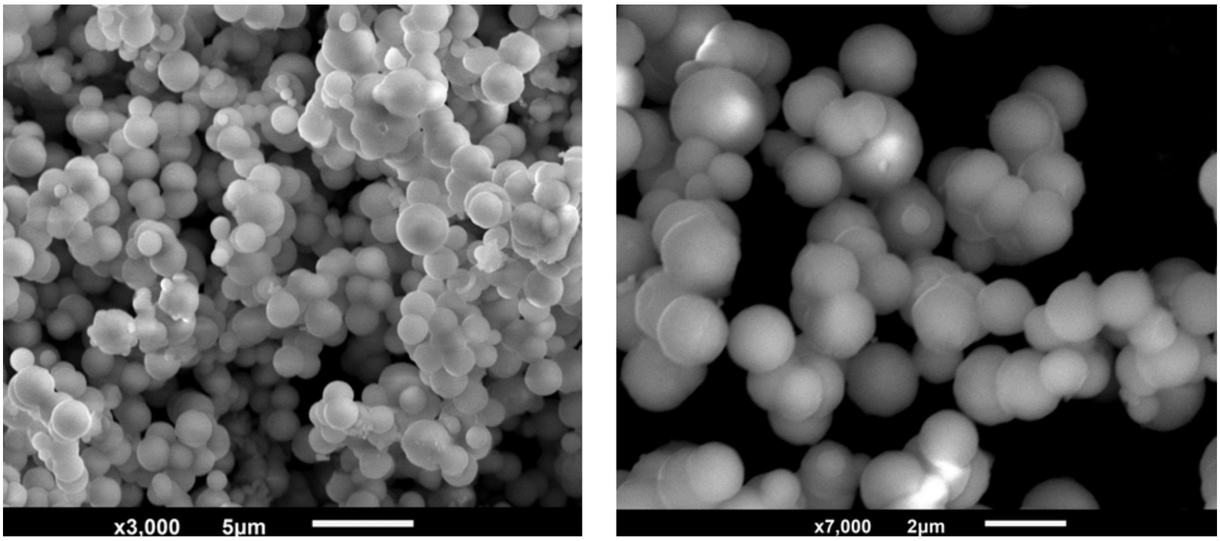
Williams *et al*. 9,10-biphenylanthracene in cyclohexane, coumarin 1 in absolute ethanol and naphthalene in cyclohexane were used as the reference organic dyes.[1] All the organic solvents were passed through a column of anhydrous magnesium sulfate to remove any adhering moisture prior to making the solutions. The stock solutions were made by dissolving 10 mg of the organic dye in the solvent mentioned above and was stirred until the entire solid was dissolved. The solutions were then filtered through a membrane filter to remove suspended impurities and series of diluted solution were made with absorbances ranging from 0.1 and 0.01. PL spectra were acquired for the exact same solutions. The slopes of integrated fluorescence intensity versus UV-Vis absorbance curves were plotted and compared to confirm the quality of the reference curves. In all cases, the experimentally determined quantum yields were in good agreement with literature values: 9, 10-biphenylanthracene, 0.9, coumarin 1, 0.73 and naphthalene, 0.23. The etched samples and the reference samples were excited at the same wavelength (325 nm) and PL was recorded with the same slit width.

Transmission electron microscopy (TEM) analyses were performed using a JOEL-2010 (LaB_6 filament) with an accelerating voltage of 200 keV. High resolution TEM analysis was performed on Hitachi H9500 TEM instrument with an accelerating voltage of 300 kV. 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. The HRTEM images were processed using DigitalMicrograph software.

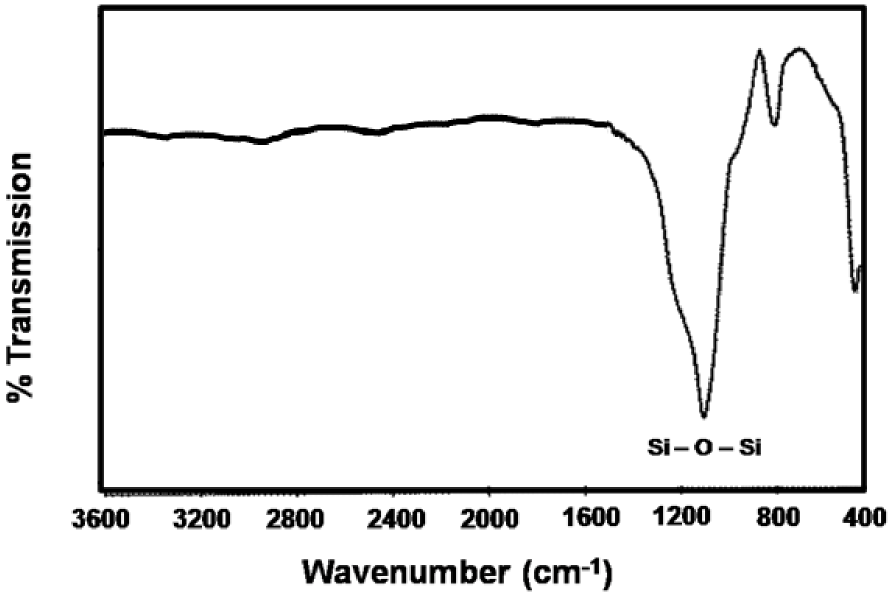
Scanning electron microscopy (SEM) was performed on JSM- 6010LA In TouchScope instrument. The powder sample was mounted on carbon tape for imaging.

[1] A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067.

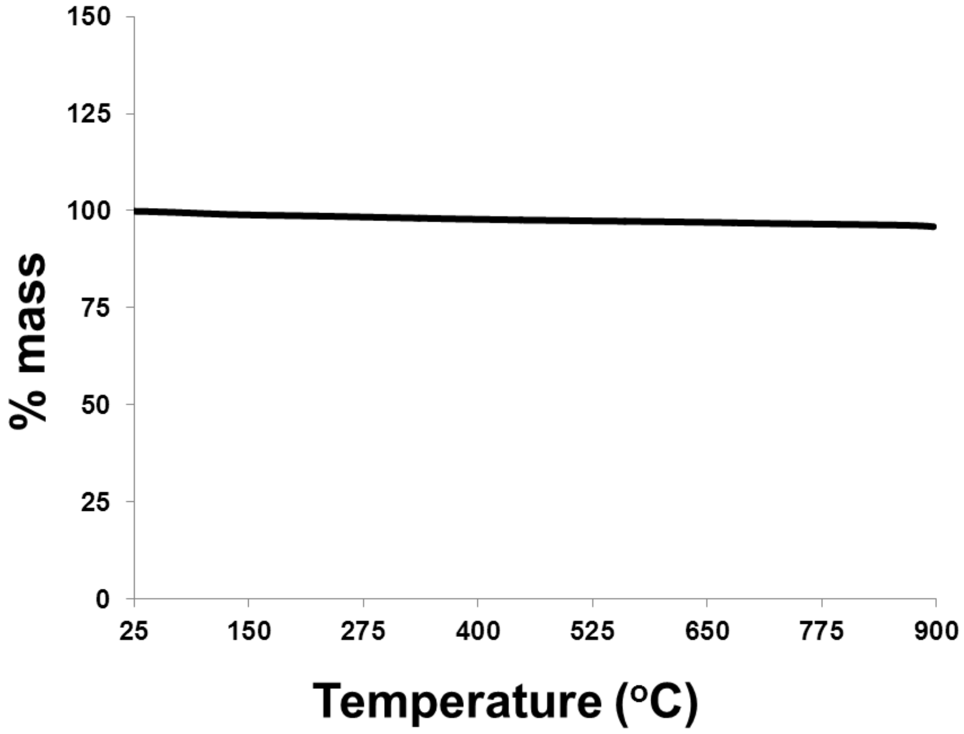
ESI Figure 1: SEM images of TEOS derived silica sol-gel polymer



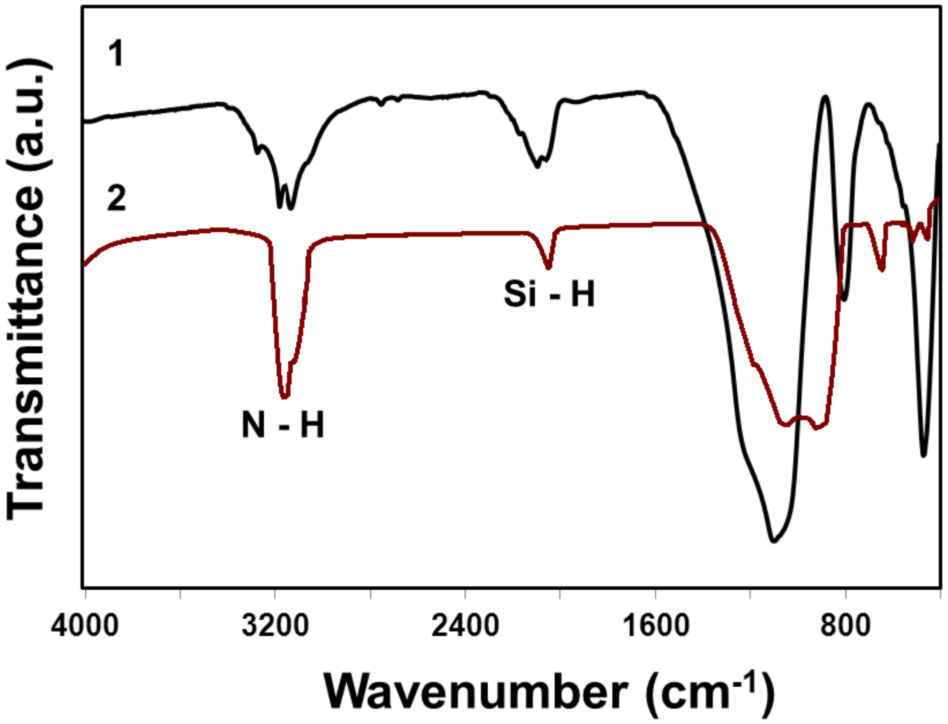
ESI Figure 2: FTIR spectrum of TEOS derived silica sol-gel polymer



ESI Figure 3: Thermogravimetric analysis of crude Si_3N_4 NCs.



ESI Figure 4: FTIR spectrum of (1) Si_3N_4 NCs prior to HF treatment (2) Freestanding Si_3N_4 NCs



ESI Figure 5: (A) Bright field Transmission Electron Micrograph image of freestanding Si_3N_4 NCs (B) Particle size distribution.