

# UV and air stability of high-efficiency photoluminescent silicon nanocrystals



Jihua Yang<sup>a,\*</sup>, Richard Liptak<sup>b,d</sup>, David Rowe<sup>a</sup>, Jeslin Wu<sup>a</sup>, James Casey<sup>c</sup>, David Witker<sup>c</sup>, Stephen A. Campbell<sup>b</sup>, Uwe Kortshagen<sup>a,\*</sup>

<sup>a</sup> Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA

<sup>b</sup> Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, MN 55455, USA

<sup>c</sup> Dow Corning Corporation, 2200 W. Salzburg Road, Midland, MI 48686, USA

<sup>d</sup> Department of Physics and Optical Engineering, Rose-Hulman Institute of Technology, 5500 Wabash Ave, Terre Haute, IN 47803, USA

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## ABSTRACT

The effects of UV light and air exposure on the photoluminescent properties of nonthermal plasma-synthesized silicon nanocrystals (Si NCs) were investigated. Si NCs with high-efficiency photoluminescence (PL) have been achieved via a post-synthesis hydrosilylation process. Photobleaching is observed within the first few hours of ultra-violet (UV) irradiation. Equilibrium is reached after ~4 h of UV exposure wherein the Si NCs are able to retain 52% of the initially measured PL quantum yield (PLQY). UV-treated Si NCs showed recovery of PL with time. Gas-phase passivation of Si NCs by hydrogen afterglow injection improves PLQY and PL stability against UV and air exposure. Additionally, phosphorous doping can also improve UV stability of photoluminescent Si NCs.

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## 1. Introduction

Silicon (Si) has unique advantages of being less toxic and naturally abundant than many other semiconducting materials. Si nanocrystals (Si NCs) have been receiving attention for ultrathin film-based electronic devices such as transistors [1] and solar cells [2–4]. At the nanoscale, Si NCs exhibit quantum confinement that manifest in radiative recombination: the NCs can absorb UV light and emit the photons at wavelengths that span across the visible-to-infrared range via tuning particle size [5,6]. This property makes Si NCs an interesting alternative for potential applications in biological labeling [7], light emitting devices [8], and luminescent concentrators [9,10]. A luminescent concentrator is designed to improve photovoltaic performance via a process termed downshifting. High-energy photons that are not efficiently absorbed by a solar cell's active layer can be absorbed by the luminescent concentrator and reemitted by photoluminescence (PL) at a lower energy that can be more efficiently absorbed by the solar cell. A viable downshifting material should have tunable emission, high PL efficiency, solubility in common solvents for the creation

of well-dispersed colloidal solutions leading to minimal light scattering of liquid or thin film-based luminescent concentrator layer, and stability against ultra-violet (UV) irradiation. Several of these characteristics have been demonstrated using Si NCs synthesized in a nonthermal plasma [11,12], however, the UV stability of such Si NCs has not been reported. The Si NC surface is sensitive to light exposure; high-energy photons have the ability to break surface Si–H or Si–Si bonds [13–15]. The light-induced dangling bonds act as charge traps and decreases PL [16,17]. The purpose of this work is to develop UV-stable silicon nanocrystals that will enable silicon–nanocrystal based luminescent concentrators to be realized.

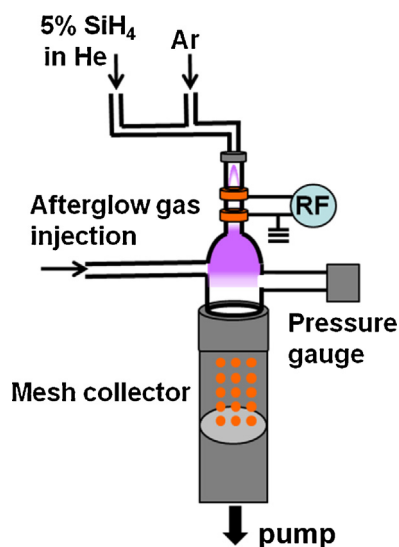
PL efficiency of Si NCs from nonthermal plasma synthesis has been improved via gas-phase passivation by afterglow hydrogen gas (H<sub>2</sub>) injection or phosphorus (P) doping [12,18]. In this article, intrinsic and P-doped NCs were synthesized in nonthermal plasmas and hydrosilylated, to create high PL efficiency NC systems. Their optical properties, specifically PL stabilities under UV irradiation in both nitrogen and air environments were studied.

## 2. Experiments

Fig. 1 shows the schematic of the plasma reactor used to synthesize the Si NCs in a plasma reactor with a side arm for injection

\* Corresponding authors.

E-mail addresses: [yangj@umn.edu](mailto:yangj@umn.edu) (J. Yang), [kortshagen@umn.edu](mailto:kortshagen@umn.edu) (U. Kortshagen).



**Fig. 1.** Schematic of plasma reactor for synthesis of Si NCs capable of gas-phase passivation by  $H_2$  afterglow injection.

of  $H_2$  into plasma afterglow region. Si NCs were produced using a nonthermal capacitively-coupled plasma using a mixture of silane ( $SiH_4$ ) precursor (5% by volume in helium (He)) and argon (Ar), as previously reported [11,12].  $H_2$  was injected into the afterglow of plasma to further passivate the Si NCs with surface hydrides [12]. Table 1 details the synthesis conditions of the Si NCs in this report. P-doped Si NCs were synthesized by flowing phosphine (15%  $PH_3$  by volume in  $H_2$ ) directly into the synthesis plasma [18]. Note: Extreme care was taken when using  $PH_3$  to prevent exposure outside of the reaction tube. Table 2 shows the synthesis conditions of the P-doped Si NCs. Si NCs and P-doped Si NCs were thermally hydrosilylated with 1-dodecene to produce clear colloidal dispersions [12]. Briefly, the collected Si NCs or P-doped Si NCs were ultrasonicated in a pre-degassed mixture of 1-dodecene (>99%) as ligand and mesitylene ( $\geq 98\%$ ) as solvent in a ratio of 1:5 by volume, at a concentration of 660  $\mu L$  of 1-dodecene per mg of Si NCs for reaction. The reagents were used as received. After ultrasonication, the suspension was transferred into a flask via cannula transfer and then refluxed under nitrogen flow at a temperature of 215  $^{\circ}C$  until the cloudy suspension became clear. The Si NCs produced with H afterglow achieved clear colloidal solution in a matter of minutes, but the reaction was allowed to proceed for 2–3 h. On the other hand, Si NCs without H afterglow passivation required more than 24 h of reaction time to produce clear colloidal solution. The resultant colloidal solutions were passed through a 0.45  $\mu m$  PTFE filter and dried at 150  $^{\circ}C$  in a nitrogen-filled glove box. The dried samples were redispersed in chloroform for structural characterization or toluene for study of PL properties.

**Table 1**  
Parameters for synthesis of Si NCs.

$SiH_4$ (5% in He in volume) (SCCM)	Ar (SCCM)	$H_2$ (afterglow) (SCCM)	Pressure (Torr)	Power (W)
13	35	100	1.4	80
13	35	0	1	80

**Table 2**  
Parameters for synthesis of P-doped Si NCs.

$SiH_4$ (SCCM)	Ar (SCCM)	$PH_3$ (15% in $H_2$ ) (SCCM)	Ar dilution (SCCM)	Diluted gas (SCCM)	Pressure (Torr)	Power (W)	Nominal P concentration (%)
0.65	47	0	0	0	0.7	150	0
0.65	47	1.03	1397	5	0.7	150	0.1
0.65	47	1.03	1397	14	0.7	150	0.3

Surface chemistry of as-grown and hydrosilylated Si NCs were studied on stainless steel meshes or as drop-casted films, respectively, using a Bruker ALPHA Fourier transform infrared spectrometer in the diffuse reflectance (DRIFTS) (for as-grown Si NCs) or attenuated total reflectance (ATR) (for hydrosilylated Si NCs) mode. Particle size was estimated to be about  $4.2 \pm 0.2$  nm by X-ray diffraction (XRD) analysis. PL quantum yield (PLQY) of colloidal Si NCs with a concentration of 0.25 mg/mL in toluene was measured using an integrating sphere in a nitrogen or air atmosphere, similar to Mangolini et al. [11]. The PL spectra were measured without additional correction for the spectral response of the instrument. Photostability of Si NCs was studied by irradiating the NCs with a mercury lamp (EXFO OmniCure S1000) coupled with a 365 nm filter at an irradiance of  $\sim 4$  mW/cm $^2$  to simulate the intensity of AM 1.5 G sunlight between 300 and 400 nm. Without exposing the sample to air, PLQY of P-doped Si NCs was measured in a nitrogen-filled glove box using a HR4000 spectrometer (Ocean Optics, Inc.) coupled with a 395 nm UV LED (ETG-5UV395-15, ETG, Inc.) and a FOIS-1 fiber optic integrating sphere. The photostability of P-doped Si NCs was examined in-situ by directly exposing the solution to the UV light source of  $\sim 4$  mW/cm $^2$  for 1 or 14 h.

### 3. Results and discussion

Fig. 2(a) shows the PL spectra of Si NCs synthesized with  $H_2$  afterglow passivation, with respect to UV irradiation time. Prior to UV exposure, the Si NCs show a PL band with a peak at 832 nm and a full width at half maximum (FWHM) of 140 nm. The PLQY was measured to be  $60 \pm 10\%$ . After UV irradiation for 1 h, the PLQY decreases to 78% of the initially measured value. Upon further UV irradiation, the PLQY continues to decrease, and after 4 h, the PLQY equilibrates at a minimum value of 52% of the initial value (as monitoring in a time of 14 h). It is noted that there is no shift in the emission peak after UV irradiation. This may imply that the UV light does not change the size of the Si NCs.

The photobleaching may be explained in the following ways. First, it could be a result of long-term charge trapping in the pre-existing deep levels, which would result in a lack of available electrons for photoexcitation. In such a situation, the light absorption of Si NCs might decrease after UV irradiation, due to decrease of electron population in valence band. The absorption of colloidal NCs was measured before and after UV exposure, and no distinguishable change was observed as shown in Fig. 3(a). Secondly, light irradiation may induce structural distortion or dangling bonds due to the cleavage of some Si– $H_x$  (3.25 eV), Si–C (3.30 eV), or Si–Si bonds (2.25 eV) [13–15,19,20]. The light-induced trap states could result in defect-mediated emission with longer wavelengths beyond the detection range of the spectrometer, or act as non-radiative recombination pathways [16,17]. FTIR spectroscopy of Si– $H_x$  bond breaking was reported for hydrogenated amorphous Si (a-Si:H) film illuminated under AM 1 light [13]. The effect of UV

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