

# In-flight Microplasma Synthesis of Luminescent Silicon Nanocrystals

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A single-step in-flight microplasma synthesis of alkyl-terminated blue-luminescent silicon nanocrystals (Si-NCs) is presented. A mixture of silicon tetrachloride and methane is activated in a medium-pressure (20 kPa), miniaturized (200  $\mu$ l) non-thermal plasma reactor. Hydrogen species derived from methane abstract chlorine from  $\text{SiCl}_n$  efficiently, while partially decomposed methane fragments terminate Si-NC surface. A miniaturized reactor works as short-residence-time reactor which suppresses excess crystal growth, leading to monodispersed 2 nm crystalline particles. Although gas temperature of the microplasma is elevated up to 1000 K, crystalline nanoparticles are obtainable at room temperature in the sense that no heating device or high temperature post-annealing is required. As-produced Si-NCs are fully passivated by short chain alkyl groups: Si-NCs are readily suspended into toluene and glow bright blue-photoluminescence (440 nm) upon irradiating UV light source. Indirect electron-hole recombination seems to dominate luminescence mechanism in the present Si-NCs.

Keywords: Microplasma, Silicon quantum dots, Photoluminescence, atmospheric pressure non-thermal plasma

## 1. Introduction

Although optical properties of silicon nanocrystals (Si-NCs) is not as excellent as II–IV semiconductor materials such as cadmium selenide (CdSe), Si-NC is highlighted as one of the promising frontiers in the future optoelectronic devices because of its non-toxicity and abundance. Furthermore, existing silicon technology based on semiconductor industry is readily available without significant modification for integrating silicon-based nanomaterials into various devices.

In the previous study, hydrogen-terminated Si-NC with size tunable photoluminescence was successfully synthesized using atmospheric-pressure microplasma reactor [1]. Microplasma is characterized as high-density non-thermal plasma where electron density reaches as high as  $10^{14}$ – $10^{15}$   $\text{cm}^{-3}$ , while gas temperature increases up to 1000–1500 K. Silicon tetrachloride ( $\text{SiCl}_4$ ) is decomposed efficiently in the microplasma reactor, whereas high-pressure condition accelerates silicon cluster nucleation via three-body reaction in the gas phase. In spite of fast crystal nucleation, excess crystal growth is suppressed because miniaturized reactor works as short-residence-time reactor which suppresses excess crystal growth, leading to in-flight synthesis of Si-NCs with sizes smaller than 3 nm. Formation of oxide shell, rather than hydrogenated surface, improves optical property of red-luminescent (670 nm) Si-NCs with sizes around 3 nm. In contrast, optical property of green-luminescent Si-NCs (520 nm) deteriorated upon exposing ambient air, resulting in faint blue-luminescence

due to silicon oxide network rather than quantum confinement effect of nanostructured silicon. Formation of silicon oxide dominates band gap energy and size-dependent tunability is no longer emerged when the crystal size is smaller than 2 nm: the maximum band gap energy of partially oxide Si-NCs is estimated to be 2.1 eV (590 nm) [2].

Blue-luminescent (< 500 nm) Si-NCs are extensively synthesized via solution route [3–6]. Liquid phase synthesis is advantageous because Si-NC synthesis and surface functionalization are possible in the oxygen-free environment. However, liquid phase synthesis requires tedious and time-consuming operations such as hours of stirring, drying, filtering, purification, and so on. Furthermore, productivity of crystalline nanoparticles is generally low because of low temperature synthesis, which is restricted by the presence of liquid solvent.

This paper presents a single-step in-flight microplasma synthesis of alkyl-terminated blue luminescent Si-NCs. Silicon tetrachloride was simultaneously activated with methane. Hydrogen species derived from methane efficiently abstract chlorine from  $\text{SiCl}_n$ , while partially decomposed methane fragments passivate particle surface: not only Si-NC synthesis, but also in-flight surface functionalization are simultaneously realized in a single-step reaction at room temperature; as-produced alkyl-terminated Si-NCs readily exhibit blue photoluminescence without high temperature post annealing or time-consuming liquid phase hydrosilylation. In this paper, detailed experimental procedure and preparation of Si-NCs containing colloidal solution is

presented. Optical property of Si-NCs was characterized by UV-Vis absorption and photoluminescence excitation spectroscopy. ATR-FTIR and TEM analysis were also performed. Finally, concluding remarks are presented.

## 2. Experimental

Figure 1 shows schematic diagram of experimental setup and digital image of microplasma. A capacitively-coupled non-thermal plasma was produced inside a quartz tube (outer diameter: 6 mm, inner diameter: 3.5 mm) having external metallic electrodes with 20 mm separation. A previously developed microplasma reactor with inner diameter of 630  $\mu\text{m}$  was also applicable for this purpose; however, reactor wall was severely contaminated by as-produced material which eventually blocks gas flow. Large agglomerate with sizes more than several micrometers, which grown on the reactor wall, was also included in Si-NCs [7]. A very-high-frequency (144 MHz) power was applied to the electrode pair, which leads to gas breakdown as shown in Fig. 1. Helium was used as carrier gas and a mixture of methane and silicon tetrachloride was premixed via gas mixing chamber. Basic condition in this report is as follows: gas flow rate: 200  $\text{cm}^3 \text{min}^{-1}$ ;  $\text{CH}_4$ , 2 %;  $\text{SiCl}_4$ , 500 ppm; total pressure, 20 kPa; synthesis time, 30 min.

Silicon tetrachloride and methane were primarily decomposed by high-energy electron impact, while hydrogen derived from methane dominantly promotes dechlorination reaction. Simultaneously, partially decomposed methane fragments are expected to passivate Si-NC surface. As-produced powder-like material was deposited directly into a quartz vial. After 30 minutes synthesis, the vial was taken out of the chamber and toluene was added. Subsequently, the material was sonicated off the vial wall and suspended into toluene, producing Si-NC containing colloidal solution. As-produced colloidal solution was centrifuged to remove bulky agglomerates or soot before optical measurement. All these procedures, except Si-NC synthesis, were performed in open atmosphere: no special care was taken to avoid air exposure. The optical property of Si-NCs was characterized by photoluminescence excitation (F-4500 Fluorescence Spectrophotometer, HITACHI) and UV-Vis absorption spectroscopy (U-3500 Spectrophotometer, HITACHI). The chemical structure of Si-NCs was characterized by ATR-FTIR (FT/IR-660, JASCO) absorption spectroscopy. The Si-NCs were also characterized by transmission electron microscope operated at 200 kV (JEM-3010, JEOL).

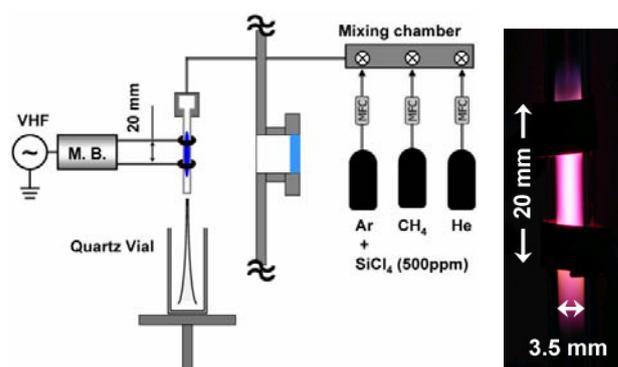
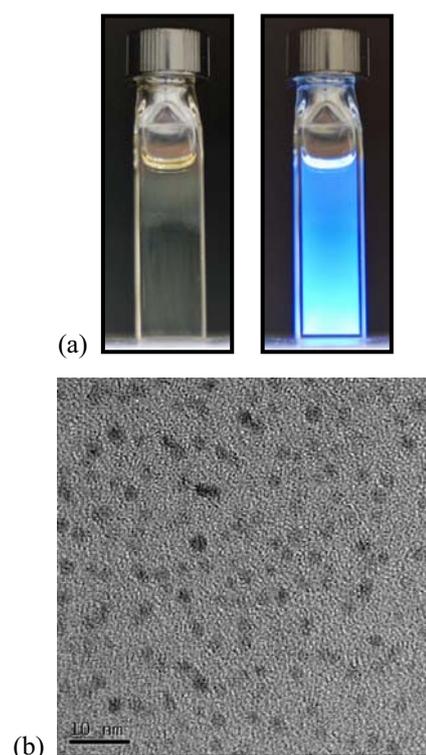


Fig. 1 Experimental setup and digital image of microplasma.

## 3. Results and discussion

### 3.1 Characterization of as-produced Si-NCs

Figure 2 shows digital image of as-produced Si-NCs suspended in toluene. The Si-NCs formed stable and clear colloidal solution (left). It is noteworthy that hydrogen-terminated Si-NCs produce cloudy solution and sedimentation of large agglomerates are soon observed [8]. A bright photoluminescence was visible by naked eyes upon irradiation of UV source (right) without high-temperature post-annealing or liquid phase surface functionalization. The solution was drop-cast onto a carbon-copper grid, then characterized by TEM. High-resolution TEM images (Fig. 2(b), (c)) revealed free-standing monodispersed crystalline particles with sizes around 2 nm. Native oxide shell which surrounds crystalline core is not observed for individual NCs.



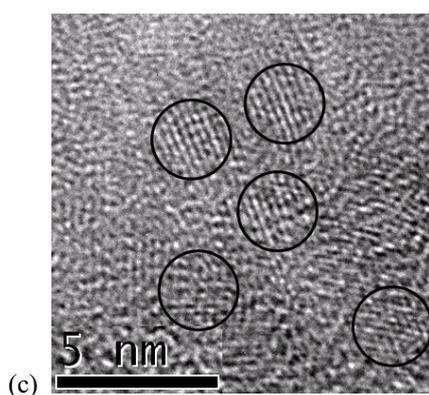


Fig. 2 (a) Digital image of surface-modified Si-NCs suspended in toluene. A clear colloidal solution in a quartz vial (left) glows bright photoluminescence (right) under UV irradiation (360 nm) during room light on. (b), (c) High-resolution TEM micrographs for the sample shown in Fig. 2(a).

Figure 3 shows ATR-FTIR absorption spectrum of sample shown in Fig. 2(a). Remarkable absorption peaks between 2800-3000  $\text{cm}^{-1}$  originate alkane C-H stretching vibration, implying that Si-NCs are successfully terminated by alkane group. Absorption due to alkyne groups such as  $\text{C}\equiv\text{C}$  (2220  $\text{cm}^{-1}$ ) and  $\equiv\text{C-H}$  (3050  $\text{cm}^{-1}$ ) vibration, which are unfamiliar with liquid phase hydrosilylation of Si-NCs, are also visible [4-6]. Acetylene is thermodynamically favorable product by methane fragmentation at elevated temperature (>1000 K), thus carbon triple bonds also contribute to Si-NC passivation. Although methane fragmentation should produce abundant hydrogen, Si-H absorption around 2100  $\text{cm}^{-1}$  is only slightly visible: Si-NCs are mainly terminated by organic ligands. Liquid phase hydrosilylation is possible with long organic chains because grafting Si-NCs with short organic chain is difficult in liquid phase due to lower boiling point with smaller molecules. Long organic chain may prevent full surface passivation due to steric repulsion, remaining some Si-H bonds on Si-NC surface. In contrast, microplasma treatment allows using small molecules such as methane that might accomplish full passivation with short organic chains.

The O-Si-O absorption is also small after 1 hour natural oxidation. It clearly increased after 12-hour natural oxidation, while alkene and alkane groups between 1400 and 1600  $\text{cm}^{-1}$  alternatively diminished. Oxidation is relatively slow because as-produced Si-NCs do not have weak Si-H bonds. In this regard, alkane group is the main component which protects Si-NCs from oxidation and also determines solubility and functionality.

There are several peaks between 730 and 900  $\text{cm}^{-1}$  as

shown in the inset of Fig. 3. A sharp peak at 760  $\text{cm}^{-1}$  may originate  $\text{CH}_3\text{SiCl}$  vibration. Other types of Si- $\text{Cl}_x$  bonds such as  $\text{HSiCl}$  (566 and 534  $\text{cm}^{-1}$ ) are also possible [9,10]; however, these short wavelength peaks are not detectable with the current FTIR setup. Generally, Si-Cl and Si-H bonds are not stable in the oxidative environment, while 760  $\text{cm}^{-1}$  peak is fairly stable after 12-hour natural oxidation. Further investigation is needed for the residual chlorine-related components. Other peaks such as 830 and 817  $\text{cm}^{-1}$  might attribute to Si-C bonds [11]. Absorption due to amorphous or crystalline SiC should occur between 780 and 800  $\text{cm}^{-1}$ . In this respect, as-produced material is unlikely SiC nanocrystal, but might be rich in Si-C bonds.

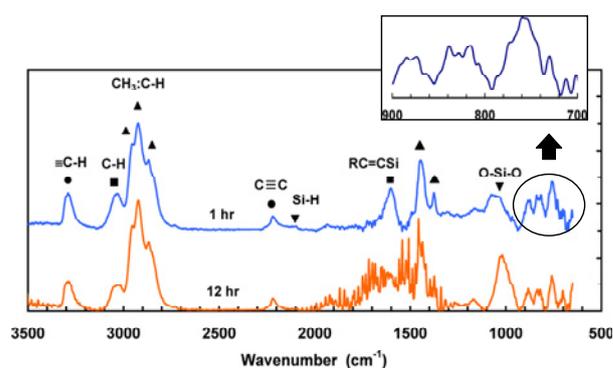


Fig. 3 ATR-FTIR spectrum of as-produced Si-NCs. The spectrum was taken after 60 min and 720 min air exposure.  $\blacktriangle$  Alkane,  $\blacksquare$  Alkene,  $\bullet$  Alkyne.

### 3.2 Optical property

Figure 4 presents UV-Vis absorption spectrum of the sample shown in Fig. 2(a). A featureless long absorption tail reflects the indirect nature of the silicon band gap. Photoluminescence excitation (PLE) spectrum is also presented in Fig. 4 with excitation wavelength between 280 nm and 600 nm. The PL intensity is fairly weak when the excitation wavelength was shorter than 280 nm in spite of strong UV absorption. Except a small variation of PL spectrum with respect to excitation wavelength, PL peak is located essentially around 440 nm (2.8 eV), which is well below the first direct band gap energy of bulk silicon (3.54 eV): indirect electron-hole recombination seems to dominate luminescence mechanism in the present Si-NCs. The Stokes shift was calculated as the difference between excitation energy and PL peak energy, and results are presented in Fig. 5. The Stokes shift is greater than 1 eV when the excitation wavelength is shorter than 350 nm (3.54 eV) which approximately corresponds to the first direct band gap energy of silicon. It drops below 0.5 eV after 350 nm where strong PL is observed. Excitation wavelength with slightly above the indirect band gap energy results in efficient PL emission.

The longer wavelength excites a population of larger Si-NCs; therefore, PL intensity gradually decreases with excitation wavelength.

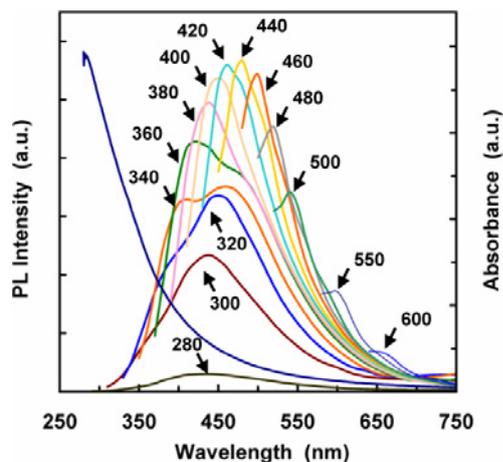


Fig. 4 UV-vis absorption and photoluminescence excitation spectrum of colloidal solution. Each number expresses excitation wavelength in nm.

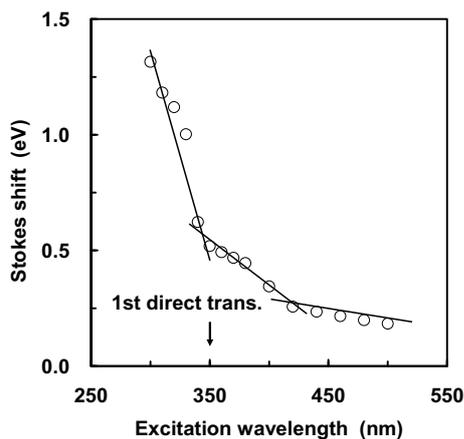


Fig. 5 Stokes shift of the sample shown in Fig. 2(a). Data was derived from PLE spectrum shown in Fig. 4.

#### 4. Concluding remarks

A microplasma reactor realized in-flight synthesis of alkyl-terminated blue-luminescent nanocrystals. Mono-dispersed 2 nm crystalline particles suspended in toluene readily exhibits blue-luminescence without high temperature post-annealing or liquid phase hydrosilylation: bright blue-luminescence was available without depletion over months. ATR-FTIR absorption spectroscopy suggests that as-produced Si-NCs do not have Si-H bonds and fully terminated by organic ligands. Unlike liquid phase hydrosilylation, in-flight plasma synthesis allows full passivation with short organic chains. Blue is one of the light's three primary colors, thus

blue-luminescent Si-NC opens variety applications including not only photovoltaic devices, but also lighting purposes. A given microplasma reactor provides simple and viable production method. However, productivity of Si-NCs is relatively small due to limited  $\text{SiCl}_4$  concentration (500 ppm) in the initial feed gas. In addition, large part of Si-NCs seems to be included in the soot which is simultaneously produced via methane decomposition: further increase in Si-NCs yield must be achieved from the practical standpoint. For future work, operating parameters such as total pressure, feed gas components ( $\text{CH}_4/\text{SiCl}_4$  ratio), and reactor size (reaction time) must be optimized for size-dependent luminescent tunability of Si-NCs.

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