Synthesis and Surface-derivatization of Silicon Nanoparticles and their Photoluminescence and Stability

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Abstract

We describe the synthesis and characterization of silicon nanoparticles prepared by the solution reduction of silicon tetrachloride by lithium naphthalenide and subsequently with n-butyllithium at room temperature. These reactions produce silicon nanoparticles with surfaces that are covalently terminated with butyl group. Reaction with lithium aluminium hydride instead of n-butyllithium produces hydride-terminated silicon nanoparticles. The butyl or hydride terminated silicon nanoparticles can be suspended in hexane and their optical behavior have been characterized by photoluminescence spectroscopy. Stabilization of silicon nanoparticles were investigated upon illumination, indicating that as-prepared silicon nanoparticles are very stable at room temperature for several days.

Key words : Silicon Nanoparticles, Surface-derivatization, Photoluminescence, Stability

1. Introduction

Over the past decade, nanoparticles and quantum dots have been touted as promising agents for their possible applications in biomedical images, optics, and sensors due to their desirable properties of high quantum yield, resistance to photobleaching, narrow emission peak, and tunable emission wavelength[1-3]. Quantum dots have several interesting characteristics due to quantum effects that appear at the nanoscale. They have unique optical and electronic properties that are not observed in their bulk counterparts.

There have been extensive studies of group II-VI annoparticles[4,5]. Recent advances have resulted in the large-scale preparation of relatively monodisperse quantum dots[6], quantum dot arrays[7], light-emitting diodes[8], and fluorescent probes[9]. Over the past decade the preparation and characterization of silicon nanocrystals has been developed due to their abundance in nature and biocompatibility[11]. The wide availability of silicon along with its electrical and chemical properties has made this semiconductor the material of choice for many electronic applications[3]. Silicon nanoparticle shows many of the characteristics of conventional III-IV nanoparticles, such as short lifetimes, high quantum yields and stimulated emission. Further they are useful for biologically sensitive materials and applied in opto-electronics[2].

Investigation of the synthesis of silicon nanoparticles by solution routes has been an active area of the research since it was first suggested that the visible luminescence seen in porous silicon could result from quantum confinement of electron-hole pairs[12]. Several different methods are available for the preparation of silicon nanoparticles such as solution phase decomposition of silanes[13], the electrochemical etching of silicon wafers[14] as well as the reaction of Zint'l salts with silicon halides[3,14]. Other applicable methods such as solution reduction of silicon halides by sodium[15], lithium naphthalenides[16], hydride reagents[17], the reduction of tetraalkoxysilanes with sodium[18] also exist simultaneously.

Here an approach has been made for the synthesis of silicon nanoparticles by an improvement in the solution reduction method. This provides a nanoparticle capped with chlorine, which is then passivated. Surface derivatization (passivation) is expected to provide long stability to the nanoparticle[19,20].

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2. Experimental Section

2.1. Materials and Methods

Lithium, naphthalene, silicon tetrachloride (99.99%), n-butyllithium, dichlorodimethylsilane were all purchased from Aldrich. Prior to use, the solvent THF was distilled over sodium/benzophenone but all other reagents were used as received without further purification. All sample manipulations were handled via standard inert atmospheric techniques. Glasswares were silonated by reaction for 1 h with a 2% solution of $(CH_3)_2SiCl_2$ in toluene followed by repeated washes with hexane and methanol and dried overnight at 120°C. The nanoparticles were characterized by photoluminescence spectroscopy (Perkin Elmer LS 55 luminescence spectrometer).

Synthesis : The lithium naphthalenide was prepared by modification of a literature procedure. 0.9 g of lithium (50 mmol) into small pieces and 3.23 g of naphthalene (25 mmol) were added in 50 mL THF and stirred vigorously overnight at room temperature. Dark greenish solution was obtained. The lithium naphthalenide solution was canulated at room temperature to a Schlenck flask containing 1.14 g (6.7 mmol) of silicon tetrachloride in 100 mL of THF with rapid stirring. It was allowed to stir for about half hour. Then 6.4 mL of n-butyllithium (2.5 M in hexane) was added in a single amount. The stirring was continued for overnight. Then the solvent and naphthalene were removed under reduced pressure with heating. The residue was extracted with hexane. The extracted solution was washed with water and the organic portion separated out. Evaporation of the hexane layer followed by heating in an oil bath under vacuum to remove residual naphthalene gave out a viscous oil of silicon nanoparticle with butyl surface-derivatization.

For the production of hydride terminated silicon nanoparticles, lithium aluminium hydride ($LiAlH_4$) solution (2.6 mL) was added via a gastight syringe at 0°C in place of n-butyl lithium. The mixture was stirred in an ice-bath at 0°C and allowed to slowly warm up to room temperature overnight. Remaining the processes being the same, the collected hexane layer was clear and colorless. This hexane was removed by evaporation. That gives an oily residue containing silicon nanoparticles surface-derivatized with hydrogen which can be further suspended in hexane.

3. Result and Discussion

3.1. Solution reduction and surface derivatization

The silicon nanoparticles were formed according to equations as follows, given in the Scheme 1. The reaction involves the reduction of silicon tetrachloride with lithium naphthalenide and the subsequent surface-derivatization of the silicon nanoparticle produced with use of an alkyl lithium reagent and contact with water.

Once the alkyl-capped product was obtained, the solvent was removed under reduced pressure and hexane was added. The hexane mixture was washed with distilled water to remove the salt by-products such as lithium chloride, excess silicon tetrachloride and n-butyllithium, and other byproducts of the reaction. The suitable method for surface-derivatization of the silicon nanoparticle was investigated by the canulation of lithium naphthalenide solution into the silicon tetrachloride dissolved in THF followed by the introduction of n-butyllithium. This indicated the more surface-derivatization of the nanoparticles.

3.2. Organic-soluble silicon nanoparticles

For both butyl and hydrogen terminated silicon nanoparticle characterization, no analytical technique can itself verify the crystallinity, size and surface-derivatization. The observation of photoluminescence suggests that there is occurrence of terminated silicon nanoparticle displaying quantum confinement effects. It does not give details of nanoparticle crystallinity or the size distribution. The identity of the termination source and its relationship to the nanoparticle (relating with structural or crystalline core) remains undefined. The pho-
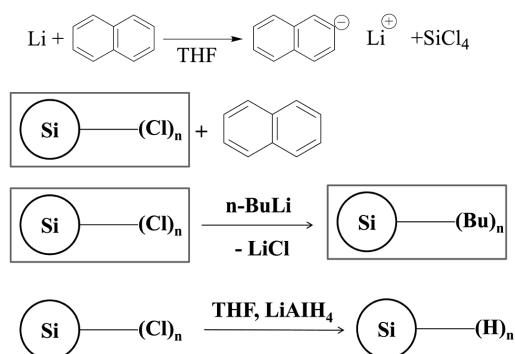
Scheme 1. Reaction method for surface derivatized silicon nanoparticles.

toluminescence data signifies only that there are surface-derivatized silicon nanoparticles suspended in n-hexane[21]. It is an obvious fact that the quantum size effect in semiconductor nanocrystals is manifested as a blue shift in the photoluminescence spectrum[22]. It has been shown that this shift is as much a function of the surface-derivatization and the organization of the nanoparticle surface in the case of silicon and germanium nanocrystals[23,24].

3.3. Photoluminescence

Since the discovery of visible photoluminescence from nanometer sized silicon such as porous silicon, silicon nanoparticles and silicon nanoparticles embedded in other materials at room temperature have attracted much attention in the study of silicon based, light-emitting materials. It is necessary to understand their luminescence processes in order to expose their potential for applications in optoelectronics. However, owing to their low stability and reproducibility, porous silicon devices still seem to be very difficult to use in the industry. Therefore it is important to clarify the stability of the silicon nanoparticles and their surfaces believed to be responsible for blue-luminescence.

Photoluminescence spectra were taken from samples dissolved in n-hexane. The photoluminescence spectra were measured at room temperature. The present synthesis produces a size distribution of which the photoluminescence spectra are inhomogeneously broadended.
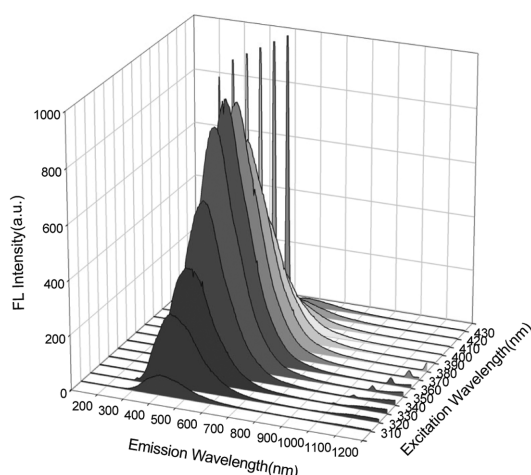
Figure 1 shows the photoluminescence spectra for the butyl terminated silicon nanoparticles. In the photoluminescence spectra, a strong UV-blue photoluminescence ranging from 390 nm to 550 nm is observed for organic-soluble silicon nanoparticle terminated with n-butyl group. The center of the UV-blue peak is located at 450 nm, with an excitation wavelength of 360 nm and shows continuous shift with the increase of excitation wavelength. One manifestation of quantum confinement in such a system is a monotonic shift of the photoluminescence as the excitation wavelength is changed. This results from the excitations of different sizes of nanoparticles that have different optical transition energies. It has been suggested that the blue-green luminescence is due to a particularly small size of the particles, where strong quantization of the electronic levels occurs, and that the red-orange luminescence is caused by larger particles which are less quantized. The photoluminescence of the silicon nanocrystals was found to be remarkably stable in terms of the sensitivity of the nanoparticle core to the surface chemistry.

The photoluminescence is considered to be the size dependent, with the larger particles emitting lower energy light than the smaller particles, regarding with the general concept of quantum confinement effects in silicon nanoparticles. The photoluminescence was found to depend on the excitation wavelength yielding the sharpest photoluminescence.

Figure 2 shows the photoluminescence spectra of the hydride terminated silicon nanocrystals. In the photoluminescence spectra, a strong UV-blue PL ranging from

Fig. 1. Photoluminescence spectra of butyl-capped silicon nanoparticles derived from n-butyllithium.
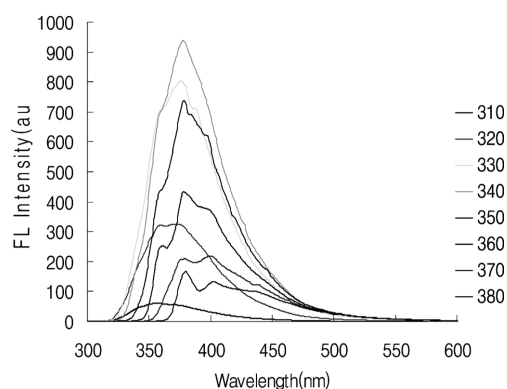

Fig. 2. Photoluminescence spectra of hydride terminated silicon nanoparticles derived from lithium aluminium hydride.

330 nm to 600 nm is observed for hydride terminated silicon nanoparticle. The center of the UV-blue peak is located at 378 nm, with an excitation wavelength of 340 nm and shows continuous shift with the increase of excitation wavelength. This UV-blue photoluminescence from these nanocrystallites occurs in a different spectral region than that from other blue emitters such as oxidized porous silicon (440 - 480 nm)[25,26] or silicon carbide (500-520 nm)[27], thus complimenting their blue output performance.

The intensity of the blue photoluminescence from these nanoparticles is affected by the cluster size and depends linearly on the excitation power density[28]. It is expected that luminescence from traps in semiconductors will saturate at high excitation powers due mainly to their lower number density relative to the band edge states of semiconductors. As a result, the observation of a linear dependence of the luminescence intensity as a function of excitation power indicates that saturation does not occur. This suggests that the origin of the luminescence is likely to be from traps, such as oxide or defect sites.

Figure 3 showed that the FT-IR spectrum of H-terminated silicon nanoparticles displayed a characteristic broad band centered at 2119 and 914 cm^{-1} for the (Si-H) stretching vibration and (Si-H) bending vibration. Strong (Si-Si) stretching vibration appeared at 611 cm^{-1}, indicating that as-prepared silicon nanoparticles consisted of only silicon and hydrogen atom.

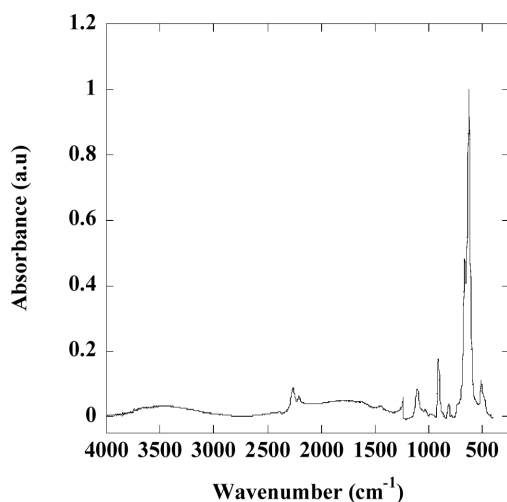## 3.4. Stability

Aging is observed after 1 hour when the particles are left in solution and stored in the dark. The aging of the particles was monitored over 4 days but after aging for 2 days, the stability seems to be constant over time. For the organic-soluble silicon nanoparticle terminated with n-butyl group as shown in Figure 4, the photoluminescence intensity is found to be dropped by a difference of around 7% and the peak position to be shifted by about 8 nm toward the blue during 100 hrs just after synthesis.

A general trend seems to be that particles with initial emission at longer wavelengths show an increase in photoluminescence intensity with time, followed by a decrease in intensity at longer times, while particles with shorter wavelength emission show a monotonic decrease in photoluminescence intensity with time. But this uniformity has always not been encountered during the observation of all the samples we prepared (as shown above).
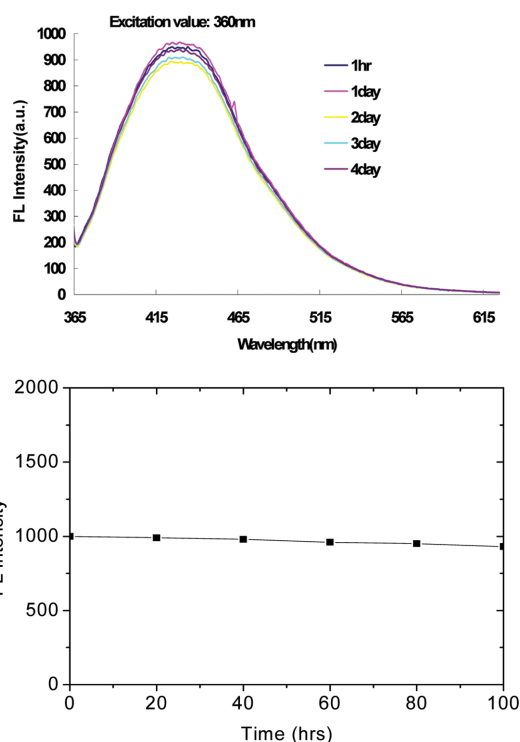
In the case of surface-derivatized silicon nanopaticles

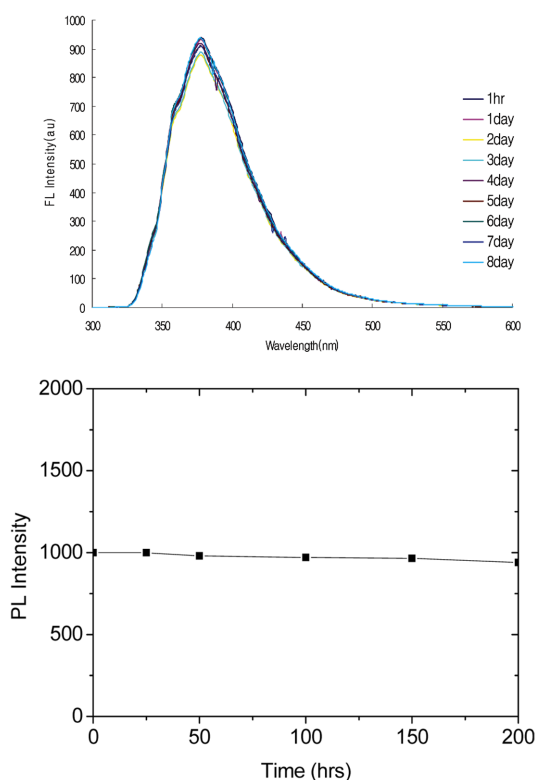Fig. 4. Time dependence of photoluminescence spectra of organic-soluble Si nanoparticles derived from n-BuLi.

Fig. 3. FT-IR spectrum of silicon nanoparticles.

Fig. 6. Photographs of as-prepared silicon nanoparticles under white light (left) and black light (right).

Fig. 5. Time dependence of photoluminescence spectra of organic-soluble silicon nanoparticles derived from LiAlH$_4$.

toluminescence spectrum with time for the same phase nanoparticle can be observed.

Figure 6 displayed the photographs of as-prepared silicon nanoparticles, indicating that silicon nanoparticles showed strong blue emission.

4. Conclusion

The surface-derivatization of silicon nanoparticle produced by reaction of the lithium naphthalenide with silicon tetrachloride has been investigated. The samples studied are the organic soluble silicon nanoparticles in hexane. This method is unique in being able to produce in a limited amount of silicon nanoparticles with brighter and visible photoluminescence. Additional efforts are needed and are underway to modify the nanoparticle surfaces and synthesize size-dependent nanoparticles and to further stabilize the photoluminescence. Stable, surface-derivatized and highly photoluminescent silicon nanoparticles can be produced in room temperature as a bench reaction.

Acknowledgements

with hydrogen, the organic-soluble silicon nanoparticles as shown in Figure 5, the photoluminescence intensity is found to be dropped by a difference of around 6% and the peak position to be shifted by about 1 nm toward the blue during 200 hrs (over 1 week) just after synthesis. The changes in photoluminescence intensity or emission wavelength may be due to slow internal effect of the particles causing a thicker layer and smaller core diameter resulting in self-limiting value[29]. Further it may result from other changes in the state of the particle surface.

The mechanism of the photoluminescence considering these factors in the case of such nanoparticles (in both the cases) is not yet strongly discussed and therefore a speculation can only be made regarding the sources of changes in it. The photoluminescence intensities can be compared directly between the two phase nanoparticles. The reason behind this is assumed to be due to the similarities in particle concentration (including other factors may be). Further the change in pho-
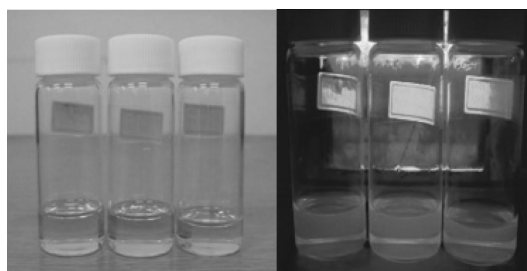
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