A New Approach to Synthesis and Photoluminescence of Silicon Nanoparticles

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Abstract

We describe the synthesis and characterization of silicon nanoparticles prepared by the solvent reduction of SiCl4. These reactions produce Si nanoparticles with surfaces that are covalently terminated. The resultant organic derivatized Si nanoparticles as well as a probable distribution of water-soluble Si nanoparticles are observed and characterized by photoluminescence (PL) spectroscopy. This work focuses originally on the organic- and water-soluble silicon nanoparticles in terms of the photoluminescence. Further this work displays probably the first layout of hydrogen terminated Si nanoparticles synthesized in solution at room temperature.

Key words: Synthesis Photoluminescence, Si Nanoparticle, Solution Route.

1. Introduction

An exciting aspect of the research at the nanoscale results as nanostructures hold the potential to display an enhanced and unexpected reactivity relative to that at the micron scale and bulk phase. Further, their formation and interactions may be accompanied by phase transformations not commonly observed in bulk systems. Interest in nanoscale materials increased in recent years with the realization that unique properties may be obtained from otherwise ordinary materials.

Nanoscale materials are being focused, nowadays, as a center of attraction for a great deal of intense scientific research such as biomedical, optical, electronic fields etc. This focus is due to the fundamental differences in properties between nanoscale and macrolevel. The properties of materials change as their size tend to approach the nanoscale. The interesting and sometimes exciting behaviors of nanoparticles are observed, partly, due to the aspects of the surface of the material dominating the properties in lieu of the bulk properties. An investigation of the silicon nanoparticles has also displayed particle size dependent optical and electronic properties. Further they are useful for biologically sensitive materials and applied in optoelectronics. The prospect of silicon possessing useful optical properties has generated extensive speculation over the possibilities of new applications for silicon. The wide availability of silicon along with its electrical and chemical properties has made this semiconductor the material of choice for many electronic applications.

Here an approach has been made for the synthesis of silicon nanoparticles by improving the solution reduction method. In particular, the use of metal naphthalenides has been reported as precursors to silicon nanoparticles with subsequent surface derivatization with organic ligands. This synthesis covers the reaction of silicon tetrachloride with lithium naphthalenide in tetrahydrofuran as a solvating medium to give rise to chloride capped silicon nanoparticles that can be further terminated by n-butyllithium as a surface-derivatization to give butyl-capped silicon nanoparticles. In another attempt, the production of hydrogen terminated silicon nanoparticles is also becoming a hot issue in the area of intense research.

To date very little investigation has been done on the hydrogen terminated silicon nanoparticles. Hydrogen terminated silicon nanoparticle is an attractive starting point for the synthesis of novel modified silicon surfaces. In the present work, hydrogen terminated silicon nanoparticles have been synthesized by the reaction of lithium aluminium hydride with chloride-capped silicon nanoparticle which being produced from silicon tetrachloride with lithium naphthalenide in tetrahydrofuran. After the synthesis, the photoluminescence and stability
of both types of silicon nanoparticles have been studied thoroughly.

2. Experimental

2.1. Materials
Lithium, naphthalene, silicon tetrachloride (99.99%), n-butyllithium, dichlorodimethylsilane, and lithium aluminium hydride (1 M in THF) were all purchased from Aldrich. Prior to use, the solvent tetrahydrofuran was distilled over Na/benzophenone but all other reagents were used as received without further purification. All sample manipulations were handled via standard inert atmospheric techniques. Glass wares were silanized by reaction for 1 hr with a 2% solution of (CH₂)₃SiCl in toluene followed by repeated washes with hexane and methanol and dried overnight at 120°C.

2.2. Syntheses
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 of tetrahydrofuran and stirred vigorously overnight at room temperature. Dark greenish solution was obtained. The lithium naphthalenide solution was cannulated at room temperature to a Schlenk flask containing 1.14 g (6.7 mmol) of silicon tetrachloride in 100 mL of tetrahydrofuran with rapid stirring. It was allowed to stir for about half an 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 (if necessary). 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. The remaining portion was washed with the distilled water, filtered and separated out. The resulting oxidized solution was handled in air. For the production of hydrogen-terminated Si nanoparticles, lithium aluminium hydride (LiAlH₄) solution (2.6 mL) was added via a gastight syringe at 0°C in place of n-butyllithium. 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 Si nanoparticles surface-derivatized with hydrogen which can be further suspended in hexane.

3. Results and Discussion

3.1. Solution Reduction and Surface-derivatization
The 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 nanoparticle produced with use of an alkyl lithium reagent and contact with water.

3.2. Organic-soluble Silicon Nanoparticles
Water is reactive to silicon and is capable of oxidizing silicon nanoparticle surfaces. The oxygen is reactive, too, to silicon surfaces. It is obvious that oxidation occurs when silicon and water as well as air come into contact with it. It is probable that a uniform oxide or hydroxide shell forms on the silicon, thereby protecting the crystalline core for a longer time. It is assumed that the nanoparticles appear to be encased in an amorphous material which is able to support nanoparticles. The amorphous material solidifies when the water evaporates. Exposure of silicon with lithium moieties to the air or water may result in significant oxidation⁴. An exposure of chloro-capped silicon nanoparticle to water results in oxide environments. The reaction of np-

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**Scheme 1.** Synthetic Routes of Hydride-capped Si Nanoparticles.

**Scheme 2.** Synthesis for hydroxyl-terminated silicon nanoparticles.

Si/Cl, with water to form np-SiOH suggests that hydroxyl groups have replaced chloro-groups for termination. (Scheme 2) The loss of chloro-groups in this reaction and the appearance of hydroxyl groups implies that the silicon surface sites are not completely passivated by Cl-groups in the np-Si/Cl, sample.

3.3. Photoluminescence Behavior
Since the discovery of visible photoluminescence from nanometer sized silicon such as porous silicon, silicon nanoparticles; 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. Pure silicon nanoparticles do not exhibit photoluminescence because they have dangling bonds on their surfaces.

PL emission spectra were taken from samples dissolved in n-hexane and water.

The photoluminescence spectra were measured at room temperature. The present synthesis produces a size distribution of which the photoluminescence spectra are inhomogeneously broadened. 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 PL of the Si nanocrystals was found to be remarkably stable in terms of the sensitivity of the nanoparticle core to the surface chemistry in the case of porous silicon.

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. The PL was found to depend on the excitation wavelength yielding the sharpest PL. Fig. 1 shows PL spectra of organic-soluble and water-soluble silicon nanoparticle derived from n-BuLi.

Fig. 1. PL spectra of of organic-soluble and water-soluble silicon nanoparticle derived from n-BuLi.

4. Conclusions

The surface-derivatization of silicon nanoparticle produced by reaction of the lithium naphthalenide with silicon tetrachloride has been investigated. Hydrogen-terminated silicon nanoparticles can be too, synthesized by reacting lithium naphthalenides with silicon tetrachloride and further with lithium aluminium hydride. The samples studied are the organic and water-soluble silicon nanoparticles. This method is unique in being able to produce in a limited amount of silicon nanoparticles with brighter and visible photoluminescence. We can arrive at a conclusion that n-butyllithium and lith-
ium aluminium hydride serve as effective ligands for surface-derivation for the synthesis of butyl-capped and hydrogen-capped silicon nanoparticles respectively. Probably stable, significantly terminated and photoluminescent silicon nanoparticles can be produced in room temperature as a bench reaction. Summing up, the Si nanoparticles have been investigated in order to understand the role of the surface in the UV-blue photoluminescence.

References