

Preparation of Luminescent Silicon Nanoparticles: A Novel Sonochemical Approach

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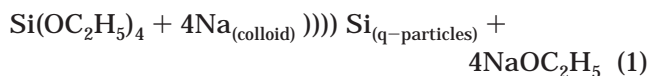
Currently porous silicon has been attracted a great deal of attention because of its novel optoelectronic properties due to visible light emission.¹ The electronic properties of bulk silicon cannot explain the above phenomenon, as silicon has the indirect band gap of 1.1 eV. In early investigations, the predominant view was that the surface structure, especially surface defects, controlled the luminescence properties.² However, recent work on quantum dot particles has suggested that the visible luminescence of porous silicon results from the quantum confinement of electron–hole pairs and controls the band gap widening into the visible range.³ Therefore, the processing of silicon nanoparticles (q-particles) has generated extensive speculation over the possibilities of new applications for silicon. In this paper we describe a novel sonochemical procedure for generating porous silicon nanoparticles in high yields that exhibit luminescence, attributed to quantum confinement effects.

In the literature, relatively little headway has been made in the solution synthesis of porous silicon nanoparticles, primarily due to the difficulty involved in devising a synthetic strategy compatible with the solution chemistry of silicon. Such a strategy would be advantageous because it would provide a better means of controlling surface passivation of the clusters. To date, three basic methods have been used to produce silicon nanoclusters. The most successful method is the gas-phase decomposition of organic compounds of silicon.⁴ This produces silicon nanoparticles with a relatively small size distribution, but does not lend itself to the easy manipulation of the surface of the particles nor to their large-scale manufacture. A second method,⁵ investigated by several groups, is the electrochemical etching of silicon wafers in various solvents to produce colloidal suspensions of silicon nanoparticles. The solution route⁶ developed to date to synthesize these nano-

particles employs reacting Zintl compound KSi with SiCl₄ to produce crystalline silicon nanoparticles (yield of ~8%). Heath⁷ has prepared nanosized silicon powders through the reduction of SiCl₄ and RSiCl₃ by sodium metal in a nonpolar organic solvent at a high temperature (385 °C) and high pressures (>1000 atm). The reduction takes place for 3–7 days under an argon atmosphere in a high-pressure bomb.

The chemical effects of ultrasound (sonochemistry) arise from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles in liquid.⁸ The implosive collapse of the bubble generates localized hot spots through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hot spots have been experimentally determined, with transient temperatures of ~5000 K, pressures of 1800 atm, and cooling rates in excess of 10¹⁰ K/s. Since sonochemical hot spots have a high-pressure component, one might be able to produce, on a microscopic scale, the same macroscopic conditions of high-temperature–pressure “bomb” reactions or explosive shock-wave synthesis of solids.

In light of these methodological perspectives, many researchers have been interested in using sonochemical methods to prepare unusual materials that cannot be obtained by conventional techniques.⁹ Herein, we report a sonochemical procedure for the preparation of technologically important luminescent silicon nanoparticles.¹⁰ The sonochemical reduction of Si⁴⁺ → Si⁰ is most conveniently carried out by using an alkali metal and a dry alkane solvent whose vapor pressure is low at the sonication temperature. The choice of the solvent and the reactant seems to be a particularly important factor. The preparation is based on ultrasound-induced reduction of tetraethyl orthosilicate (TEOS) by colloidal sodium in toluene solvent at –70 °C. The combined cavitation effects and the highly electropositive character of metallic sodium are believed to provide the driving force for the formation of silicon nanoparticles. The primary reaction for the sonochemical generation of silicon particles can be written as:



All manipulations for the preparation of silicon nanoparticles were carried out in a dry nitrogen glovebox (<10 ppm level of oxygen). Dry toluene was used as the solvent. Sulfur free toluene was refluxed over

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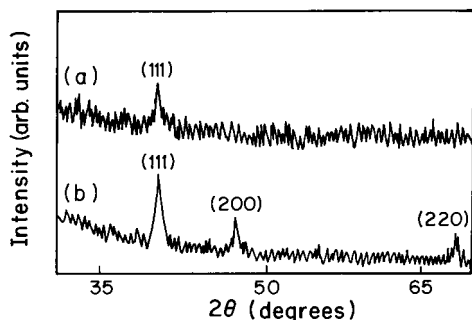


Figure 1. 1. XRD pattern of silicon: (a) initially and (b) annealed at 400 °C.

sodium wire and distilled out under dry nitrogen atmosphere. Absolute methanol was prepared by distilling out from magnesium methoxide. The reactant TEOS (99.999% Aldrich) was used without further purification. Sodium dispersion (40% Aldrich) was used as reducing agent. Mineral oil in the sodium dispersion is removed by careful, repeated washing and decanting with dry toluene. The reduction took place under an Ar atmosphere for about 3 h at -70 °C (Julabo FT 901 cooler). The solutions to be irradiated were purged with Ar gas for 30 min and kept under an argon atmosphere (0.2 MPa) throughout the sonication. Specifically, ultrasound irradiation (Misonix XL sonifier, 20 kHz, 100 W cm^{-2} , continuous mode) of a slurry of 1 mL of colloidal sodium and 2 mL of TEOS in toluene (100 mL) under an argon atmosphere yielded gray-black powders. The excess reactants were removed by washing with absolute methanol. The solid insonation product was washed with dry toluene and absolute methanol and was recovered by centrifugation. The total yield of the sonochemical solid product was $70 \pm 5\%$. The product was characterized by various different physical methods.¹¹ A similar sonochemical reduction of tetrachlorosilane (SiCl_4) by colloidal sodium to silicon has also been observed. However, washing the insonation product by water to remove the sodium chloride byproduct quenches the optical properties of the resulting solid.

The powder X-ray diffraction pattern (Figure 1) of a bulk initial sample indicates that the diffraction feature corresponds to silicon. The absence of lower intensity peaks can be attributed either to the lack long-range ordering to generate a constructive diffraction pattern due to the smallness of the particles or to the presence of a large extent of surface defects.¹² However, further annealing of the product at 400 °C for 5 h under a flow of nitrogen yields diffraction peaks characteristic of polycrystalline silicon (JCPDS card no. 35-1158). The FT-IR data collected for the different samples show

(11) The X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, Cu $K\alpha$). IR spectra were recorded using a Nicolet (Impact 410) FT-IR spectrometer, using transparent pellets of the compounds in KBr matrixes. The transmission electron micrographs were obtained by employing a JEOL-JEM 100SX electron microscope. The photoluminescence spectrum was obtained using an Perkin-Elmer luminescence spectrophotometer (model LS50B). The excitation wavelength was 260 nm. The UV-visible absorbance spectrum of the silicon was obtained using a Varian (model-DMS 100S) UV-visible spectrophotometer. ESR spectra were recorded on a Bruker ER 083 CS spectrometer, operating at X-band frequency ($\nu = 9.7$ GHz), with a 100 kHz magnetic field modulation.

(12) Because of the rapid thermal quenching and interparticle collisions associated with the acoustic cavitation, a large amount of surface defect concentration is likely to be present in the sonochemical product. See Suslick, K. S. *Sci. Am.* **1989**, *111*, 2342.

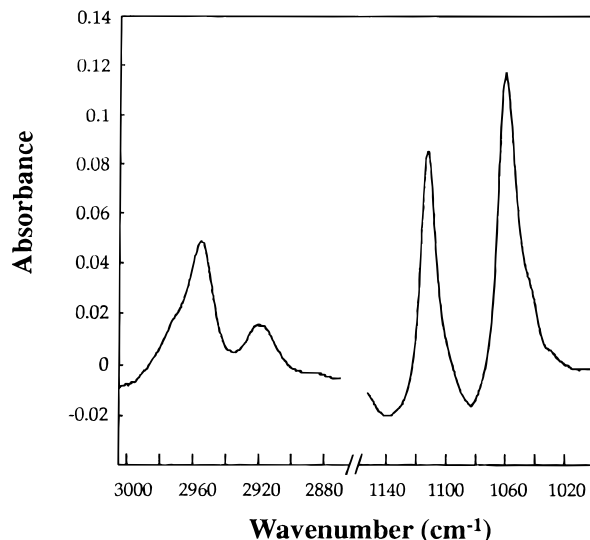


Figure 2. 2. FT-IR spectrum of silicon nanoparticles surface-capped with methoxide.

(Figure 2) only the silicon–oxygen peak near 1060 cm^{-1} and the saturated hydrocarbon peak just below 3000 cm^{-1} . This indicates that the silicon surface is probably terminated with an OC_2H_5 group, i.e., $\equiv\text{SiOC}_2\text{H}_5$. One might reasonably expect such ethoxide termination in the silicon product, since it is processed from the ethoxide precursor.

A small amount of washed sonochemical product was taken up in absolute methanol and deposited onto an amorphous carbon-coated copper grid for transmission electron microscopy (TEM) analysis. The TEM (Figure 3) study revealed the porous and spongy structure of the silicon particles. It can be seen that the porous structure is irregularly assembled/aggregated on the TEM grid, ranging from a monolayer (grey region) to multilayers (black region). A magnified TEM image shows the particulate morphology and the nature of the aggregation. The silicon nanoparticles are held together by an irregular network, with diameters ranging from 2 to 5 nm. The particle size of the silicon powder was also analyzed using a dynamic light scattering (Coulter N4 plus instrument) method. These measurements reveal the particles to be highly agglomerated.

Figure 4 shows the photoluminescence (PL) spectrum of the sonochemical product. The PL spectrum is very broad, with a maximum centered at 680 nm, while amorphous silicon emits in the range of 600–800 nm, depending upon the particle size.¹³ The observed emission spectrum of porous silicon obtained by the sonochemical process can be attributed to the expected behavior for the silicon q-dot ensembles. The UV-visible absorption spectrum of the representative silicon (Figure 5) was similar to the published spectrum of silicon particles synthesized from silane pyrolysis and electrochemical etching. The presence of an absorption peak at around 250 nm can be attributed to the charge carriers generated by light absorption of q-silicon particles. On the other hand, the strong absorption band at around 200 nm probably stems from the charge transfer of both $\text{O} \rightarrow \text{Si}$ (from surface $\equiv\text{SiOC}_2\text{H}_5$) and $\text{Si} \rightarrow \text{Si}$.

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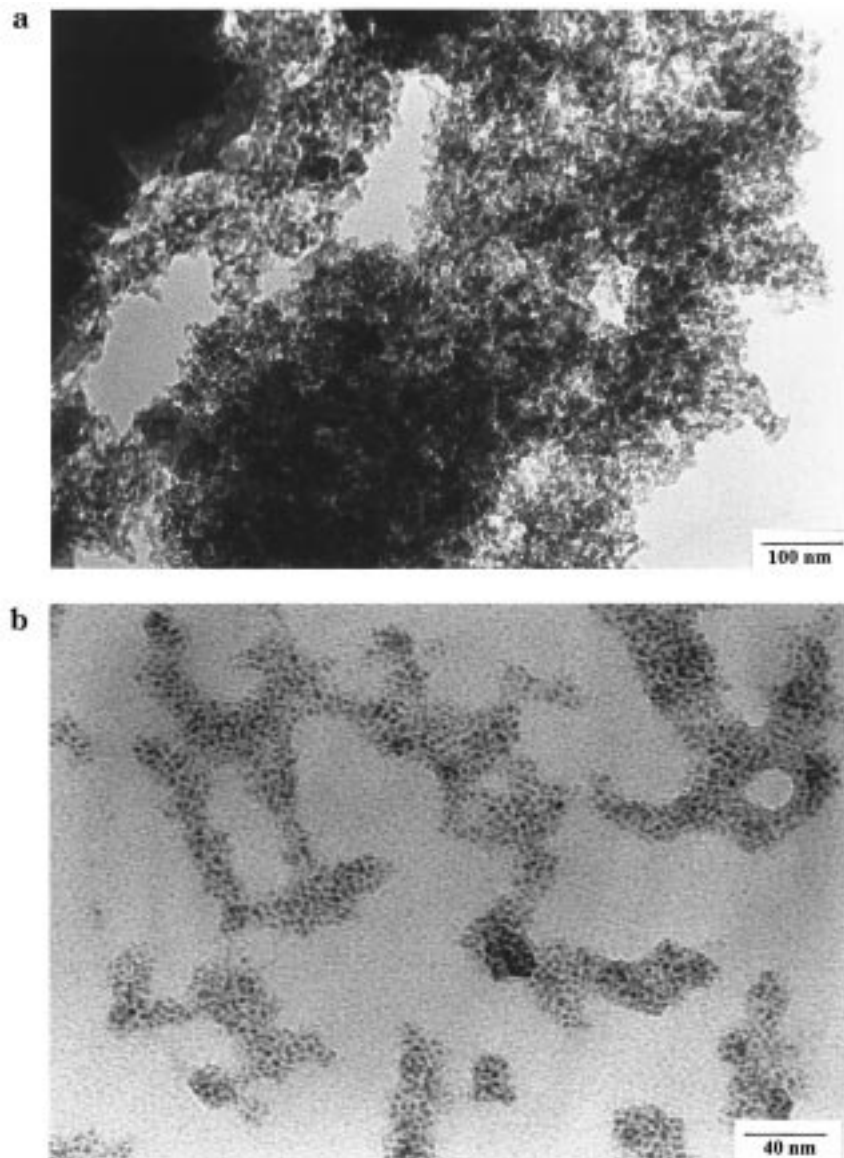


Figure 3. 3. TEM images of porous silicon: (a) bar = 100 nm and (b) bar = 40 nm.

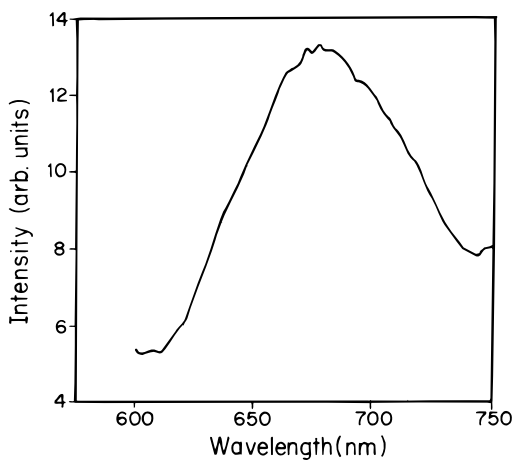


Figure 4. 4. PL spectrum of sonochemically prepared silicon q-particles.

The ESR spectrum of the sonochemical product (Figure 6) shows a very sharp signal, with a g -value of 2.0056, due to the dangling bonds of the silicon nanoparticles. The literature g -value of 2.0054(± 5) for porous silicon varies depending upon the preparation

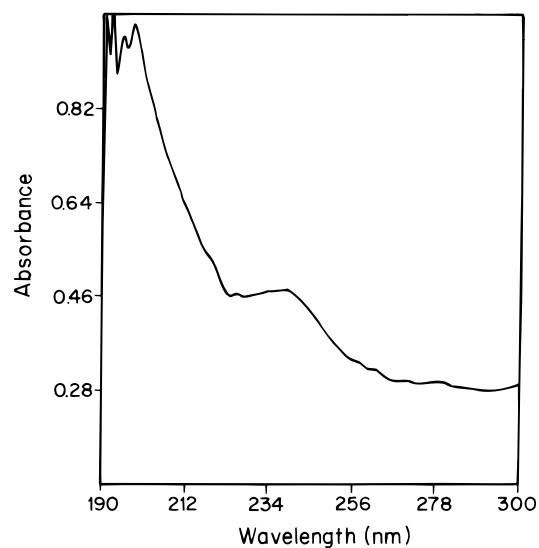


Figure 5. 5. Absorption spectrum of silicon particulates cast on a quartz plate using a methanol suspension.

method and the extent of surface defects.¹⁴ The dangling bond signals are due to the Si-Si[•] radical sites

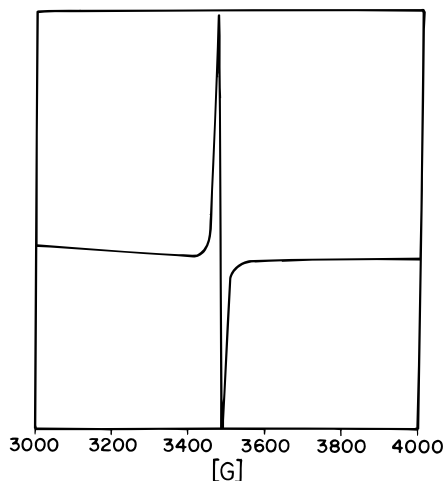


Figure 6. ESR spectrum of silicon powder.

created by breaking weak Si–Si bonds in the cluster or, alternatively, by carrier trapping in the preexisting charge defects. The narrow bandwidth of the ESR signal of the sonochemical product can be interpreted as a manifestation of quantum confinement effects; as the particle size gets smaller, the ESR signal becomes sharper.¹⁵

In conclusion, a simple sonochemical synthetic procedure has been discovered to generate silicon nanoparticles which exhibit luminescence that can be attributed to the quantum confinement effects. TEM images show the presence of porous silicon nanoparticles with diameters ranging from 2 to 5 nm. The observed PL spectral features and the ESR narrow bandwidth suggest the formation of q-dot silicon particles produced by the sonochemical reduction process. The primary advantages of the present investigation include reduced reaction time and temperatures, energy saving, and increased yields. This synthetic strategy, moreover, is potentially applicable for a variety of technologically important, simple and binary alloys of classical semiconductor nanoclusters.

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