

Sonochemically Synthesized Silicon Nanoparticle Inks

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ABSTRACT

We report on a scalable and surprisingly simple method of synthesizing silicon nanoparticles using semiconductor-grade purity trisilane (Si_3H_8) and ultrasound. The method relies on the chemical effects associated with acoustic cavitation, in particular, on the generation of localized hot spots upon bubble collapse. We demonstrate via spectroscopic techniques (FTIR, XPS) and scanning electron microscopy that sonication leads to the synthesis of discrete, unoxidized, hydrogenated, and amorphous silicon nanoparticles of size in the range 1.5 to 30 nm. Moreover, we show that the addition of a hydrocarbon additive such as 2-pentyne (C_5H_8) to the trisilane silane solution can lead to the synthesis of composite silicon carbide particles.

Keywords: silicon, nanoparticles, lithium-ion batteries, nanomedicine, solution-processing

1 INTRODUCTION

Silicon nanoparticles (Si-NPs) have become increasingly relevant in several important fields ranging from lithium-ion batteries [1], solar cells [2], and because silicon is biodegradable, their use as drug carriers or fluorescent markers has also begun to be explored [3,4].

Several methods based on gaseous silanes (e.g. monosilane, SiH_4) and vacuum processes such as plasma-assisted and hot-wall reactor techniques for producing Si-NPs are known [5,6]. However, not many practical routes based on liquid silanes have been discovered, especially ones relying on ambient temperature and pressure methods. Methods for producing Si-NPs based on liquid silanes include one relying on the gas-phase pyrolysis of cyclohexasilane (Si_6H_{12}) [7] and another on the thermal decomposition of trisilane in super critical solvents [8]. These methods have the drawback of requiring elevated temperatures (several hundred °C) or high pressures (several hundred bar) for producing particles.

The present paper discusses a convenient ambient temperature and pressure method of producing Si-NPs in trisilane solutions irradiated with ultrasound. Besides a liquid silane precursor and a source of ultrasound, the only other requirements for carrying out the synthesis are an inert atmosphere and an organic solvent.

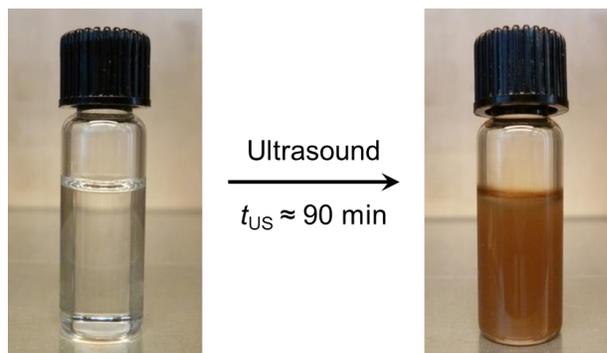


Figure 1: Color and opacity changes of a typical trisilane solution after about 90 min of ultrasonic irradiation.

2 EXPERIMENTAL

The synthesis of the Si-NPs and composite particles is carried out in a N_2 -filled glove box with H_2O and O_2 values < 1 ppm. The source of the ultrasound is a 26 kHz *Hielscher Ultrasonics* UP200St ultrasonic horn. The solvent used is cyclooctane (C_8H_{16}) from *Sigma Aldrich* and the silicon hydride precursor is trisilane (Si_3H_8) from *Voltaix LLC* (Silcore®). The additive used for the silicon carbide particles is 2-pentyne (C_5H_8) from *Sigma Aldrich*. The solutions are actively cooled and typically kept at temperatures of between -5 °C and 30 °C during sonication.

A *Zeiss* LEO 1550 VP scanning electron microscope was used for the SEM image. The FTIR spectrum was acquired using a *ThermoFischer Scientific* Nicolet 5700 spectrometer. The XPS measurements were carried out on a *Scienta Omicron* MXPS system with an Al- K_α x-ray source.

3 RESULTS

3.1 Standard Synthesis

As illustrated in Fig. 1, as-mixed solutions of trisilane are transparent. Within a few minutes of sonication, however, the mixture takes on a semi-transparent light-brown color. After about 90 min an opaque brown dispersion results. For such highly concentrated dispersions, the particles and particle agglomerates generally precipitate

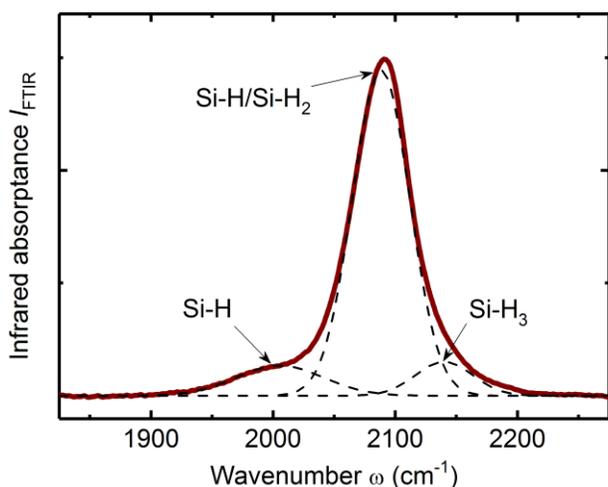


Figure 2: FTIR spectrum of a silicon nanoparticle thin film depicting the silicon hydride stretching band between 1900–2200 cm^{-1} . The various modes indicate that hydrogen is bonded to silicon both in the core (mainly at $\sim 2000 \text{ cm}^{-1}$) and at the surface ($\sim 2090\text{--}2130 \text{ cm}^{-1}$) of the particles.

at the bottom of the vial after some hours. These colloids can be collected and redispersed in other solvents for subsequent modification or coating of substrates.

Additionally, sonicated solutions can be subsequently irradiated with ultraviolet light to produce silicon nanoparticle – silicon hydride polymer composite inks [9]. These inks can be used to deposit semiconducting hydrogenated amorphous silicon thin films for a variety of optoelectronic applications, including solar cells and surface defect passivation layers [2].

3.2 Nanoparticle Properties

In general, the Si-NPs produced are amorphous and hydrogenated. The non-crystalline nature of the particles is attributed to their rapid formation inside collapsing microbubbles generated by the ultrasound.

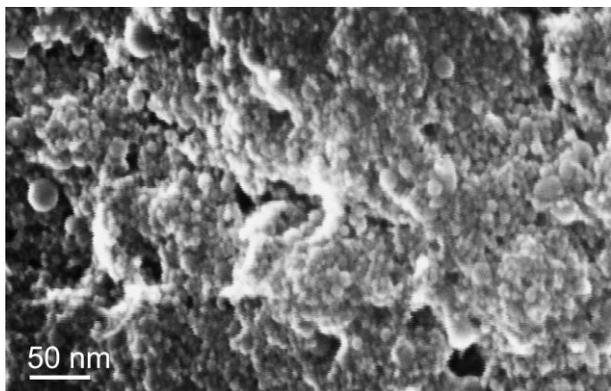


Figure 3: SEM image of a section of a silicon nanoparticle thin film showing distinct spherical particles with diameters varying from ca. 5 to 20 nm.

The presence of bonded hydrogen in the Si-NPs can be demonstrated using FTIR. Evident in the spectrum shown in Fig. 2 are the stretching modes of silicon hydride groups of the form of SiH_x ($x = 1, 2, 3$) centered at about 2100 cm^{-1} . The modes at $2000\text{--}2090 \text{ cm}^{-1}$ correspond to SiH/SiH_2 bulk hydrides in the interior and those at $2090\text{--}2130 \text{ cm}^{-1}$ to $\text{SiH}_2/\text{SiH}_3$ hydrides at the outer surface of the particles. The hydrogen termination of the surface is beneficial because it not only protects the surface from rapid oxidation, but also makes the Si-NPs ready for surface functionalization without the need for additional etching or hydrogenation steps.

The Si-NPs have been shown to range in size from about 1.5–30 nm in diameter and are predominantly spherical in shape. Two ways of varying their size have been investigated, namely by changing the amplitude of vibration of the ultrasonic horn or by simply changing the concentration of trisilane in the solution [2]. For instance, large amplitudes or high concentrations yield larger particles (average diameter $D_{\text{av}} \sim 10 \text{ nm}$). Such particles can be seen in the SEM image of Fig. 3. Conversely, smaller amplitudes or lower concentrations yield smaller particles ($D_{\text{av}} \sim 3 \text{ nm}$).

Standard solutions consist of trisilane dissolved in cyclooctane solvent. The question arises as to what happens when an additive is mixed in before sonication. Like trisilane, will the additive likewise diffuse into the acoustic bubbles to be assimilated into nanoparticles?

3.3 Composite Nanoparticle Synthesis

The nanoparticles produced with trisilane are composed of only silicon and hydrogen [10]. In order to synthesize nanoparticles composed of additional elements, such as carbon, we used 2-pentyne as additive.

Shown in Fig. 4 is a high-resolution XPS spectrum of the C 1s core-level of silicon carbide composite nanoparticles synthesized using a solution with a trisilane to 2-pentyne volumetric ratio of approx. 2. The dominant peak at $\sim 285 \text{ eV}$ corresponds to adventitious carbon or residual solvent. The smaller chemically shifted peak at $\sim 283.4 \text{ eV}$ is assigned to carbon chemically bonded to silicon. The inset shows a photograph of a typical dispersion in a glass vial. In contrast to synthesis with only trisilane and cyclooctane, the resulting dispersions with 2-pentyne additive are usually semi-transparent and stable.

4 CONCLUSIONS

A sonochemical synthesis route for silicon-based nanoparticles was shown that can be carried out in inert atmosphere at ambient temperature and pressure. The main

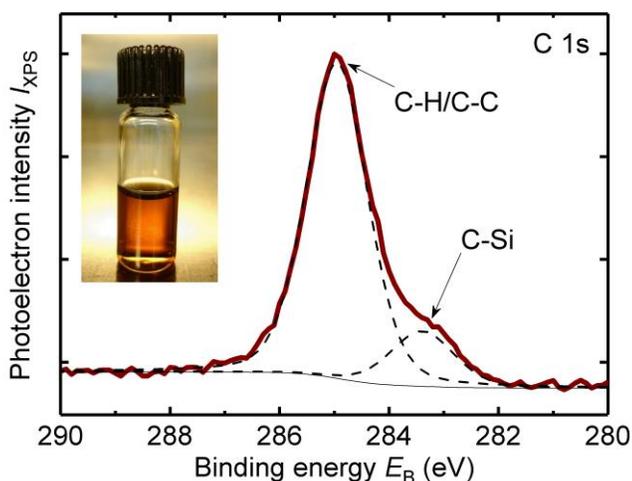


Figure 4: XPS spectrum depicting the components of the C 1s core-level of silicon carbide composite nanoparticles synthesized using 2-pentyne additive. The smaller chemically shifted peak at ~ 283.4 eV corresponds to carbon chemically bonded to silicon. The photograph in the inset shows a typical dispersion in a glass vial.

precursor used was commercially available trisilane and the produced particles were demonstrated to consist of hydrogenated silicon. Addition of a hydrocarbon additive such as 2-pentyne to the mixture was shown to produce silicon carbide composite particles upon sonication.

There are several aspects of this work which are currently under investigation. For instance, with regard to the silicon carbide nanoparticles, the precise amount and location (surface, bulk, or both) of the carbon is being investigated. The results of these experiments will guide future work focused in embedding other molecules or perhaps even nanotherapeutics.

Finally, the silicon nanoparticles are found to form highly porous sponge-like thin films when deposited onto substrates like copper. The lithiation properties of these layers are being assessed in lithium-ion half-cells and preliminary results show that they are stable for several dozen charge and discharge cycles.

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