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Functionalized Silicon Nanoparticles from Reactive Cavitation Erosion of Silicon Wafers

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A new sonochemical process for the top-down production of silicon nanoparticles (<1 nm) with surface functional groups is described. The procedure involves a combination of acoustic cavitation erosion of a single-crystalline silicon surface coupled with simultaneous reaction with a reactive organic compound such as 1-Hexyne. The sonochemical formation of the photoluminescent silicon nanoparticles by reactive cavitation erosion can be easily up-scaled.

As the list of available techniques for the production of functionalized semiconductor nanoparticles continues to grow, the search for fast, efficient, and scalable processes that produce nanoparticles with controlled properties continues. Numerous top-down and bottom-up techniques exist for semiconductor nanoparticle production, including supercritical colloids [1] [2], Zintl salts [3] [4], electrochemical reduction [5], nonthermal plasma [6], laser pyrolysis [7] [8], and mechanical attrition [9]. A subset of these processes have been employed to form functionalized nanoparticles – particles less than 100 nm in diameter with a semiconductor core and organic moieties covalently bound to the surface. The importance of surface functionalization, as opposed to simple surface passivation with a native oxide or physisorbed organic layer, lies in the combination of long-term stability and control of nanoparticle properties necessary for such end uses as photonics [10], photovoltaics [11], nanobiotechnology [12] [13] [14], surface coatings [15] [16], and intracellular delivery of biological agents [17] [18] [19]. Of particular scientific interest are the effects of surface functional groups and processing parameters on the optoelectronic properties of the semiconductor cores, principally the fluorescence excitation and emission spectra. Unlike other semiconductor nanoparticles or quantum dots such as CdS and CdSe in which the principal influence on fluorescence emission characteristics is size, functionalized semiconductor nanoparticles exhibit band gap structures and resulting emission properties that are a complex combination of core size [20], surface defect structure [21], impurities [22], surface functional group [23] and passivation effects [24] [25]. The process that can best control these parameters while simultaneously producing large quantities of material will have the best potential for meeting the wide variety of possible applications.

Top-down processes have the advantage over bottom-up processes for many of these manufacturing considerations. First of all, the core size is controllable to some extent, either through process parameter manipulation such as power input and processing time in mechanochemical methods, or through subsequent size separation when a large distribution of particles sizes is formed. Second, not only can surface chemistry be controlled, but the purposeful introductions of defect structures (both structural and impurity) can be controlled, again through control of process parameters. Finally, and perhaps most importantly, top down methods provide an opportunity for large-scale production of nanoparticles that may be impractical with bottom-up techniques. We report here on a new method for the top-down formation of functionalized silicon nanoparticles utilizing a sonochemical approach.

In general, the use of sonochemistry in organic [26] and organometallic [27] syntheses is well studied. Sonoelectrochemistry in particular has emerged as a sub-field of study in the formation of alloy and semiconductor nanoparticles and nanocomposites [28]. The detrimental effects of acoustic waves on surfaces have also been studied, particularly with respect to the erosion of hard surfaces due to material fracture over long exposure times [29]. However, an important combination of these sub-fields has not been previously studied: the formation of organically-modified semiconductor nanoparticles from the erosion of surfaces by acoustic cavitation in reactive liquids. In this paper we introduce the simultaneous nanoparticle formation by cavitation erosion with surface reactions to form functionalized Silicon nanoparticles in a process called Reactive Cavitation Erosion (see Supplemental Material, Figure S1). 1-Hexyne was selected as the functionalizing compound as it has been shown to react rapidly with no side reactions in similar top-down nanoparticle functionalizing studies [30].

There is compelling evidence that functionalized nanoparticles were formed in the RCE process as described in the Supplemental Materials. This evidence comes in the form of chromatographic results, UV-Vis and PL spectroscopic results, and elemental analysis from TEM/EDS investigations. There is also evidence of impurity formation in this sonochemical process. These impurities confound the ability to isolate pure, functionalized Silicon nanoparticles in the current manifestation of the process, but the results provide sufficient reason to believe that these impurities can eventually be identified and eliminated, either through proper control of process parameters (solvent selection, sonication conditions) or through post-processing purification such as continuous flow chromatography.

GPC results (See Supplemental Material, Figure S2) indicate that there are three distinct products in the reaction solution, even after purification by centrifugation and dialysis. The earliest products (first peak) are presumably the nanoparticles since they give a relatively broad distribution and elute first. The two sharper peaks at longer elution times are most likely from molecular impurities. The presence of these three components is consistent with the results from other characterization techniques.
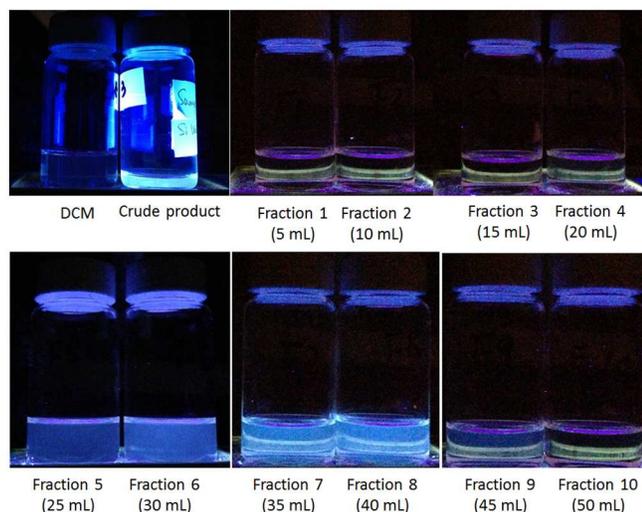
Figure 1 Ultraviolet light photographs of functionalized Si nanoparticle solutions obtained by Reactive Cavitation Erosion after fractionation by size exclusion chromatography (SEC). Total elution volume is indicated in parentheses for each fraction.

Evidence for the presence of the functionalized nanoparticles (first GPC peak) first comes in the form of UV images of the SEC fractionated samples (Figure 1), which show that the strongest emission comes from SEC Fractions 5 through 9. The fact that photoluminescent product begins to elute at Fraction 5 (25 mL elution volume) indicates that there were smaller size particles in this sample than those formed by mechanochemical methods reported in the literature which have diameters in the 5-10 nm range and elute with only ~15 mL of the mobile phase [31] [32]. The small nanoparticle sizes (< 1 nm) are further supported by TEM investigations which show a proliferation of sub-1 nm nanoparticles down to the resolution of the instrument (about 1 nm), with EDS analysis of these same samples indicating the presence of elemental Si (see Supplemental

Material Figure S3). We do not believe that the Silicon signal in the EDS comes from Si-containing molecular compounds: neither ^{29}Si-NMR spectra (not shown) nor mass spectrometry of the GC sample (see Supplemental Material, Figure S4) show evidence of Si-containing compounds. Rather, the MS spectra suggest that in addition to the presence of Si-hexyne, the impurities are due to fragments of the THF solvent at the lower end of the molecular weight spectrum, and low-molecular weight oligomers of poly-hexyne at the higher end. We would not expect to see species attributable to the Si nanoparticles in the MS spectra as the nanoparticles would be too large to volatilize. Evidence for nanoparticles, however, comes from ^{1}H-NMR, (Figure 2) which is consistent with previously published NMR spectra of surface-bound alkenyl groups on Si nanoparticles [33] [34]. The ^{1}H-NMR results also verify the presence of organic impurities, likely the poly-hexyne species, as indicated by an asterisk on the peaks.
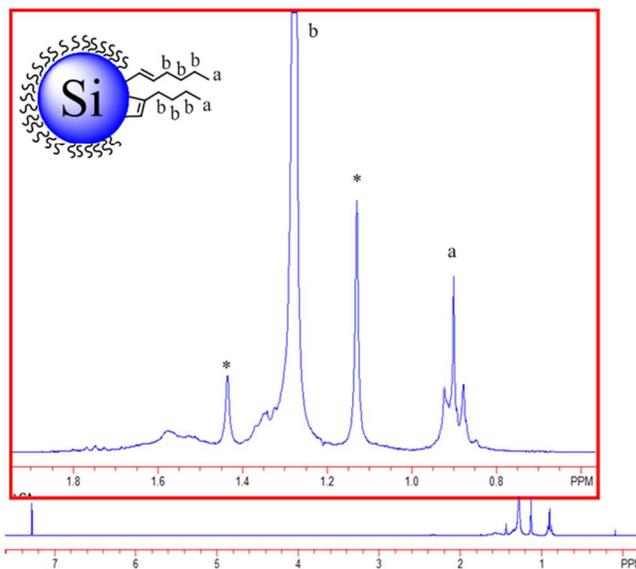
Figure 2 1H-NMR of post-SEC sample. ^{29}Si-NMR showed no evidence of Si-containing compounds. Asterisk (*) indicates likely impurity peaks.

Further evidence for nanoparticle formation comes in the form of UV-vis and Photoluminescence spectroscopic results. Characterization of SEC Fractions 5-9 by UV/Vis and Photoluminescence (PL) spectroscopy (Figure 3) show that although impurities are clearly still present in the sample as indicated by molecular species absorptions and re-emissions at 300-350 nm wavelengths, the slope of the UV-Vis absorption curve and the Stokes shift present in the PL emission spectrum from Fraction 7 are nearly identical to those observed in Si nanoparticles formed by other techniques [20]. Furthermore, the strong molecular absorption at 300 nm in Fraction 8 is an indication that molecular impurities are eluting after the nanoparticles as first discovered in the GPC results. The radiative surface states model can be used to roughly estimate the nanoparticles size from the PL emission wavelength [8]. The emission wavelengths for the three most intense PL emission peaks in Figure 3 are 370, 390 and 395 nm (300, 320 and 340 excitation wavelengths, respectively). These correspond to particle diameters of 1.46, 152 and 1.55 nm, respectively, using the radiative surface states model. The majority of nanoparticles are thus estimated to be below about

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1.5 nm in diameter, which is below the resolution of the TEM employed.
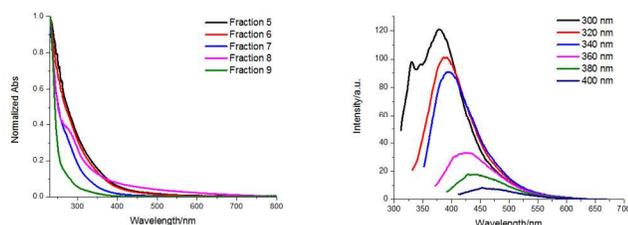
Figure 3 UV-Vis (left) spectra for Fractions 5-9 of Si nanoparticles formed by Reactive Cavitation Erosion and corresponding Photoluminescence (right) spectra for Fraction 7 only as a function of excitation wavelength.

Unlike cavitation bubble dynamics in a continuous, homogeneous liquid, cavitation near a solid surface alters the dynamics of cavity collapse due to the interaction between the cavitation interface and the solid surface. The asymmetric collapse of a cavitation bubble near a solid boundary results in a high-speed liquid jet with velocities exceeding 100 m/sec [35]. These jets impinge upon the surface and cause erosion which depends in the size of the cavitation microbubble and its distance to the solid surface. Erosion in brittle materials such as Silicon occurs due to the creation of pits by the impact of a single bubble collapsing close to the surface [36] accompanied by the expulsion of the Silicon excess in the form of nanoparticles with size depending on the intensity and duration of the ultrasonic treatment.

The rate of nanoparticle formation from reactive cavitation erosion can be estimated from the final mass of nanoparticle recovered and the sonication time. Approximately 10 mg of nanoparticles were recovered from a 100 minute sonication experiment, indicating a preliminary nanoparticle production rate of 6 mg/h, consistent with the linear weight loss with time of 1-10 mg/h found in ceramic materials eroded with a commercial sonication device [37].

The mechanisms of ablation and subsequent erosion of solid surfaces by vibratory cavitation bubble generation have been studied in non-reactive environments; for example, with Silicon [38] and Silicon Nitride surfaces [29]. Cavitation erosion in ceramic systems is believed to be controlled by the extent to which these materials can plastically deform prior to fracture [39]; that is, plastic deformation inhibits pitting. This dependence of erosion on mechanical properties has been further confirmed by studies with Silicon, which indicate that damage during cavitation erosion is inflicted due to brittle fracture. The brittle-ductile transition in pure, single-crystal Silicon occurs at around 2/3 of the melting point, or 1122K (depending on strain rate) [40]. In this same study, brittle fracture was found to occur due to dislocation nucleation and motion, with an activation energy barrier of 2.1 eV that depended on strain rate and electronic doping level. This ablative process is viewed as beneficial for the formation of nanoparticles, as it can potentially lead to a narrower particle size distribution than those found in mechanochemical (comminutive) processes.

In this communication, we demonstrate for the first time that ultrasonic cavitation erosion of Silicon described in the literature can be adapted to a special reactive environment for the one-step formation of functionalized photoluminescent Silicon nanoparticles in considerable quantities. More detailed investigation of the ablative mechanism of nanoparticle formation from Reactive Cavitation Erosion (RCE) will be the main topic of the future research work.

Conclusions

Silicon nanoparticles functionalized with 1-Hexyne have been formed by Reactive Cavitation Erosion. The process involves a combination of acoustic cavitation erosion of a single-crystalline silicon surface at 20 kHz ultrasonic treatment coupled with simultaneous reaction with a reactive organic compound. The nanoparticles are in the sub-1 nm size range, and exhibit stable, blue-green photoluminescence that is characteristic of functionalized Si nanoparticles. We believe that developed top-down ultrasonic approach can be applied for synthesis of other functionalized nanoparticulate elemental semiconductors like Ge or In. Detailed investigation of the mechanism of Si nanoparticle formation by Reactive Cavitation Erosion is the main task for the future research work.

Notes and references

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