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Hydrogen-Capped Silicon Nanoparticles as a Potential Hydrogen Storage Material: Synthesis, Characterization, and Hydrogen Release

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Chemical hydrides are compounds that can potentially uptake and release hydrogen without the use of hydrogen gas. Nanostructure silicon may have great potential as a chemical hydride. The surface can be capped by hydride and dihydride, and hydrogen can be thermally desorbed from the surface. We have prepared large-scale (1−2 g) samples of hydrogen-capped silicon nanoparticles with average diameters of 60, 10, 5, and 4 nm via a low-temperature chemical method to explore the release of hydrogen from the surface as a function of size. The 60- and 10-nm-diameter particles have only hydrogen on the surface. The 60-nm-diameter particles are crystalline, and the 10-nm-diameter particles are amorphous according to powder X-ray diffraction (XRD). The 5- and 4-nm-diameter particles have both hydrogen and solvent capped on the surface. The 4-nm-diameter particles are amorphous and the 5-nm-diameter particles are crystalline by powder XRD. Weight percentages of ~3.5% at 350 °C are observed for the 10-nm-diameter particles. The largest weight loss is observed for the amorphous 4-nm-diameter particles, which show a weight loss of ~4.5%, which is attributed primarily to hydrogen. The products have been investigated by powder XRD, scanning electron microscopy (SEM), transmission electron microscopy (TEM), solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR), Fourier transform infrared (FTIR) analysis, thermogravimetry/differential scanning calorimetry (TG/DSC), and thermogravimetry/mass spectroscopy (TG/MS).

Introduction

Hydrogen economy constitutes a subject of controversy, not only in the scientific community but also in everyday life.[1,2] In terms of chemical energy per mass, hydrogen stands out as the primary candidate, because it can release more (at least 3-fold) than that of any other conventional fuel. Hydrogen is also a clean fuel, which does not produce any CO_2 and keeps NO_x emissions at a low level.[1−3] One problem that still must be solved is the storage of the hydrogen gas. The conventional way of storing hydrogen is in high-pressure tanks, which can store only 4% hydrogen by mass and are potentially dangerous. Condensation is an attractive alternative to the storage of gaseous hydrogen; however, H_2 condenses at −252 °C at 1 bar and the losses associated with heat transfer are large.

To address this problem, chemical and physical storage in metal hydrides (MgH_2 or $LaNi_5H_6$), chemical hydrides ($NaBH_4$ or $LiBH_4$), metallorganic frameworks (Zn_4OL_3), hydrogen clathrates, carbon-based materials, ammonia boranes, and zeolites are only a few examples sought to be alternative solutions for hydrogen storage.[3,4]

It is a well-known fact that hydrogen has a great affinity for amorphous or crystalline silicon.[4−7] In addition, studies on silicon have shown that hydrogen desorbs from silicon surfaces upon annealing. Therefore, silicon can be considered a possibility for the use of high-surface-area main-group-element nanomaterials as hydrogen storage materials.[5,6] Indeed, efforts toward this goal are underway with porous silicon.[7,8] Moreover, the high surface area of hydrogen-terminated silicon makes its use as a hydrogenation agent possible.[9] Also, hydrogen-terminated silicon nanocrystals can be modified further via a hydrosilylation process to form chemically robust Si−C bonds on the surface.[8,10] Upon size reduction of a particle, the surface area increases dramatically. Assuming a Si:H ratio of ~1:1, which has been proposed for a silicon particle that is 1 nm in size,[11] the hydrogen storage potential will be 3.4% by weight. It also has been shown

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experimentally that, for 100-nm amorphous particles, the Si:H atomic ratio can be as high as 1:1.[12] Moreover, hydrogen has been shown to desorb from such materials between 300 °C to 600 °C.[12−14]

Recently, a simple method for producing free-standing, hydrogen-terminated nanoparticles has been introduced.[15] In this method, sodium silicide is reacted with ammonium bromide in a solvent to produce hydrogen-capped silicon nanoparticles.[15−21] It has been shown that ammonium salts can react with alkali silicides and germanides to produce amorphous material.[22] Herein, we report the synthesis and characterization of hydrogen-terminated silicon nanoparticles of different sizes and their potential use for hydrogen storage.

Experimental Section

Sample Preparation. The samples were prepared by reacting sodium silicide with ammonium bromide in the solid state (60 and 10 nm) or in solution (5 and 4 nm). Sodium silicide (NaSi) has been prepared according to literature methods.[23] Typically, stoichiometric quantities of sodium metal and silicon powder are loaded in a tantalum or niobium tube and the tube is sealed in a quartz jacket under argon or vacuum. The reaction mixture is heated to 650 °C at a rate of 60 °C/h and dwell at 650 °C for 4−5 days. Purity of the product is assessed using powder X-ray diffraction (XRD). Ammonium bromide (NH_4Br) and sodium bromide (NaBr) have been dried under dynamic vacuum at 100 °C for 2 days. The larger-size nanoparticles (60 nm in size, denoted as **S60**) have been prepared via a solid-state reaction between NaSi and NH_4Br. In a drybox, NaSi and NH_4Br have been weighted in a 2:1 molar ratio, 0.5 g of NaSi were mixed with 0.48 g of NH_4Br. The smaller-size nanoparticles (10 nm in size, denoted as **S10**) also were obtained from a mixture of NaSi and NH_4Br with the addition of NaBr as a diluting agent. Typically, 0.5 g of NaSi were mixed with 0.48 g of NH_4Br and 1 g of NaBr for a NaSi:NH_4Br:NaBr ratio of 2:1:1. The reactants have been intimately mixed in an agate mortar (or ball-milled) and pressed into pellets. The pellets were loaded in alumina boats and placed in Pyrex tubes. The reaction occurs within 17 h under dynamic vacuum conditions at 200 °C. The furnace is preheated at 200 °C, and the one-open-end quartz tube is purged with argon three times and evacuated at room temperature. The tube then is inserted in the preheated oven. The furnace temperature stays at 200 °C for the entire duration of the experiment. There is a 1 °C variation in temperature, as expected when inserting a cold object (quartz tube) into a hot one (furnace at 200 °C). It is important that the temperature does not increase to 250 °C, because, under these new conditions, a mixture of silicon nanoparticles and sodium silicon clathrate has been observed. Note that this solid-state reaction can be performed from 200 °C to 300 °C (not ramped but in a preheated furnace) under no-flow conditions (it is protected from air by the positive pressure of ammonia, checked with pH paper). The reaction is considered completed when ammonia gas evolution ceases. Under these conditions, amorphous silicon is formed. This is presumably the effect of having an ammonia gas pressure above the reaction mixture and has been also observed in the solution particle synthesis under no-flow conditions.

Table 1. Summary of Samples with the Method of Preparation and Average Particle Diameter

sample	preparation method	nanoparticle size (nm)
S60	solid state	60
S10	solid state + NaBr	11
S5	solution DME	5
S4	solution DOE	4

The powders were washed under argon by cannulating degassed acidified water ([HF] ≈ 2%) over them to remove the salt byproduct, NaBr. The material was rinsed with water and hexane and dried under vacuum for 4 h. The yield on all of the solid-state reaction is quantitative, 0.26 g of silicon hydrogen-capped nanoparticles, yield 97%, and this reaction can be scaled up to produce grams of silicon nanoparticles. To reduce the particle size, the reaction between sodium silicide and ammonium bromide has also been performed via a solution route. The details on the synthesis via solution in both dimethoxyethane (**S5**) and dioctyl ether (**S4**) have been published elsewhere.[15] Typically, 0.50 g of sodium silicide was stirred and heated at 40 °C overnight in 200 mL of solvent. The mixture of solvent and sodium silicide was cannulated over 0.55 g of ammonium bromide in a Schlenk degassed flask. The reaction flask was connected to a water condenser and heated under flowing argon. The dimethoxyethane (DME) and dioctyl ether (DOE) reactions were performed at 70−80 °C (DME, boiling point (bp) of 85 °C) and at 260−280 °C (DOE, bp =289 °C), respectively. The reaction can be performed under the no-flow conditions case in which there will be an ammonia pressure over the solution, which leads to the formation of amorphous silicon nanoparticles, regardless the nature of the solvent or temperature of reaction. The reaction was considered complete when ammonia gas stopped coming off, as indicated by pH paper. After the reaction, the powder was washed under argon by cannulating degassed acidified water (HF ≈ 2%) over it to remove the salt byproduct, NaBr. The material was rinsed with water and hexane and dried under vacuum for 4 h (0.284 mg in DME and 0.20 mg in DOE). The yield in the powder product was ~103 wt % in DME and ~75 wt % in DOE. A summary of all of the prepared samples, along with the nanoparticle sizes and the corresponding method, is provided in Table 1.

Caution must be taken when washing all of the alkali-metal silicide reaction products with water. Traces of alkali-metal silicides have a very exothermic reaction with water that generates sufficient heat to ignite the hydrogen byproduct of the reaction. This can result in an explosion and fire. It is recommended that water addition should be performed slowly under inert atmosphere.

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Characterization. *Powder X-ray Diffraction (XRD) Data.* The powder XRD patterns were obtained on a Scintag PAD V instrument (Cu Kα radiation, λ =1.5418 Å) equipped with a graphite monochromator. Data were collected in a step scan mode between 20° and 80° 2θ, with a step size of 0.02° 2θ. The line widths were estimated using the Jade MDI software after background subtraction. The size of the particles was calculated using the Scherrer equation: $L = \frac{0.9\lambda}{\beta \cos \theta}$ where λ is the X-ray wavelength (in nanometers), β the width of the diffraction peak (in nanometers), and θ the Bragg angle (in degrees 2θ); the value 0.9 is the Scherrer constant for spherical-shaped crystallites. Based on the obtained powder XRD data, the particle size of **S60** is 60 ± 1 nm and that of **S5** is 8 ± 1 nm. These sizes are calculated from the Si[111] peak. **S10** and **S4** are amorphous, and the particle sizes for these samples were obtained from TEM data.

Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) was performed on a JEOL Model SEM FEI XL-30s FEG system. For the bigger nanoparticles, 0.05 g of **S60** was dispersed by sonication in 30 mL of chloroform or toluene. The dispersion was layered on an SEM stub, and then the solvent was evaporated by heating in air at 100 °C overnight.

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) analysis was performed on a Philips Model CM-12 system, operating at 100 keV. Typically, 0.01 g was sonicated in 20 mL of toluene or chloroform for 1 h, and the grid was prepared by dipping the holey, carbon-coated 400-mesh grid in this solution, followed by heating at 200 °C overnight. The size distribution of the as-prepared silicon nanoparticles was 10.99 ± 2.23 nm for **S10**, 4.95 ± 1.33 nm for **S5**, and 4.15 ± 1.25 nm for **S4**. The size distribution of the as-prepared samples was calculated based on 600 nanoparticles.

Solid-State NMR. All solid-state NMR experiments were performed on a Bruker Advance 500 WB spectrometer equipped with an 11.75 T magnet. The ^{23}Na and ^{1}H NMR data were recorded using a Bruker 4-mm CP-MAS probe with zirconia rotors spinning at 15 kHz with Larmor frequencies of 132.288 and 500.1086 MHz. The samples were loaded into the zirconia rotors inside a drybox filled with flowing dry nitrogen gas. A Hahn Echo pulse program (90-tau-90-tau-acq) was used, with tau being synchronized the rotor time. For ^{23}Na NMR, the datablock size was 32 k, the line broadening was 1 Hz, the relaxation delay was 2 s, the 90° pulse width was 1 μs, and the total number of scans was 1024. The chemical shift was referenced to 0.5 M NaCl solution. For ^{1}H NMR, the datablock size was 64 k and zero-filled to 32 k, the line broadening was 1 Hz, the relaxation delay was 5 s, the 90° pulse width was 2 μs, and the total number of scans was 1024. The chemical shift was referenced to trimethyl silane (TMS). For the ^{29}Si CP-MAS NMR experiment, a Bruker 7-mm CP-MAS probe was used, with a Larmor frequency of 99.348 MHz. The sample was loaded into a 7-mm zirconia rotor in a drybox filled with flowing dry nitrogen gas. A ramp-contact and TMMP decoupling pulse program was used. The magic-angle spinning rate was 5 kHz, the contact time was 5 ms, the relaxation time was 2 s, and the datablock size was 8 k. The chemical shift was referenced to TMS.

FTIR. FTIR data were obtained using a Shimadzu IR Prestige 21 system that was equipped with a diffusive reflectance accessory. Silicon powder was mixed with KBr, using a 1:100 molar ratio dilution of the sample in the KBr matrix. The samples were mixed with KBr in a nitrogen-filled drybox, then loaded in vials and brought out of the drybox just before the measurement. The IR measurements were performed in air.

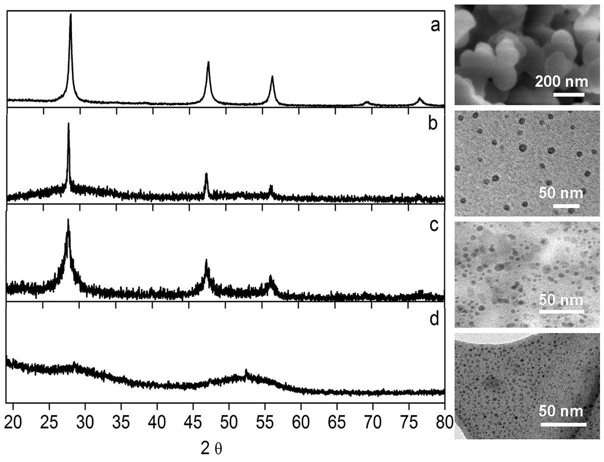

Figure 1. Powder X-ray diffraction (XRD) patterns and scanning electron microscopy/transmission electron microscopy (SEM/TEM) images for silicon nanoparticles of various size: (a) 60 nm, (b) 10 nm, (c) 5 nm, and (d) 4 nm.

Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Mass Spectrometry (MS). The TGA/DSC/MS measurements were performed on a TG/DSC Model STA 409 Netzsch instrument and a Aelos Model QMS 300 MS apparatus were used to identify the gases, by heating the sample under argon. Typically, 40 mg of Si NP powder were loaded in alumina crucibles in the drybox. The samples were brought under inert atmosphere and loaded in the TG/DSC instrument. The data were obtained by heating the samples under argon gas from room temperature to 600 °C at intervals of 10 °C in a stepwise manner. The samples were heated with 10 K/min to 100 °C, held at 100 °C for 1 h, and then heated at a rate of 10 K/min to 600 °C under flowing argon. The argon flow rate was set to 25 mL/min. In the case of DOE, an isotherm at 350 °C was employed (DOE is a high-boiling-point solvent, 289 °C). All of the MS channels have been checked from mass 1 to 100. The strongest signals were always, in this order: He $>$ H_2 $>$ N_2 $>$ CO_2. No water has been detected, and no weight loss has been seen below or at 100 °C.

Results and Discussion

Silicon nanoparticles (Si NPs) were prepared according to the reaction below:

$$\mathrm{NaSi} + \mathrm{NH_4Br} \rightarrow \mathrm{Si{-}H\ nanoparticles} + \mathrm{NaBr} + \mathrm{NH_3}$$

It was found that the reaction conditions can be controlled to produce various sizes of hydrogen-capped Si NPs as either crystalline, amorphous, or mixed crystalline and amorphous powders in high yield. In all cases, the product of the reaction is washed with slightly acidified, deoxygenated water to remove the NaBr. The material is then dried en vacuo to remove any trace amounts of water and then is further characterized.

Powder XRD data of the nanoparticles obtained by the aforementioned reaction, denoted here as **S60**, **S10**, **S5**, and **S4**, along with the corresponding SEM/TEM images of these materials are presented in Figures 1a–d. The particle size, based on the powder XRD pattern (full width at half maximum, fwhm) of the 28.7° 2θ peak for **S60** (Figure 1a), is 60 nm. The SEM image is consistent

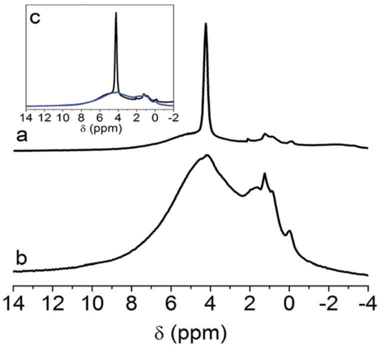

Figure 2. ^{1}H MAS NMR data (a) before and (b) after washing; (c) overlay of panels (a) and (b) for the 60-nm silicon nanoparticles (Si NPs).

with such a particle size, and the particles are spherical. The powder XRD data on **S10** shows that this material is a mixture of amorphous and crystalline silicon. The amorphous silicon peaks are observed at 28° and 49° 2θ, and the crystalline silicon diffraction peaks are observed at 28.7°, 47.5°, 56.5°, 69.3° and 76.6° 2θ, corresponding to Miller indices of [111], [220], [311], [400], and [331]. No attempt to calculate the particle size from X-ray data was made in this case. The size of the particles, based on the TEM data, was 10.99 ± 2.23 nm. The powder XRD patterns and the TEM images for **S5** and **S4** are presented in Figures 1c and 1d. The **S5** particles were crystalline; the particle size, based on the fwhm from the XRD data, was 8 nm and that from TEM data is 4.95 ± 1.33 nm. The powder XRD analysis of the **S4** nanoparticles shows two broad diffraction peaks at 28 and 49° 2θ, which are consistent with amorphous silicon. The average particle size of these nanoparticles was measured from TEM data and determined to be 4.15 ± 1.25 nm.

^{23}Na MAS NMR and powder XRD of the samples before washing with water were performed on the **S60**, **S10**, and **S5** silicon nanoparticles. The XRD pattern only indicated NaBr. In the reaction previously described, a NaSi:NH_4Br ratio of 1:0.5 was used, because when the ratio is 1:1, the product is a mixture of Si NPs and Na_xSi_{46}.[22] Because less NH_4Br is used than the stoichiometric amount, there should be unreacted NaSi left in the product and the amount can be ascertained from the ^{23}Na NMR provided in the Supporting Information. These spectra show that there is still unreacted NaSi at the end of the reaction, as indicated by the ^{23}Na chemical shifts for NaSi of δ =53 ppm, 46 ppm, and 38 ppm, and NaBr, which has a ^{23}Na chemical shift at approximately zero (referenced to NaCl). From the integrated intensities, on the NaSi peaks, there is 20% unreacted NaSi in the **S60** and **S10** Si NP samples, and 12% unreacted NaSi in the 5-nm Si NP samples. The powder XRD patterns show only NaBr, which is consistent with the reaction equation previously provided.

The ^{1}H MAS NMR spectra of the **S60**, **S10**, and **S5**, before and after washing, are presented in Figures 2, 3, and 4, respectively. Figure 2a shows the ^{1}H NMR of **S60** before wash. The spectrum shows a very sharp peak at 4.29 ppm on top of a broad signal that is difficult to distinguish. Figure 2b shows the ^{1}H NMR of **S60** after washing with water. Figure 2c shows both spectra, to illustrate the fact that Figure 2b is the same spectrum as that shown for Figure 2a, except without the sharp resonance at 4.29 ppm. The spectrum shows that there are four types of hydrogens with chemical shifts at 4.29 ppm, 1.3 ppm, 0.95 ppm, and −0.042 ppm and the sharp signal at 4.29 ppm is not present. The sharp resonance is consistent with the presence of very mobile hydrogen, most likely surface or physically adsorbed species. It is possible that when NH_4Br reacts with NaSi, H_2 is produced, which is present in the final product mixture. From the integrated intensity of the sharp resonance, this represents 22% of the total amount of hydrogen. When the mixture (Si−H nanoparticles and NaBr) is washed with water, the physisorbed hydrogen is removed and the spectrum is consistent with chemically bonded Si−H_x species. Chemical shifts for most organosilanes are in the range of 3−5 ppm, a tentative assignment could be 0−1.3 ppm SiH, 4.29 ppm SiH_2.[24] The slightly negative signal at −0.042 ppm might correspond to a hydride species present on the surface of this material.[25] Similar chemical shifts have been reported for aerosol particles of amorphous hydrogenated silicon.[26] In this case, the ^{1}H NMR spectra has been deconvoluted into a broad feature and three narrow signals.[26] The broad

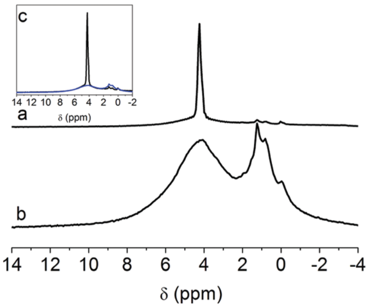

Figure 3. ^{1}H MAS NMR data (a) before and (b) after washing; (c) overlay of panels (a) and (b) for the 10-nm Si NPs.

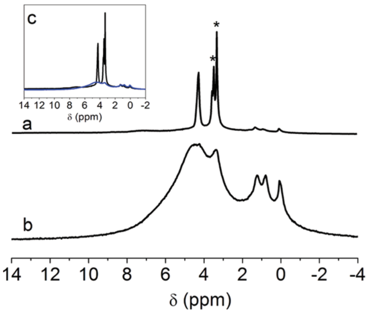

Figure 4. ^{1}H MAS NMR data (a) before and (b) after washing; (c) overlay of panels (a) and (b) for the 5-nm Si NPs. The asterisk symbols indicate solvent peaks.

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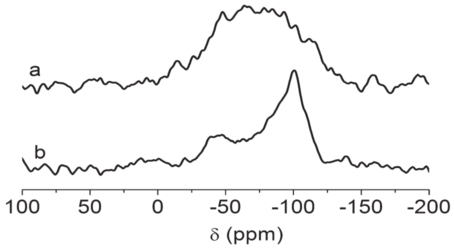

Figure 5. ^{29}Si CP MAS NMR data (a) before and (b) after washing for the 60-nm Si NPs.

feature was assigned to clustered monohydride SiH groups and polymeric species, SiH_x.[26] A similar situation is apparent in **S10** nanoparticles whose ^{1}H NMR spectra, before and after washing, is shown in Figure 3. The shape and resonances observed are similar to that observed in Figure 2 for the 60-nm-diameter nanoparticles. The percentage of physisorbed hydrogen, calculated based on the integrated intensity of the sharp resonance, is 24% of the total amount of hydrogen present initially in the sample. However, after washing, the resonances assigned to Si−H and hydride (in the range of −0.042 ppm to 1.3 ppm) are more intense, compared to the broad resonance at 4.29 ppm. This suggests that a larger percentage of the surface for the 10-nm-diameter particles is a Si−H or hydride bonded species. Figure 4 shows the before-washing and after-washing ^{1}H NMR spectra for **S5**, the 5-nm-diameter nanoparticles prepared in DME. The amount of physisorbed hydrogen is 6% in this case. In addition to the aforementioned signals, the ^{1}H MAS NMR spectra of the 5-nm nanoparticles obtained via the solution reaction, show that the surface of these nanoparticles also has solvent, in this case DME, which is indicated by astericks.[27] Again, the mobile hydrogen species, presumably hydrogen physisorbed on the surface is present before washing at 4.29 ppm.[23] After washing, the broad resonances become more apparent and the relative amounts of each resonance are slightly different, when compared to the larger sizes. This may be due to the fact that the DME resonances are also present. The results for the three different sizes suggests that, even for the smallest sizes presented herein, both $Si-H_2$ and Si−H and hydride are present on the surface of the nanoparticles.

^{29}Si CP MAS NMR was performed on the same samples before and after washing the sample with acidified water. As a general feature, the silicon cross-polarized hydrogen spectra are broad, implying that there is great local variation in electron density. The spectra for **S60** are presented in Figure 5. The before wash spectrum reveals the presence of a broad signal centered about −75 ppm. After washing with acidified water, four signals specifically, those at −20 ppm, −50 ppm, −86 ppm, and −100 ppm can be seen in the ^{29}Si CP MAS NMR. The first peak can be attributed to hydrogenated silicon nuclei, possibly polyhydride species.[28,29] The peaks at −50 ppm corresponds to diluted monohydritic SiH species.[23,26,28−30] The peak at −86 ppm could be attributed to SiH_2 species.[29] The peak at −100 ppm can be assigned to clustered SiH, monohydride species. The peak at −100 ppm could also be a mixture of the OSi−H and SiH groups, because it is in the range of Si−O bonds seen in amorphous SiO_2.[22,31] Figure 6 shows the NMR spectra for the 10-nm nanoparticles. The 10-nm-diameter nanoparticles show features similar to those described for the 60-nm nanoparticles, suggesting that the surface chemistry is similar. However, the peak relative intensities change. Thus, the signal at −100 ppm is smaller in intensity than that for the 60-nm nanoparticles, suggesting that there is less monohydride silicon in these particles. Also, the peak at −86 ppm is more intense in this case, meaning that more of the Si−H bonds are similar to those of the dihydride. The peak at −50 ppm is smaller and slightly shifted, suggesting that there are still diluted monohydride species, but their concentration decreases. Another aspect that can be noticed and it would be further amplified as the size of the particles gets even smaller (e.g., 5 nm), is that the ^{29}Si CP becomes even broader and featureless as the particle size decreases. Figure 7 displays the NMR obtained before and after washing the 5-nm particles. The CP MAS NMR spectra of the 10-nm particles are also quite similar to that for the 60-nm particles, indicating that the particles have similar Si−H environments. For the 5-nm nanoparticles, the CP ^{29}Si NMR retains some of the features of the 10-nm nanoparticles. The signal at −100 ppm is similar in

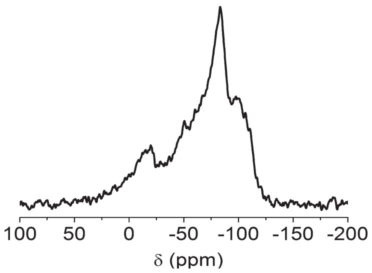

Figure 6. ^{29}Si CP MAS NMR after washing for the 10-nm Si NPs.

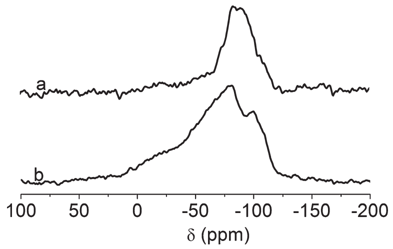

Figure 7. ^{29}Si CP MAS NMR data (a) before and (b) after washing for the 5-nm Si NPs.

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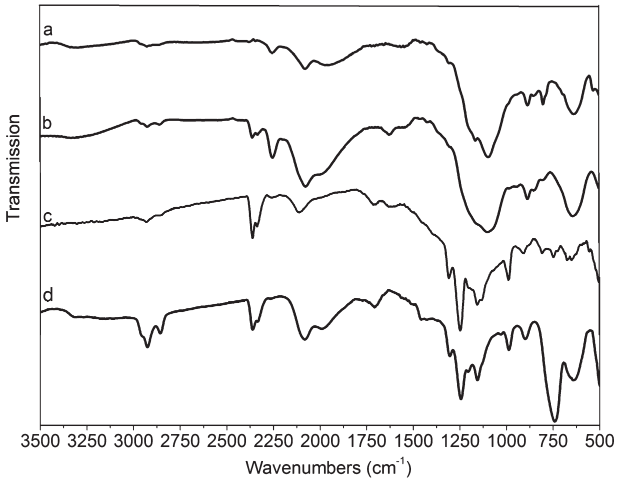

Figure 8. FTIR data after washing for Si NPs of various sizes: (a) 60 nm, (b) 10 nm, (c) 5 nm, and (d) 4 nm.

intensity to the one obtained from the 10-nm nanoparticles, the monohydride, relative to dihydride and polyhydride, becomes the predominant species. In addition, this peak has contributions for the Si−OR groups of the solvent, which are also seen in the FTIR. The solvent makes Si−OR bonds on the surface of these particles and protects the surface from oxidation during washing. The peak at −86 ppm is smaller in intensity, compared to the spectra of the 10-nm nanoparticles, which might indicate that the dihydride species are not the preferred configuration of the surface of these particles. This might be understood taking into consideration the size of these nanoparticles, as the size gets smaller, one would expect a higher concentration of monohydride and a lower concentration of dihydride and trihydride species. The rest of the spectrum is very broad and featureless, making an unequivocal analysis difficult.

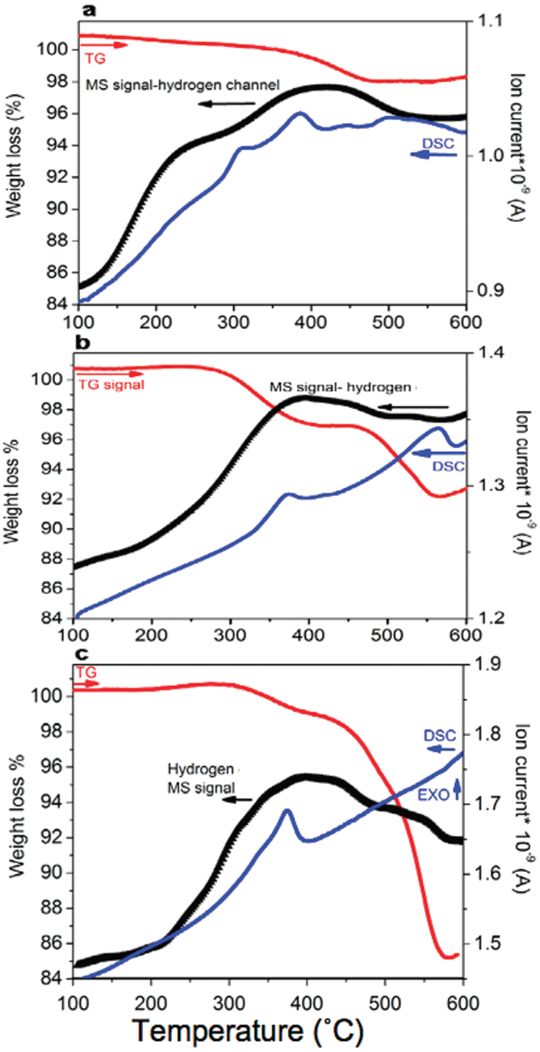

Figure 9. TG/DSC/MS (hydrogen channel only) data recorded in argon for (a) 10-nm DME-prepared Si NPs, (b) 5-nm DME-prepared Si NPs, and (c) 4-nm DOE-prepared Si NPs.

The FTIR data for **S60**, **S10**, **S5**, and **S4** after washing with water are presented in Figure 8. The FTIR data are consistent with all the nanoparticles containing Si−H and Si−H_2 bonds.[32,33] All of the FTIR spectra show the 900 cm^{-1} and 1900−2100 cm^{-1} region, characteristic for the SiH_2 scissors mode in the low wavenumber region, and for the Si−H and dihydride stretches in the 2000 cm^{-1} region.[10,34] These signals can be attributed to monohydride, dihydride, or polyhydride species present on the surface of the silicon nanocrystals. In addition, in the low wavenumber region, 600−700 cm^{-1}, silicon lattice vibrations are present. In the case of the bigger particles obtained via the solid-state reaction, the Si−O−Si stretch mode is present at 1100 cm^{-1}. Presumably, the oxidation of the surface occurred during washing the nanoparticles with water. The Si−O−Si can be removed with HF, so it is due to oxidation during washing with water. The solvent systems do not show this sensitivity to oxygen, presumably because they are protected from further oxidation through some Si−OR linkages. In the FTIR analyses of the solvent-prepared nanoparticles (see Figures 8c and 8d), alkyl C−H stretching modes (aliphatic ν(C−H) stretching modes at 2800−2900 cm^{-1}), deformation modes at 1300−1400 cm^{-1}, and C−C stretching modes for alkyl chains at 1500−1600 cm^{-1} are also observed.[10,32,34]

The TG/DSC/MS data obtained under flowing argon for the 10-nm-diameter (solid-state), 5-nm-diameter (DME), and 4-nm-diameter (DOE) nanoparticles obtained in this study are presented in Figures 9a, 9b, and 9c, respectively. The weight loss occurs in two steps, which is reflected in the DSC data. The weight loss for the 4-nm particles starts at ~300 °C with a plateau at ~450 °C, with all weight loss completed at 600 °C. The weight loss for the 5-nm particles is continuous; it starts at 300 °C and finishes at 600 °C. The DSC data show two exotherms associated with the two weight losses. The first one is observed at ~350 °C for both the 5-nm-diameter particles (DME) and ~410 °C for the 4-nm-nanoparticles prepared in DOE. This exotherm is consistent with

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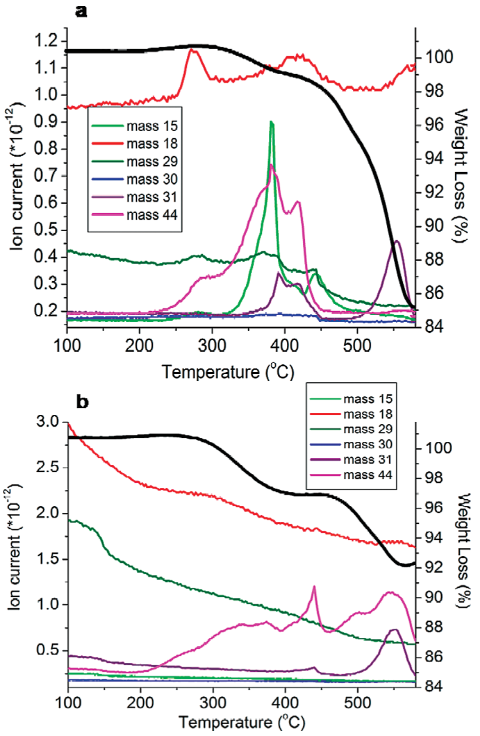

Figure 10. TG/MS data obtained from the (a) 4-nm and (b) 5-nm Si NPs. This figure presents the other volatiles evolved from the Si NPs in argon upon heating.

hydrogen removal from the surface. The second exotherm is observed at 560 °C for both the 5-nm nanoparticles and the 4-nm nanoparticles. This exotherm may be attributed to hydrocarbon loss from solvent molecules adsorbed to the surface. There is an additional exotherm observed above 600 °C for the 4-nm-diameter nanoparticles, which is consistent with the amorphous-to-crystalline silicon phase transition. This additional exotherm is expected as the powder XRD analysis showed that the 4-nm-diameter particles were amorphous. This transition was confirmed by powder XRD before and after the TG/DSC experiment, with an amorphous pattern initially and a crystalline diffraction pattern afterward.

The TG/MS data for the volatiles (other than hydrogen) evolved from the silicon nanoparticles prepared in solvent are presented in Figure 10. Figure 10a presents the volatiles desorbed by the 4-nm nanoparticles prepared in DOE. These data show that, above 200 °C, masses 18 (H_2O), 44 (CO_2), 15 and 31 (hydrocarbons or silanes) are coming off this sample. However, the volatiles are three orders of magnitude lower than the hydrogen signal from the MS (necessitating a separate figure to demonstrate their presence). Also, most of these volatiles are desorbed above 350 °C. Figure 10b presents the volatiles evolved by the 5-nm nanoparticles prepared in DME. These data show that most of the hydrocarbon and carbon dioxide are evolved above 400 °C. To be able to separate out the hydrogen evolution from the other volatiles, an isothermal experiment was run at 350 °C. In addition, an FTIR spectrum was collected on the sample before and after this experiment. The isotherm of the 4-nm-diameter particles at 350 °C under argon shows a weight loss of 4.5%. This is presented in Figure 11, along with the FTIR data obtained on the same sample batch before and after the isothermal heating. The FTIR on the sample before and after the isotherm confirms the disappearance of the SiH stretches in the 2000 cm^{-1} region.

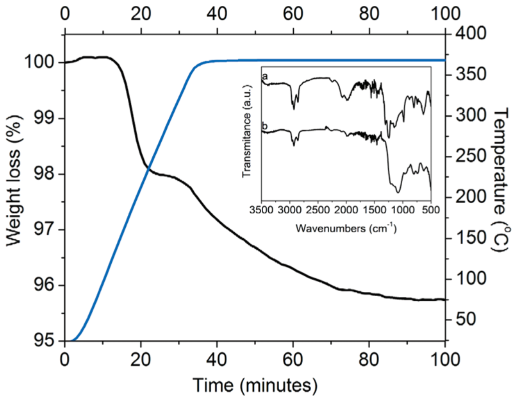

Figure 11. TG isothermal data at 350 °C under argon for the 4-nm Si NPs obtained in DOE. The inset presents the FTIR data obtained from the same sample batch before and after heating at 350 °C under argon.

Summary

Different-sized silicon nanoparticles (Si NPs) have been prepared via solid-state and solution chemistry. The 60- and 5-nm nanoparticles are crystalline, the 10-nm nanoparticles are a mixture of amorphous and crystalline silicon, and the 4-nm nanoparticles are amorphous. Regardless of particle size and crystallinity, these materials show similar SiH and SiH_2 entities on their surface. The particles prepared in solvent bind solvent to their surface, while the particles prepared via solid-state methods are oxidized. In all cases hydrogen evolution from these particles is observed above 300 °C. The highest amount of hydrogen is associated with the smallest particles prepared in DOE. As a possible hydrogen storage system, the surface of nanoparticles may provide a good platform. In the case of this study, the increase in the amount of hydrogen with surface area is demonstrated. Reversibility through chemical hydrogenation may also be possible; however, the rather high temperature for hydrogen release, along with the air sensitivity of hydrogen-capped Si NPs discourages further development of this system for hydrogen storage.

Supporting Information Available: ^{23}Na MAS NMR of the samples before washing with water for the **S60** and **S10** silicon nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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