Inorganic Chemistry

Silicon Nanoparticles by the Oxidation of [Si₄]^{4–}- and [Si₉]^{4–}- Containing Zintl Phases and Their Corresponding Yield

Bradley M. Nolan,[†] Thomas Henneberger,[‡] Markus Waibel,[‡] Thomas F. Fässler,[‡] and Susan M. Kauzlarich^{*,†}

[†]Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, United States [‡]Department of Chemistry, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Supporting Information

ABSTRACT: The Zintl phases with nominal compositions Na_4Si_4 , Rb_7NaSi_8 , and $A_{12}Si_{17}$ (A = K, Rb, Cs) were utilized as precursors in the synthesis of silicon nanoparticles (Si NPs). The present study characterizes and compares the yields of Si NPs synthesized from Na_4Si_4 , Rb_7NaSi_8 , and $A_{12}Si_{17}$ (A = K, Rb, Cs). Na_4Si_4 and Rb_7NaSi_8 Zintl phases consist of anionic silicon tetrahedra stabilized by group I cations. The $A_{12}Si_{17}$ (A = K, Rb, Cs) Zintl phases that contain $[Si_9]^{4-}$ and $[Si_4]^{4-}$ clusters have been speculated to be more soluble than the A_4Si_4 (A = Na, Rb, Cs) Zintl phases that contain Siegl Y = 34.



Cs) Zintl phases that contain solely $[Si_4]^{4-}$ clusters due to the lower charge density of the $[Si_9]^{4-}$ cluster. The Zintl phases were reacted with NH₄Br in dimethylformamide (DMF) and subsequently capped with allylamine. The Si NPs were characterized by transmission electron microscopy (TEM), energydispersive spectroscopy (EDS), UV-vis, and photoluminescence (PL) spectrophotometry. Furthermore, the Si yields were characterized by inductively coupled plasma mass spectrometry (ICP-MS) to evaluate if the reactions of $[Si_9]^{4-}$ cluster containing Zintl phases resulted in higher yields of Si NPs. The yield of Si increased with larger or mixed alkali metal Zintl phases, leading to the conclusion that Coulombic interactions between the cations and anions affect the Zintl phase's reactivity. The size of the Si NPs also increased with larger and mixed alkali metal cations, resulting in similar NP concentrations regardless of the starting material. With respect to ease of synthesis and yield, Na₄Si₄ remains the most practical precursor for the solution synthesis of Si NPs; however, the larger and mixed alkali metal precursors show promise for further development.

INTRODUCTION

Subsequent to Canham's seminal paper on the fluorescence of nano-Si, silicon nanomaterials have received intense attention within the scientific community.¹ Synthesis, size/morphology, photoemission, and surface functionalization have dominated silicon nanoparticle (Si NP) research.^{2–10} Because silicon is an inexpensive and abundant semiconductor material that is already ubiquitous in technology, extending the applications of bulk silicon to the nanoscale holds much appeal in areas related to energy conversion and other optoelectronics.^{11–13} Furthermore, Si NPs exhibit the advantageous size-dependent quantum confinement effects of the group II–VI and group III–V quantum dots without the inherent toxicity, making them desirable for bioapplications.^{8,14–16}

The syntheses of Si NPs include both top-down and bottomup approaches. The etching of silicon wafers is the most notable top-down approach, while synthetic methods such as the gas-phase decomposition of molecular silicon species, reduction of silicon halides, oxidation of Zintl phase materials, and others comprise the bottom-up approaches.^{10,17,18} Two recent examples of bottom-up synthetic routes are the thermal processing of hydrogen silsesquioxane under a reducing atmosphere, where the Si NPs are formed encapsulated in a silica matrix and liberated by HF treatment, and a facile microwave-assisted aqueous synthesis of Si NPs produced by the reduction of (3-aminopropyl)trimethoxysilane using trisodium citrate.^{19,20} Of the many synthetic methods known in the literature to produce Si NPs, no route has yet been established as synthetically superior. The use of pyrophoric materials, HF, and high temperatures is evidence that a simple synthetic route to colloidal Si remains elusive. Moreover, there is a lack of information regarding the yield of Si NPs produced by the various methods in the literature. When the mass of the produced nanoparticles has been reported, little information has been provided as to how this number was acquired: i.e., what percentage of the mass is attributed to silicon versus the ligand or the percent yield relative to the initial silicon source. Knowing the yield of Si NPs for a synthetic route is important, considering the future industrial role that Si NPs are expected to fulfill. The yield of Si NPs, along with the cost of synthesis, will define the scope of the application for a particular synthesis. Our investigation focuses on determining the yield of Si NPs as produced by the oxidation of the Zintl phases Na₄Si₄, Rb₇NaSi₈, and $A_{12}Si_{17}$ (A = K, Rb, Cs) with NH₄Br.

Received: November 13, 2014 Published: December 8, 2014

The Zintl phases Na₄Si₄, K₄Si₄, and Mg₂Si have been previously explored as reactive precursors to synthesize Si NPs.^{18,21–23} However, the application of the heavier Zintl phases Rb₇NaSi₈ and A₁₂Si₁₇ (A = K, Rb, Cs) toward Si NP production has not been evaluated. The A₁₂Si₁₇ (A = K, Rb, Cs) Zintl phases are composed of two distinct silicon clusters present in a ratio of two [Si₄]⁴⁻ clusters to one [Si₉]⁴⁻ cluster (Figure 1). Isolating and characterizing the individual clusters



Figure 1. $[Si_4]^{4-}$ and $[Si_9]^{4-}$ clusters that comprise the $A_{12}Si_{17}$ (A = K, Rb, Cs) Zintl phases.

has been the focus of research on these Zintl phases. The solvate structure of the $[Si_9]^{*-}$ cluster has been isolated with charges of 2–, 3–, and 4–.^{24–28} Moreover, the nine atomic silicon cluster has been isolated as the complexes $[Si_9 - {\rm Ni}({\rm Co})_2)_2 - {\rm Si}_9]^{8-}$ and $[Si_9 - {\rm Zn}({\rm C}_6{\rm H}_5)]^{3-.29,30}$ While there are several reports in the literature of the isolation of both the solvate and coordinated $[Si_9]^{*-}$ clusters, the only known isolated structure of $[Si_4]^{4-}$ is $[Si_4({\rm CuMes})_2]^{4-.28}$ Recently, the first NMR signal of a bare silicide in solution was reported as the $[Si_4]^{4-}$ ion in liquid ammonia.³¹ The difficulty in isolating the $[Si_4]^{4-}$ cluster arises from the high charge per atom, which causes Na₄Si₄, for example, to be nearly insoluble in all solvents. The A₁₂Si₁₇ (A = K, Rb, Cs) Zintl phases also exhibit low solubility, but these materials can be solubilized in liquid ammonia. In addition, the $[Si_9-Zn(C_6H_5)]^{3-}$ complex mentioned above was isolated from a pyridine solution and the more oxidized $[Si_9]^{2-}$ is soluble in DMF. Using a more soluble Zintl phase precursor in the synthesis of Si NPs may lead to a higher yield of Si NPs relative to what can be obtained from Na₄Si₄.

Herein, we report a comparative study of Si NPs synthesized from the $A_{12}Si_{17}$ (A = K, Rb, Cs) Zintl phases to Si NPs produced from the Zintl phases composed solely of $[Si_4]^{4-}$ clusters (i.e., Na₄Si₄ and Rb₇NaSi₈). Inductively coupled plasma mass spectrometry (ICP-MS) was used to quantify the silicon concentration of each reaction. Transmission electron microscopy (TEM) provided information regarding the nanoparticle size and morphology. The absorbance and photoluminescence properties of the Si NPs synthesized from the various Zintl phases were measured. Using the ICP-MS and TEM data, we calculated the Si NP concentration in accordance with previously reported values for the number of silicon atoms contained within a Si NP with respect to the Si NP diameter.¹⁷

EXPERIMENTAL SECTION

Synthesis of Na₄Si₄, Rb₇NaSi₈, and A₁₂Si₁₇ (A = K, Rb, Cs). Na₄Si₄ was purchased from SiGNa Chemistry, Inc. (80%) and used as received.³² Powder X-ray diffraction showed the presence of both Na and Si, along with Na₄Si₄. Sodium and potassium were purified from impurities such as alkali metal oxides by liquating, i.e., melting and careful decanting the alkali metal melt. This process was repeated twice. Rubidium was distilled as previously reported.³³ Cesium (ABCR, 99.98%) and silicon (Wacker Chemie AG, 99.9%) were used without further purification. $\rm Rb_7 NaSi_8$ was synthesized following a previously reported method.³⁴ According to this method stoichiometric quantities of Rb, Na, and Si (6.23, 0.89, and 7.12 mmol, respectively) were loaded into a tantalum tube, which was crimped shut in an argon-filled glovebox and then sealed by an argon-filled arc welder. The tantalum tube was further enclosed within an evacuated silica ampule. The ampule was heated at 2 K/min to 600 °C, allowed to dwell for 10 h, and then cooled to room temperature (0.2 K/min). The product was characterized by powder X-ray diffraction to be phase pure.

 $A_{12}Si_{17}$ (A = K, Rb, Cs) Zintl phases were synthesized following a procedure similar to that previously reported.^{28,35} The alkali metals were mixed with Si powder (6.52 mmol of alkali metal, 9.24 mmol of Si), sealed in a tantalum tube, and enclosed within an evacuated silica ampule. The ampule was heated at 2 K/min to 900 °C, allowed to dwell for 10 h, and then cooled to room temperature (0.5 K/min). The products were characterized by powder X-ray diffraction. $K_{12}Si_{17}$ was phase pure, and $A_{12}Si_{17}$ (A = Rb, Cs) were found to be primarily the A_4Si_4 phase.

Caution! Na₄Si₄, Rb₇NaSi₈, and A₁₂Si₁₇ (A = K, Rb, Cs) Zintl phases as well as the alkali metals K, Rb, and Cs are highly reactive to air and moisture. These materials must be handled carefully under inert atmosphere conditions.

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 Advance diffractometer using Cu radiation (Cu K α : $\lambda = 1.54$ Å). Samples were ground with a mortar and pestle and loaded into an airtight sample holder in an argon-filled drybox. Powder diffraction patterns were collected in a 2θ range of $10-90^{\circ}$ with a step size of 0.02° . However, because of poor signal-to-noise ratios at low and high 2θ , only $20-60^{\circ}$ 2θ is displayed. The PXRD patterns are provided as Supporting Information.

Synthesis of 3-Aminopropenyl-Capped Silicon Nanoparticles. All reactions were performed under inert atmosphere conditions on a Schlenk line. To maintain consistency within the Zintl phase series, all reactions were performed with 2.55 mmol of Si from the respective nominal composition Zintl phases. This quantity corresponds to 0.64, 0.32, and 0.15 mmol of Na4Si4, Rb7NaSi8, and $A_{12}Si_{17}$ (A = K, Rb, Cs), respectively. In an argon-filled glovebox, the Zintl phase was added to a three-neck round-bottom flask containing a magnetic stir bar along with 3.83 mmol of NH4Br (Sigma-Aldrich, ≥99.99%) and 150 mL of previously distilled dimethylformamide (DMF) (Sigma-Aldrich, 99.8%). The reaction flask was closed with an adapter and stopcock, glass stopper, and a rubber septum and transferred to the Schlenk line. Once connected to the Schlenk line, the glass stopper was replaced with a water-cooled reflux condenser. The mixture was heated to 150 °C for 12 h under an argon flow (Scheme 1).^{36,37} After 12 h of heating, the reaction mixture was cooled to room temperature. While the reaction mixture was under air-free conditions, 0.57 mL of allylamine (Sigma-Aldrich, 98%) was injected. The reaction mixture was then heated at 150 °C for 4 h to produce 3aminopropenyl-capped Si NPs. The product consisted of a yellow solution and a black precipitate. The black precipitate was determined to be a mixture of amorphous and crystalline Si.

Scheme 1. Reaction Scheme for the Synthesis of Amine-Terminated Si NPs



A = K, Rb, Cs

Purification of Silicon Nanoparticles. To separate the bulk silicon precipitate from the yellow solution, the DMF mixture was centrifuged for 40 min. The supernatant was decanted and the black solid discarded. The yellow solution contains the alkylamine-capped Si nanoparticles, which were further purified and characterized accordingly. The DMF supernatant was exchanged for 18 M Ω cm nanopure water by successively concentrating and diluting the solution multiple times using a rotary evaporator. The final aqueous solution was characterized by UV–vis, photoluminescence, TEM, EDS, and ICP-MS.

Spectrophotometry. UV–vis data were collected for aqueous samples on a Shimadzu UV-1700 spectrophotometer with a sampling interval of 1.0 nm and a fixed slit width of 1.0 nm. Samples were analyzed in 18 M Ω cm nanopure water. Photoluminescence (PL) spectra were acquired on a Jobin Yvon Horiba FluoroMax-P spectrophotometer. The scan increment was set to 1.00 nm with an integration time of 1.00 s. The excitation and emission slit widths were fixed at 5.00 nm. The spectra are provided in the Supporting Information.

TEM Imaging/EDS Spectroscopy. TEM samples were prepared by drop-casting the Si NP solution onto a holey carbon grid (SPI). Si NPs were imaged on a 200 kV JEOL 2500SE TEM. Energy-dispersive spectra were collected on a Thermo Corporation EDS spectrometer coupled to the TEM. Gatan Digital Micrograph software was used to collect the images acquired on the TEM. The histograms are provided in the Supporting Information.

ICP-MS. Quantitative silicon concentrations were acquired by inductively coupled plasma mass spectrometry (ICP-MS). Silicon samples from individual reactions were each concentrated to a volume of 10 mL. From the 10 mL silicon nanoparticle solution, 200, 400, and 600 μ L aliquots were diluted to 5 mL in 3% trace element HNO₃. The prepared samples were analyzed by the Interdisciplinary Center for Plasma Mass Spectrometry at the University of California, Davis (ICPMS.UCDavis.edu), using an Agilent 7500CE ICP-MS (Agilent Technologies, Palo Alto, CA). The samples were introduced using a MicroMist Nebulizer (Glass Expansion, 4 Barlow's Landing Road, Unit 2A, Pocasset, MA 02559, USA) into a temperature-controlled spray chamber with He as the collision cell gas. Instrument standards were diluted from Certiprep ME 2A (SPEX CertiPrep, 203 Norcross Avenue, Metuchen, NJ 08840, USA) to 50, 100, 250, 500, and 1000 ppb and from Certiprep ME4 to 50, 100, 250, 500, and 1000 ppb, respectively, in 3% trace element HNO₃ (Fisher Scientific) in 18.2 M Ω cm water. A standard consisting of ME 2A and ME4 with a concentration of 100 ppb was analyzed every 12th sample as a quality control.

RESULTS AND DISCUSSION

As described above, Na4Si4 and Rb7NaSi8 are composed of isolated silicon tetrahedra, whereas the $A_{12}Si_{17}$ (A = K, Rb, Cs) Zintl phases contain both tetrahedra and nine-atom monocapped-square-antiprismatic silicon clusters. Powder X-ray diffraction of Na4Si4 obtained from SiGNa displayed the expected Na4Si4 phase (monoclinic space group, C2/c) along with Si and Na impurities. The calculated PXRD reflections for Rb₇NaSi₈ (cubic space group, Pa) confirmed that the product was phase pure. Due to the larger unit cell, complex structure, and disorder of K₁₂Si₁₇, the K₁₂Si₁₇ PXRD pattern showed poor diffraction intensities; however, no other products were identified.³⁸ The synthesis of the $Rb_{12}Si_{17}$ and $Cs_{12}Si_{17}$ Zintl phases did not yield a phase pure product. Both Rb₁₂Si₁₇ and Cs₁₂Si₁₇ showed mainly reflections of A₄Si₄. While reflections of Rb₁₂Si₁₇ can be found in the Rb sample, it was not possible to determine if $Cs_{12}Si_{17}$ was present in the Cs sample, due to the high background and weak reflections. The experimental PXRD patterns of the SiGNa Na₄Si₄ and the as-prepared Rb₇NaSi₈, K12Si17, Rb12Si17, and Cs12Si17 Zintl phases are provided in Figure S1 (Supporting Information).

Si NPs capped with allylamine were prepared by Schlenk line synthesis using the Zintl phase precursors according to Scheme 1. The reactions produced air-stable NP dispersions in DMF that were subsequently exchanged into an aqueous solvent. UV-vis and photoluminescence spectra were acquired for the Si NPs synthesized from each of the respective Zintl phase precursors (Figure S2 (Supporting Information)). The average emission wavelength of the Si NPs synthesized from Na₄Si₄ was 430 \pm 5 nm. The photoluminescence emission maxima of the Rb₇NaSi₈ and nominal A₁₂Si₁₇ (A = K, Rb, Cs) Zintl phases ranged between 421 and 434 nm (Table 1). These data are in

 Table 1. Emission Maxima of the Silicon NPs Synthesized

 from the Corresponding Zintl Phases

	Zintl phase				
	Na ₄ Si ₄	K ₁₂ Si ₁₇	Rb ₇ NaSi ₈	$Rb_{12}Si_{17}$	Cs ₁₂ Si ₁₇
$\lambda_{\rm em}~({\rm nm})$	429	434	427	429	421

agreement with literature values of the reported emission maxima for Si NPs synthesized from the reaction of Na₄Si₄ with NH₄Br.⁴ A recent study on the origin of red and blue photoluminescence of Si NPs best explains the observed photoluminescence.^{39,40} In that paper the authors concluded that trace amounts of nitrogen and oxygen were responsible for producing defects in the Si NPs, which give rise to blue photoluminescence. Further investigation into the role of surface groups determined that the Si NP photoluminescence could be tuned across the visible spectrum by carefully selecting the surface ligand.⁴¹

The presence of the Si NPs from $K_{12}Si_{17}$ was confirmed by energy-dispersive spectroscopy (EDS) (Figure 2) with the presence of the characteristic Si K α peak. The Cu K α is attributed to the copper grid on which the sample was prepared.



Figure 2. EDS spectrum of silicon nanoparticles synthesized from $K_{12}Si_{17}\!.$ The image of the analyzed area is shown in the inset.

TEM showed that the NPs have a spherical morphology with diameters of 3.1 ± 0.8 , 3.7 ± 1.2 , 4.5 ± 1.9 , 4.2 ± 1.4 , and 4.0 ± 1.1 nm for Si NPs synthesized from Zintl phases with the nominal compositions Na₄Si₄, K₁₂Si₁₇, Rb₇NaSi₈, Rb₁₂Si₁₇, and Cs₁₂Si₁₇, respectively (Figure 3 and Figure S2 (Supporting Information)). All of the TEM images show NPs, and Figure 3C displays additional amorphous material, which is attributed

Inorganic Chemistry



Figure 3. Silicon nanoparticles synthesized from (A) Na_4Si_4 , (B) $K_{12}Si_{17}$, (C) Rb_7NaSi_8 , (D) $Rb_{12}Si_{17}$, and (E) $Cs_{12}Si_{17}$. The scale bar is 100 nm.

to an organic polymer byproduct of hydrosilylation that was not completely removed during the purification of the solution.⁴

ICP-MS measurements show an increase in Si concentrations as the mass of the alkali metal in the Zintl phase increases (Figure 4, Table 2). To account for non phase pure starting materials, upper and lower boundary limits of the initial moles



Figure 4. Silicon yields related to the respective alkali metal Zintl phase precursor.

of Si from the Zintl phases were calculated on the basis of the purity of the precursor. With the calculated initial moles of Si and the yield of Si determined by ICP-MS, the percent yields of each Zintl phase reaction were calculated. Consistent with the literature, we expected that the lower charge density of the $[Si_9]^{4-}$ cluster should increase the solubility of the Zintl phase in DMF and lead to a higher yield of Si. However, comparison of the Si yields from the Rb7NaSi8 and K12Si17 precursors showed that the reactions from the $K_{12}Si_{17}$ Zintl phase containing [Si₉]⁴⁻ clusters had a lower Si yield than reactions from Rb₇NaSi₈, which contains only [Si₄]⁴⁻ clusters. Both Rbcontaining precursors Rb7NaSi8 and the nominal composition Rb₁₂Si₁₇ had nearly the same yield. This observation was not unexpected, as the nominal Rb₁₂Si₁₇ was primarily indexed as Rb₄Si₄ by PXRD. The insolubility of the highly charged Zintl phases in DMF explains the overall low yield of the reaction, but not the increasing amount of Si yielded by the reaction with larger and mixed alkali metal containing Zintl phases. The cation size is more important to the chemical reactivity than the Si anionic clusters in these Zintl phases. Smaller cations (e.g., sodium) will have more stabilizing Coulombic interactions with the anionic clusters and therefore be less reactive toward NH₄Br. This conjecture is supported by comparing the yield of Si between Na₄Si₄ and Rb₇NaSi₈, where both phases contain only $[Si_4]^{4-}$ clusters. The Rb_7NaSi_8 Zintl phase produced ${\sim}2.5$ times more Si in solution in comparison to Na₄Si₄. The larger Rb cation will disrupt the Coulombic interactions and increase the reactivity of the mixed metal containing phase, leading to a higher yield of Si.

To approximate the NP concentration, we related the average NP size to the number of Si atoms necessary to form the nanoparticle along with the yield of Si determined by ICP-MS.¹⁷ In contrast to the trend of increasing Si yield with larger cation size, the concentrations of NPs were similar, ranging between 0.137 μ M (Rb₇NaSi₈) and 0.208 μ M (Cs sample) (Table 3). Na₄Si₄ yielded the least Si and produced on average the smallest nanoparticles; however, due to the exponential increase in Si atoms with increasing NP size, the Si NP concentrations from Na₄Si₄ and the nominal Cs₁₂Si₁₇ sample are comparable.

CONCLUSIONS

Si NPs from the oxidation of a variety of Zintl phases containing $[Si_4]^{4-}$ and $[Si_9]^{4-}$ clusters have been characterized. The optical properties of the Si NPs produced from Rb₇NaSi₈ and $A_{12}Si_{17}$ (A = K, Rb, Cs) are similar to the properties of Si NPs synthesized from the previously studied Na4Si4, with emission wavelengths ranging from 421 to 434 nm. ICP-MS results show that, from millimolar quantities of the Zintl phase precursors, micromolar Si yields were achieved. A comparison of the Si yield from the oxidation reaction of the $[Si_4]^{4-}$ containing Rb₇NaSi₈ and the oxidation reaction of the mixed $[Si_4]^{4-}$ and $[Si_9]^{4-}$ -containing $K_{12}Si_{17}$ did not support the hypothesis that the $[Si_9]^{4-}$ cluster was more soluble in DMF. In fact, Rb₇NaSi₈ produced more than double the Si yield in comparison with K₁₂Si₁₇ when both initial precursor quantities contained the same amount of Si. The Si yield also increased with larger and heavier alkali metal containing Zintl phases. The trend of increasing Si yield for the heavier alkali metal Zintl phases is best explained by decreasing Coulombic interactions of the anionic silicon clusters with the group I countercations going down the group. The high yield of Si for the mixed metal Rb₇NaSi₈ phase further supports this hypothesis. The Si NP

Table 2. ICP-MS Data Quantifying the Silicon Yield from the Corresponding Zintl Phase

	^a SiG1	Na Na ₄ Si ₄			^b Rb sample		^c Cs sample	
	Na ₄ Si ₄	80% Na ₄ Si ₄	K12Si17	Rb ₇ NaSi ₈	Rb ₄ Si ₄	Rb ₁₂ Si ₁₇	Cs ₄ Si ₄	$Cs_{12}Si_{17}$
molar mass (g/mol)	204.30	204.30	946.63	845.95	454.21	1503.07	643.98	2072.37
amt of Si (mmol)	2.55	2.04	2.55	2.55	1.99	2.55	1.93	2.55
mass (g)	0.130	0.104	0.142	0.270	0.226	0.226	0.311	0.311
yield of Si (μmol)	1.22	$t \pm 0.10$	1.96 ± 0.12	3.19 ± 0.13	3.13	± 0.21	3.38	± 0.12
yield (%)	0.048	0.060	0.077	0.125	0.157	0.123	0.175	0.133

^{*a*}The experimentally acquired Si yield from SiGNa Na₄Si₄ (80% pure) was used to extrapolate a theoretical percent yield of pure Na₄Si₄. ^{*b*}Rb₄Si₄ and Rb₁₂Si₁₇ represent the boundary limits of the initial mmol of Si and the percent yield. ^{*c*}Cs₄Si₄ and Cs₁₂Si₁₇ represent the boundary limits of the initial mmol of Si and the percent yield.

Table 3. Calcu	lated Silicon	Nanoparticl	le Concentrations
----------------	---------------	-------------	-------------------

	Na ₄ Si ₄	K ₁₂ Si ₁₇	Rb ₇ NaSi ₈	Rb ₁₂ Si ₁₇	$Cs_{12}Si_{17}$
NP size (nm)	3.1 ± 0.8	3.7 ± 1.2	4.5 ± 1.9	4.2 ± 1.4	4.0 ± 1.1
Si atoms	759	1290	2321	1887	1630
Si yield (µmol)	1.22 ± 0.10	1.96 ± 0.12	3.19 ± 0.13	3.13 ± 0.21	3.38 ± 0.12
[Si NP] (µM)	0.161 ± 0.013	0.152 ± 0.009	0.137 ± 0.005	0.166 ± 0.011	0.208 ± 0.007

size increased with the size of the alkali metal cation. When the NP average size was considered, an approximate NP concentration was calculated to be near the micromolar regime per reaction. The overall low yield of Si NPs, which varied between 0.137 and 0.208 μ M, is attributed to the low solubility of the Zintl phases in DMF, limiting these reactions to the surface of the material. Therefore, increasing the surface area of the Zintl phase, reducing Coulombic attractions through metal cations, and employing a metathesis reaction with SiX₄ (X = Cl, Br, I) may be more promising routes for achieving higher yields of Si NPs.

ASSOCIATED CONTENT

S Supporting Information

Figures of the PXRD patterns of the starting materials, the UV-vis and photoluminescence spectra, and TEM NP histograms for each reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for S.M.K.: smkauzlarich@ucdavis.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-1035468) and the *Bavaria California Technology Center* (BaCaTeC-Precursor Methods for Silicon based Materials). We thank Joel Commisso from the Interdisciplinary Center of Plasma Mass Spectrometry for ICP-MS. Furthermore, we thank Dr. Oliver Janka and Dr. Elayaraja Muthuswamy for many insightful discussions.

REFERENCES

- (1) Canham, L. T. Appl. Phys. Lett. 1990, 57, 1046–1048.
- (2) Batu, G.; Naoto, S. Sci. Technol. Adv. Mater. 2014, 15, 014207.
- (3) Veinot, J. G. C. Chem. Commun. 2006, 4160-4168.
- (4) Atkins, T. M.; Louie, A. Y.; Kauzlarich, S. M. Nanotechnology 2012, 23, 294006.

(5) Biesta, W.; van Lagen, B.; Gevaert, V. S.; Marcelis, A. T. M.; Paulusse, J. M. J.; Nielen, M. W. F.; Zuilhof, H. *Chem. Mater.* **2012**, *24*, 4311–4318.

(6) Shiohara, A.; Hanada, S.; Prabakar, S.; Fujioka, K.; Lim, T. H.; Yamamoto, K.; Northcote, P. T.; Tilley, R. D. *J. Am. Chem. Soc.* **2009**, *132*, 248–253.

(7) Romero, J. J.; Llansola-Portolés, M. J.; Dell'Arciprete, M. L.; Rodríguez, H. B.; Moore, A. L.; Gonzalez, M. C. *Chem. Mater.* **2013**, 25, 3488–3498.

(8) Gupta, A.; Swihart, M. T.; Wiggers, H. Adv. Funct. Mater. 2009, 19, 696-703.

- (9) Buriak, J. M. Chem. Mater. 2014, 26, 763-772.
- (10) Hessel, C. M.; Henderson, E. J.; Veinot, J. G. C. Chem. Mater. 2006, 18, 6139–6146.

(11) Pi, X. D.; Li, Q.; Li, D. S.; Yang, D. R. Sol. Energy Mater. Sol. Cells 2011, 95, 2941–2945.

(12) Mastronardi, M. L.; Henderson, E. J.; Puzzo, D. P.; Chang, Y.; Wang, Z. B.; Helander, M. G.; Jeong, J.; Kherani, N. P.; Lu, Z.; Ozin, G. A. *Small* **2012**, *8*, 3647–3654.

(13) Cho, E. C.; Park, S.; Hao, X.; Song, D.; Conibeer, G.; Park, S. C.; Green, M. A. *Nanotechnology* **2008**, *19*, 245201.

- (14) Shiohara, A.; Prabakar, S.; Faramus, A.; Hsu, C.-Y.; Lai, P.-S.; Northcote, P. T.; Tilley, R. D. *Nanoscale* **2011**, *3*, 3364–3370.
- (15) Bhattacharjee, S.; Rietjens, I. M. C. M.; Singh, M. P.; Atkins, T. M.; Purkait, T. K.; Xu, Z.; Regli, S.; Shukaliak, A.; Clark, R. J.; Mitchell,
- B. S.; Alink, G. M.; Marcelis, A. T. M.; Fink, M. J.; Veinot, J. G. C.;
- Kauzlarich, S. M.; Zuilhof, H. Nanoscale 2013, 5, 4870-4883.
- (16) McVey, B. F. P.; Tilley, R. D. Acc. Chem. Res. 2014, 47, 3045–3051.
- (17) Zou, J.; Sanelle, P.; Pettigrew, K. A.; Kauzlarich, S. M. J. Cluster Sci. 2006, 17, 565–578.

(18) Pettigrew, K. A.; Liu, Q.; Power, P. P.; Kauzlarich, S. M. Chem. Mater. 2003, 15, 4005–4011.

(19) Hessel, C. M.; Reid, D.; Panthani, M. G.; Rasch, M. R.; Goodfellow, B. W.; Wei, J.; Fujii, H.; Akhavan, V.; Korgel, B. A. *Chem. Mater.* **2011**, *24*, 393–401.

(20) Zhong, Y.; Peng, F.; Bao, F.; Wang, S.; Ji, X.; Yang, L.; Su, Y.; Lee, S.-T.; He, Y. J. Am. Chem. Soc. **2013**, 135, 8350–8356.

(21) Mayeri, D.; Phillips, B. L.; Augustine, M. P.; Kauzlarich, S. M. Chem. Mater. 2001, 13, 765–770.

(22) Bley, R. A.; Kauzlarich, S. M. J. Am. Chem. Soc. 1996, 118, 12461-12462.

(23) Cho, B.; Baek, S.; Woo, H.-G.; Sohn, H. J. Nanosci. Nanotechnol. 2014, 14, 5868–5872.

(24) Goicoechea, J. M.; Sevov, S. C. Inorg. Chem. 2005, 44, 2654–2658.

Inorganic Chemistry

- (25) Goicoechea, J. M.; Sevov, S. C. J. Am. Chem. Soc. 2004, 126, 6860-6861.
- (26) Joseph, S.; Suchentrunk, C.; Kraus, F.; Korber, N. Eur. J. Inorg. Chem. 2009, 2009, 4641–4647.
- (27) Joseph, S.; Suchentrunk, C.; Korber, N. Z. Naturforsch. B 2010, 65, 1059–1065.

(28) Waibel, M.; Kraus, F.; Scharfe, S.; Wahl, B.; Fässler, T. F. Angew. Chem., Int. Ed. 2010, 49, 6611–6615.

(29) Joseph, S.; Hamberger, M.; Mutzbauer, F.; Härtl, O.; Meier, M.; Korber, N. Angew. Chem., Int. Ed. 2009, 48, 8770–8772.

(30) Goicoechea, J. M.; Sevov, S. C. Organometallics **2006**, 25, 4530–4536.

(31) Neumeier, M.; Fendt, F.; Gärtner, S.; Koch, C.; Gärtner, T.; Korber, N.; Gschwind, R. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4483–4486.

(32) SiGNa Chemistry, Inc., Davis, CA, 2013.

(33) Brauer, G. Handbuch der Präparativen Anorganischen Chemie, 3rd ed.; Ferdinand Enke Verlag: Stuttgart, Germany, 1975.

(34) Goebel, T.; Prots, Y.; Ormeci, A.; Pecher, O.; Haarmann, F. Z. Anorg. Allg. Chem. 2011, 637, 1982–1991.

(35) Waibel, M.; Benda, C. B.; Wahl, B.; Fässler, T. F. Chem. Eur. J. 2011, 17, 12928-12931.

(36) Neiner, D.; Chiu, H. W.; Kauzlarich, S. M. J. Am. Chem. Soc. 2006, 128, 11016–11017.

(37) Zhang, X.; Neiner, D.; Wang, S.; Louie, A. Y.; Kauzlarich, S. M. Nanotechnology **2007**, *18*, 095601.

(38) Quéneau, V.; Todorov, E.; Sevov, S. C. J. Am. Chem. Soc. 1998, 120, 3263-3264.

(39) Dasog, M.; Yang, Z.; Regli, S.; Atkins, T. M.; Faramus, A.; Singh, M. P.; Muthuswamy, E.; Kauzlarich, S. M.; Tilley, R. D.; Veinot, J. G. C. ACS Nano **2013**, *7*, 2676–2685.

(40) Fuzell, J.; Thibert, A.; Atkins, T. M.; Dasog, M.; Busby, E.; Veinot, J. G. C.; Kauzlarich, S. M.; Larsen, D. S. *J. Phys. Chem. Lett.* **2013**, *4*, 3806–3812.

(41) Dasog, M.; De los Reyes, G. B.; Titova, L. V.; Hegmann, F. A.; Veinot, J. G. C. ACS Nano **2014**, *8*, 9636–9648.