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Sanaa Semlali, Benoit Cormary, Maria de Marco, Jérôme Majimel, Alix Sournia-Saquet, et al.. Effect of solvent on silicon nanoparticle formation and size: a mechanistic study. *Nanoscale*, 2019, 11 (11), pp.4696-4700. 10.1039/C9NR00619B . hal-02071674

HAL Id: hal-02071674

<https://hal.science/hal-02071674v1>

Submitted on 18 Mar 2019

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DOI: 10.1039/C9NR00619B

Effect of solvent on silicon nanoparticle formation and size: a mechanistic study

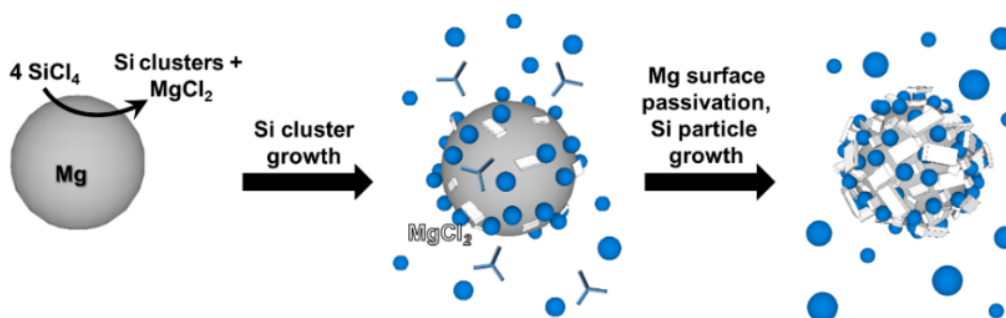
Sanaa Semlali,^a Benoit Cormary,^{a*} Maria L. De Marco,^a Jérôme Majimel,^a Alix Saquet,^b Yannick Coppel,^b Mathieu Gonidec,^a Patrick Rosa,^a Glenna L. Drisko^{a*}

Silicon has emerged as the most desirable material for optics, however chemists struggle to control its morphology and dimensions for larger diameters. Here the average diameter of silicon nanoparticles is varied between 3 and 15 nm by changing the reaction solvent. Electrochemistry and NMR elucidate the role of solvent on the synthetic mechanism. Surprisingly the solvent does not stabilize the nanoparticles and there is no trend associated with chain length or open-chain versus cyclical solvent molecules. The solvents' main role is to stabilize the by-products, which prolongs the reaction lifetime.

Silicon has exceptional optical properties spanning from photoluminescence to Mie resonance, which has generated frenetic activity among physicists in recent years.¹ Silicon is an abundant and nontoxic element, thus commercial applications are expected from optically active biomedical probes to telecommunications.¹⁻³ One particularly exciting application is the prospect of forward-light scattering, which can be used for beam shaping. In pursuit of optical metamaterials, large particle

diameters, that is ≥ 75 nm, are required.¹ It is especially difficult to grow nanoparticles larger than 10 nm using solution chemistry. The size restriction can be attributed to the sluggish particle growth kinetics compared to nucleation rate. It is well-known that a strong reducing agent favours fast nucleation, consuming most of the precursor.⁴ As small nanoparticles are typically obtained by strong reductants,⁵ a gentle reductant is required to promote particle growth over nucleation. Magnesium (Mg) is a gentler reducing agent than the others commonly used, i.e. naphthalenides, alkylides, metal hydrides and Zintl salts. This synthetic protocol is similar to one published by S. Kauzlarich and coworkers, where SiCl_4 was reduced by the Zintl salt Mg_2Si .⁶ This metathesis reaction producing particles in glyme with a diameter between 2-5 nm,⁶ where the Mg reduction reported here generates particles around 10 nm. However, Mg does not reduce SiCl_4 in all solvents,⁷ begging two questions: What is the reduction mechanism? And what is the solvent's role in this reaction?

Scheme 1. Formation mechanism of Si NPs (blue spheres). The Mg (grey sphere) is not drawn to scale, being millimetric in size, where the silicon is nanometric. Clusters of Si are represented by a blue Y, the MgCl_2 as white crystals.



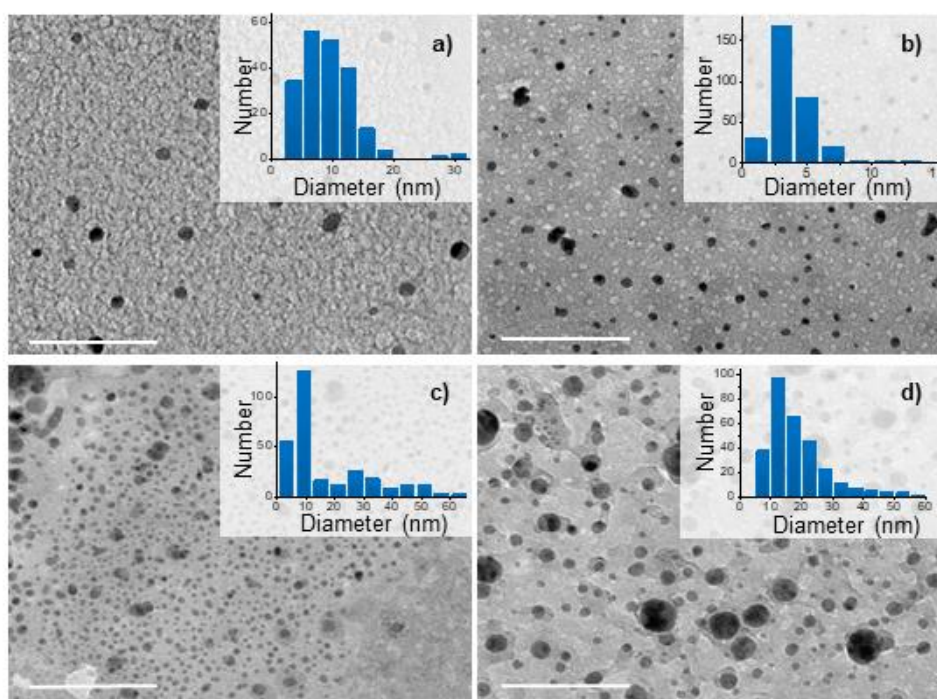


Fig. 1 Bright field TEM and particle size distribution of Si NPs synthesized in (a) THF, (b) diglyme, (c) glyme, and (d) tetraglyme. Scale bars represent 100 nm.

No one has yet studied the solvent effect on silicon nanoparticle (Si NP) size, even though the solvent changes the reactivity of reducing agents and precursors, while either stabilizing the nanoparticles or promoting their aggregation. For example, in the preparation of CdS nanoparticles, the particle size was ten times smaller in pure alcohol than in an alcohol/water mixture.⁸ Here we tested six solvents, in the form of glycol ethers and heterocyclic ethers. We have chosen to use Mg as a reductant, due to its relatively mild reactivity and because it does not pollute the silicon structure, as hydrogen can.⁹ Using Mg and SiCl_4 , we were able to vary the mean nanoparticle size between 3-15 nm simply by changing the solvent. This reaction is relatively easy, as it occurs at room temperature and ambient pressure, using commercially available products. It is also easy to handle and poses less security risks than most other reducing agents. We have investigated the reaction mechanism using NMR and by determining the reduction potentials in the respective solvents. SiCl_4 was reduced by Mg grit at room temperature and ambient pressure in the presence of THF, glyme, diglyme and tetraglyme. The reaction had little induction time, with a visible colour change occurring within a few minutes of mixing the reagents. Reduction did not occur in diethyl ether and dioxane. A previous report claims that the reaction does not occur in toluene or anisole.⁷

By producing Si NPs under different conditions and studying the synthesis using solution-state NMR and electrochemistry, we propose that these nanoparticles form via the mechanism shown in Scheme 1. SiCl_4 reduction is observed through a colour change, from colourless to yellow, to red, to brown, as an evolution in nanoparticle size. The SiCl_4 reduction occurs at the Mg surface. We can eliminate a mechanism based on the formation of silanylmagnesium complexes, the analogue of the carbon-based Grignard reagent, a mechanism that was proposed previously.⁷ Silanylmagnesium compounds cannot be produced from chloride-based silicon precursors at room temperature, and if they did form, they would cleave the glycol ether solvents.¹⁰ At the onset of the reaction, the Mg grit is covered by a thin oxide layer. Upon SiCl_4 addition, the surface of the Mg is partially scrubbed, generating a very small amount of SiO_2 and a reactive magnesium surface. The SiCl_4 then grows into clusters of several silicon atoms, generating MgCl_2 as a by-product. The vast majority of the silicon clusters and the MgCl_2 detach from the surface of the Mg grit. However, as time progresses, the surface eventually becomes encumbered with a skin of salt and Si NPs. Elemental analysis of pieces of Mg grit at the end of the reaction in different solvents was conducted using a scanning electron microscope (SEM) (Fig. S1, S2 ESI). The surface was covered with two types of zones: One rich in silicon and one rich in both magnesium and chloride. This skin

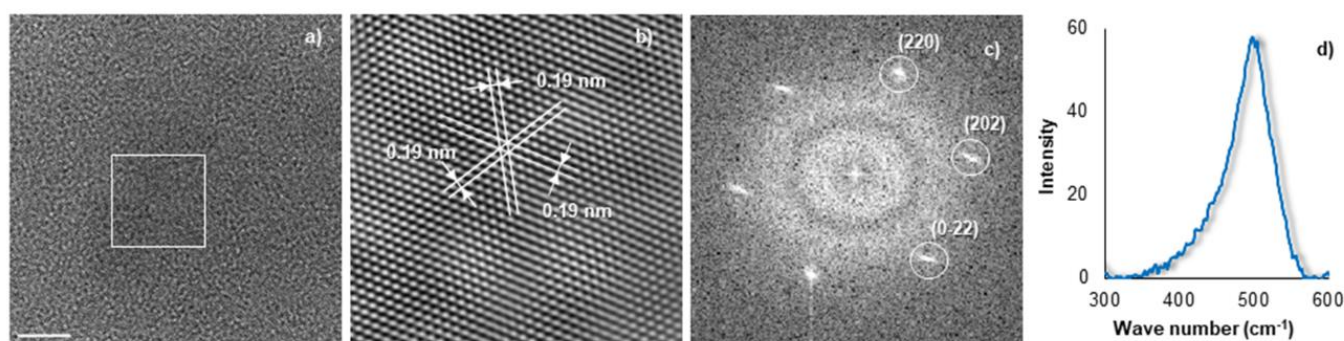


Fig. 2 (a) HRTEM (scale bar = 5 nm), (b) filtered HRTEM image, (c) SAED, and (d) Raman spectroscopy of a nanoparticle produced in glyme.

passivates the Mg surface and prevents further reaction, even if SiCl_4 still exists in the solution, terminating nanoparticle growth. The solvent does not intervene directly in the reaction. We believe that the solvent's main effect on the final size of the Si NPs is due to its capacity to solvate MgCl_2 and Si species, and its physical properties (e.g. viscosity, reduction potential of the SiCl_4 , polarity and density). NMR and electrochemistry studies provide evidence supporting this mechanism.

By simply changing the solvent from one glycol ether to another, the Si NP size distribution is significantly altered. Fig. 1 shows representative TEM images and histograms of the size distribution of Si NPs synthesized in four different glycol ethers. The results are not immediately logical, the trend in size is not linearly connected to the number of ether units, and oddly THF produces particles where its linear analogue, diethyl ether, does not. The smallest Si NPs were obtained in diglyme, having an average diameter of 6 ± 2 nm. Si NPs synthesized in THF have a size centred around 8 ± 8 nm. The synthesis in glyme offers a large range of Si NP sizes: from 5 to 60 nm; however half of the NPs have a diameter between 5 and 10 nm. In tetraglyme, a size maximum distribution occurs at 15 nm, with a substantial quantity of particles being larger than 20 nm. Perhaps the substantially larger size observed in tetraglyme is due to its viscosity, slowing NP diffusion away from the reactive surface. Pure, crystalline Si NPs are produced by this room temperature method, as confirmed with high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy (Fig. 2). The Si NPs contain diffraction planes, visible using HRTEM (Fig. 2a). The d-spacing for the planes in this orientation were 0.19 nm, which correspond to the $\{220\}$ hkl plane for the diamond cubic structure. The selected area electron diffraction (SAED) pattern indexes to the $[-111]$ zone axis of cubic silicon, the expected crystallographic structure. Si nanoparticles with a chlorinated surface become charged by observation under the electron beam and thus leave the TEM grid after ~ 6 s of exposure time. This short window of observation did not allow us to do EDX spectra of the silicon nanoparticles. However, we performed electron diffraction on particles of all sizes and

consistently found that the particles were silicon. The Raman spectrum of the Si NPs possesses a peak at 510 cm^{-1} that corresponds to crystalline silicon.¹¹ No other peaks were observed, indicating the purity of the sample. Thus, crystalline silicon can be successfully produced using this room temperature reaction.

Analytic electrochemistry was used to probe the observed trend in Si NP size as a function of solvent (Fig. 3). The reductive potential of the Mg fluctuated rather dramatically according to the solvent used. The starting potential ($E_{t=0}$) indicates the role of the solvent on the electrode. The starting potentials measured in glycol ethers are similar to the potential observed for a Mg electrode in DMF with NBu_4Cl as the electrolyte salt.¹² Upon SiCl_4 addition, an initial oxidation occurs. The oxidation is likely due to the reaction of SiCl_4 with the passivating oxide layer present at the surface of the Mg electrode. This initial oxidation is observed in all of the solvents studied. In the case of dioxane, once the oxidation is complete, the silicon precursor no longer reacts with Mg. The starting potential in dioxane is 1.4 V/SCE.

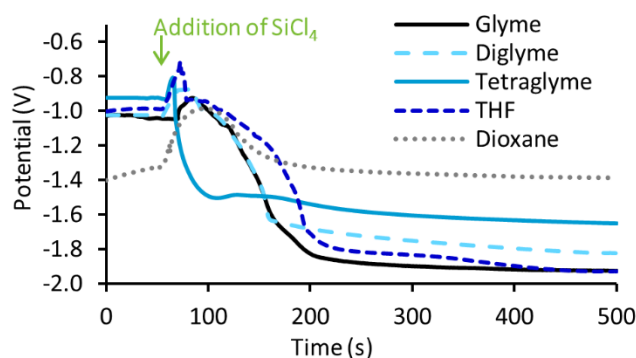


Fig. 3 Chronopotentiometry measurement using a Mg electrode of the equilibrium potential in various solvents before and after adding SiCl_4 .

Although dioxane shows the lowest potential in the presence of Mg and absence of SiCl_4 , after addition of SiCl_4 , dioxane shows the highest potential of the set and does not form nanoparticles. In the other solvents studied, the reaction was

spontaneous. After SiCl_4 injection, there are different reduction kinetics. Within 200 s, the potential stabilizes at a lower value. The final potential value ranged from -1.6 to -2.0 V/SCE, and is probably the standard potential of the MgCl_2/Mg couple.

Upon cycling the Mg electrode in the presence of SiCl_4 , in all solvents except dioxane (Fig. S3, ESI) the surface became highly resistive and eventually passivated. Thus, no further reaction between Mg and SiCl_4 was possible. The passivation results from the side product of the reduction, which is probably the magnesium chloride salt.¹³ In dioxane, the Mg surface remained unchanged (Fig. S3b, ESI). When platinum was used as the working electrode in place of Mg, the SiCl_4 was not reduced (Fig. S4, ESI). Thus, platinum does not intervene in the reaction in the same way as Mg does. The electrochemistry confirms what was observed synthetically, no nanoparticles are formed when dioxane is employed. Moreover, the reduction in the other solvents is spontaneous on the surface of the Mg. While differences in the redox potential of Mg/MgCl_2 appear to induce noticeable differences in the final sizes of Si NPs in each solvent, the relationship between solvent and reductant is not univocal: diglyme yielded smaller sizes than THF and glyme while having a higher potential. It is likely that other factors, such as viscosity, come into play.

NMR experiments help shed light upon the interaction between the solvent and the nanoparticles and show which species are present in solution. *In situ* growth NMR studies were performed without agitation and as a result, the reduction occurred much slower than the reactions taking place in a Schlenk flask.

When monitoring the reaction over time using ^{29}Si NMR spectroscopy, at the onset only SiCl_4 is present (δ -18 ppm, Fig. S5 ESI). After 4 h, peaks appeared at 0 and 30 ppm. The peak at 0 ppm later disappears, indicating that it is a relatively stable intermediate species, which is then consumed. At longer times, a peak is still observed at 30 ppm, but with a strongly increased width. F. Meyer-Wegner, *et al.* have published the chemical shifts for Si in SiCl_{2n+2} species of $n=1-5$.¹⁴ These species can only be detected if they are free in solution, species bound to the Mg grit cannot be observed. The peaks that we observe do not correspond to those reported by Meyer-Wegner and co-workers, thus we believe that they correspond to clusters larger than 5 silicon atoms. Alternatively, however, these downfield shifts may correspond to SiCl_2 silylene adducts: examples of ternary amine adducts are reported in the literature in cleavage reactions of chlorosilanes in the presence of reductants, so solvent adducts in our likewise reducing conditions could be a possibility. There is little evolution after 6 h, indicating that the Mg surface is no longer active. The SiCl_4 peak at -18 ppm is consistently present. Another peak appears at -128 ppm after 4 h of reaction, which then shifts to -140 ppm by 6 h. After 46h, two new peaks appear at -39 and -46 ppm, which we cannot explain at this time. The peaks are only present when THF is used as a solvent, thus it is perhaps due to a degraded THF molecule attacking a silicon chloride species, as silicates can appear in this region of the spectrum. After a second addition of Mg, these three peaks disappear, which is probably because the THF becomes so crosslinked that it is no longer sufficiently

mobile to be detected by liquid NMR. The solution had gellified by the end of the reaction. The mechanism is further clarified using ^{35}Cl NMR.

The consumption of the SiCl_4 precursor is monitored using ^{35}Cl NMR (Fig. 4). It is possible to observe the ^{35}Cl signal due to the tetrahedral geometry of the chloride, which averages to zero the quadrupolar coupling. Chlorides occurring in other geometries are not observable. At the beginning of the experiment, SiCl_4 is added to 4 equivalents of Mg grit in deuterated THF. The intensity of the Cl peak initially decreases at a linear rate, and then stabilizes. Twenty% of the initial concentration of SiCl_4 is consumed after 5.5 h. At this point, a fresh quantity of Mg (4 equivalents) is added. The SiCl_4 reacts with the fresh Mg and stabilizes by 8 h. By this time, 62% of the SiCl_4 has been consumed. For comparison, in the case of a reaction with just one single addition of 10 equivalents of Mg grit, the SiCl_4 concentration decreases by only 35%. The second addition of Mg yields a faster consumption of the silicon precursor. The same behaviour is observed in the case of 2 successive additions of 2 equivalents of Mg (Fig. S6, ESI). These results illustrate that a successive addition of reductant is more efficient than a single addition. The NMR experiments confirm the electrochemistry results: the reaction occurs rapidly until the Mg surface becomes passivated and the reaction stops.

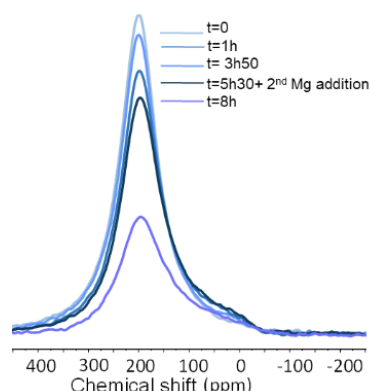


Fig. 4 ^{35}Cl NMR of SiCl_4 and Mg grit in THF-D8 at different time intervals and with 4 equivalents of Mg.

^1H NMR studies show no visible species, with the exception of THF (data not shown). THF shows a minor chemical shift over time, probably due to its polymerization. The NMR studies show no interaction between the solvent and the growing Si NPs, indicating that the solvent molecules are not in fast exchange between a surface-bound and solvated state, and thus it is unlikely that the solvent is behaving as a ligand as has been observed for other semiconductor nanoparticles.¹⁵ Solvent does not seem to stabilize the formed Si NPs. Thus, the changing particle size as a function of solvent must be mainly due to its effect on the reduction potential of SiCl_4 and its capacity to solvate MgCl_2 and Si species.

Physicists challenge chemists to develop silicon particles, but the difficulty of working with silicon leads to slow progress. In pursuit of a bottom-up chemistry synthesis of Si NPs large enough to support a Mie resonance, it is important to examine

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each reaction parameter separately: the silicon precursor, the reducing agent, the solvent and the reaction conditions. Here, solvent was the subject of study, where tetraglyme proved to produce nanoparticles much larger on average than in other glycol ethers. The Mg reduction of SiCl_4 was studied because Mg is a gentle reducing agent, which should favour growth over nucleation. In all cases, the Si NPs obtained were cubic crystalline silicon. The Mg donates its electrons without polluting the silicon structure. Electrochemistry and NMR experiments indicate that the reaction occurs quickly and spontaneously on the Mg surface. Mg reduction did provide larger nanoparticle sizes, however polydispersity in nanoparticle size was large. Thus, Mg may not be the right reductant for solution-based routes to optically resonant silicon nanoparticles. Although silicon-based optical metamaterials still cannot be achieved using solution chemistry, this work shows that solvent needs to be considered in order to maximize nanoparticle size.

Conflicts of interest

There are no conflicts to declare.

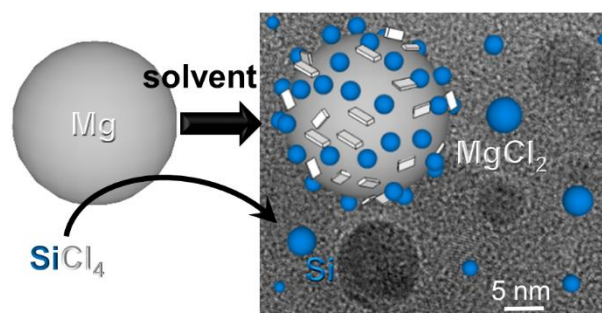
Notes and references

SS, BC, MLDM and GLD were supported by the LabEx AMADEus (ANR-10-LABX-42). They and MG acknowledge the framework of IdEx Bordeaux (ANR-10-IDEX-03-02), i.e. the Investissements d'Avenir program of the French government managed by the Agence Nationale de la Recherche. PLACAMAT (UMS 3626CNRS-Bordeaux University) provided technical support with imaging. FEGSEM and EDX instrumentation was facilitated by the Institut des Matériaux de Paris Centre (IMPC FR2482) and was funded by Sorbonne Université, CNRS and by the C'Nano projects of the Région Ile-de-France. We thank David Montero for performing the FEGSEM and EDX analysis.

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TOC graphic



Silicon nanoparticle size is adjusted by simply changing the reaction solvent. The role of solvent on nanoparticle formation is investigated.