

Supporting information

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

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## 1. Experimental section

**General.** Silicon tetrachloride (99%), magnesium grit (99%), and the anhydrous grade of tetrahydrofuran (THF), glyme, diglyme, tetraglyme and dioxane were purchased from Sigma Aldrich. The solvents were purified via distillation before use, by heating to the boiling point or by heating under vacuum, in the case of high boiling solvents. In a typical procedure, 10 g of benzophenone and approximately 1 g of metallic sodium shavings were added to 1 L of the solvent. When the solution turned blue, indicating the absence of peroxides and water, distillation was initiated. The solvents were then stored over activated molecular sieves (4Å, 10 to 18 mesh from Fisher scientific).

**Silicon nanoparticle synthesis.** All experiments were performed in an Ar filled dry box to avoid exposure to air and water. Silicon tetrachloride (1 mL, 8.7 mmol) was mixed with magnesium grit (420 mg, 17.3 mmol) in 20 mL of one of the solvents, be it either diethyl ether, THF, dioxane, glyme, diglyme or tetraglyme. The solution was then stirred at room temperature for 20 h in a Schlenk flask. The magnesium chloride salt precipitates were separated from the colloidal silicon solution by centrifugation at 10 000 rpm for 10 min. No observable quantity of nanoparticles was obtained in diethyl ether. In the presence of glyme and tetraglyme a brown solution was obtained, where the THF solution was blood red and diglyme yielded a yellow solution. These are the colours expected for this size regime (reference C. M. Hessel, E. J. Henderson, J. G. C. Veinot, *Chem. Mater.* **2006**, *18*, 6139.).

**Electrochemistry.** Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 (ECO Chemie, The Netherlands) controlled by GPES 4.09 software. Experiments were performed at room temperature using a custom-built airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. A platinum wire served as the counter electrode. A bare magnesium rod (Sigma Aldrich, 6 mm in diameter) was used as the working electrode. The electrolyte (n-Bu<sub>4</sub>N)[PF<sub>6</sub>] was dissolved in the dry solvent of interest (either dioxane, THF, glyme, diglyme or tetraglyme) to form the media for the electrochemical reactions. Diethyl ether is a very poor solvent for the electrolyte, thus this solvent could not be measured.

The Mg electrode was polished using sand paper and then conditioned by cyclic voltammetry in glyme before each measurement to ensure an identical surface. The pretreatment consisted of 20 cycles between +3 and -3V/SCE at a rate of 0.1 V/s. After conditioning, the solvent was changed to the medium of interest. The parameters of the new electrochemical medium were checked by cyclic voltammetry (10 cycles). SiCl<sub>4</sub> (0.1 mL) was added to the electrochemical cell and then using chronopotentiometry for a period of 500 s with no applied current. Afterwards the reactivity of the surface was checked by performing an additional

cyclic voltammetry between +3 and -3V/SCE at a rate of 0.1 V/s. The chronopotentiometry and the cyclic voltammetry curves were obtained under static conditions, that is the solutions were not stirred.

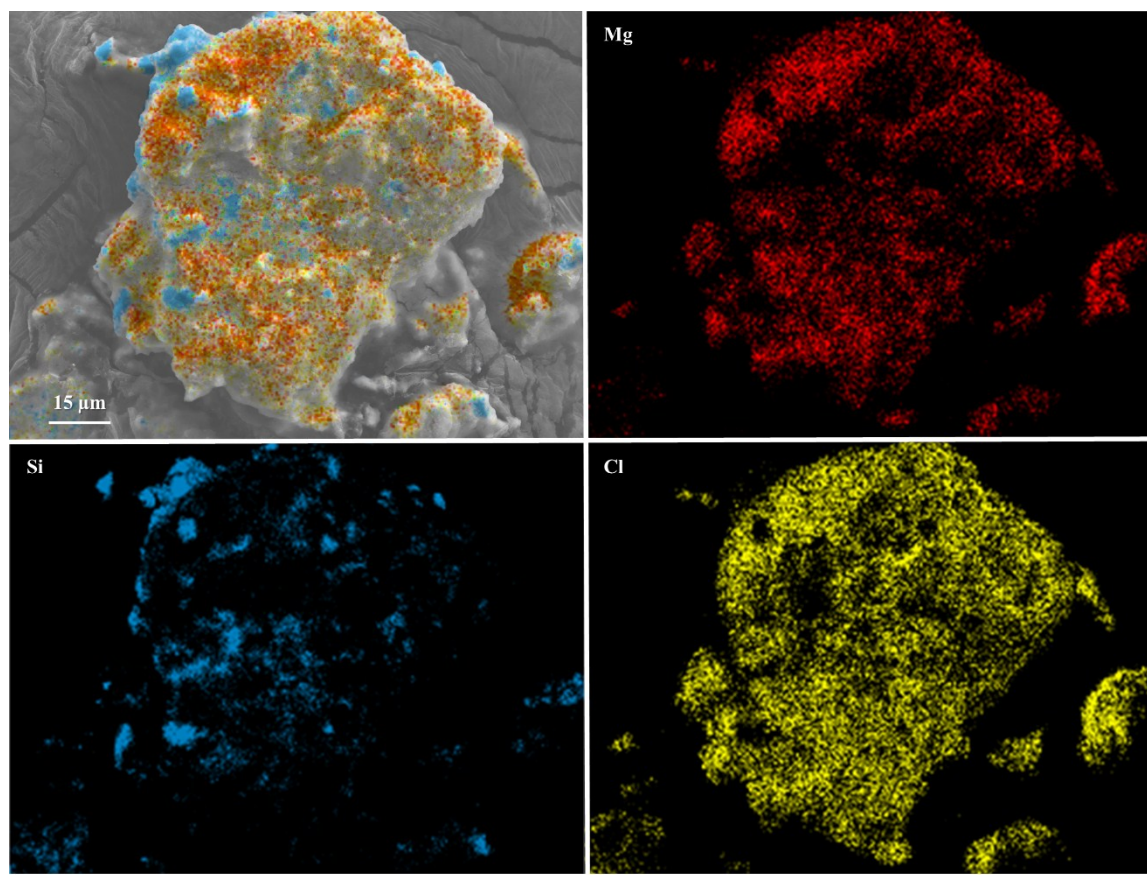
Experimental peak potentials can be referenced to the standard ferrocene redox potential, with our SCE reference electrode yielding in THF  $E_{1/2}(\text{Fc}^{2+}/0) = +0.55$  V. This value is in line with literature (see e.g. J. Ruiz Aranzaes, M.-C. Daniel, D. Astruc, *Can. J. Chem.* **2006**, *84*, 288.).

**High resolution transmission electron microscopy.** HRTEM was carried out using a JEOL 2200FS (JEOL, Tokyo, Japan) microscope operating at an acceleration voltage of 200 kV (wavelength  $\lambda = 2.51$  pm) equipped with a Schottky type FEG. For HR-TEM studies, a few droplets of the Si particles suspension were deposited over copper/carbon grids. High-resolution transmission electron microscopy micrographs were acquired with a Gatan Ultrascan CCD 2k x 2k and digital diffractograms were calculated using the Gatan Digital Micrograph program. Moreover, in order to be representative and statistically significant, many images from several regions of various samples were recorded and the most characteristic results are presented here.

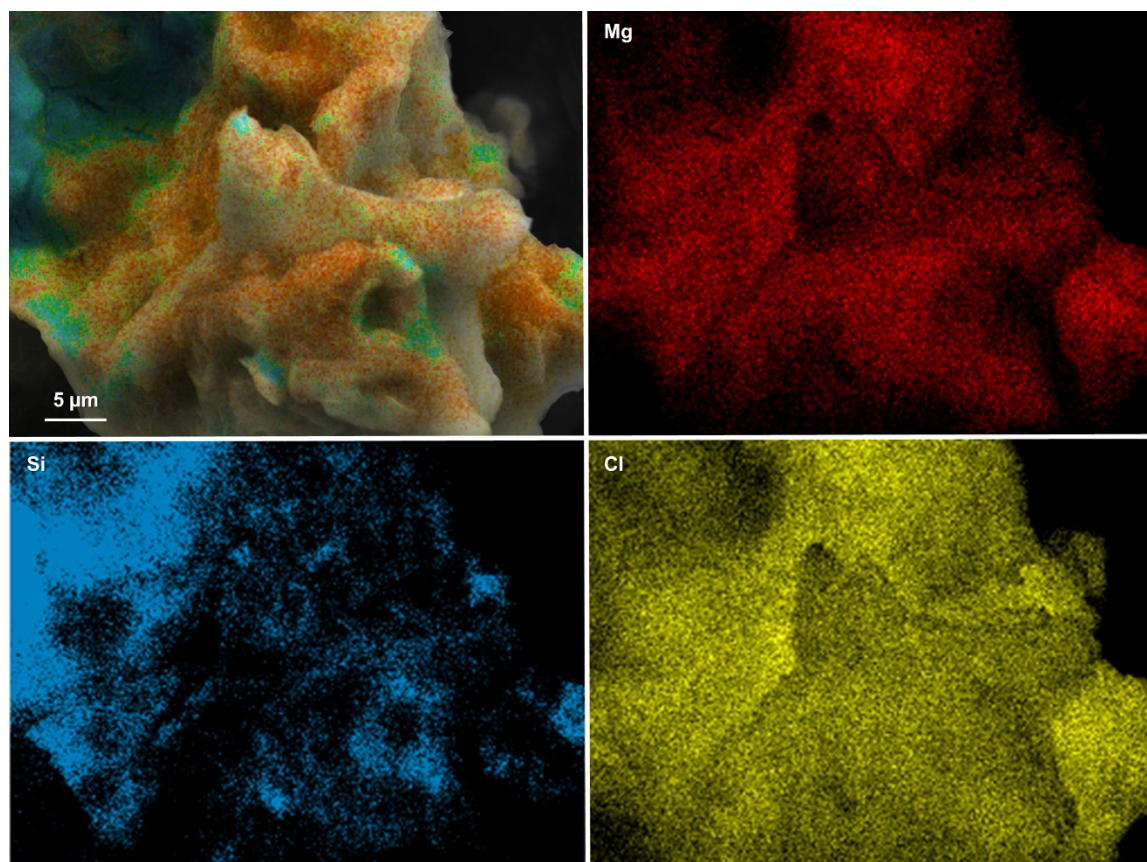
Bright field TEM images were acquired using a JEOL 1400+ (JEOL, Tokyo, Japan) microscope operating at an acceleration voltage of 120 kV and equipped with a Smart Orius 1000 camera obtained from GATAN.

**Raman.** Raman spectra were recorded with an Xplora spectrometer (Horiba), equipped with a 532 nm laser. The power of the laser was attenuated to 50% of the maximum power for all experiments. The laser beam was focused on the sample using a microscope with a 50x objective lens.

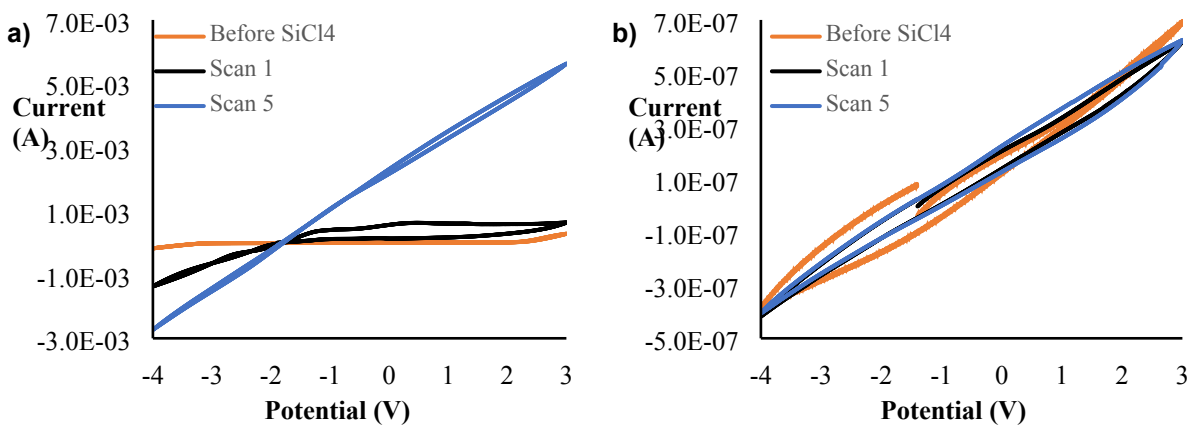
**NMR spectroscopy.** Liquid state 1D  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^{35}\text{Cl}$  NMR experiments were recorded on a Bruker Avance NEO 600 spectrometer equipped with a 5 mm double resonance inverse Z-gradient probe (BBFO  $^1\text{H}$ ,  $^{31}\text{P}$ - $^{109}\text{Ag}$ ). The samples were prepared in THF- $d_8$  at 298K.  $^{29}\text{Si}$  and  $^{35}\text{Cl}$  spectra were acquired with an inverse-gated decoupled methodology and the Bruker aring pulse sequence, respectively. The relaxation delays for  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^{35}\text{Cl}$  have been set to 1 s, 20 s and 0.05 s, respectively. Chemical shifts for  $^1\text{H}$  and  $^{29}\text{Si}$  are relative to TMS.  $^{35}\text{Cl}$  chemical shifts were referenced to a NaCl solution (0.1M in  $\text{D}_2\text{O}$ ).



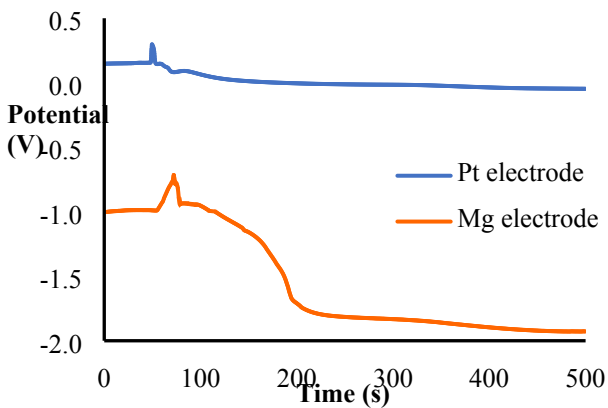
**Figure S1.** Scanning electron microscopy image (top left) of a piece of magnesium at the end of the reaction with elemental analysis showing zones rich in magnesium (red), silicon (blue) and chlorine (yellow).



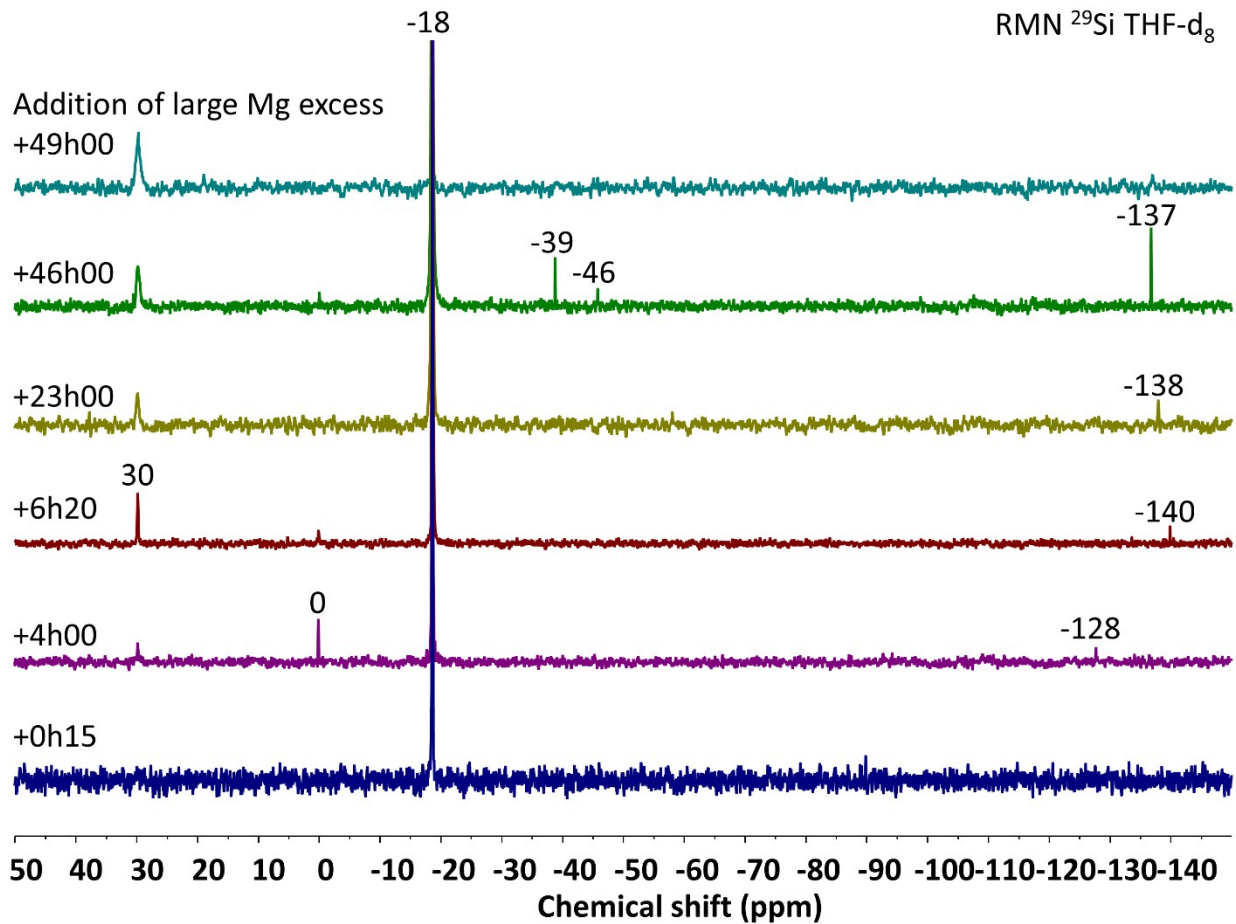
**Figure S2.** A second example of scanning electron microscopy image (top left) of a piece of magnesium at the end of the reaction with elemental analysis showing zones rich in magnesium (red), silicon (blue) and chlorine (yellow).



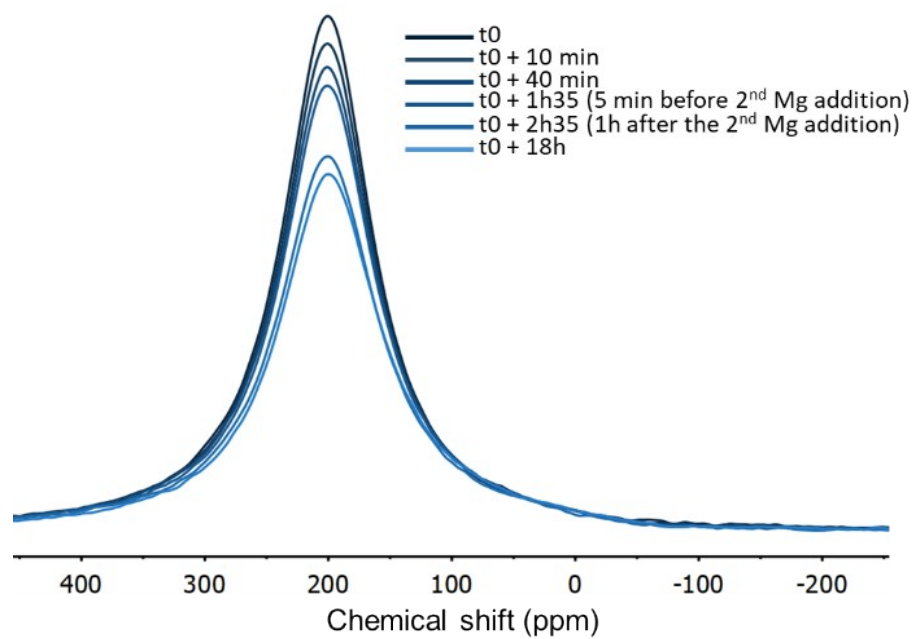
**Figure S3.** Cyclic voltammograms before (orange) and after (1<sup>st</sup> cycle, black and 5<sup>th</sup> cycle, blue) adding SiCl<sub>4</sub> in (a) THF, and (b) dioxane. The cycles after adding SiCl<sub>4</sub> were obtained after 500 s of stabilization, at which point equilibrium had been established.



**Figure S4.** Chronopotentiometric curves of  $\text{SiCl}_4$  in THF, measured using a magnesium (orange curve) and a platinum (blue curve) electrode.



**Figure S5.**  $^{29}\text{Si}$  NMR of reaction carried out with 2 equivalent of Mg and a second addition of large excess of Mg after 49 hours of reaction time.



**Figure S6.**  $^{35}\text{Cl}$  NMR of  $\text{SiCl}_4$  consumption with 2 equivalents of Mg grit in THF d8 as a function of time.