

Seeded Germanium Nanowire Synthesis in Solution

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Supplementary Data

Figure S1 shows the chemical structures of the high boiling solvents examined in this study.

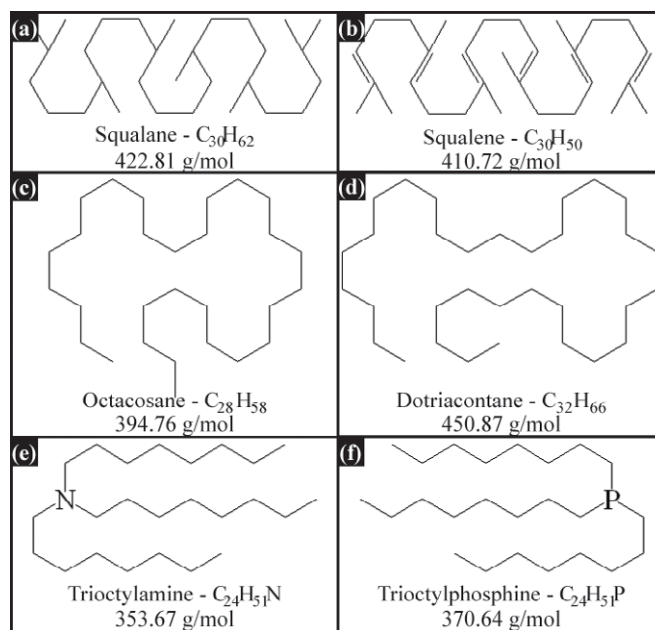


Figure S1: Solvents used in this study: Chemical structure, name, formula and molecular weight for (a) squalane, (b) squalene, (c) octacosane, (d) dotriacontane, (e) trioctylamine and (f) trioctylphosphine. Trioctyl-amine and -phosphine both have coordinating groups, whereas the others are long chain hydrocarbons.

Figure S2 shows SEM images of some of the unwanted reaction byproducts observed with Ge nanowires in some reactions. Figure S3 shows the amorphous Ge particles that are formed in when DPG was heated to 400°C without the addition of Au nanocrystals.

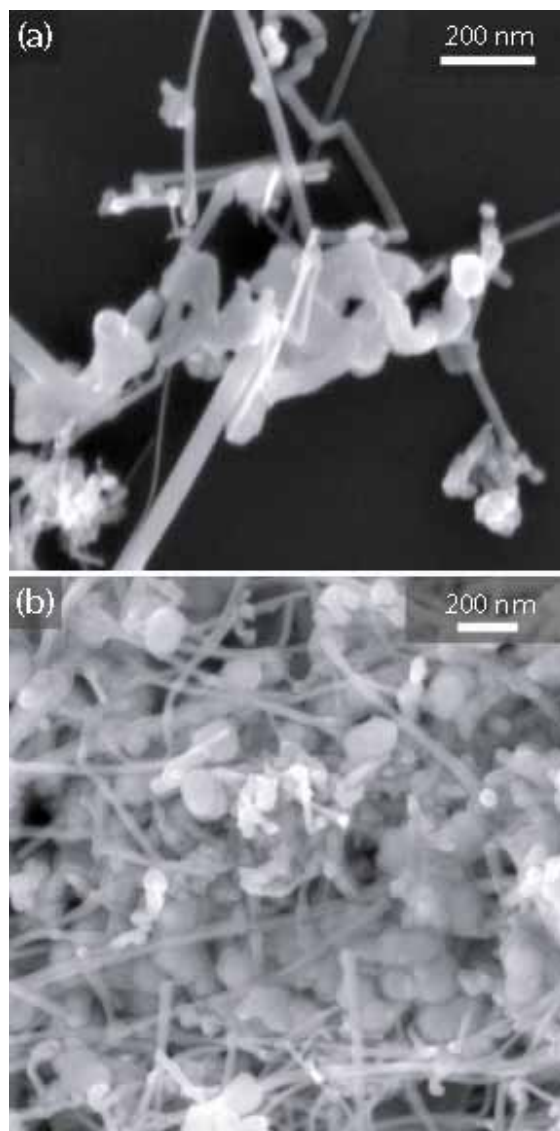


Figure S2: SEM images of reaction byproducts formed during SLS Ge nanowire growth: (a) kinked nanowires and (b) homogeneously nucleated amorphous Ge particles.

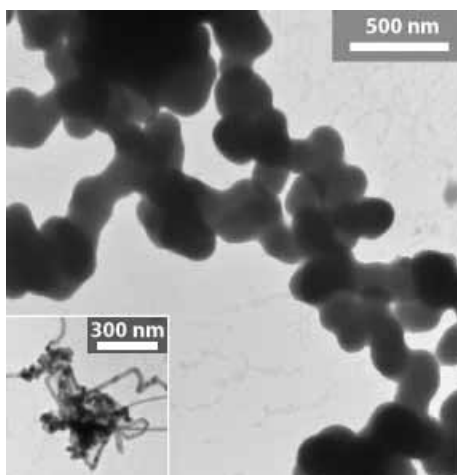


Figure S3: TEM images of the solid reaction product obtained when DPG was heated in squalane at 400°C for 2 hrs in the absence of Au nanocrystals. The product is primarily necked amorphous Ge particles, but there are also a very small number of Ge nanowires that form, such as those in the TEM image in the inset.

Phenylgermane identification by mass spectroscopy.

Positive and negative chemical ionization mass spectroscopy (PCI-MS and NCI-MS) was performed on a Thermo Finnigan TSQ700 mass spectrometer. PCI-MS and NCI-MS of as-received DPG was acquired with 300 mM DPG in toluene solutions. PCI-MS and NCI-MS data of the squalane reaction mixture were obtained by diluting a 500 μ L aliquot drawn from the reaction flask with 5 mL of additional toluene.

Several phenylgermane species have similar molecular weights, *e.g.*, a (phenyl)_(x)germane and a (phenyl)_(x-1)digermane. For example, DPG and MPG₂, differ by less than 2 mass units due to the difference of a phenyl ring (C₆H₅, MW = 77.11 g/mol) and a germane radical (GeH₃, MW = 75.67). Their nearly equivalent molecular weights make it difficult to distinguish them in the MS data. The same similarities in molecular weights exist for phenylated trigermane compounds as well. These similarities do not exist for all species,

however, and the data indicates conclusively the presence of phenyldigermanes, for example through the peaks observed at mass to charge ratios of 455 (QPG₂) and 530 (PPG₂ – not shown). The existence of trigermanes, however, could not conclusively be determined and due to the stability of the Ge-Ge bond were excluded from the analysis.

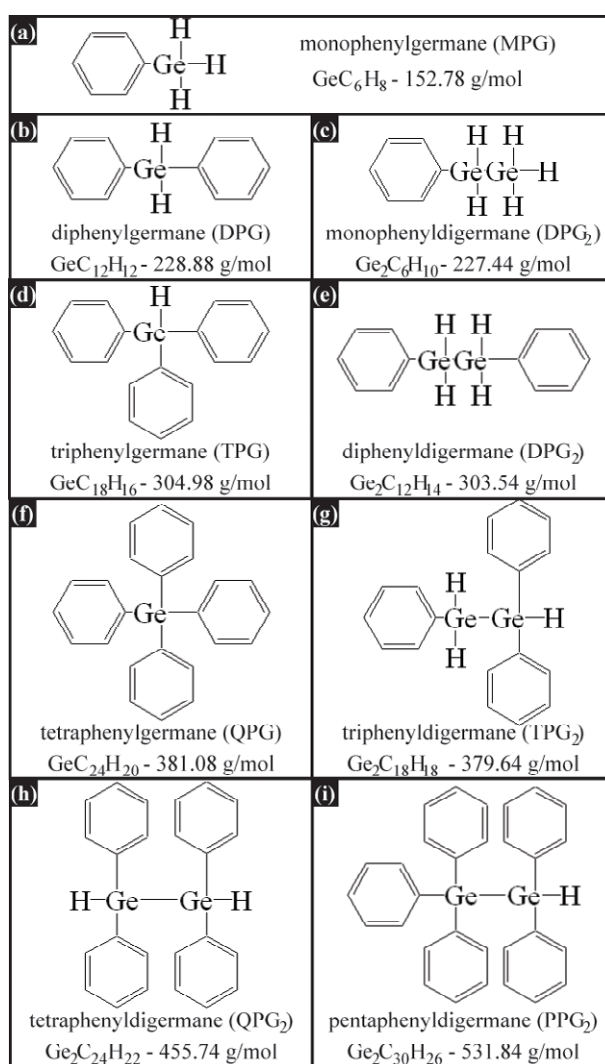


Figure S4: Phenyldigermanes observed by mass spectrometry: (a) monophenylgermane, (b) diphenylgermane, (c) monophenyldigermane, (d) triphenylgermane, (e) diphenyldigermane, (f) tetraphenylgermane, (g) triphenyldigermane, (h) tetraphenyldigermane and (g)

pentaphenyldigermane. Molecules with similar molecular weights are displayed side-by-side for ease of comparison.

Figure S5 shows PCI-MS and NCI-MS scans of DPG as-received from the supplier and aliquots taken from a DPG decomposition reaction in squalane at 380°C (without Au nanocrystals). MS showed that in addition to DPG, other phenylgermane compounds were present in the as-received compound, including monophenylgermane (MPG), triphenylgermane (TPG), tetraphenylgermane (QPG), tetraphenyldigermane (QPG₂) and pentaphenyldigermane (PPG₂) (peaked at a mass/charge ratio of 530, not shown). When DPG was heated in squalane at 380°C, heavier phenylgermanes increased in relative concentration and DPG disappeared after about 10 minutes of heating. TPG also disappeared from the reaction mixture after ~10 minutes. This MS data shows that DPG decomposes under these conditions by phenyl redistribution.

Redistribution leads to tetraphenylgermane as a thermally stable, reaction byproduct (which is insoluble in the solvent and therefore does not appear in the MS data). The MS data also revealed that dimeric species like tetraphenyldigermane end up as relatively stable reaction byproducts. (It is possible that some Ge oligomers form in the ionizer during analysis as well). These dimeric species are not desirable because they lead to lower DPG conversions to Ge nanowires.

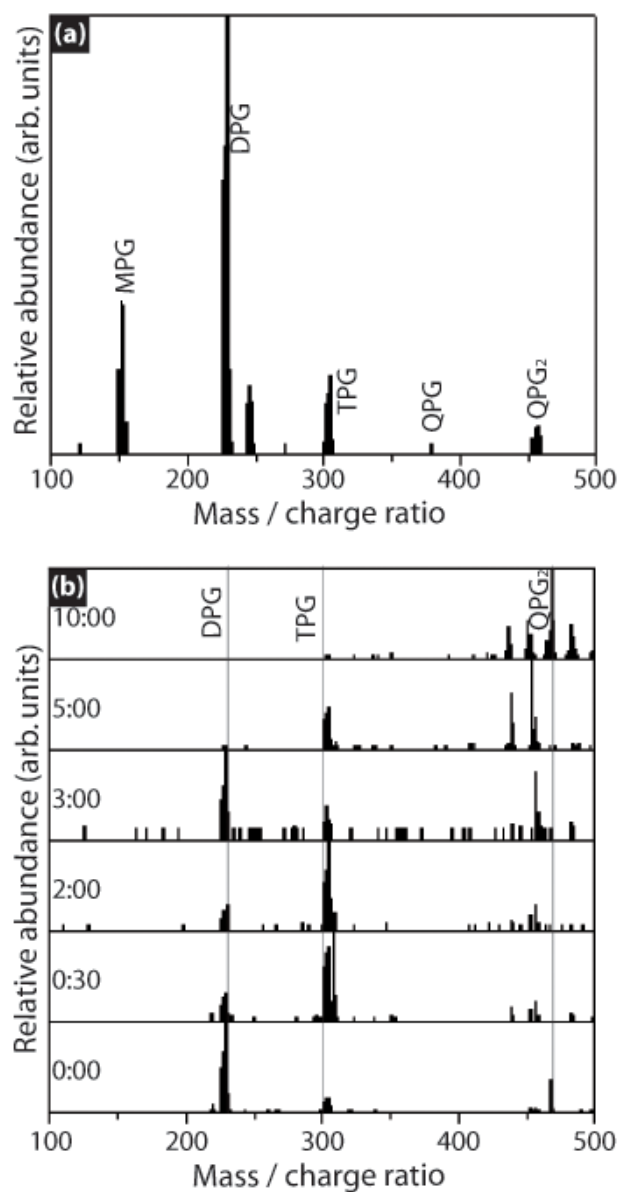


Figure S5: (a) PCI-MS scans of (a) DPG as received from Gelest. (b) NCI-MS scans of aliquots taken from a DPG decomposition reaction in squalane at 380°C without Au nanocrystals. The reaction times are noted in units of minutes next to each spectrum. Peaks are labeled that correspond to diphenylgermane (DPG), triphenylgermane (TPG) and tetraphenyldigermene (QPG₂).