Size Controlled Growth of Germanium Nanorods and Nanowires by Solution Pyrolysis Directly on a Substrate

Supporting Information

Experimental

Substrate preparation and post synthetic treatment.

Cu foil was purchased from Goodfellows with a 0.25 mm thickness and 99.9 % purity. The Cu was cleaned with 0.1 M nitric acid and rinsed repeatedly with deionized water and then dried before introduction into the reactor setup. After reaction, the NW covered substrates were removed from the glovebox and dried under a N_2 line prior to characterization.

Chemicals used

All chemicals were used as received unless otherwise stated. The high boiling point solvent squalane (99%) was received from Sigma-Aldrich. Diphenylgermane (DPG, 97%) and triphenylgermane (TPG, >95%) supplied by Gelest, all of which were stored and dispensed from a nitrogen filled glove box.

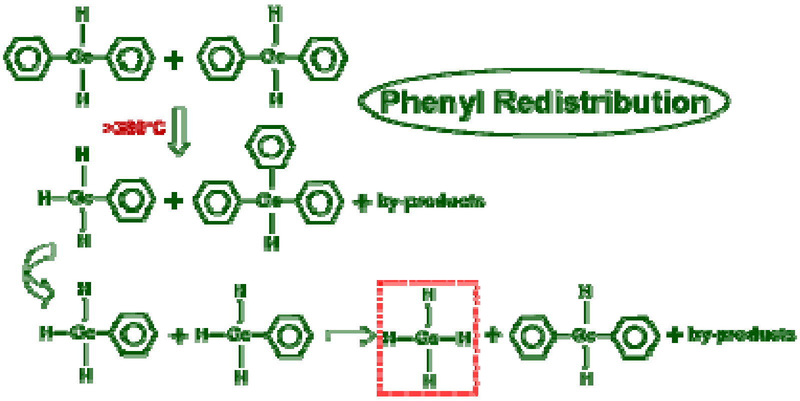
Reaction setup

Reactions were carried out in an Ar filled glovebox using an Electronic Microsystems Ltd. hotplate with a maximum temperature of 405 °C. Typically the (100) Si substrates (with a native oxide covering) for reaction were placed on the hotplate and the temperature was allowed to equilibrate for 10 minutes prior to reaction. The Cu 'confiner' was placed on to the Si substrate just before reaction. The appropriate volume and concentration of the precursor and HBS mixture was then dropcast on to the substrate. The HBS was allowed to evaporate thus terminating the reaction and the substrate was removed from the hotplate for analysis.

By weighing a number of substrates after the reaction, it was found that undiluted DPG gave approximately 25-30% conversion to Ge NWs. The highest reported conversion to date of DPG to Ge NWs was 52.8 % and was conducted within the solution phase of squalane in a closed system.[1] The losses here can be attributed to some vaporization of the DPG and Cu_3Ge seed formation on the bulk Cu foil. Nevertheless, the reaction scheme employed here was sufficient to allow the formation of high density NWs directly on the Si substrate.

Precursor Decomposition Route

The DPG precursor decomposes along previously reported pathways[1] as illustrated below.



Role of the solvent:

Squalane was chosen as solvent as its boiling point closely matched the reaction temperatures investigated. This allowed the amount of Ge monomer being supplied to the evolving Ge nanostructures to be accurately controlled. The majority of other well known HBS either have a lower boiling point (i.e. squalene,oleylamine) which would have hampered precursor decomposition or are solid at room temperature (i.e hexatriacontane) which would not have been compatible with the dropcast method employed.

Analysis

SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. For TEM analysis, the NWs were removed from the substrates through the use of a sonic bath. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. EDX analysis of the NWs was conducted on Au TEM grids. XRD analysis was conducted using a PANalytical X'Pert PRO MRD instrument with a Cu-K_{α} radiation source (λ= 1.5418 Å) and an X'celerator detector.

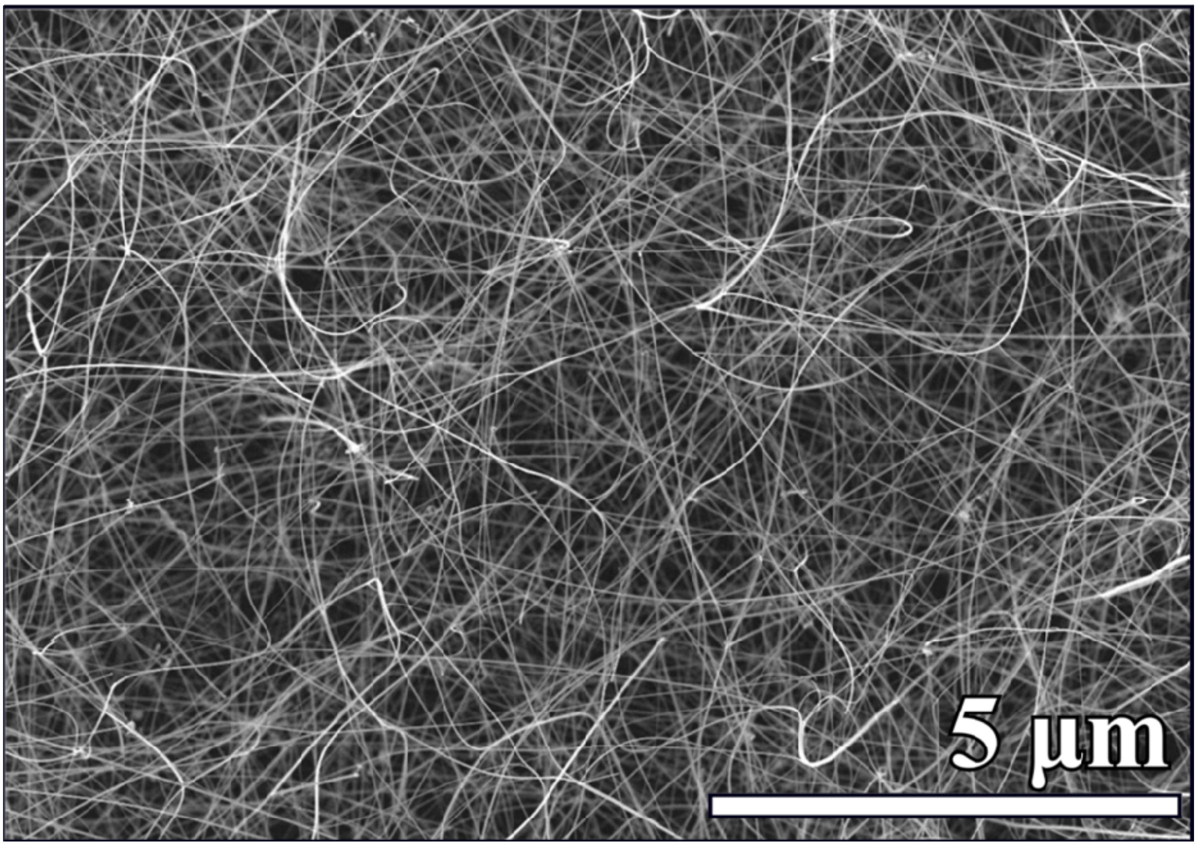


Fig. S1: SEM image showing high aspect ratio Cu_3Ge seeded Ge NWs, using DPG without dilution, which are >10 microns in length.

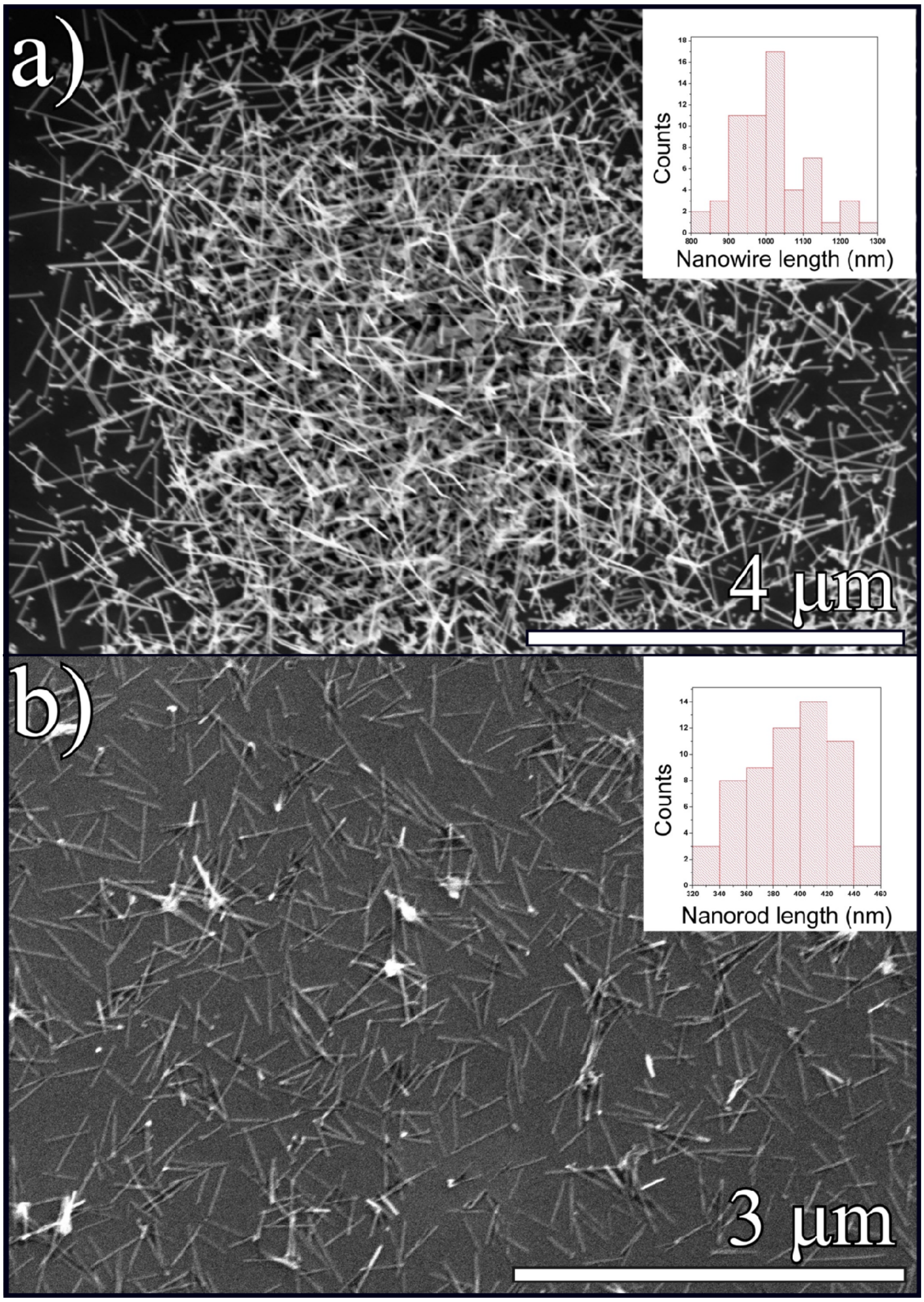


Fig. S2: SEM images of 1D Ge nanostructures formed using a) 1:1 DPG in squalane with corresponding length distribution showing a mean of 1016 ± 97 nm (inset), b) 1:4 DPG in squalane and corresponding length distribution with mean 393 ± 30 nm (inset).

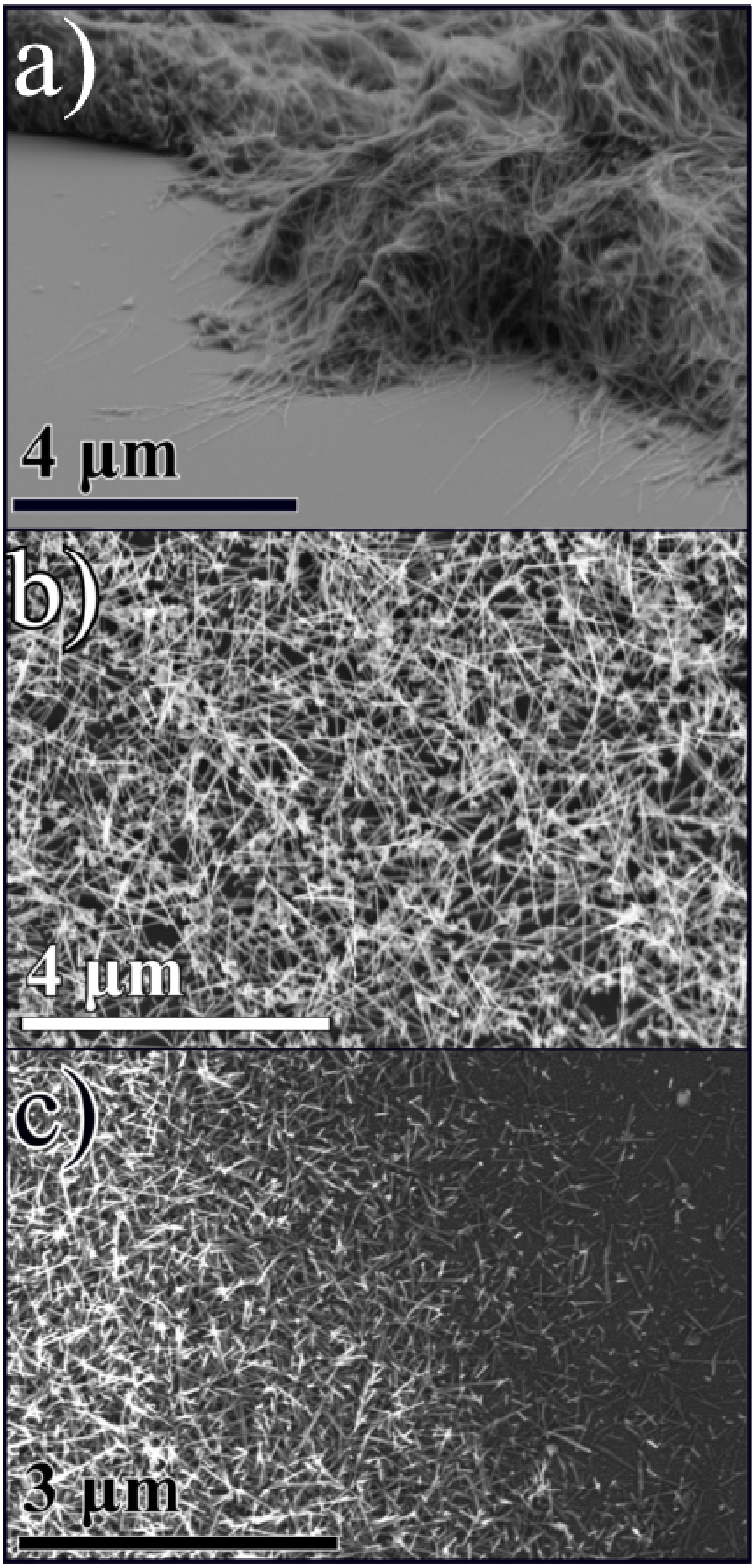


Fig. S3: SEM images showing high density regions of NWs/NRs. a) A tilted view of high aspect ratio NWs using DPG as received. b) 1D structures obtained using 1:1 DPG in squalane. c) Shorter aspect ratio NRs using 1:4 DPG in squalane.

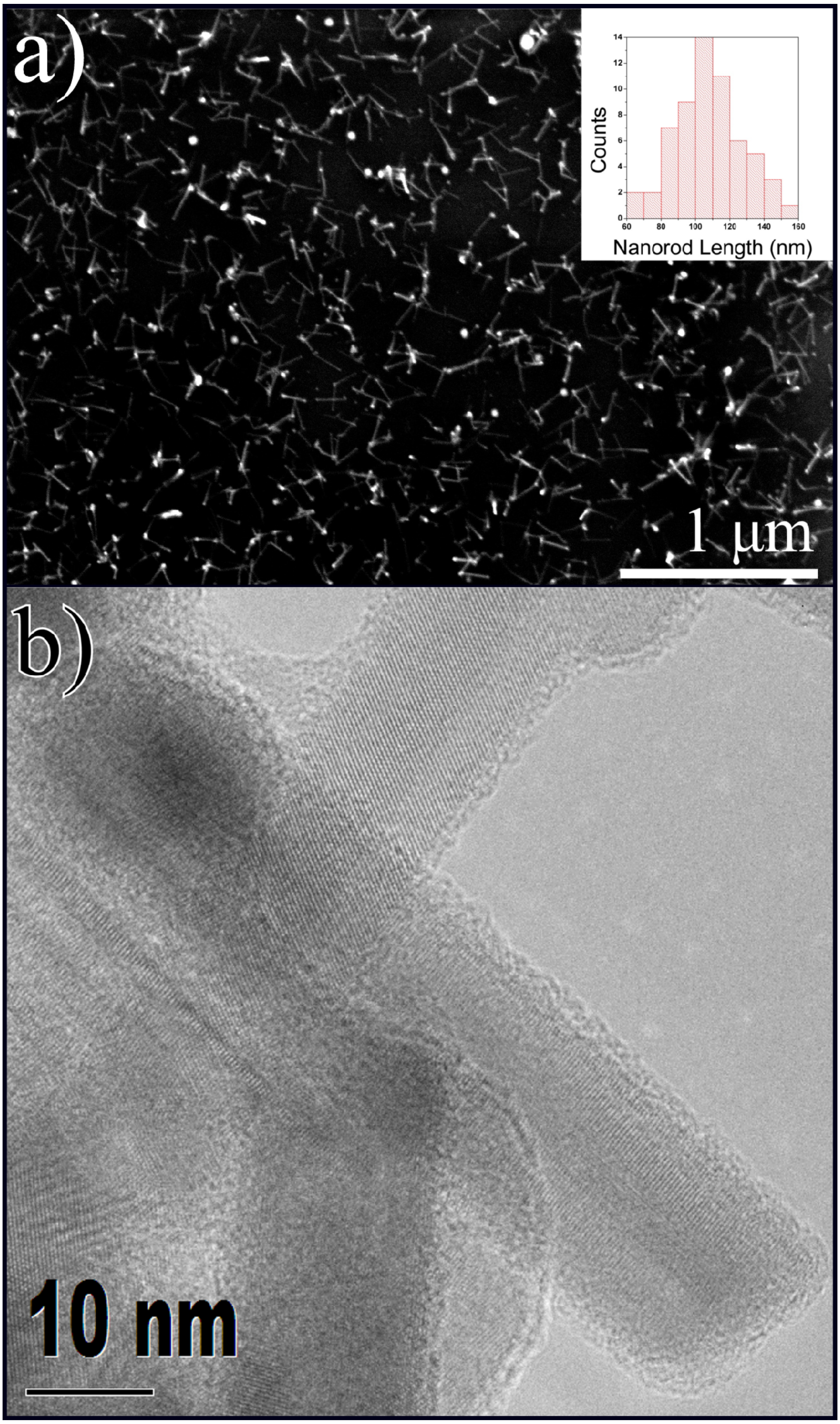


Fig. S4: Additional images showing low aspect ratio NRs achieved using TPG as a Ge source. a) Low resolution SEM image of TPG formed NRs and corresponding length distribution with mean 108 ± 20 nm. b) TEM image of individual NR.

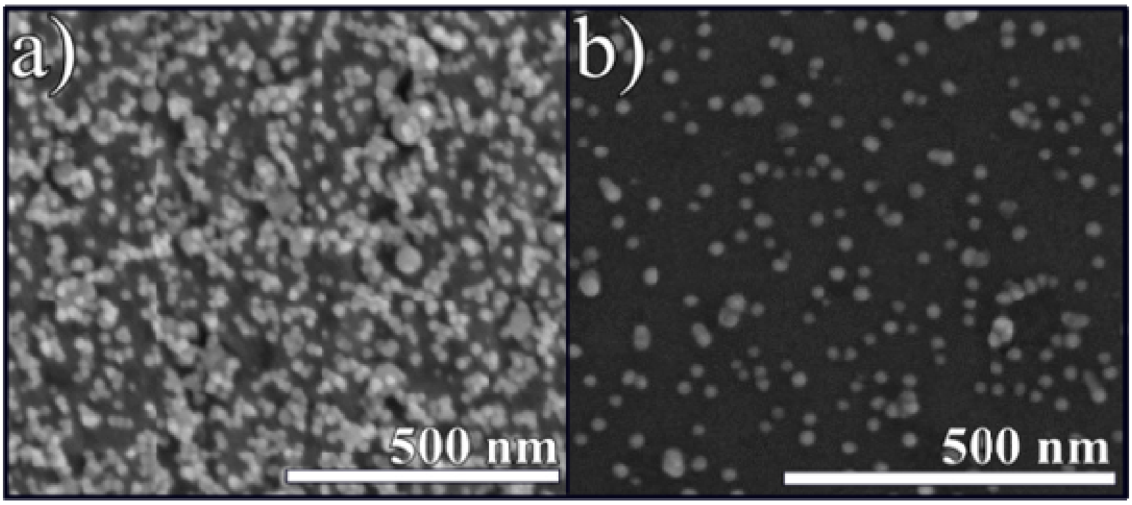


Fig. S5: a) Cu_3Ge nanoparticles formed directly on the unrolled Cu foil confiner. b) Cu_3Ge seeds transferred onto the Si substrate from Cu foil by the solvent migration at reaction temperature.

References:

(1) Chockla, A. M.; Korgel, B. A. *J. Mater. Chem.* **2009**, *19*, 996-1001.