



Tough sheets of nanowires produced floating in the gas phase†

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Assembling nanostructured building blocks into network materials unlocks macroscopic properties inaccessible with monolithic solids, notably toughness and tolerance to electrochemical alloying. A method is reported for large-scale, continuous synthesis of silicon nanowires (SiNWs) suspended in the gas phase and their direct assembly into macroscopic sheets. Performing gas-phase growth of SiNWs through floating catalyst chemical vapor deposition using an aerosol of gold nanoparticles eliminates the need for substrates, increasing the growth rate by a factor of 500, reaching $1.4 \mu\text{m s}^{-1}$ and leading to very long SiNWs. The combined high aspect ratio (> 210) and large concentration of SiNWs in the gas-phase ($1.5 \times 10^7 \text{ cm}^{-3}$) enable the formation of macroscopic solids solely composed of percolated SiNWs, such as free-standing sheets and continuous metre-long SiNW tapes. Sheet samples of small diameter SiNWs ($< 25 \text{ nm}$) combine extraordinary flexibility in bending, tensile ductility around 3%, and over 50-fold higher toughness than Si-based anodes (fracture energy $0.18 \pm 0.1 \text{ J g}^{-1}$). This synthesis and assembly process should be applicable to virtually any one-dimensional inorganic nanomaterial producible by thermochemical methods.

New concepts

We present a new universal route to produce continuous sheets of inorganic nanowires directly assembled through their growth suspended in a gas stream, with textile-like properties and an order-of-magnitude higher toughness than monolithic analogues. Drawing on evidence that chemical vapour deposition can be conducted with catalyst aerosols, the manuscript demonstrates the synthesis of silicon nanowires (SiNWs) floating in the gas phase, at high particle concentration and unprecedented fast growth rate, enabling the direct formation of percolating networks and fabrication of continuous macroscopic solids solely composed of SiNWs. Their network structure of bundled nanowires makes them flexible in bending and tolerant to knotting, similar to fabrics and in stark contrast with monolithic ceramics. Deformation through network reorganisation and nanowire stress transfer in shear lead to high tensile toughness, with exceptionally high fracture energy compared to regular Si materials, and similar to sheets of high-performance nanocarbons or boron nitride nanotubes. The synthesis method should be applicable to virtually any one-dimensional inorganic nanomaterial producible by thermochemical methods. Moreover, controlling percolation through aspect ratio and concentration in the gas phase gives access to novel network materials ranging from transparent conductors to dense fibres using the same process; with an inherent toughness attractive for mechanically augmented devices.

1 Introduction

One-dimensional (1D) inorganic nanostructures are fascinating objects that combine quantized optoelectronic properties, enormous surface-to-volume ratio and often an extremely high degree

of crystallinity. As an archetypal example, silicon nanowires (SiNWs) of small diameter show visible photoluminescence,¹ high photocatalytic activity,² and tolerance to large expansions under electrochemical conversion reactions,³ all distinct from the properties of bulk silicon. Exploiting the properties of 1D nanostructures requires integrating a large number of them into macroscopic ensembles. 1D inorganic nanostructures can be assembled into a range of architectures,⁴ but most often bound to a rigid supporting surface, reminiscent of a substrate-growth process or because the macroscopic ensemble lacks mechanical integrity. Some exceptions include growth of ultra-light silicon carbide aerogels using sacrificial templates,⁵ plasma-assisted synthesis of boron nitride nanotube (BNNT) felt,⁶ and spinning of fibres of carbon nanotubes (CNTs).^{7–10} In the latter case, controlled growth of long carbon nanotubes and their direct assembly from the gas phase into aligned fibres⁷ has led to mechanical

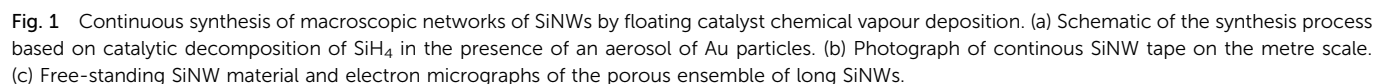
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We have found a wide window of reaction conditions leading to the successful growth of SiNWs, but optimum sample quality in terms of crystallinity, reduced content of self-nucleated Si nanoparticles and low tapering is currently obtained by conducting the reaction at 650 °C, using silane at a concentration of 1.0% in a mixture of N₂ and H₂ as carrier gases. A typical sample produced under these conditions has over 95 vol% of SiNW, with around 1 vol% Au residual catalyst. The SiNWs are long, straight and mono-crystalline (diamond structure), with their

We performed the synthesis of SiNWs through chemical vapour deposition of silane (SiH_4) using an aerosol of Au nanoparticles to enable SiNW growth unsupported and suspended in the



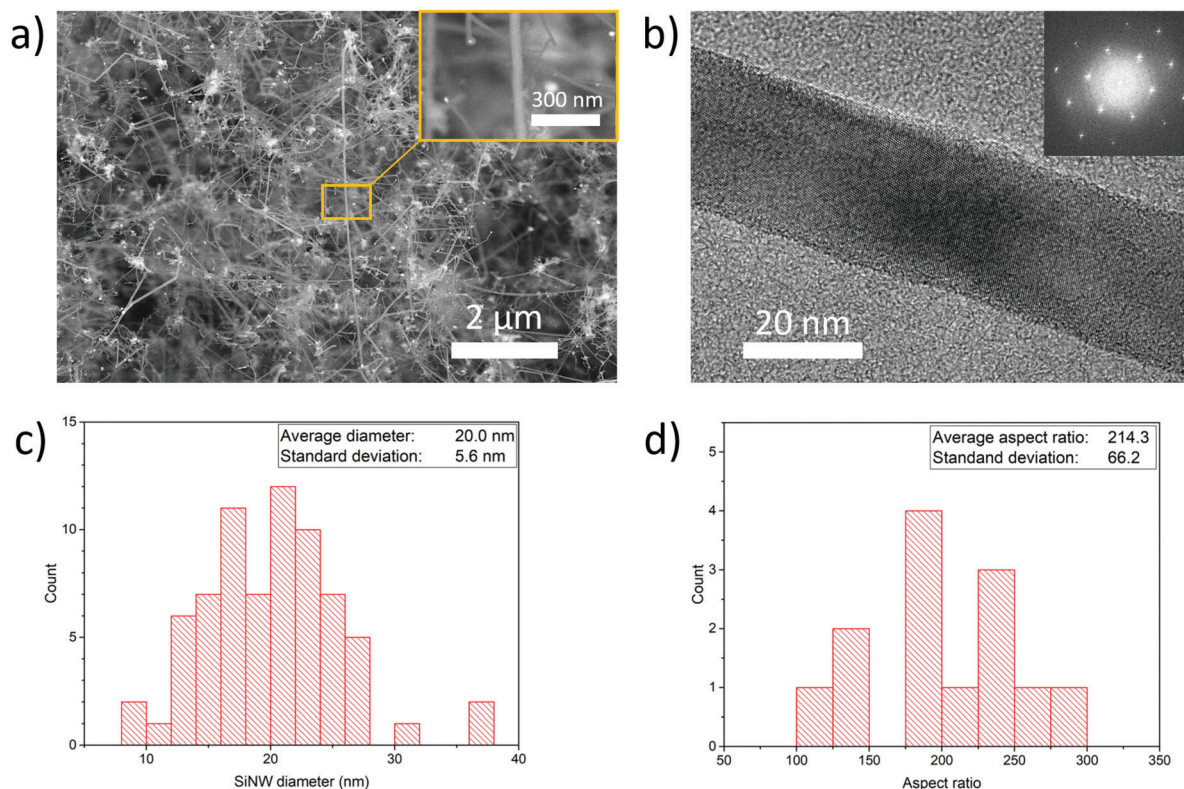


Fig. 2 Size distribution of SiNWs produced in the gas-phase. (a) Electron micrograph of a network of long SiNWs. (b) HRTEM and FFT inset of monocrystalline SiNWs with the growth direction $\langle 110 \rangle$. (c) Diameter and (d) aspect ratio distributions of SiNWs determined from electron micrographs. The product of average diameter and aspect ratio gives an average length of $L = 4.3 \pm 2.3 \mu\text{m}$.

main axis parallel to $\langle 110 \rangle$. Examples of electron micrographs are shown in Fig. 2. We determined the distributions of SiNW diameter and aspect ratio by image analysis of electron micrographs (Fig. 2 and Fig. S3, ESI†). They show an average diameter of $\Phi = 20.0 \pm 5.5 \text{ nm}$ and an aspect ratio of $s = 214.3 \pm 63.8$. There is no observed correlation between nanowire aspect ratio and diameter; it then follows that thicker nanowires tend to be longer (reaching up to $13 \mu\text{m}$) (Fig. S4, ESI†). This suggests that the availability of SiH_4 is not the reaction rate-limiting step and that growth rate depends on the catalyst particle size. To avoid overestimating the length in case electron micrograph analysis is biased towards thicker SiNWs, the average length can be calculated from the product of average diameter and average aspect ratio, which results in $L = 4.3 \pm 2.3 \mu\text{m}$.

A key aspect of the reaction enabling the formation of macroscopic networks of SiNWs lies in the simultaneous achievement of a very fast growth rate and high throughput. For a typical residence time of 8 s, a high estimate calculated from gas velocity through the reactor hot zone, the average growth rate can reach 1400 nm s^{-1} , which is orders of magnitude higher than conventional gold-catalysed substrate growth of SiNWs, typically at around $2\text{--}15 \text{ nm s}^{-1}$ (Fig. S1, ESI†). Similar enhancements in growth rate compared to substrate-based processes have been observed in CNTs⁷ and GaAs NWs¹⁴ grown by FCCVD, and thus seem to be a generic feature of this

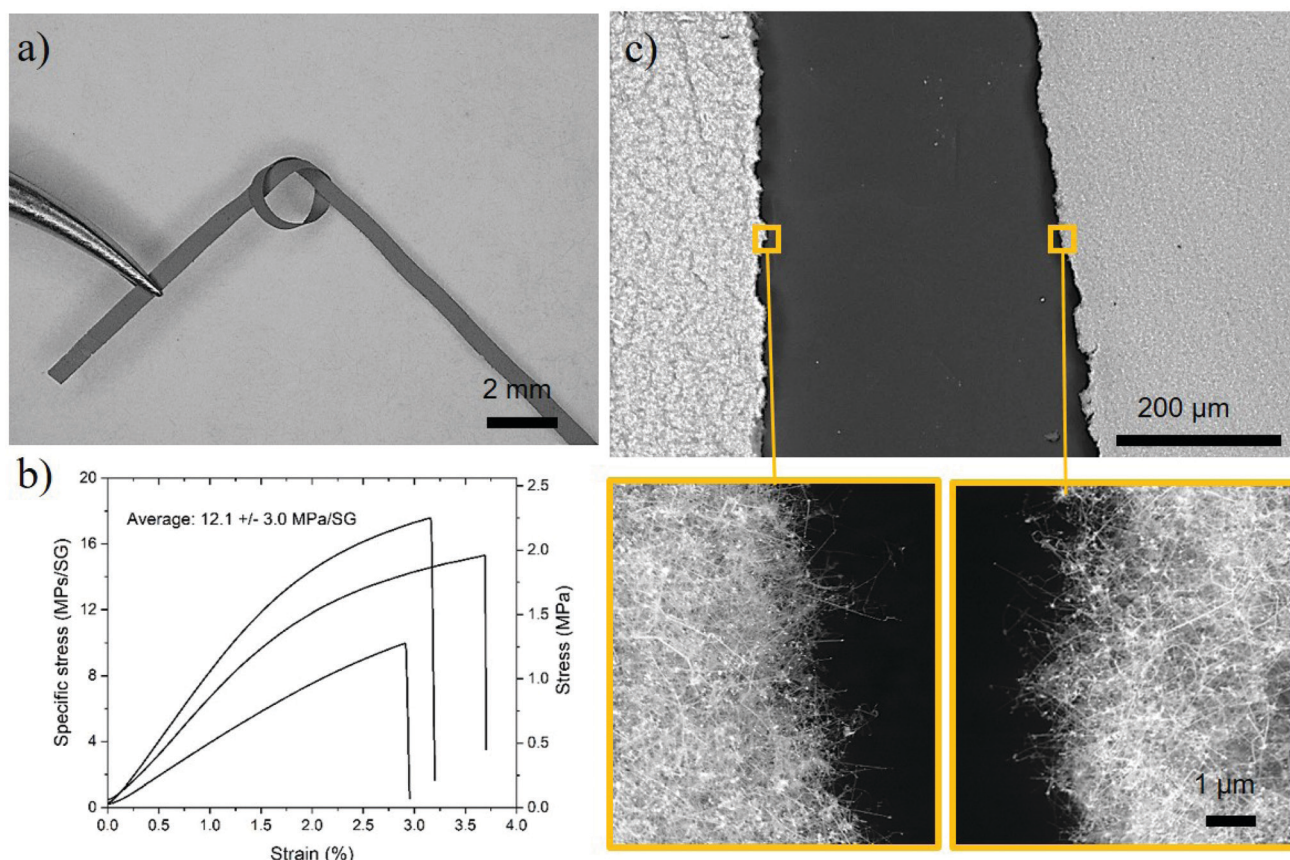
synthesis mode. We attribute them to faster kinetics for precursor transport in floating catalyst conditions resulting from a much larger separation between NWs, which avoids reactant depletion zones, and the fact that both the precursors and the catalyst can diffuse simultaneously. But very importantly, the growth of long, highly crystalline SiNWs reported here is achieved at high 1D nanoparticle concentration in the reactor. Based on throughput determined from direct measurement of sheet sample mass, we estimate a typical nanowire number concentration of $1.5 \times 10^7 \text{ cm}^{-3}$ in the gas phase.

The combined high aspect ratio and high concentration in the reactor favour the aggregation of SiNWs through the formation of entanglements and contact between SiNWs, thus enabling collection into mechanically robust macroscopic ensembles. A useful process descriptor can be derived from the general theory of particle networks: a continuous (percolating) particle network forms above a critical volume concentration (v_p), determined by the particle excluded volume and thus related to its aspect ratio (s) as $v_p \approx 0.5/s$.²¹ Drawing from this simple relation, we use the product of aspect ratio and particle volume concentration in the reactor (vs) as a figure of merit to describe the probability for 1D objects produced in the gas-phase to form continuous networks. Expressed in terms of particle diameter (Φ), length (L) and number concentration (n) it leads to $vs = 0.25\pi\Phi nL^2$. This simple “aerogelation parameter” captures, for example, the importance of increasing



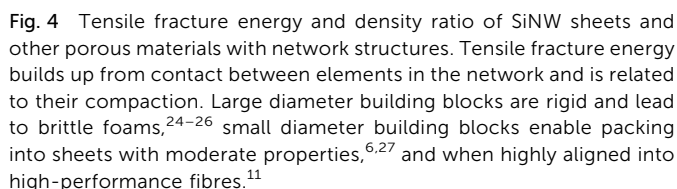
Nanomaterial type	Particle number concentration (# cm ⁻³)	Average aspect ratio	Aerogelation parameter	Throughput (g per day)	Ensemble format
SiNW (this work)	1.5×10^7	214	4.3×10^{-6}	0.2	Sheets
CNT ¹⁶	1.1×10^9	33 000	2.5×10^{-2}	2.33	Fibres
CNT ¹⁷	5×10^5	4000	6.3×10^{-9}	$\approx 4.8 \times 10^{-6}$	Thin film
GaAs ¹⁴	1×10^6	20	4×10^{-8}	≈ 0.024	Thin film
BNNT ^{18,19}	$\approx 7.8 \times 10^8$	31	1.6×10^{-7}	≈ 0.48	Powder
BNNT ²⁰	4.2×10^{10}	5000	5.3×10^{-2}	840	Fibres

Free-standing macroscopic samples can be easily produced by collecting the SiNWs on a filter during gas-phase synthesis, and then manually removing the sample from the filter. They resemble thin fabrics in terms of their overall toughness during handling. As a result of their network structure of building blocks with a diameter much smaller than the sample thickness, as in a regular textile fabric, they have large flexibility in bending. In Fig. 3a, we show a strip of SiNW sheet with an overhand knot, equivalent to withstanding deformations at a



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Finally, we compared different materials with a network structure made up of nanoscale building blocks. Fig. 4 shows a plot of the density-normalized tensile fracture energy against the ratio of sample density over its theoretical bulk density. This representation enables visualisation of the build-up of toughness with increasing compaction of 1D elements in the network. At the low end are materials with ultra-low density such as SiO₂ aerogels composed of a rigid cellular structure of thick nanofibres (>200 nm), which behave as foams that can withstand transverse compaction but have otherwise low tensile toughness, with a fracture energy of around 0.01 J g⁻¹. When of a smaller diameter (<50 nm), 1D nanostructures can compact more easily and form larger interfacial areas of contact, thus forming tougher materials resembling fabrics that are capable of reaching higher tensile fracture energies of 0.1–1 J g⁻¹. The SiNW sheet samples produced by FCCVD in this work are in this category, as well as sheets of BNNTs⁶ or of CNTs,²⁷ often referred to as buckypapers. In these sheets, the 1D nanostructures are predominantly aligned along the main axis but randomly oriented in the plane. Increased density and load-bearing capacity requires a higher packing



Another interesting aspect of the direct conversion of gas precursors to fully integrated solids is the elimination of processing steps requiring handling of the nanomaterials in powder form. As powders, nanomaterials are generally more prone to individualisation, often requiring special safety handling measures.³³ Although in most envisaged applications, nanowires are contained by some form of encapsulation, toughness resulting from strong interparticle forces and entanglements inherently minimises exposure to individualised particles during mechanical manipulation. Nevertheless, a precautionary approach should be applied to SiNWs, even in light of *in vivo* studies indicating early rapid SiNW clearance after being intratracheally instilled in rats³⁴ and promising applications when interfaced with living cells.³⁵

3 Conclusions

In conclusion, we show continuous synthesis of SiNW networks in the gas-phase and direct association into macroscopic solids. Conducting SiNW growth using an aerosol of catalyst nanoparticles increases the growth rate by orders of magnitude compared to substrate-based CVD, attributed to faster kinetics for precursor transport in floating catalyst conditions by avoiding reactant depletion zones and enabling diffusion of both the precursors and catalyst. Critically, the growth of long building blocks is achieved at high particle concentrations in the reactor, thus favouring the formation of percolated networks of SiNWs and association into macroscopic solids. An implication of this work is the demonstration of a generic route for the growth of ultralong 1D inorganic nanostructures in the gas phase and their direct assembly into macroscopic solids. This strategy should be applicable to a large number of 1D nanostructures producible through substrate-based CVD. Controlled organisation into porous solids seems particularly promising for energy storage and conversion applications.

The product of aspect ratio and volumetric concentration (ν_s) is introduced as a descriptor to guide improvements towards the fabrication of high-performance materials made up of 1D nanostructures. Large increases in the aspect ratio may be attainable by temperature-gradient control³⁶ or using alternative Si precursors,³⁷ previously shown to produce SiNWs of 1–20 mm grown on substrates. Related gas-phase synthesis processes for ultrahigh aspect ratio CNTs^{8,16} or large throughput in plasma-based growth of BNNTs,²⁰ suggest promising avenues for the simultaneous improvement of both aspect ratio and volumetric concentration. Increases in SiNW length and reaction conversion will also translate into a large cost drop from the corresponding reduction of Au concentration in the final material. Sheets of SiNWs of small diameter, long SiNWs resemble textiles and with orders of magnitude higher toughness than ceramic materials and Si microparticle electrodes. This augurs high capacity retention as lithium ion battery electrodes, for example.

4 Experimental

Synthesis of SiNWs by FCCVD

The FCCVD reactor consists of a chamber for catalyst nanoparticle generation, a reaction tube and a collection chamber. An aerosol of gold particles was generated *via* resistive heating of a gold source at approximately 1500 °C. A nitrogen gas flow was introduced at the heated gold source with a continuous flow rate of 2 slm. Just before the reactor tube (stainless steel tube, diameter of 10 cm), silane gas and hydrogen gas were added. The typical nitrogen, hydrogen and silane ratio used is 41:58:1. The temperature of the reactor was set to 650 °C. As SiNWs were grown in the reaction tube, the structures were collected down-stream *via* filtration using a conventional porous paper. These synthesis conditions led to an approximate throughput of 0.2 g per day, based on the mass of collected material. Samples of thicker NWs and lower purity could also

be produced at a throughput of 1 g per day. Typical sample weight was around 20 mg.

SiNWs and residual Au nanoparticles were calculated from image analysis of SEM micrographs using brightness, contrast and shape differences to produce areal maps of filtered composition.

SiNW diameter and length determination

SiNW diameter and aspect ratio distributions were obtained by image analysis of scanning electron micrographs at high magnification (Fig. S3, ESI†). Length was calculated from the product of diameter and aspect ratio.

Sample preparation

Preparation of free-standing samples consisted in depositing SiNWs on a vacuum filter at the end of the FCCVD reactor, typically for a collection time of 30 minutes. The material was then mechanically removed from the filter and then densified with isopropanol. This densification procedure was applied to all samples shown in the manuscript except those in Fig. 1 and 2. By weighing the sheets we could easily determine the areal density. Samples for tensile tests were cut out from the sheet using a scalpel.

Tensile tests

Tensile tests were performed with a Textechno Favimat tensile tester, at a strain rate of 10% min⁻¹. Sample dimensions were determined from optical micrographs of each sample. The typical width was 0.6 mm, and the thickness was 25 µm. Volumetric density could then be determined from areal density and thickness. Discarding specimens that broke at the grips, 36 samples were tested in total, 23 at a gauge length of 5 mm, 5 at 2 mm, and 8 at 1 mm. No significant difference in tensile strength was found at smaller gauge lengths. Data were corrected for machine compliance, obtained from tensile tests on commercial poly-aramid fibres. Stress-strain curves in the main manuscript are for 5 mm gauge-length samples. Tensile fracture energy values for the main paper were calculated from the data in Table S1 (ESI†). For SiNWs, data are calculated from the 10 best measurements with clear evidence of a genuine fracture not induced by grips or defects introduced during manipulation. Density ratios are calculated assuming a maximum density corresponding to hexagonal closed packed bundles of solid rods each with the theoretical bulk density of the material.

Conflicts of interest

There are no conflicts to declare.

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