THE RIGHT STUFF

The space elevator's tether could be built soon using lightweight, ultra-strong materials such as single crystal graphene, hexagonal boron nitride or carbon nanotubes

By Adrian Nixon, John Knapman and Dennis Wright | Diagrams courtesy ISEC/Adrian Nixon

A space elevator could be built in the near future with acceptable risk and less funding than some current space programmes, according to a 2003 NASA Innovative Advanced Concepts (NIAC) space elevator feasibility study. One of the most important elements is the space elevator tether, stretching from Earth to well beyond geosynchronous altitude, which must support itself and any devices which climb it. Without the tether there is no elevator. The tether material must be lightweight and very strong, preferably with a tensile strength of at least 100 GPa. The NIAC study concluded that carbon nanotubes (CNTs) could be the tether material of choice. One year later in 2004 graphene was discovered adding a new candidate to the possible tether materials list.

To take full advantage of the material strength the tether needs to be made as a continuous piece of material and it needs to be about 100,000 km long. This means the material must be capable of being manufactured at industrial speeds. For example, at a material manufacturing rate of one metre per second, it would take 3.17 years of continuous production to produce a tether of sufficient length. Manufacturing ultra-high strength material in ultra-long lengths at very high speeds requires industrial mass production on an unprecedented scale. These are daunting numbers but there are processes on the horizon which can make this possible.

One of the strongest materials available for the tether is Aramid, with a tensile strength of 4 GPa. This can be compared to other materials in an Ashby plot. Here, in the accompanying image, straight lines represent specific strength, or tensile strength divided by density. Aramid sits on the red line. A tensile strength of 50 GPa and a density of one is a point on the green line. Almost all the available materials fall below the red line, with combinations of strength and density well below that required for a space elevator.

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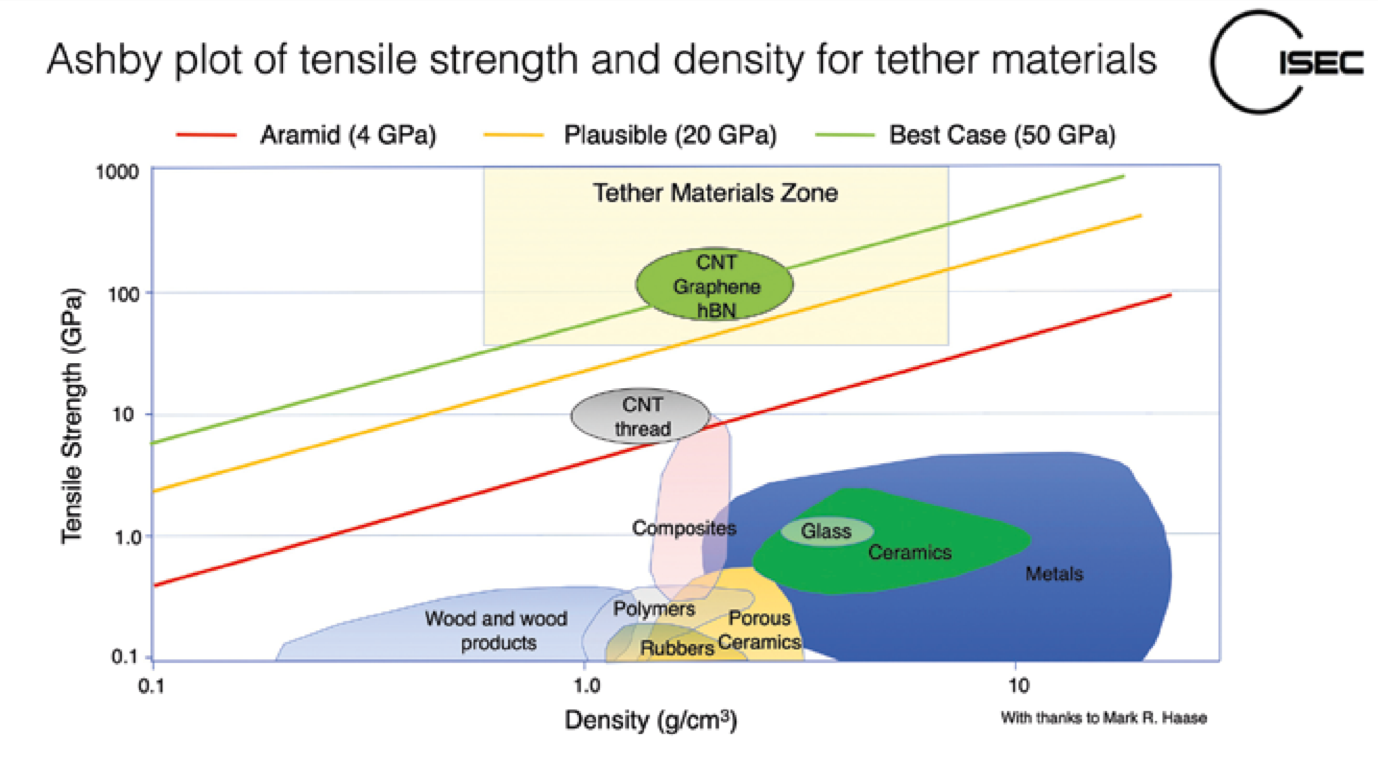
There are, however, three materials which do have the strength to make them viable candidates. They are, the aforementioned CNTs, single crystal graphene (SCG) and hexagonal boron nitride (hBN). Laboratory tests show that CNTs have a range of tensile strengths between a theoretical 200 GPa and an actual 77 GPa. Graphene has a tensile strength of 130 GPa, while hBN has a measured tensile strength of 100 GPa. A unique thing about these materials is that they can be classified not as three-dimensional (3D) materials, but as one-dimensional (1D) or two-dimensional (2D).

Dimensions in this context refers to the number of spatial dimensions in which a molecule can grow while still retaining the same characteristics. For example, carbon nanotubes can grow from either end of the tube, provided it is not capped, and remain the same material. However, if extra carbon atoms were to be added to the sides of the tube this would change the nature of the material. The immense strength of the candidate materials comes from their single crystal nature.

A single crystal, or grain, can be either a 1D or 2D molecule. In many materials the size of the grain may vary from nanometres to millimetres. An uninterrupted repetition of the crystal, also referred to as a unit cell, creates a layer, referred to as a polycrystalline layer. The polycrystalline layer consists of a patchwork of these single crystal unit cells, which can individually be orientated differently to each other. The crystals can be orientated as parallel columns, "columnar," or they can be aligned with approximately equal dimensions in all directions – equiaxed. The size, orientation and whether the crystal grains are equiaxed or not, is the result of mechanisms of nucleation and growth.

Because the single crystals with differing orientations are not lined up, the strength of



polycrystalline materials is always much less than the single crystal variety. Each patch, or domain, that makes up the polycrystalline layer's patchwork is separated from its neighbour by grain boundaries organised by the competing forces of growth rate and suppression of nucleation. Nucleation is the molecules' proto-aggregation that leads to macroscopic crystal growth. This process leads to 2D defects in the structure that become those crystal grain boundaries.

GRAPHENE NUCLEI

The greater the number of graphene nuclei, the smaller the size of the crystal before it encounters an incoming nucleation driven growth front and forms a defective grain boundary. In 2D materials these crystal domains can take the form of hexagons, stars or snowflakes depending on the growth conditions. These features are typical of polycrystalline materials and their presence makes the job of controlling size, shape and eventual functional quality more difficult.

In graphene, grain boundaries are effectively lines of defects which can take the form of carbon rings made from pentagons and heptagons, so-called Stone-Wales defects, which are non-periodic. Defects can also take the form of vacancies where one or more carbon atoms are missing. The ideal is to form a defect-free sheet of a single grain, boundary-free lattice of graphene – known as single crystal graphene, or carbon nanotubes.

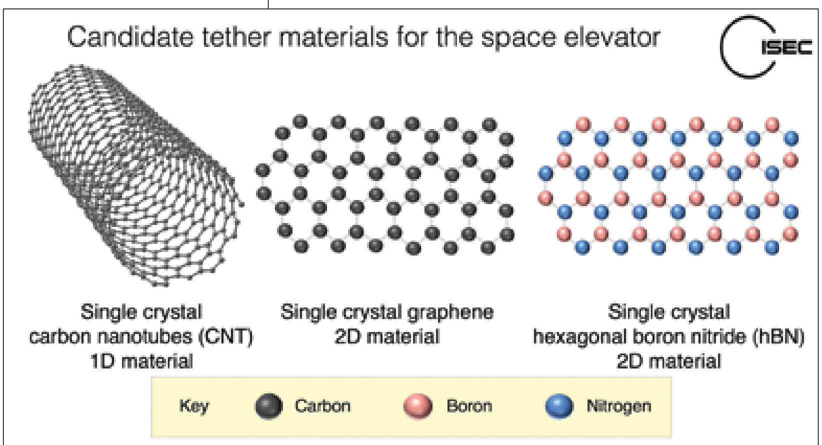
While single crystal graphene is probably one of the required materials for the space elevator tether, it has not yet been produced in significant quantities. However, polycrystalline graphene (PCG) is now being produced at ever-increasing rates and could serve as a useful proxy for SCG when undergoing tests – which must distinguish between the two. One way to do this is by electron microscopy and Raman spectroscopy which can easily identify the grain size and grain boundaries in PCG, and by their absence confirm the presence of SCG.

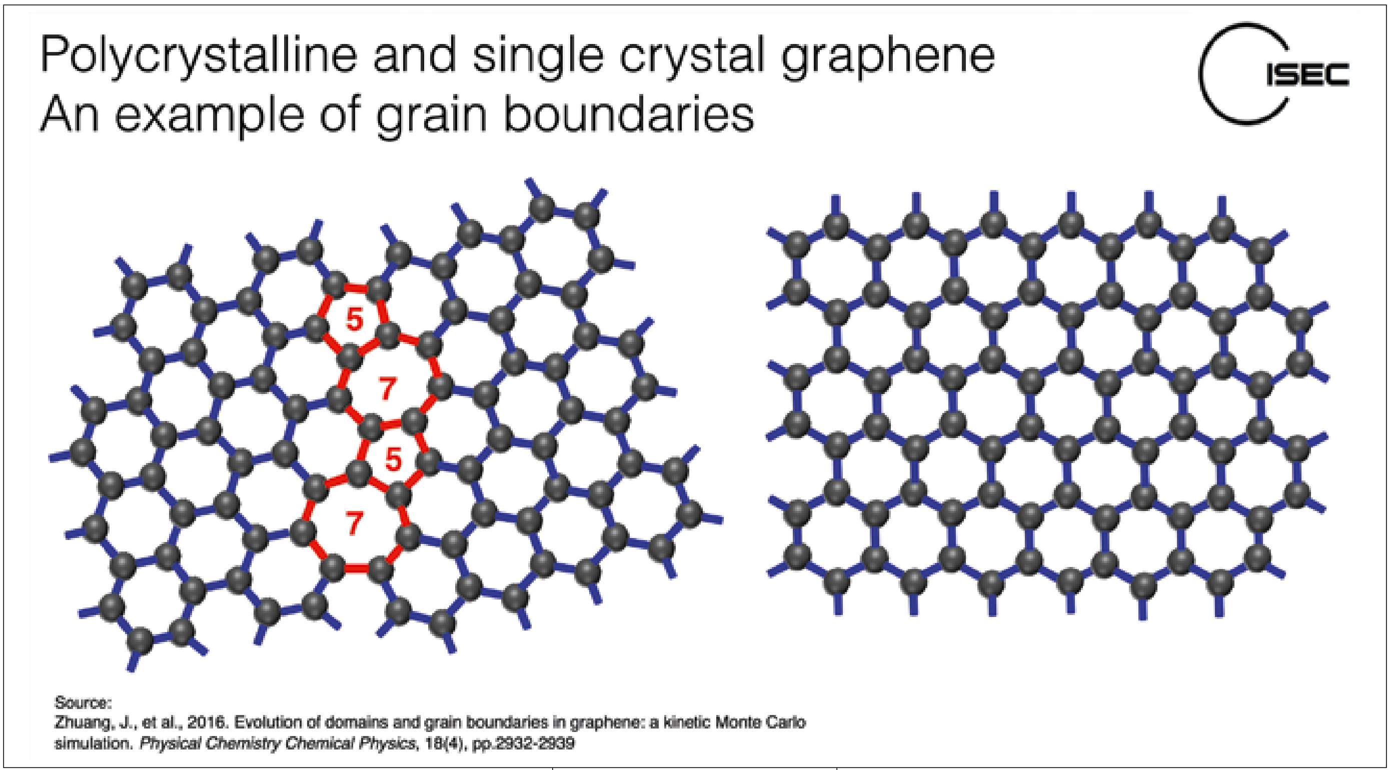
Carbon nanotubes, graphene and hexagonal boron nitride are all made by variants of the chemical vapour deposition (CVD) method. This involves a feedstock gas containing the atoms needed for the final material. In the case of carbon nanotubes and graphene this is usually methane (CH_4). A transition metal catalyst, typically copper or nickel, mediates the formation of the 2D material at elevated temperatures, around 1,000° Celsius. The metal acts as both a catalyst and a substrate enabling the carbon material to form and providing a platform for growth. For the 1D material, a slightly lower temperature of 750° Celsius and a catalyst made from iron, gadolinium and aluminium oxide has been used to grow a carbon nanotube forest using this method.

The longest single molecule carbon nanotube (500 mm) was made in 2013, but since then, no further improvements in length have been reported. The state of the art of carbon nanotube manufacture seems to be to make nanotube forests with a length of 140 mm and an average growth rate of 1.5 microns per second »

FROM ABOVE
An Ashby plot of tensile strength versus density of candidate tether materials.

The crystalline structures of candidate space elevator tether materials are shown here.





CLOCKWISE FROM ABOVE
Examples of grain boundaries in graphene crystal quality.

This shows the steps required for the industrial scale manufacturing of graphene.

The basic concepts of how chemical vapour deposition is used in laboratory-scale manufacturing of graphene and carbon nanotubes is shown here.

« and a growth lifetime of 26 hours. If the growth conditions could be sustained this would mean a production speed of one metre in 186 hours. The carbon nanotubes made by this method were not single crystals and did have defects. The tensile strength of the carbon nanotubes was not measured, but the electrical conductivity improved upon annealing at 2,800° Celsius.

Hexagonal boron nitride is being made in powder form by several manufacturers. The most significant manufacturer of large-area sheet hBN is the California-based company Grolltex – a graphene manufacturer, specialising in CVD graphene and hexagonal boron nitride. The company has developed a batch process that manufactures hBN by a CVD method on metal foil and can transfer the material to other substrates. However, this is restricted to 200 mm diameter wafers for the semiconductor industry. The longest sheet of single crystal graphene manufactured so far is 500 mm by 50 mm, made at Peking University in Beijing in 2017. The largest area of single crystal graphene to date has been reported by researchers from Oak Ridge National Laboratory, Tennessee. They have demonstrated the manufacture of single crystals with an area of 300 mm by 300 mm.

INDUSTRIAL PRODUCTION

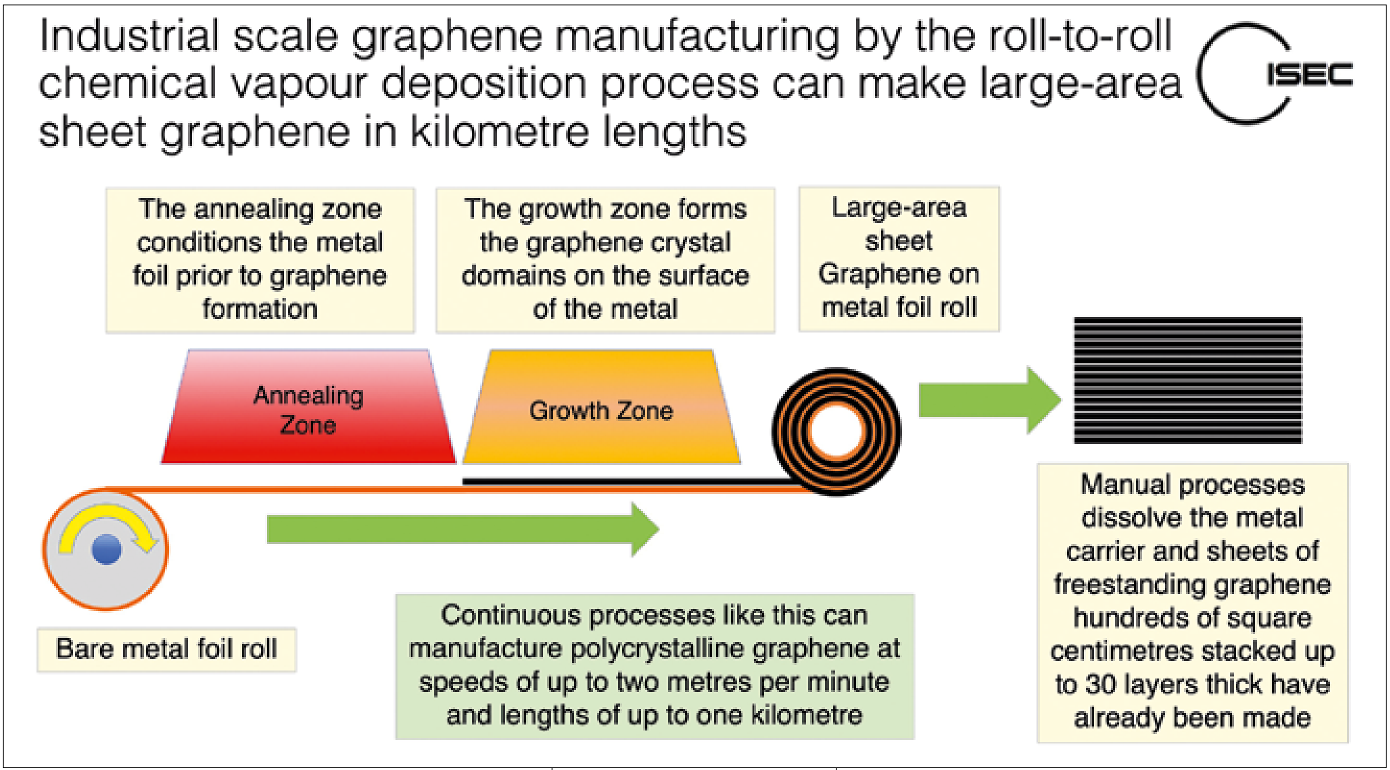
The Luxembourg firm OCSiAl claims to be the world's largest industrial manufacturer of single wall carbon nanotubes. Its carbon nanotube production capacity through its Tuball subsidiary company is stated to be 90 t per year which the company says is more than 97% of the global CNT market. However, it must be noted that the carbon nanotubes it produces are just five microns in length and seem to be used as powdered additives to enhance the performance of other materials.

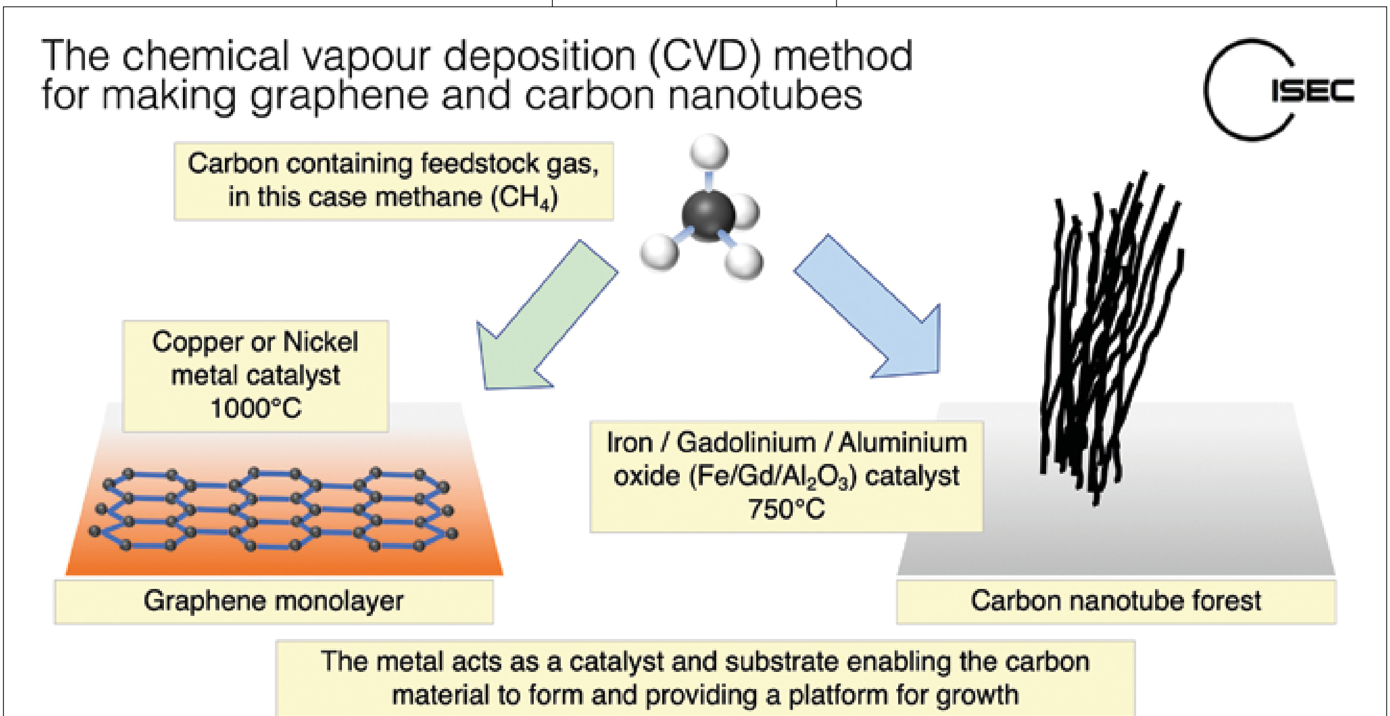
Carbon nanotube manufacturing development appears to have focussed on making very short fibres as powder additives in other materials and existing manufacturing methods to make ultra-long carbon nanotubes appear to have stalled. The state of the art of carbon nanotube manufacture can make at most 0.5 m long samples at slow speeds. While CNTs have been touted as the wonder material, it lags behind its competitor materials for the tether. As does hexagonal boron nitride which is only being manufactured in 200 mm sheets for the electronics industry and for research applications.

Graphene is being manufactured by industrial-scale processes at General Graphene in Knoxville, Tennessee. It has announced that its Gen 3.0 roll-to-roll graphene production line has been commissioned and can make graphene on copper foil at the rate of 100,000 square metres per year. General Graphene has also demonstrated the ability to separate the graphene from the copper foil and create multi-layered graphene samples coming in one, five, 10 and 30 layer thicknesses.

Two companies in South Korea have also created industrial-scale graphene manufacturing plants. The LG Corporation, headquartered in Seoul, has developed a roll-to-roll production method that can make graphene on copper foil at speeds of up to 1 m per minute and lengths of up to 1 km. Charmgraphene in Korea's Suwon Venture Valley is a manufacturer and developer specialising in next-generation new material graphene films and graphene ink. It can produce graphene on copper foil at speeds of two metres per minute and lengths of one kilometre.

Charmgraphene has automated the separation of graphene from the copper foil and its transfer to other substrates. The firm has also demonstrated the ability to separate graphene from the copper foil surface to create free-standing multi-layered graphene. Free-standing means there is no substrate support. The atomic layers of graphene support themselves. A sample of 20 to 30 layers of freestanding graphene can





Source:
Sugime, H., Sato, T., Nakagawa, R., Hayashi, T., Inoue, Y. and Noda, S., 2021. Ultra-long carbon nanotube forest via in situ supplements of iron and aluminum vapor sources. *Carbon*, 172, pp.772-780.

be 110 mm wide by 144 mm in length. While these industrial-scale manufacturing processes can make graphene at square-metre scales, the current state of the art is to manufacture polycrystalline material.

General Graphene is probably manufacturing the largest pieces of single crystal material in square-centimetre domains but the material is not space elevator tether quality at present. However, given that graphene was isolated as a 2D material for the first time in 2004, this represents an astonishing rate of industrial progress. In the past decade much academic and industrial research effort has resulted in the manufacture of graphene as a large area material that can be manufactured at speeds of 2 m per minute and lengths of up to 1 km.

The manufacture of tether-quality material for a space elevator still needs more development, but the trajectory to a high-quality industrial product is clear. It is not unreasonable to think that, as this graphene process continues apace, space elevator tether production could begin in five to 10 years using graphene as its material.