UK-Japan workshop on health, environment and social impacts of nanotechnology

Current status and future development of carbon nantubes as an innovative nanomaterial

M.Endo

Shinshu University, Japan

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2. CCVD process, historical aspect and present status of mass-production
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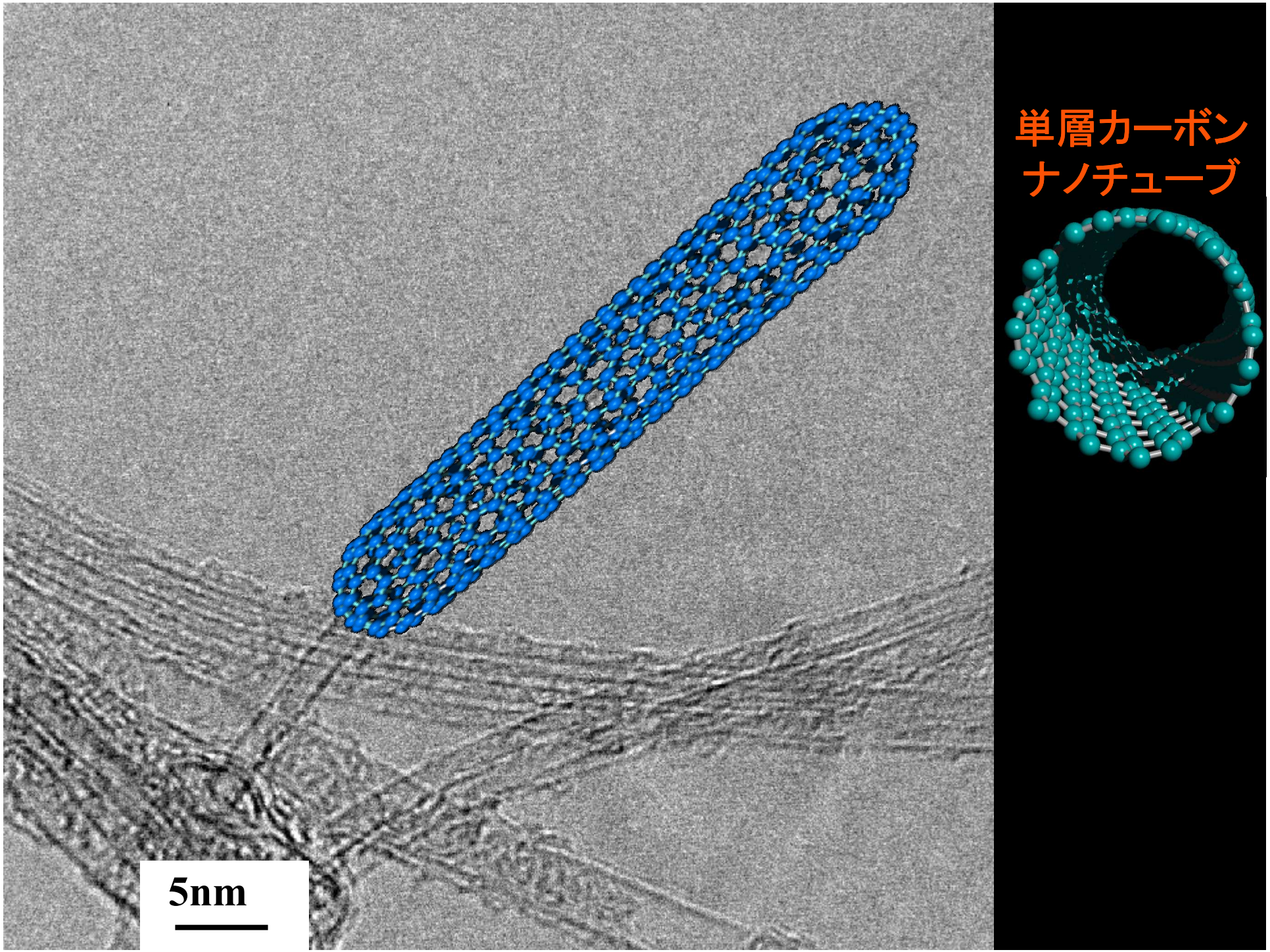
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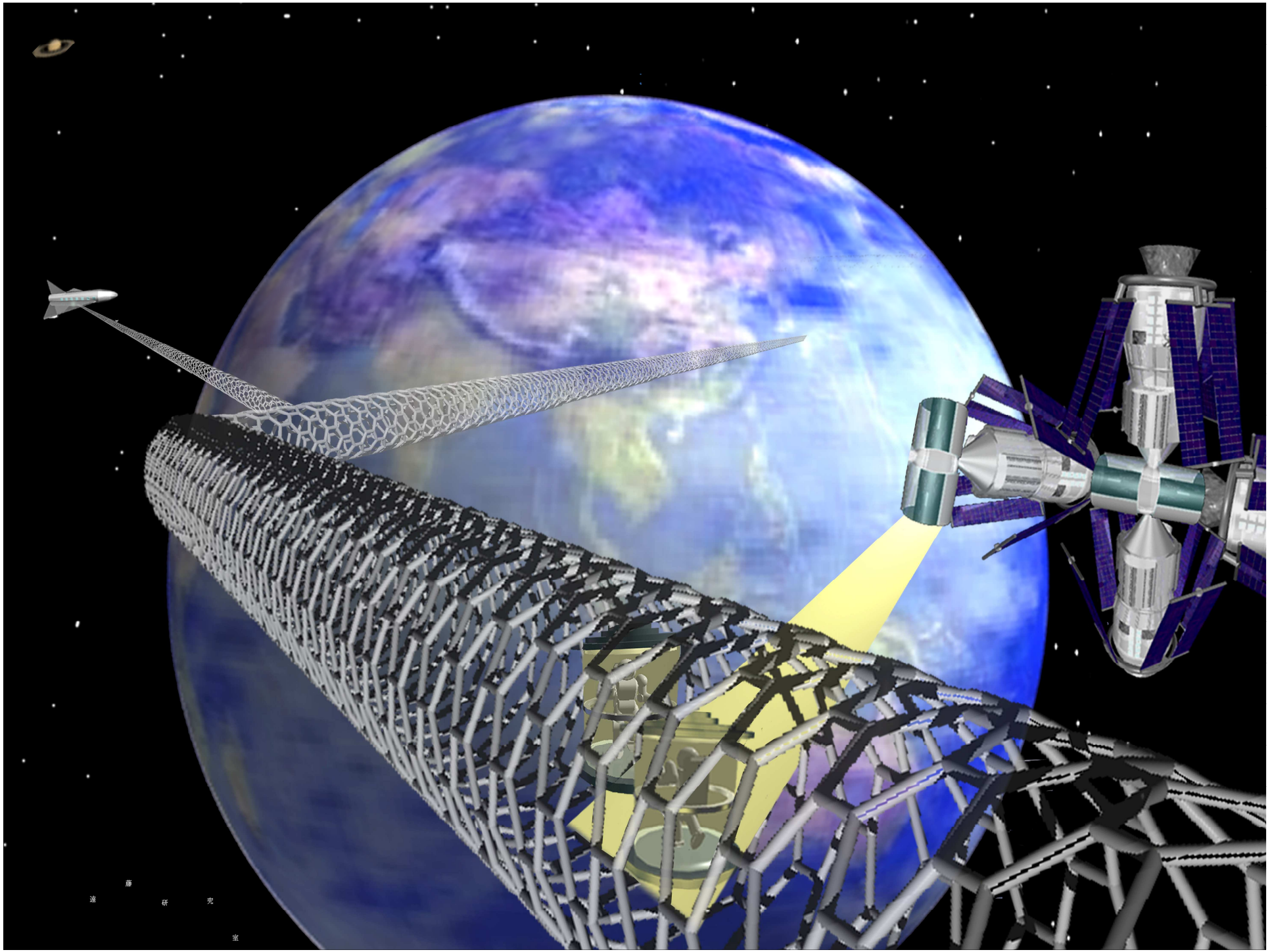
ナノチューブ
5nm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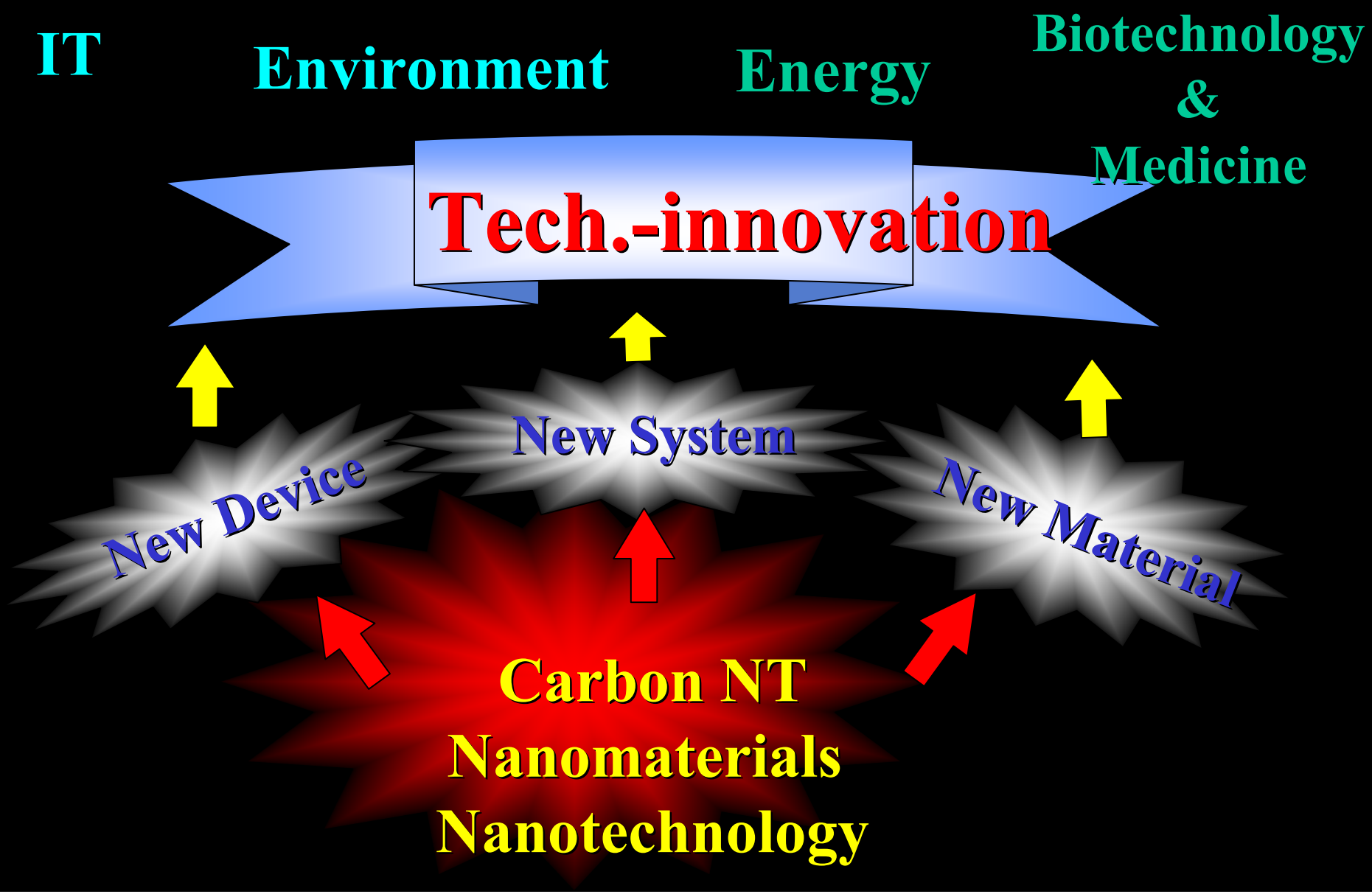
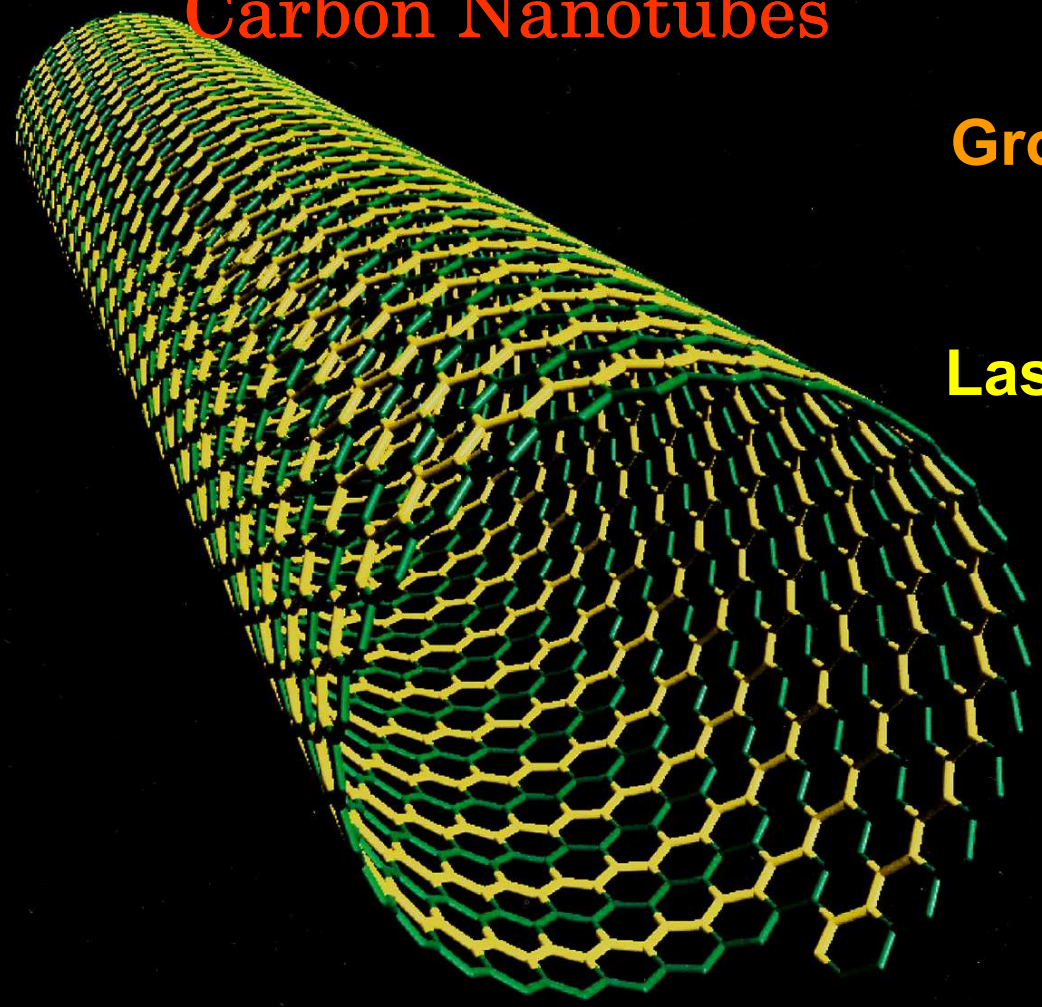
Technical Innovation



Carbon Nanotubes



Growth method

Arc

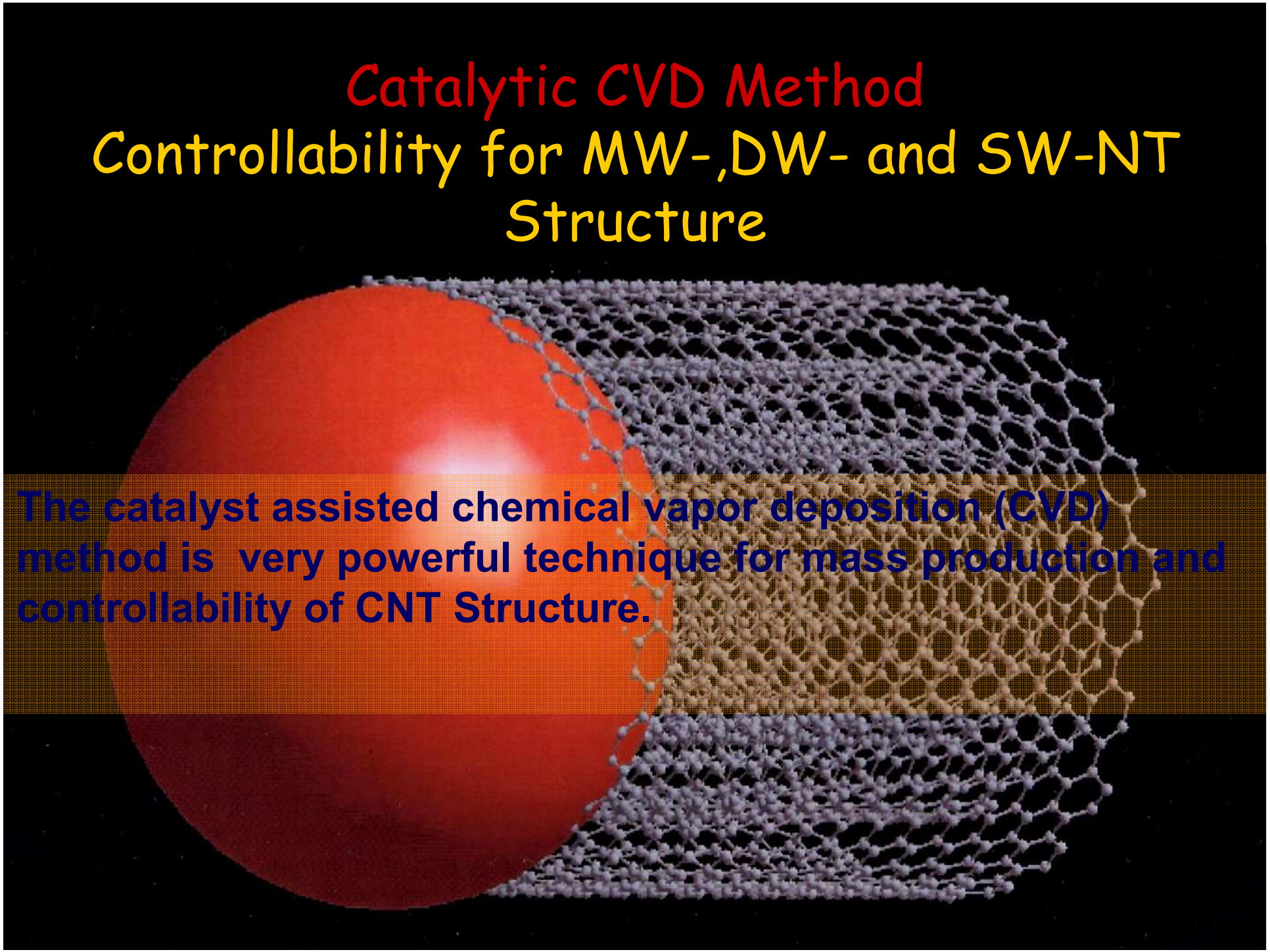
Laser Abrasion

CCVD

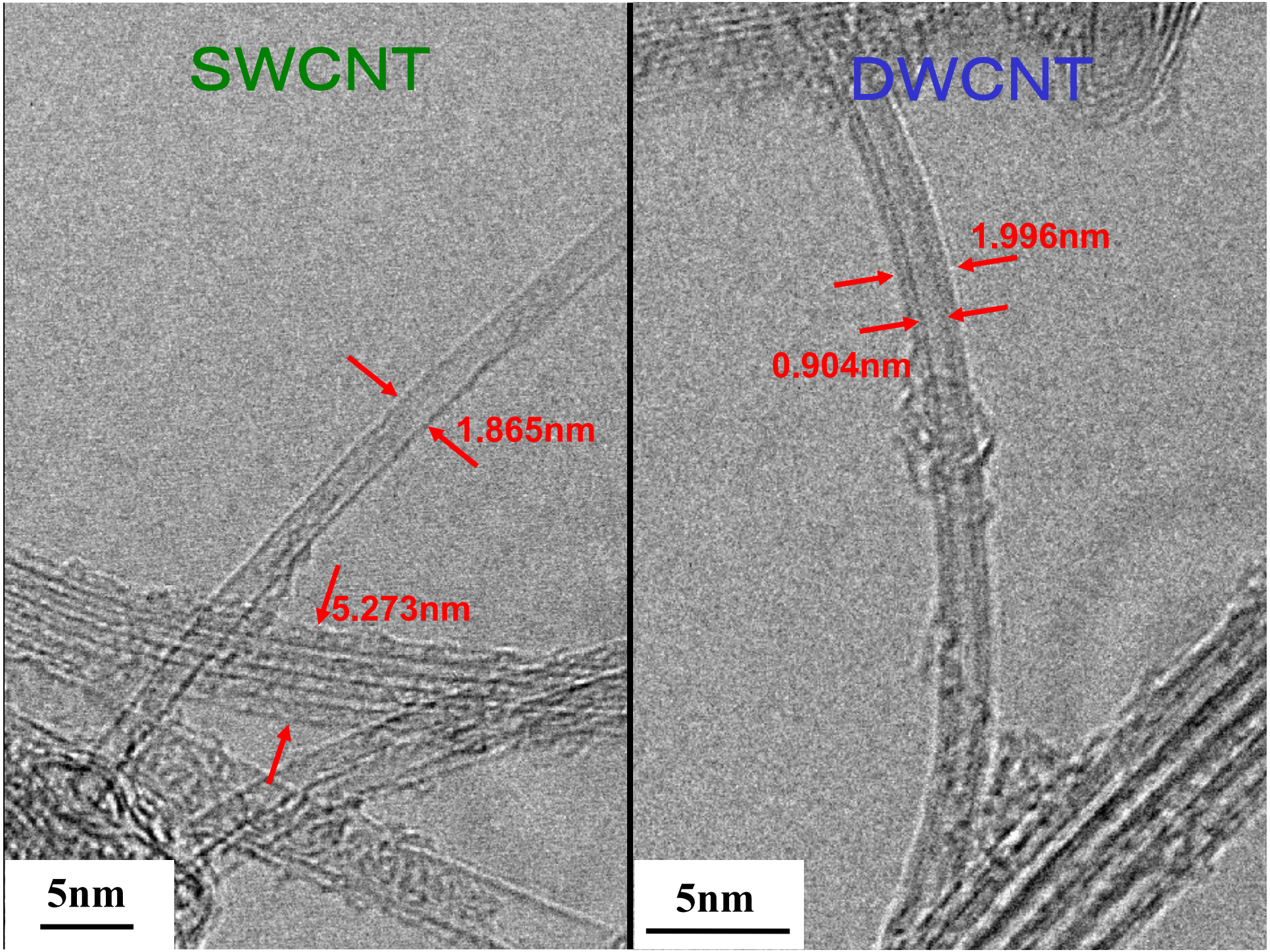
Nanotechnology = Controllability

Catalytic CVD Method

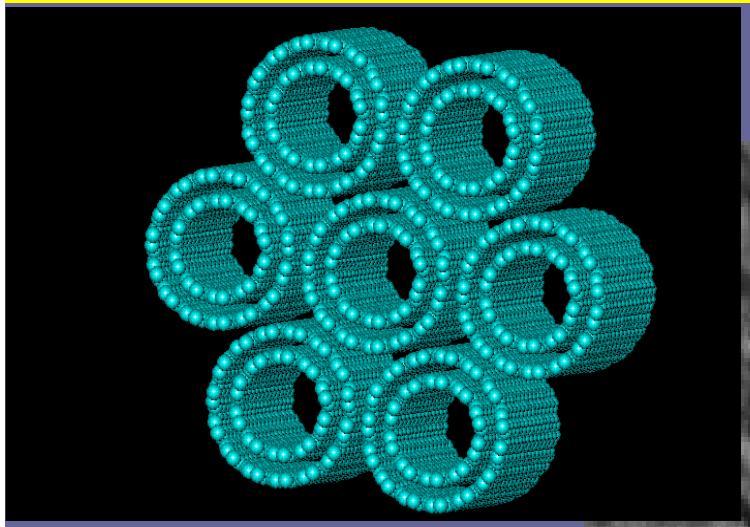
Controllability for MW-,DW- and SW-NT Structure

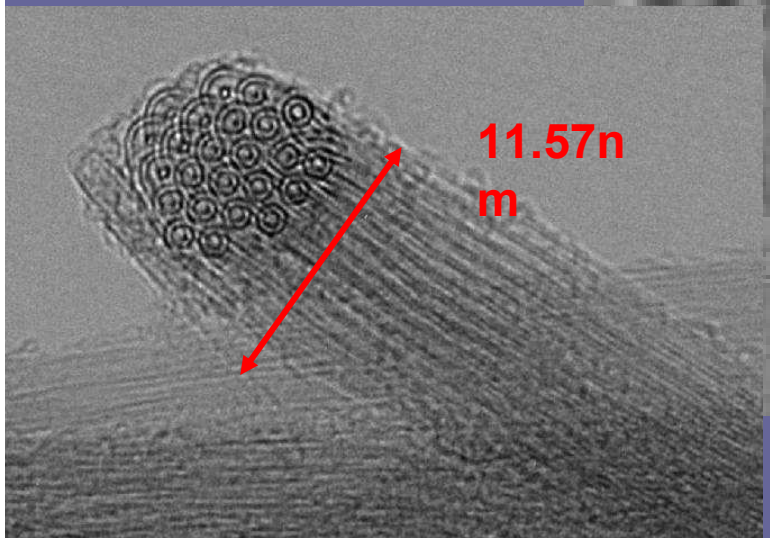


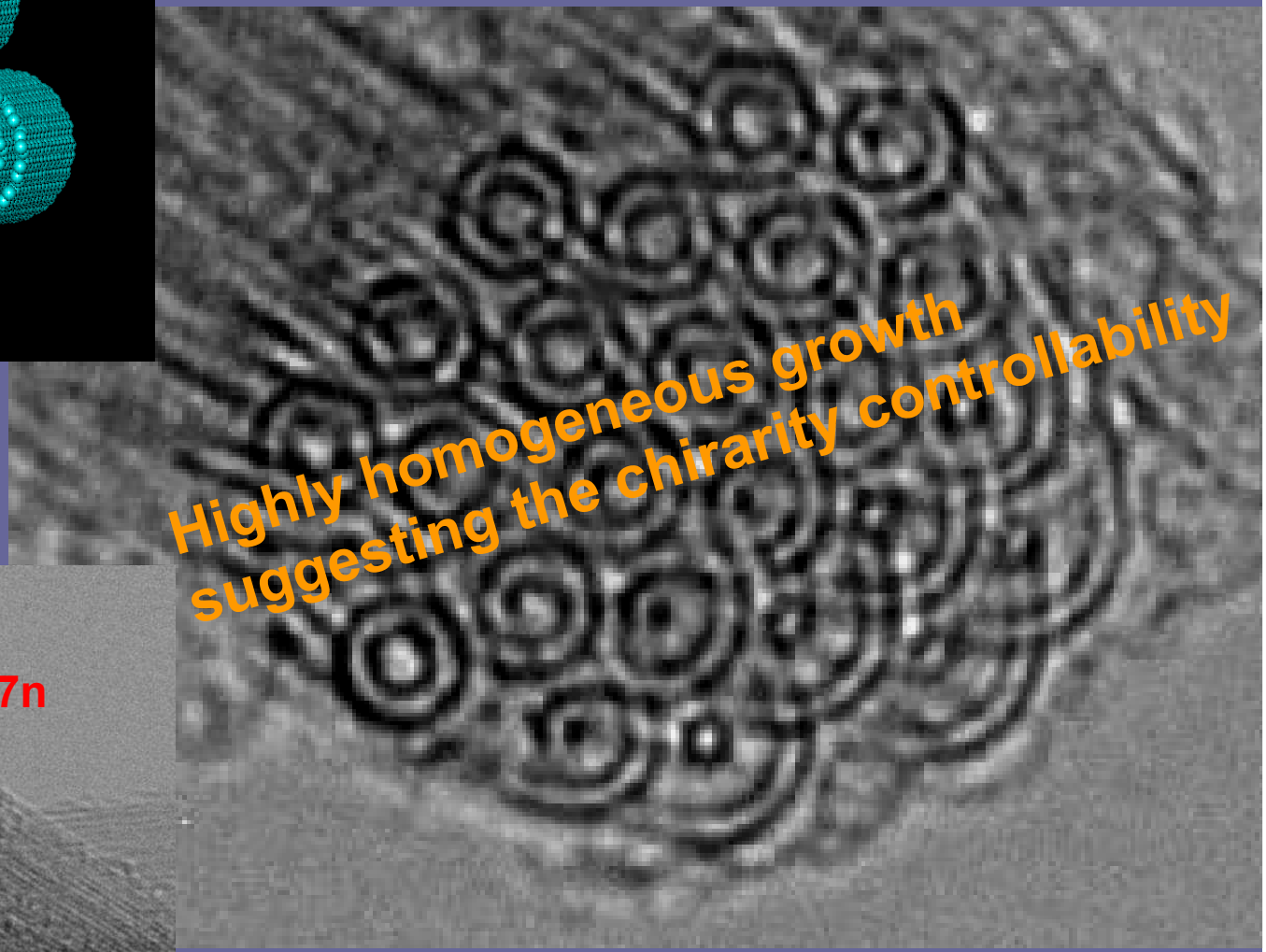
The catalyst assisted chemical vapor deposition (CVD) method is very powerful technique for mass production and controllability of CNT Structure.


SWCNT
1.865nm
5.273nm
5nm
DWCNT
1.996nm
0.904nm
5nm

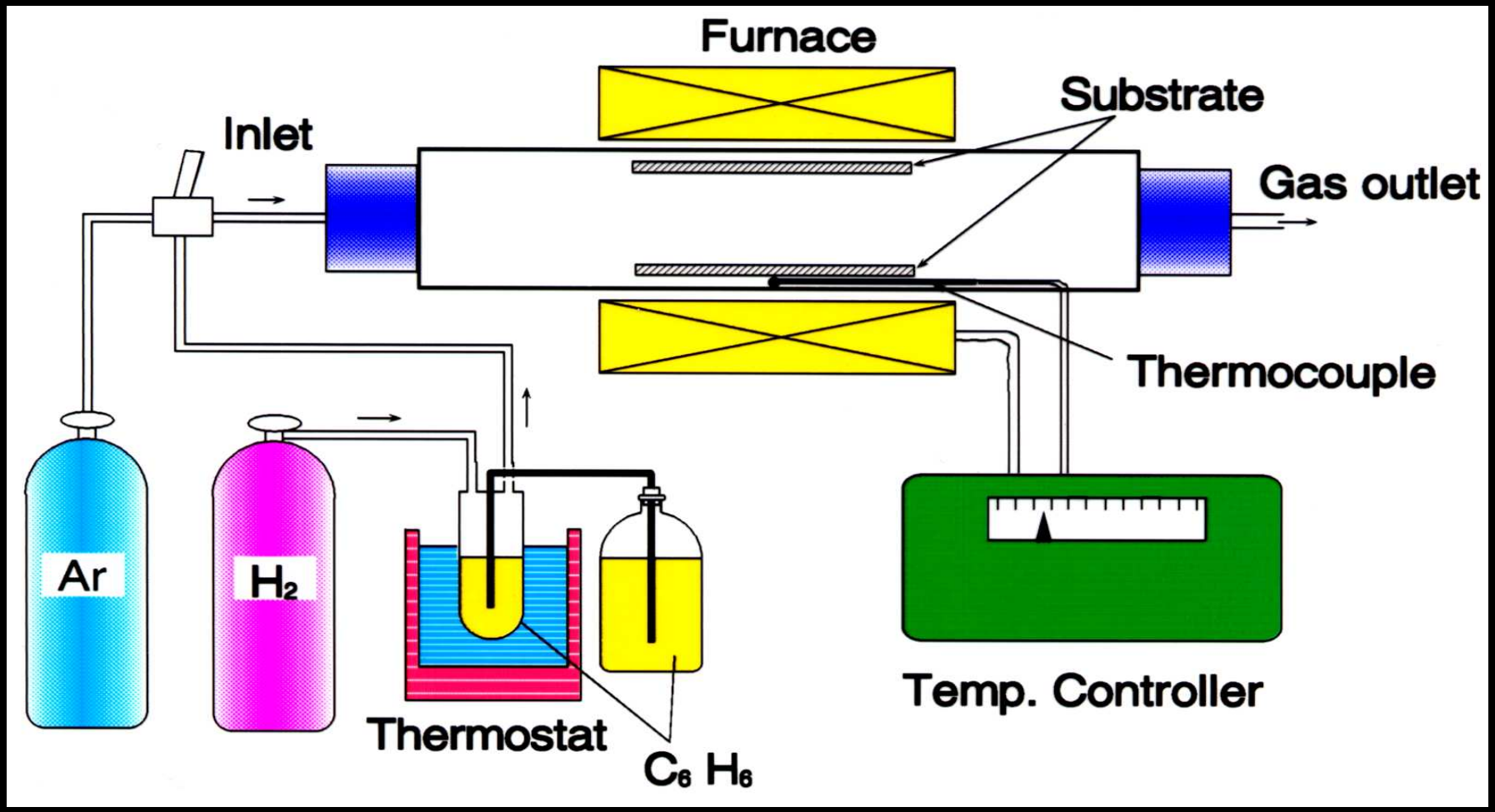
High purity DWNT by CCVD Method, by M.Endo et al., Nature ,2005, 433, 476

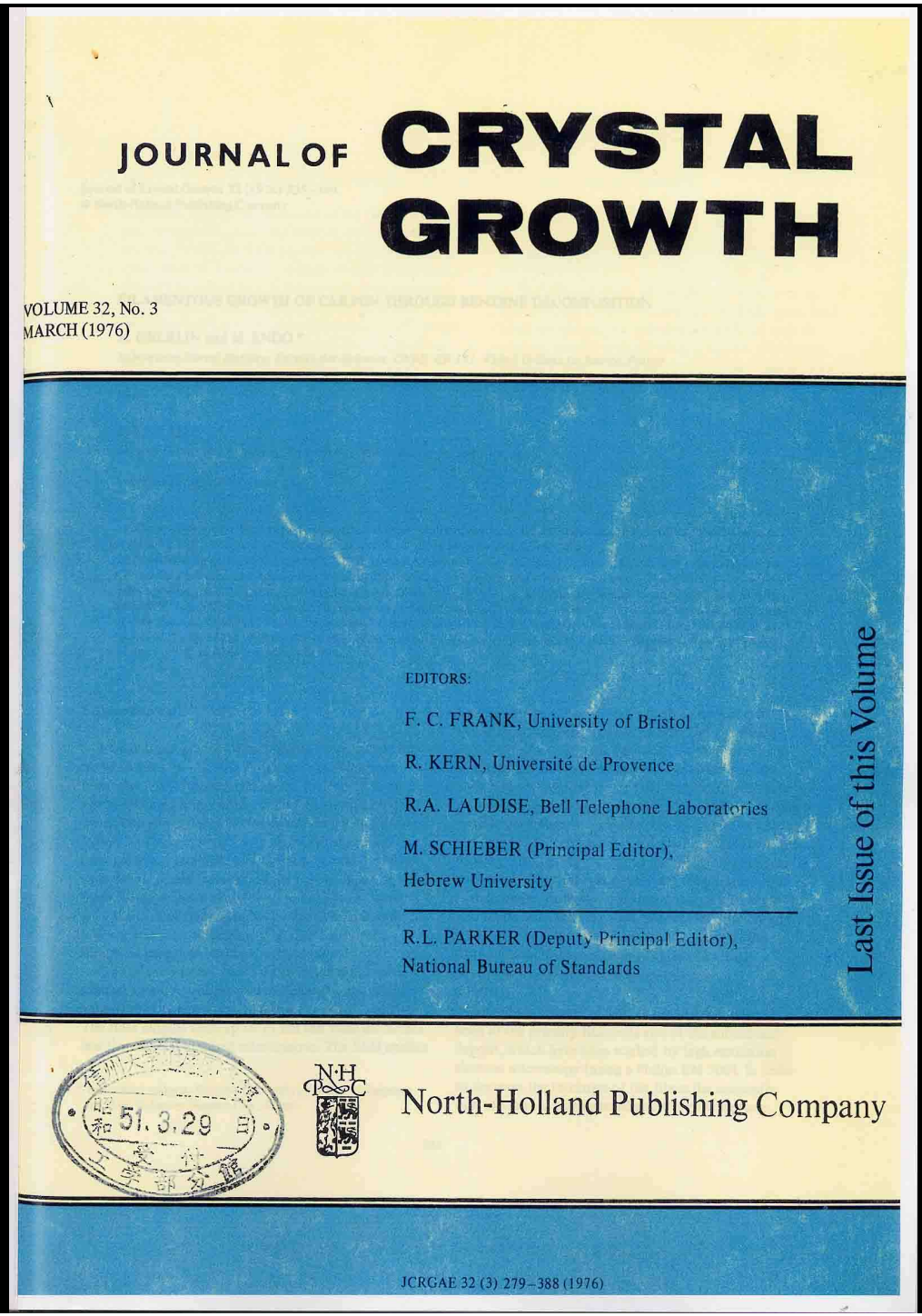






Manufacturing Apparatus for VGCFs





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A. Oberlin,
M. Endo,
and
A. T. Koyama

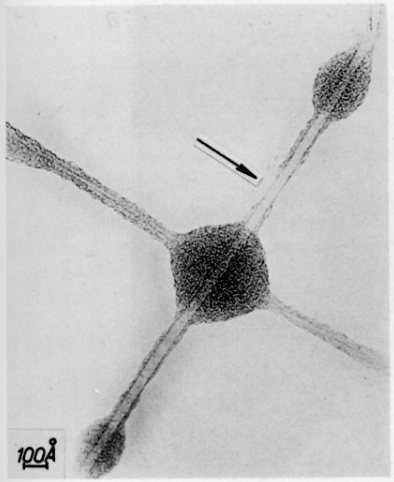

Fig. 11. Bright-field image of branched inhomogeneous fibres.

carbon atoms in a single carbon layer. Fig. 10c also shows that, near the hollow tube, the 00.2 fringes, i.e. the carbon layers, are very long, straight and perfectly parallel. The parallelism of the layers is so perfect in the vicinity of the tube that they always seem to form only one stack, thus explaining the 00.2 Bragg fringe production (which is not necessarily related to any three-dimensional order but only due to the perfect parallelism of the layers). The length of the fringes is usually more than 1000 Å. On the contrary, fig. 10d corresponding to the external part of the fibre only shows short fringes (less than 10 Å) piled up by two or three. The misorientation of one stack relatively to its neighbour ranges from 20 to 30°. This value satisfactorily agrees with the results deduced from SAD patterns. Sizes of the carbon layer stacks obtained from fringes are also in good agreement with those deduced from dark-field pictures.

The above results strongly support the occurrence of two growth processes. The first one is responsible for the formation of the inner core containing long, straight and parallel carbon layers cylindrically rolled around a hollow tube. The secondary process is the thickening of the fibre by a pyrolytic deposit. Some

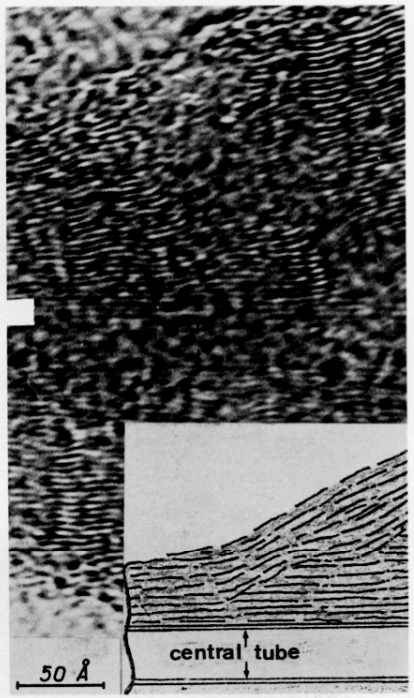

Fig. 12. (a) 00.2 lattice fringes of a constricted fibre, (b) schematic drawing of (a).

examples may be found where the internal core is only present in some part of a given fibre (see arrow in fig. 11). The same figure shows that some secondary deposit has been formed from place to place. This fact explains the conical shape of some fibres (see fig. 1c) which is probably due to an additional continuous pyrolytic deposit on an ancient one, similar to the one pictured in fig. 11. This mechanism is illustrated by lattice-imaging in the case of figs. 12a and 12b.

2.2. Tip of the fibres

Most of the fibre extremities are broken, but some of them are naturally terminated. In this latter case,

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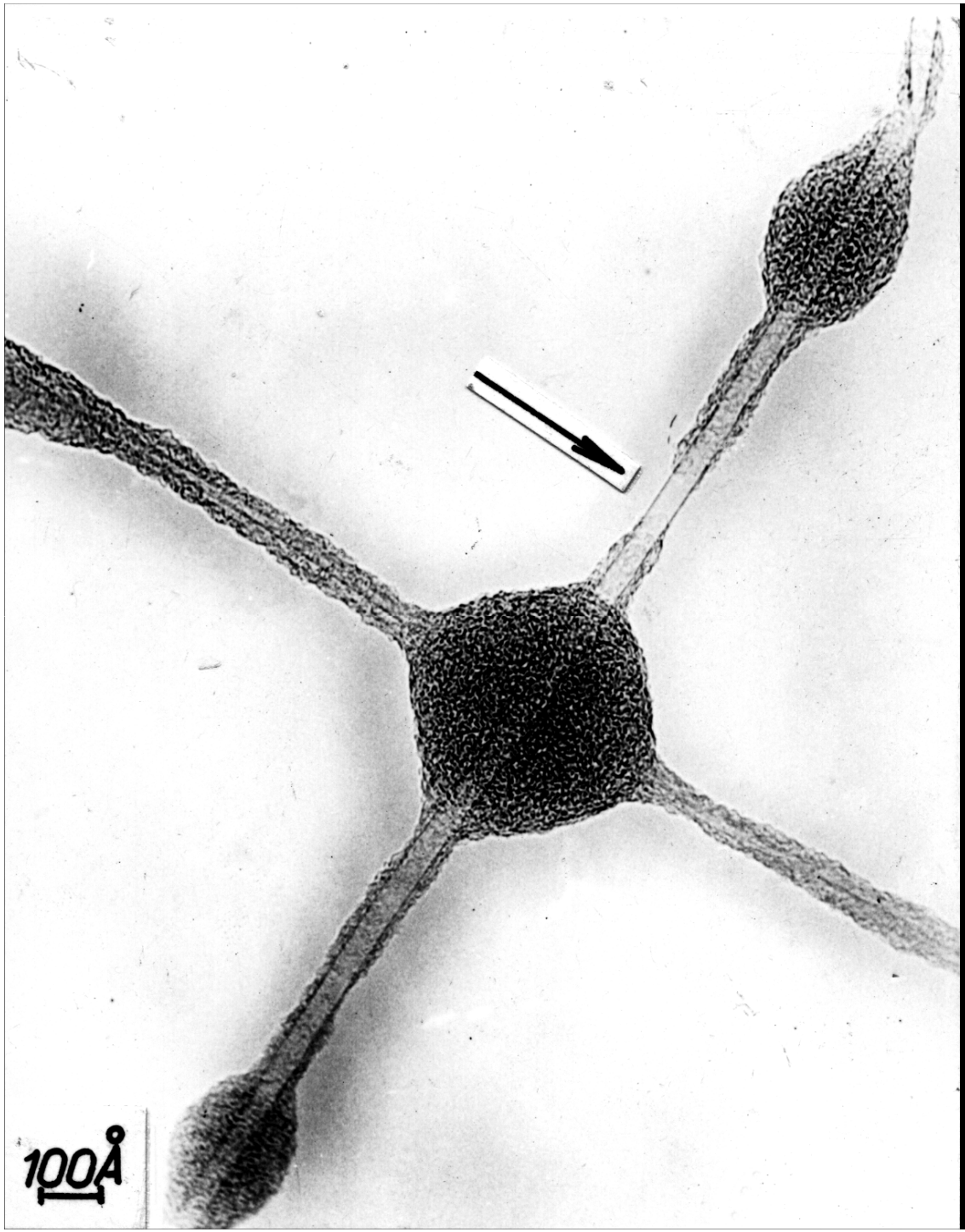

Exposed SWNT during the growth of crossing the tubes；

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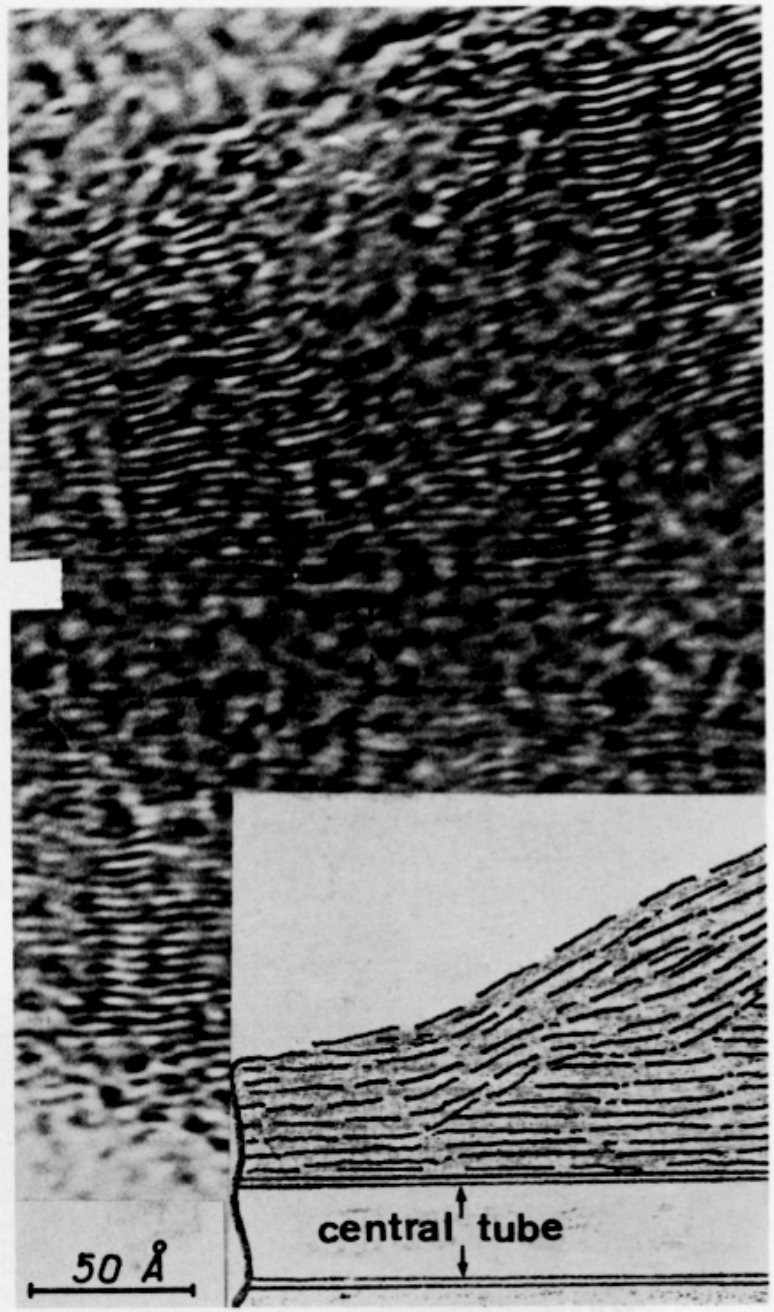

Fig. 12. (a) 00.2 lattice fringes of a constricted fibre, (b) schematic drawing of (a).

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and T. Koyama

Double layered carbon nanotube in the core of the VGCF

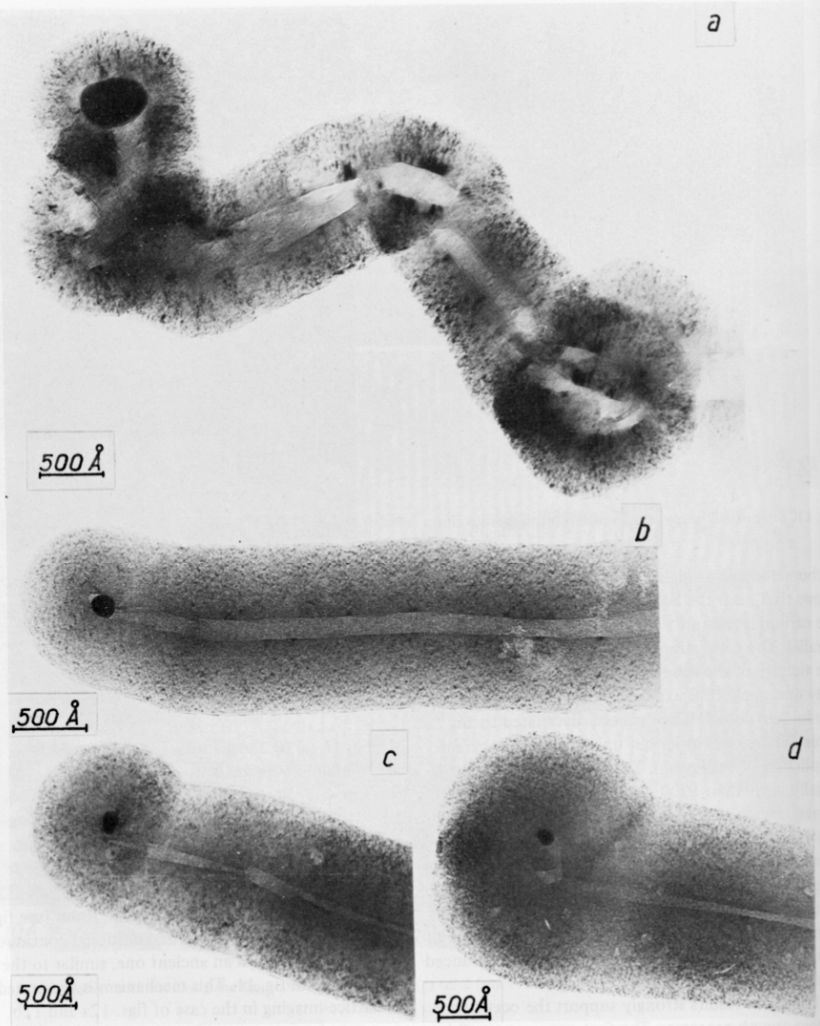

Fig. 13. Bright-field images of fibre tips showing catalyst particles.

whatever the size and shape of the fibres are, each of them contains at its tip a very small particle opaque to electrons (fig. 13). The size of these particles widely varies as it can be seen in the figure; it ranges

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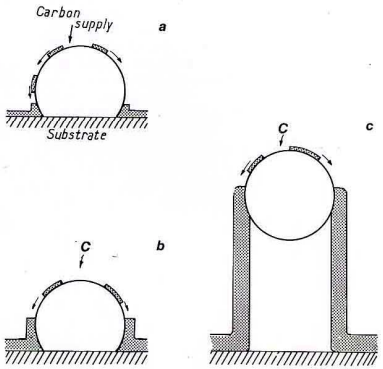

Fig. 21. Schematic illustration of fibre growth through catalytic effect.

the droplet. The carbon thus tends to nucleate on the side portions of the drop unprotected from carbon deposition because of their contact with the furnace. All these interpretations consider the diffusion of carbon atoms either through the metal or through the carbide and do not take into account any possible diffusion of metal into carbon. Moreover all of them do not really satisfactorily explain anisotropy of the growth and the occurrence of a central hollow tube.

An explanation which seems more satisfactory has been proposed by Baird et al. [26] involving a surface diffusion of "metal–metal hydrocarbon species" across the edge of the carbon layer planes. At the beginning small "liquid-like" droplets of iron get fixed on the wall of the furnace, resulting from the reduction by hydrogen of iron oxide soots. On that clean surface begins to nucleate an association of metal and hydrocarbons which diffuses on the surface and dissociates at the contact angle between the droplet and the wall of the furnace acting as a substrate. The beginning of a carbon shell is then produced. New metal hydrocarbon species dissociate on its edges and the carbon layers develop by lateral growth following the external surface of the catalyst (figs. 21a and 21b). Such a lateral growth exerts a force strong enough to lift up the catalyst particle above the surface of the substrate (fig. 21c). Layers always progress laterally in the same way and result in a filament. The hollow channel in the centre is due to the fact that no carbon supply can reach the back of the droplet, the surface of which is protected from downward surface migration by the lateral carbon layers. Growth of carbon layers would continue as long as there is a supply of metal from the top of the catalyst particle (the metal being progressively trapped between the carbon layers). When the whole droplet is covered by carbon layers at the tip, the diffusion stops and growth ends. This kind of mechanism is strongly supported by the existing relics of cementite found inside the carbon shell (see fig. 20). It must be noticed that cementite crystals are obviously formed only when cooling occurs. Such a mechanism also well explains branching of the fibres.

Increase in thickness by pyrolytic deposit on the primary thin fibres is a common phenomenon leading to graphitizable carbon. The constricted aspects often encountered at that stage of growth are probably due to the temperature gradient created along the fibre axis by a catalyst particle existing in that place. This may also be due to fluctuations of the gas flow in the reaction furnace. Anyway, such a deposit is similar to pyrolytic carbon, i.e. it is strongly oriented with its carbon layers approximately parallel to the substrate; but it is made of small turbostratic stacks with tilt and twist boundaries and thus looks more defective than the catalytic carbon contained in the core.

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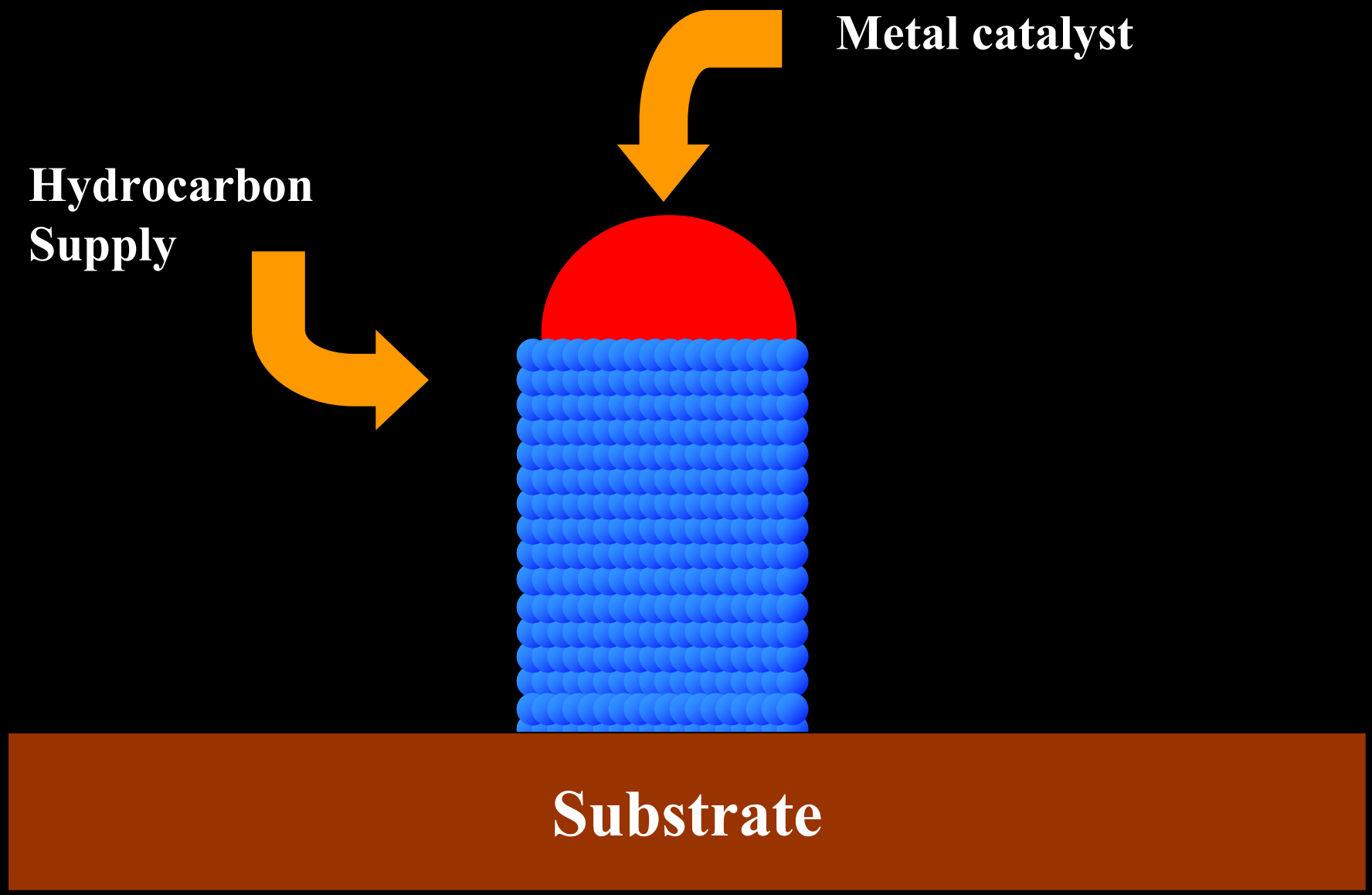

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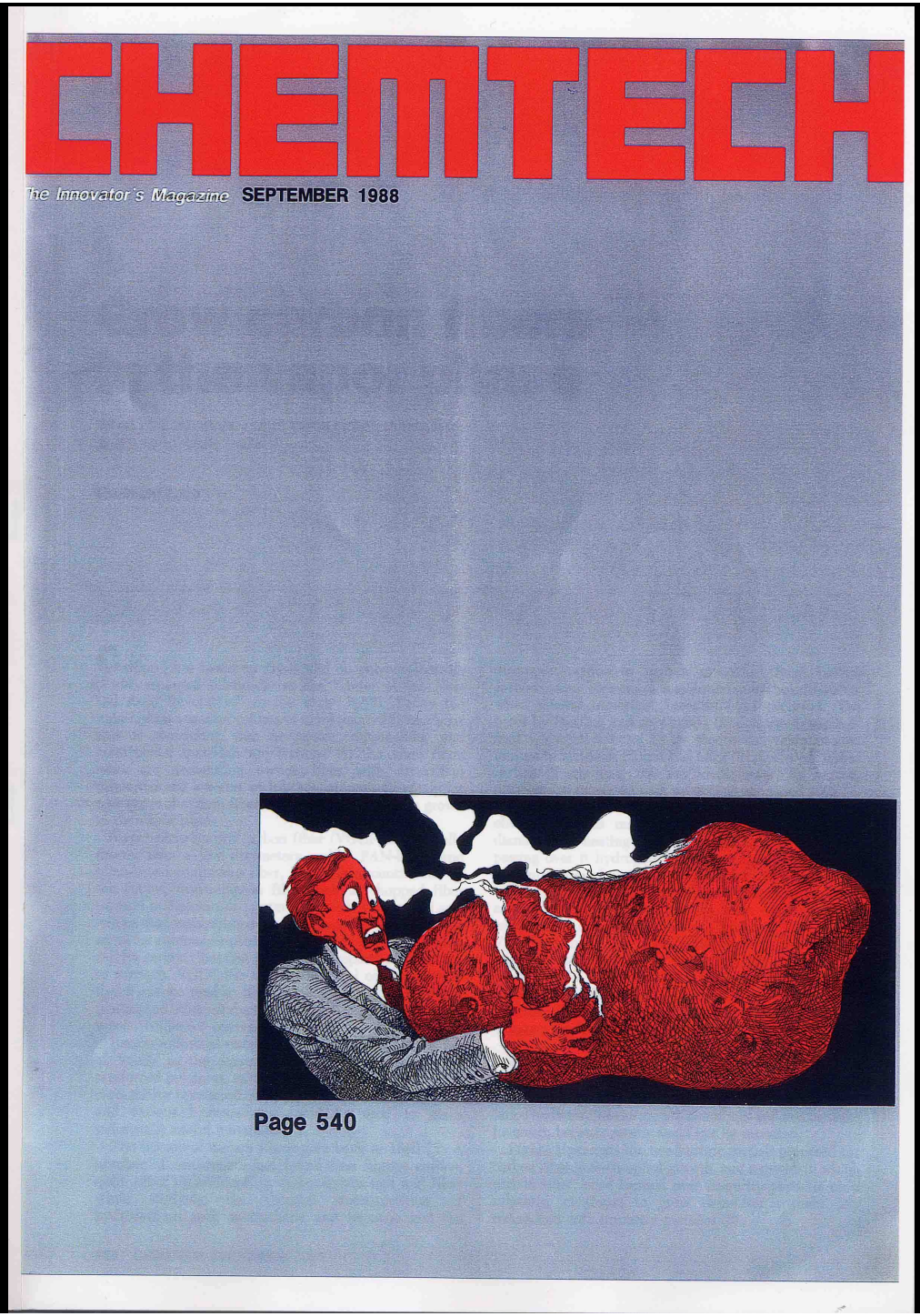

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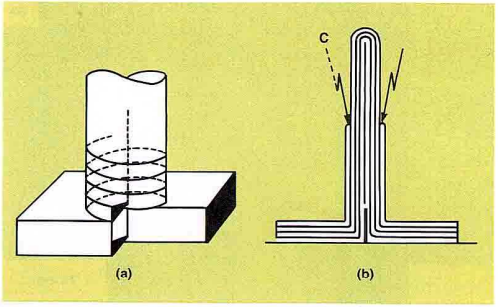

Figure 1. **Historical growth models of carbon fiber from gas phase; (a) spiral model; (b) impurity model (*3*)**

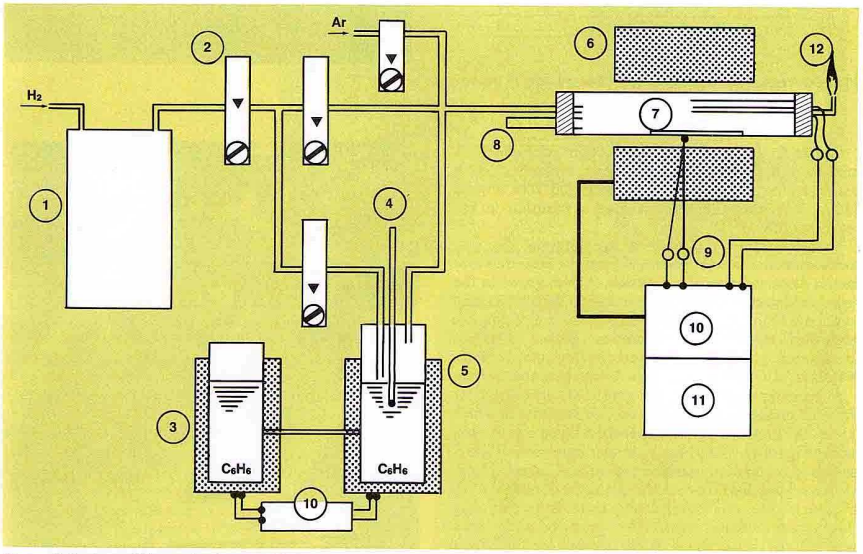

Figure 2. **Equipment for production of VGCF. 1, hydrogen purification unit; 2, flowmeter; 3 and 5, benzene; 4, thermometer; 5, thermostatic bath; 6, electrical furnace; 7, substrate; 8, observation window; 9, thermocouples; 10 and 11, temperature controller and recorder; 12, gas exhaust**

New electron microscopic analysis techniques have allowed the detailed study of these carbon fibers. Formation of mold-like or vermicular-like carbon fibers grown at 300–900 °C had been frequently reported as an abnormal phenomenon, particularly in the carbon industry. At the same time, catalyst researchers had collected detailed data relating various metallic impurities and fibrous carbon (*6*). The tiny mold-like carbon fiber, although noted as a product of interesting catalytic effects, had not been applied commercially, such as in the production of composite materials.

Carbon fiber can be made from various compounds, including benzene, hexane, allenes, and carbon monoxide. Macroscopic and microscopic characteristics of these fibrous carbon products depend on the carbon source.

We have studied schemes to mass produce carbon fibers by growing them in the vapor phase, analyzed their properties and structures, and examined applications of them. VGCF has desirable properties and is potentially competitive with PAN- and pitch-based carbon fibers (*7–9*). VGCF may be a product that "carries knowledge into a new field."

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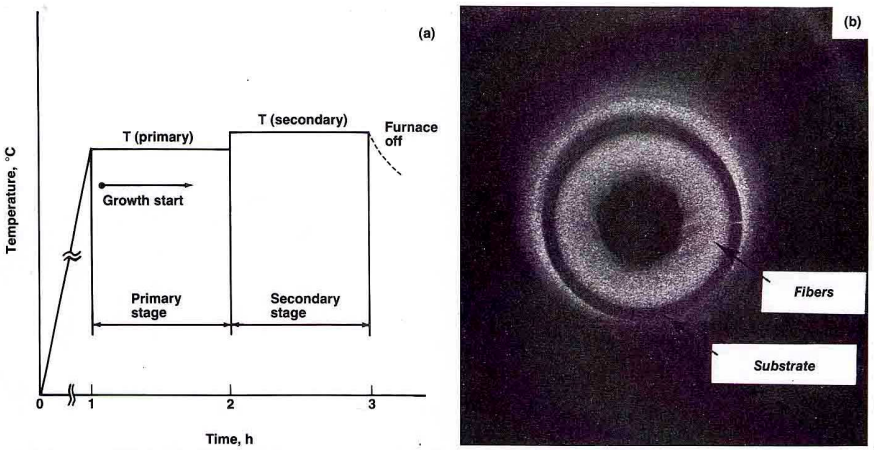

Figure 3. **Temperature program (a); fiber growing in the furnace at 1100 °C (b)**

Figure 2 depicts VGCF production equipment. A mixture of hydrogen and hydrocarbon is admitted into a reaction tube in an electrical furnace and kept around 1100 °C. Carbon fiber forms over a substrate in the reaction tube.

VGCF thus formed is grown in two steps: the fiber first forms over fine catalyst particles of iron or other relevant metals dispersed over the substrate; it then grows in the radial direction, resulting in fibers several decimeters long and about 10 μm in diameter. Temperature and timing are controlled throughout the process. Figure 3 shows temperature profiles and the fibers growing in the furnace. Note that VGCF is produced by a relatively simple system.

A scanning electron microscope (SEM) photograph of the fiber cross-section reveals a unique structure in which layers like growth rings lie concentrically on top of each other (Figure 4). VGCF has a circular cross-section and a preferred orientation in which networks of carbon planes are placed parallel to one another along the direction of the fiber axis. The orientational alignment is greater than those of conventional carbon fibers prepared in the same temperature range, which might account for the higher electrical conductivity and modulus of elasticity of VGCF.

One of the distinguishing structural features of VGCF is the presence of a hollow tube, about 10 nm or less in diameter, along the fiber axis (Figure 5a). The tube wall is composed of linearly extended, single-crystalline-like carbon layers, as shown in Figure 5c. Each layer, however, has a turbostratic stacking structure (i.e., is not a three-dimensional crystal) and does not form a three-dimensional graphite structure. The fiber periphery, on the other hand, is microcrystalline, in which two or three carbon basal networks are layered. This structure is common with thermally decomposed carbon films (Figure 5b). Thus it is apparent that the VGCF is composed of two different structures formed by different mechanisms: the catalytic growth of the fine, precursor fiber consisting of the hollow tube and linearly extended, parallel carbon layer faces near the fiber core; and the subsequent thermal decomposition of the hydrocarbons introduced by chemical vapor deposition that allows the fiber to grow in the radial direction. The physical properties of the resultant fibers are largely determined by the structures of the exterior region in thermal decomposition of hydrocarbons.

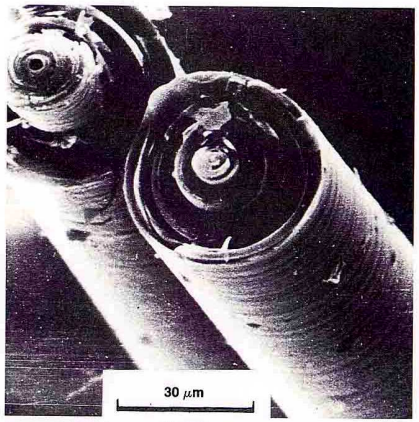

Figure 4. **SEM image of VGCF cross-section**

Mass production

The VGCF production process consists of three steps:

- seeding, in which ultrafine metallic catalyst particles serving as nuclei for the fiber growth are dispersed over the substrate surface,

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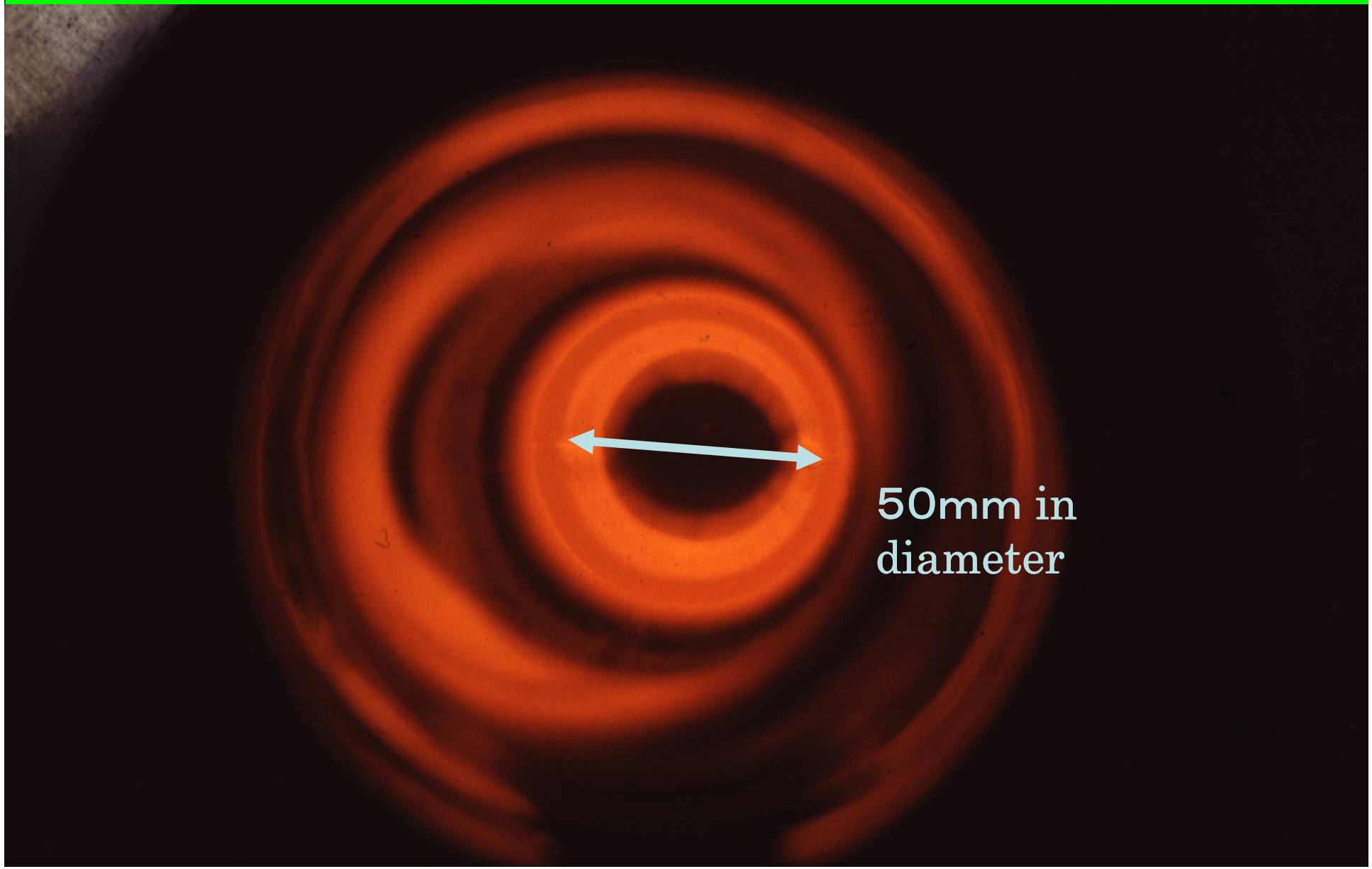
Growth Rate; $10^{4\sim5}$nm/sec

Miracles of CCVD growth by seeded Fe nano-catalyst



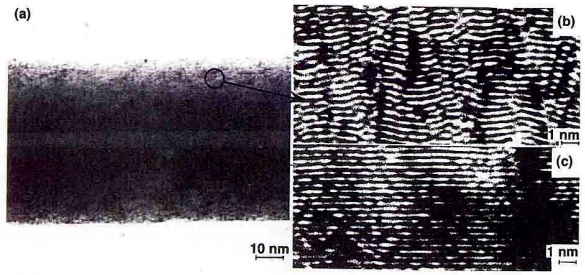
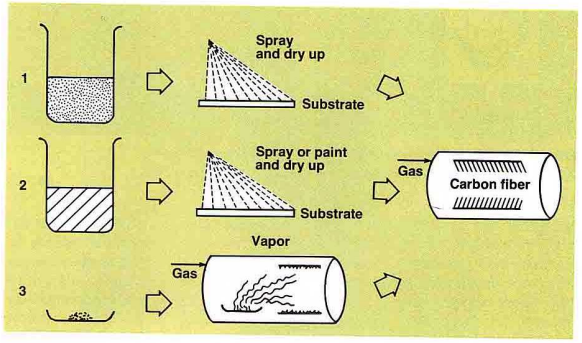


Figure 5. **Hollow tube (a) and two different structures (b, c)**

Figure 6. **Substrate seeding methods**



- growth of fine precursor fiber, and
- deposition of the thermally decomposed hydrocarbons over the precursor fiber to increase its radial size.

The dispersion of the fine catalyst particles, such as those of iron, is the key process for the mass production of VGCF. The seeding step largely determines the density of the growing fiber, i.e., the number of fibers per unit area of the substrate, and hence the productivity (7).

Figure 6 shows the three seeding approaches currently available. Approach 1 involves preparation of superfine particles of iron or other metals of 50 nm or less in size by an appropriate method such as evaporation in inert gas; the iron particles are suspended in alcohol to be sprayed and dried over a substrate. Particles having a magnetically or chemically active surface must be independently dispersed to achieve a dense growth of the fibers. Use of surfactants can promote uniform dispersion. Approach 2 attempts to spray a solution of a metal compound, such as iron nitrate, over a substrate; when heated to about 1100 °C in an electric furnace, ultrafine metal particles form. Approach 3 represents the direct seeding, in which ferrocene or other organic, metal-containing compounds are thermally decomposed and deposited over a substrate. This approach allows integration of the seeding with the subsequent fiber formation processes (9).

The seeded substrate is then heated in an electric furnace and a hydrogen–hydrocarbon mixture is passed over the substrate in a programmed process (Figure 3) to form VGCF (10 μm in diameter, 50–60 mm long). The density of the fiber formed in this manner will be about 600–1200 fibers/mm^2.

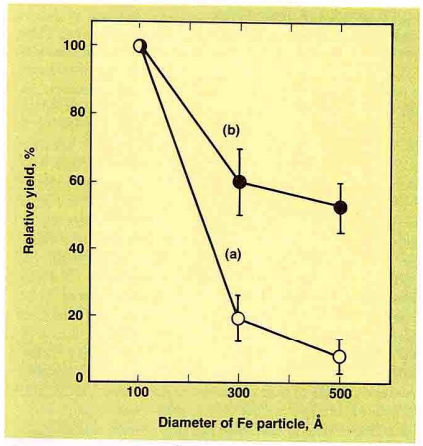


Figure 7. **Effects of catalyst particle size on VGCF yield; catalyst with narrow (a) and broad (b) size distribution**

Fiber yield increases with smaller catalyst particle size (Figure 7). Growth rate of VGCF in the axial direction is 1–50 mm/min, which is 3–4 orders of magnitude higher

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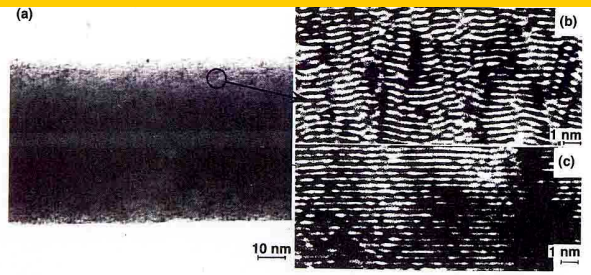

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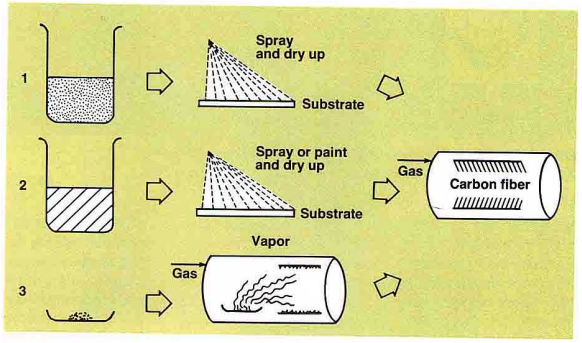

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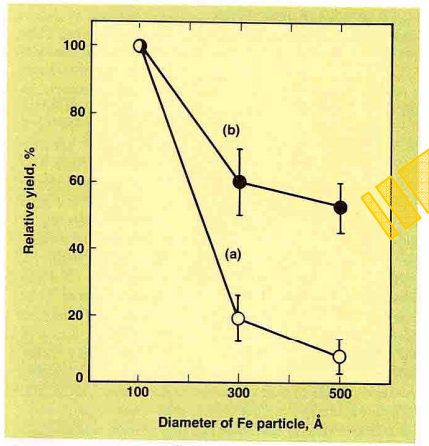

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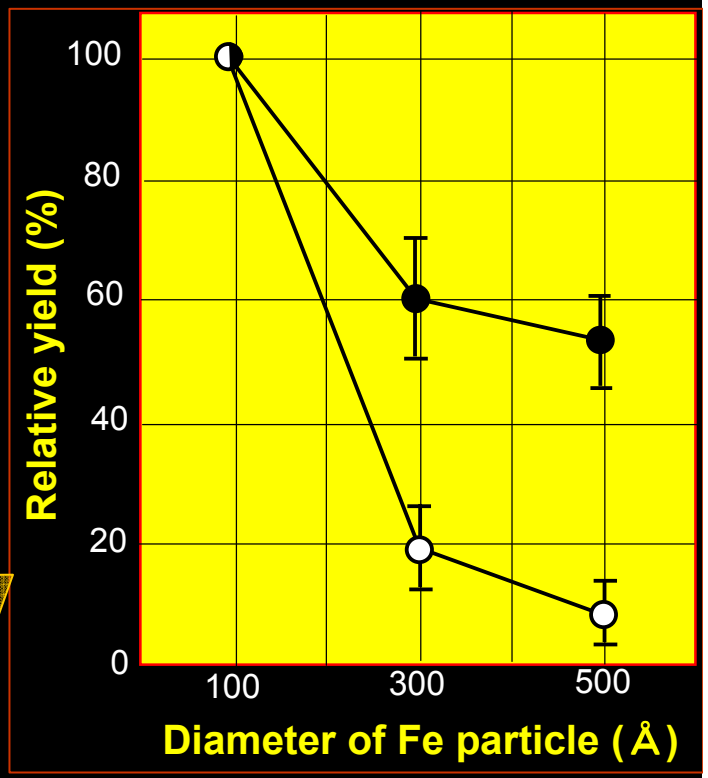
600–1200 fibers/mm².

Fiber yield increases with smaller catalyst particle size (Figure 7). Growth rate of VGCF in the axial direction is 1–50 mm/min, which is 3–4 orders of magnitude higher



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M. Endo American Chemical Society, CHEMTECH, September, pp.568-576, (1988).

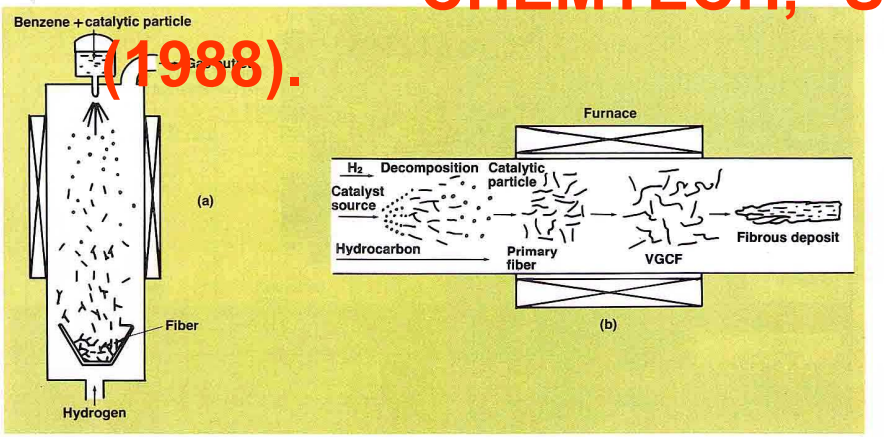


Figure 8. **Conceptual scheme of VGCF production over fluidizing catalyst particles by direct (a) and indirect (b) methods**

than those of conventional metallic or nonmetallic crystalline whiskers. This is largely due to the actions of the superfine catalyst particles.

We have developed fluidization seeding in which the initial fibers are formed over fluidized catalyst particles (Figure 8). It is much more efficient than substrate seeding for fiber formation (*9*).

Growth model and mechanism

As mentioned earlier, VGCF grows much faster than conventional whiskers, which grow at about 50 μm/s. VGCF having an aspect ratio (length/diameter) of 100 can be produced in several seconds. This ratio is equivalent to that of commercial whiskers like SiC. A reaction time of several seconds is sufficient for fine fibers to grow in a hydrocarbon atmosphere with virus-size or smaller catalyst particles. In the fluidization seeding process, the catalyst may be introduced into the reactor either directly or indirectly (Figure 8). The indirect method, by which the catalyst particles and VGCF form simultaneously, is based on Approach 3 (Figure 6). It can efficiently produce fine particles of several tens of angstroms, which, by fluidizing ultrafine metal particles introduced into the reactor in a controlled manner, greatly promotes fiber growth in the three-dimensional space of the reaction chamber. Fluidization seeding permits better control of the catalyst-feed ratio and the product aspect ratio. Fluidization-produced VGCF has a crystallographic structure similar to that of substrate-produced VGCF, but with much smaller hollow tubes of 2–3 nm (Figure 9).

It is interesting to note that the fluidization method can produce carbon fibers ranging from carbon black-like fibers with an aspect ratio of about 1 to ordinary continuous fibers, in which the aspect ratio is essentially infinite. Products having low aspect ratios can be used as reinforcing agents for various matrices, such as rubber, plastics, and cement.

Figure 10 shows the tip of a growing fiber with a crystal of iron carbide at the end of the hollow tube. The iron particle—which is either deposited on the substrate or fluidized—remains as it is while the fiber is growing but might react with the cementite particles when cooled. High-resolution transmission electron microscopy (TEM) has revealed that catalyst particles found at the fiber ends have fairly uniform sizes, mostly below 20–30 nm. Many fluidization-seeded particles are around 5 nm, which agrees with the observation that the fiber forms more efficiently with decreasing particle size. Baker and co-workers have reported that a finer particle grows the filamentous carbon faster (*10*), which may support our results for the ultrafine catalyst particles.

The fiber will continuously grow as long as the particles dispersed on the substrate or the fluidizing catalyst particles are active; the fiber ceases to grow when the particle surfaces are covered with carbon layers, oxygen, or other impurities, thus retarding movement of the carbon species. It is therefore vital to control the hydrocarbon partial pressure in the system and to keep the atmosphere free of impurities such as moisture and oxygen, in order to obtain long fibers. The TEM image (Figure 11) shows the catalyst particle at the end of the growing precursor fiber; it is not yet covered with hard, graphite-like carbon layers and can still actively assist fiber growth in the longitudinal direction. The resultant thin fibers have a continuous, thin, hollow tube as shown in Figure 11b.

We can illustrate the formation of VGCF by the model shown in Figure 12 (*11*). A reducing atmosphere of hydrogen at ~1100 °C reduces the catalyst particle of a transition metal such as iron, or cleans its surface, which promotes the polymerization and condensation of the hydrocarbon to develop hexagonal planar networks of carbon. They grow perpendicular to the substrate surface in the space between the particle and the substrate. The particle is driven upward, away from the substrate—presumably by osmotic pressure, surface tension, or

Fluidization seeding permits better control of the catalyst-feed ratio and the product aspect ratio. Fluidization- produced VGCF has a crystallographic structure similar to that of substrate-produced VGCF, but with much smaller hollow tubes of 2-3 nm (Figure 9).

The TEM image shows the catalyst particle at the end of the growing precursor fiber; it is not yet covered with hard, graphite-like carbon layers and can still actively assist fiber growth in the longitudinal direction. The resultant thin fibers have a continuous, thin, hollow tube as shown in Figure 11b.

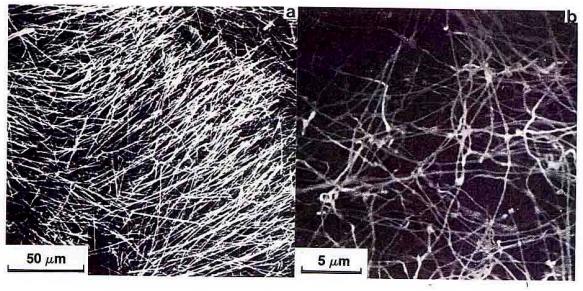


Figure 9. VGCF produced by the fluidized seeding method; straight (a) and vermiculate (b) fibers

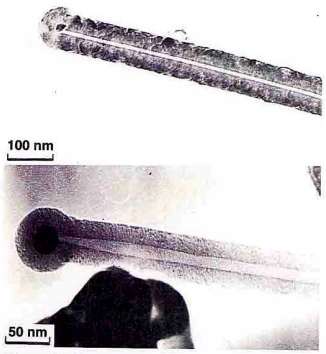


Figure 10. Microparticle (cementite) at the tip of the hollow tube

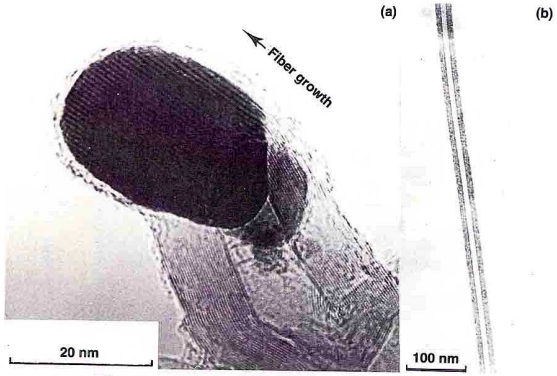


Figure 11. Seeded microparticle at the end of the growing VGCF (a) (from a collaboration with A. Oberlin) and a thin fiber with continuous hollow tube (b)

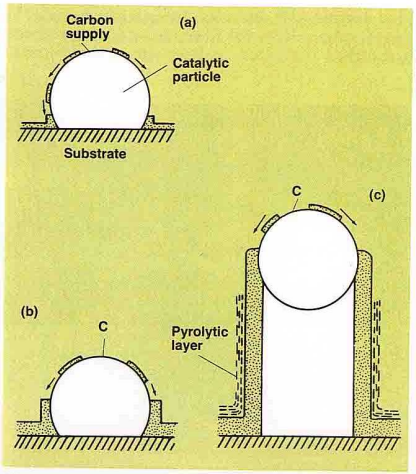


Figure 12. Proposed growth mechanisms of VGCF (*11*)

diffusion—and the precursor fiber formation is continued to elongate the fiber. The reactions occur in selective regions such as the surface of the catalyst particle or in some direction of the crystal. As the particle moves, it leaves behind the hollow tube. The carbon molecules within the particle move more briskly near the melting point of the catalyst, thus greatly contributing to the rapid growth of VGCF. It should be noted that the intraparticle temperature gradient provides an important force that drives the carbon species. This force, which consists of the net heat generated by the thermal decomposition of the hydrocarbon and the subsequent formation of solid carbon, promotes fiber formation. On the other hand, no fibrous carbon has been observed in net endothermic systems, such as those involving the decomposition of paraffins.

We don't yet clearly understand the extent to which intraparticle diffusion affects the overall reaction rate. Substrate seeding and fluidization seeding share common growth conditions and product structures, and, hence, growth mechanisms. If that is the case, the carbon layer plane should grow with a selective orientation for the fibrous matter to be formed over the fluidizing catalyst particles. It is therefore interesting to examine whether the catalytic effects show anisotropy. Audier (*12*) has studied

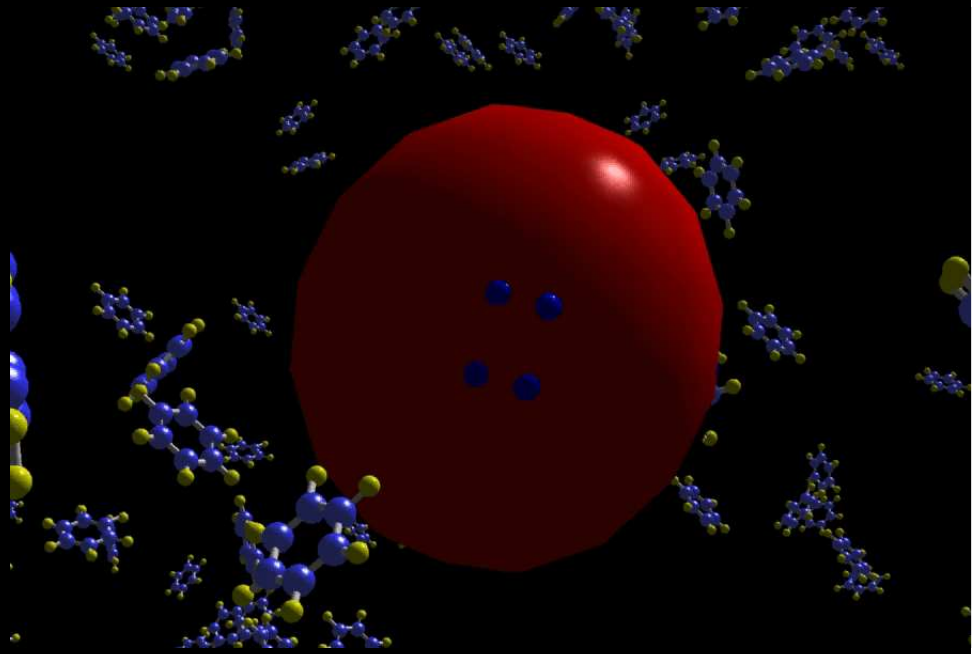
M. Endo

American Chemical Society,

CHEMTECH, September, pp.568-576, (1988).

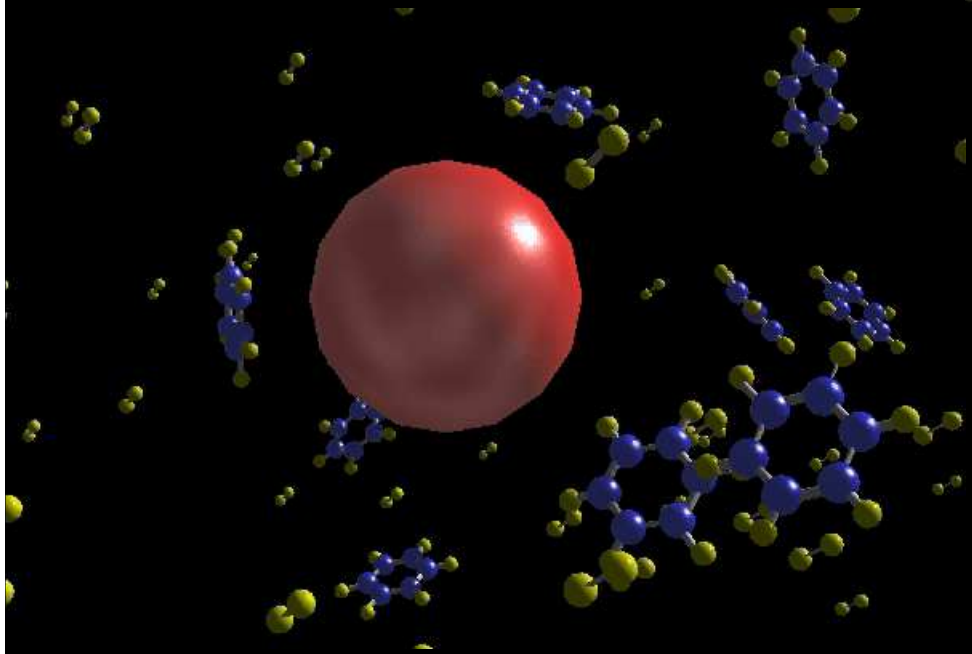
Floating Catalyst System

By M. Endo,
CHEMTECH,
American Chemical Society,
September, pp.568-576, (1988)



DWCNT

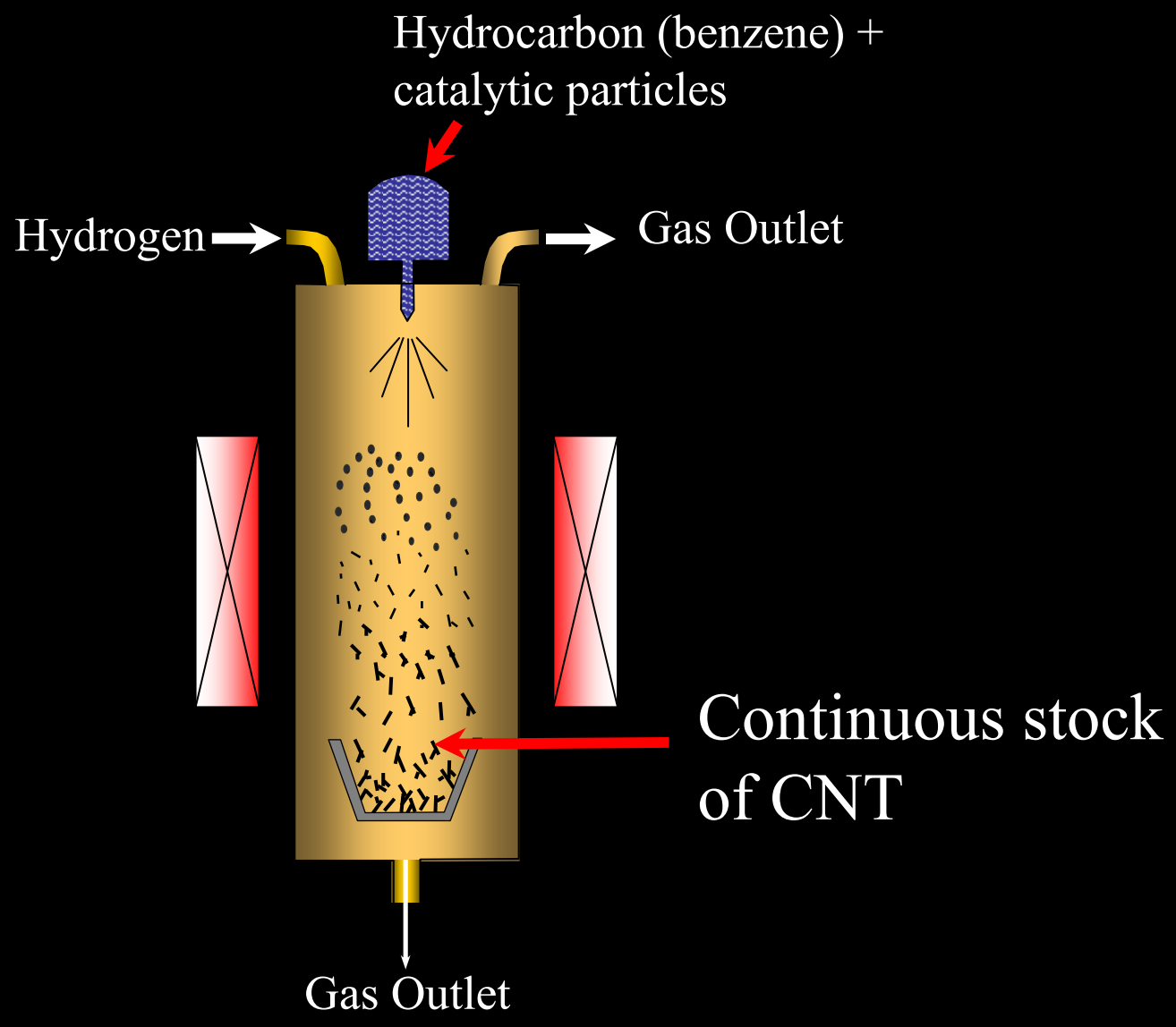
SWCNT

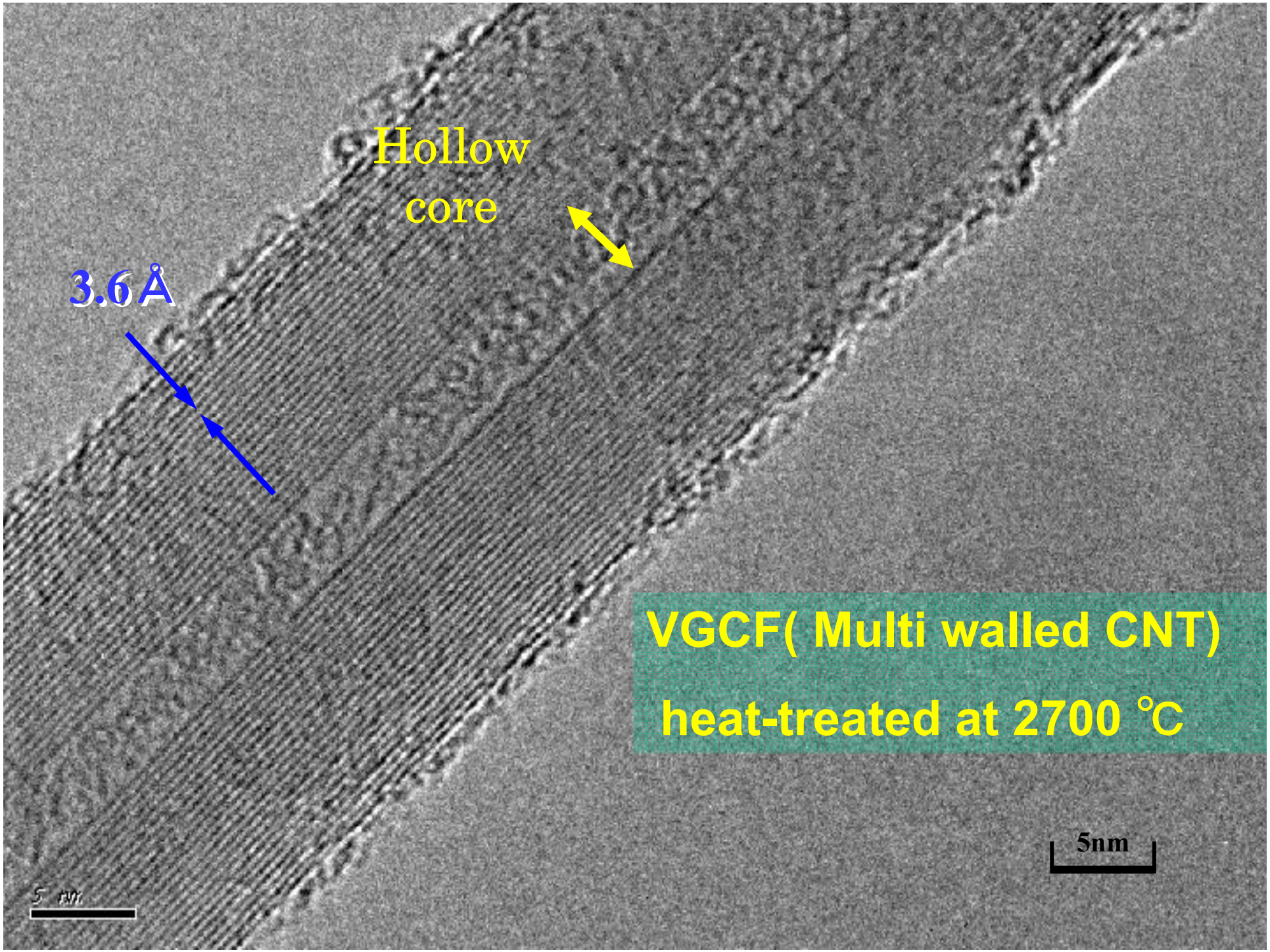


By M. Endo, *CHEMTECH, American Chemical Society, September, pp.568-576, (1988)*

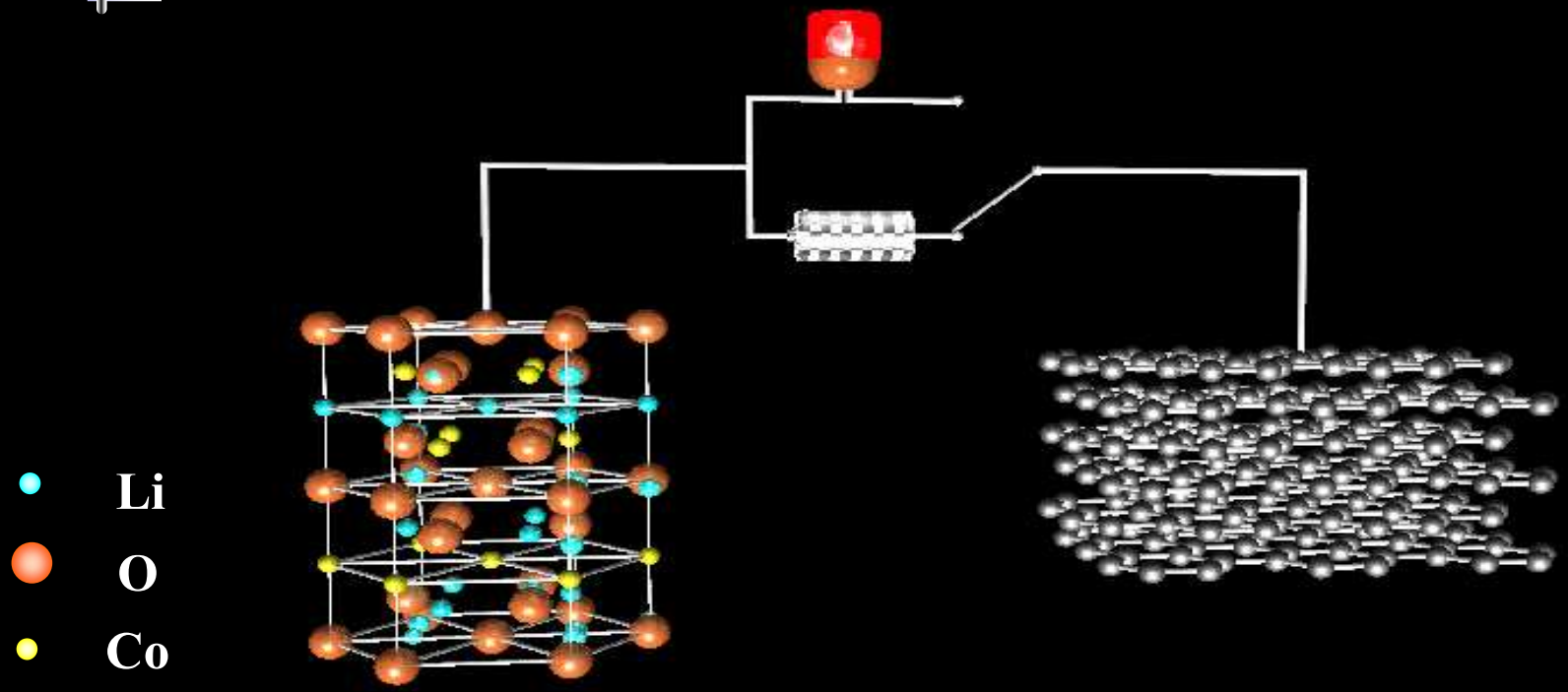
The Floating Seeding Method (Vertical type)

M. Endo; American Chemical Society, CHEMTECH, September, pp.568-576, (1988).




Hollow
core
3.6 Å
VGCF(Multi walled CNT)
heat-treated at 2700 ℃
5nm
5 nm

Principle of operation of Li-ion-Battery

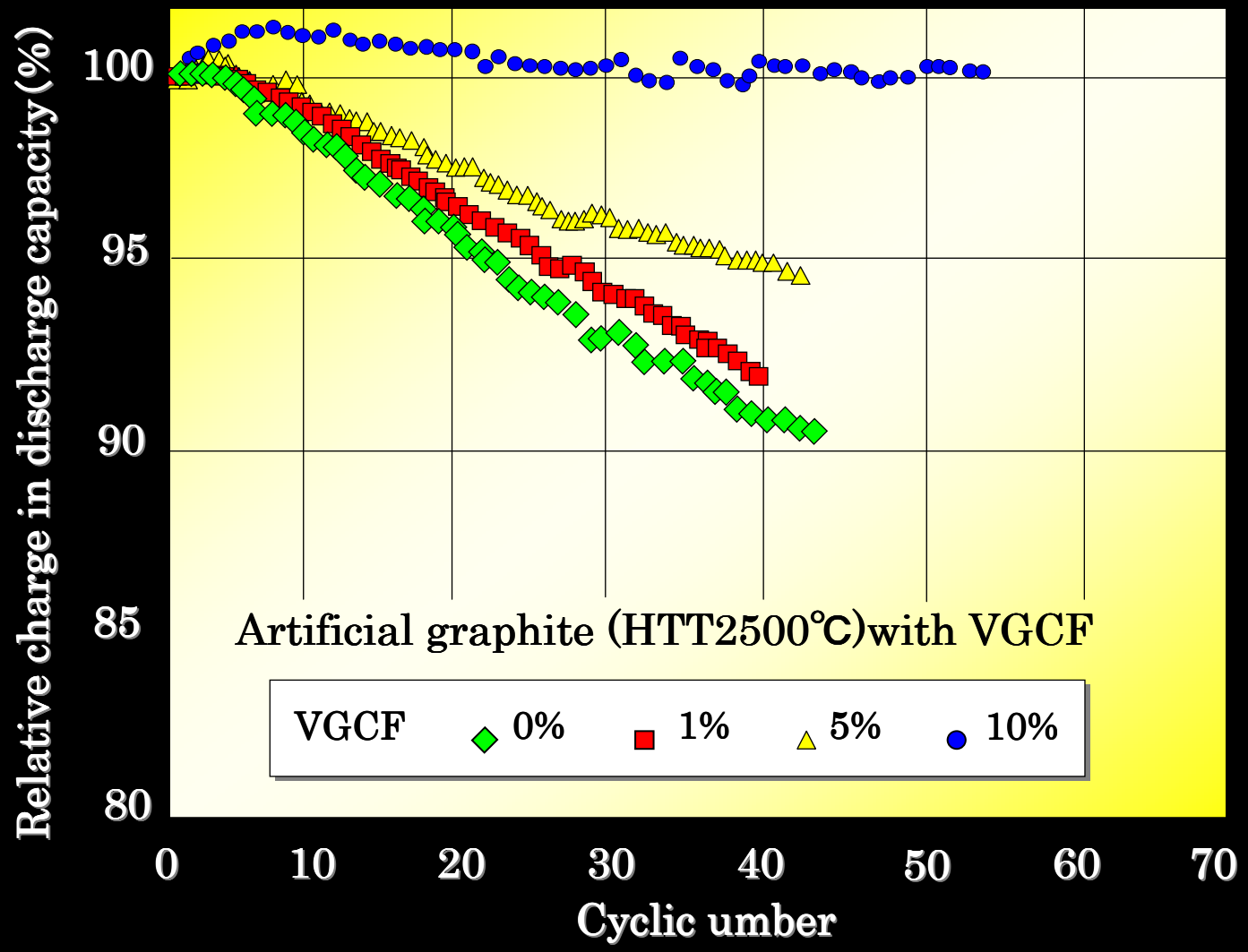


- Li
- O
- Co

$LiCoO_2$

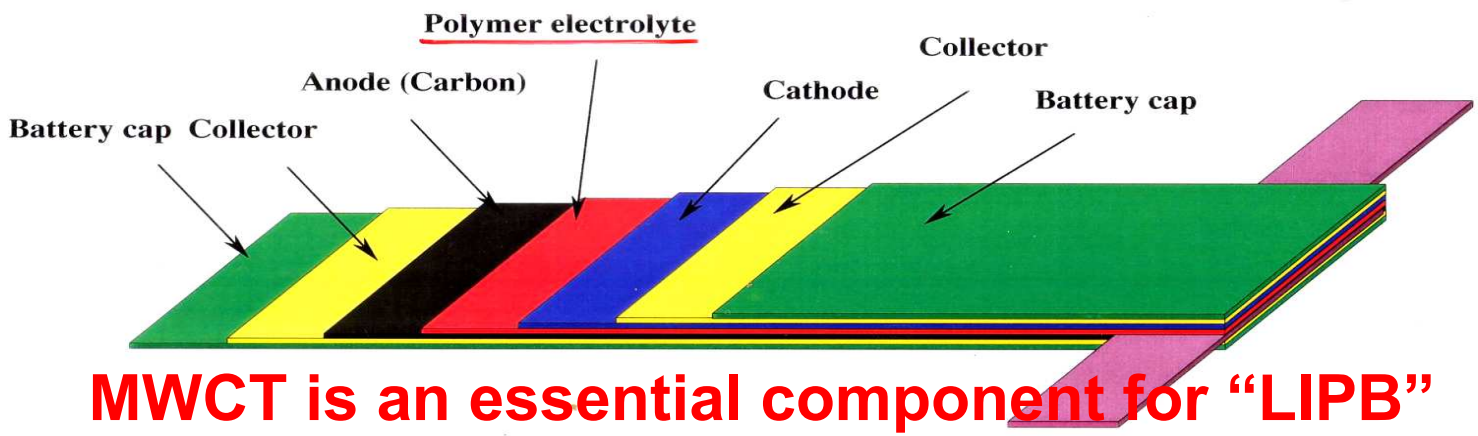
Graphite

Cyclic characteristics of synthetic graphite as a function of weight percent of CNF(MWCT)



M.Endo, Y.A.Kim, T.Hayashi, K.Nishimura, T.Matsushita, K.Miyashita and M.S.Dresselhaus; Carbon, Vol.39, pp1287-1297, (2001).

Li-Polymer Battery (LIB)

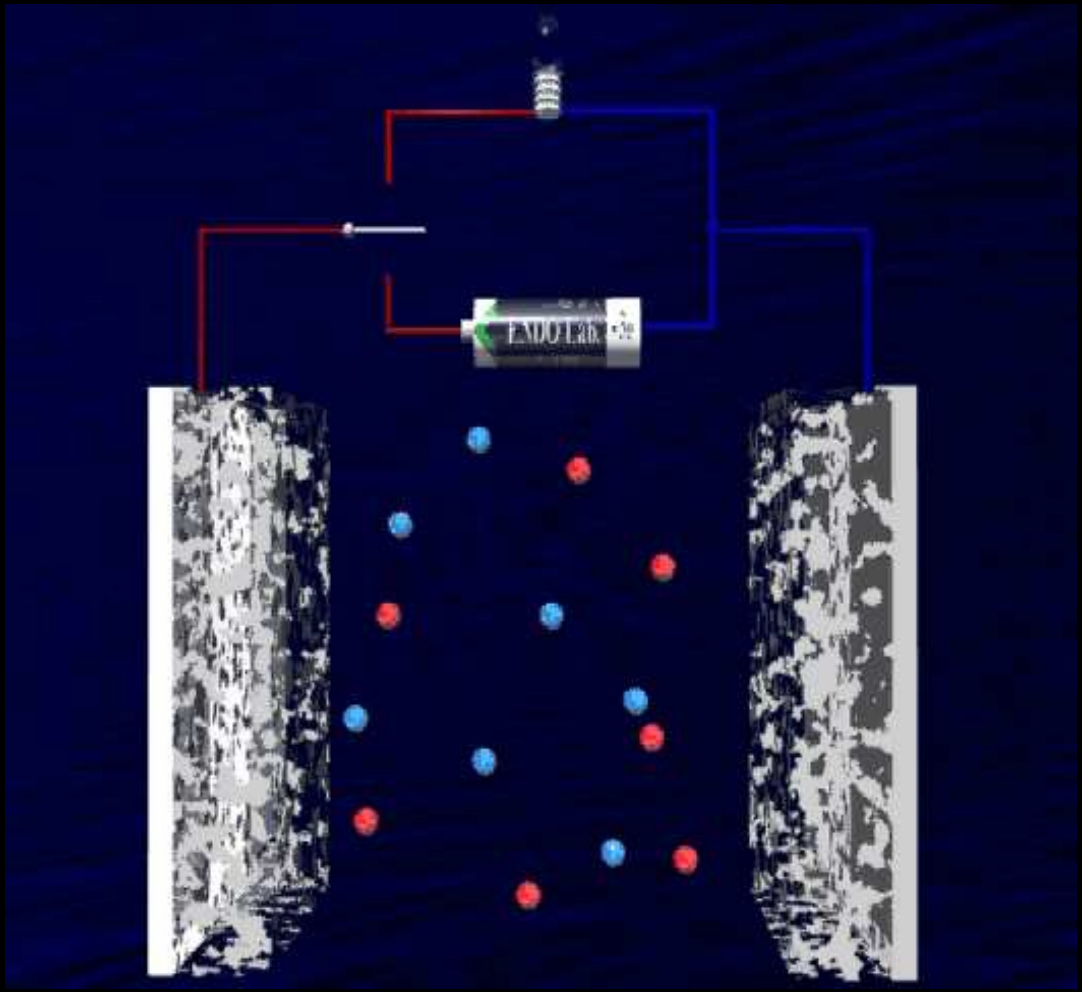


MWCT is an essential component for "LIPB"

- Safety ;solid electrolyte
- No liquid leakage
- Light weight and thin thikness(1mm)
- Shape-design freedom (back side of LC display)

http://ascii24.com/news/i/topi/article/1999/10/12/604874-000.html

Schematic diagram of electric double layer capacitor conception diagram



Cation

Anion

Positive Charge

Negative Charge

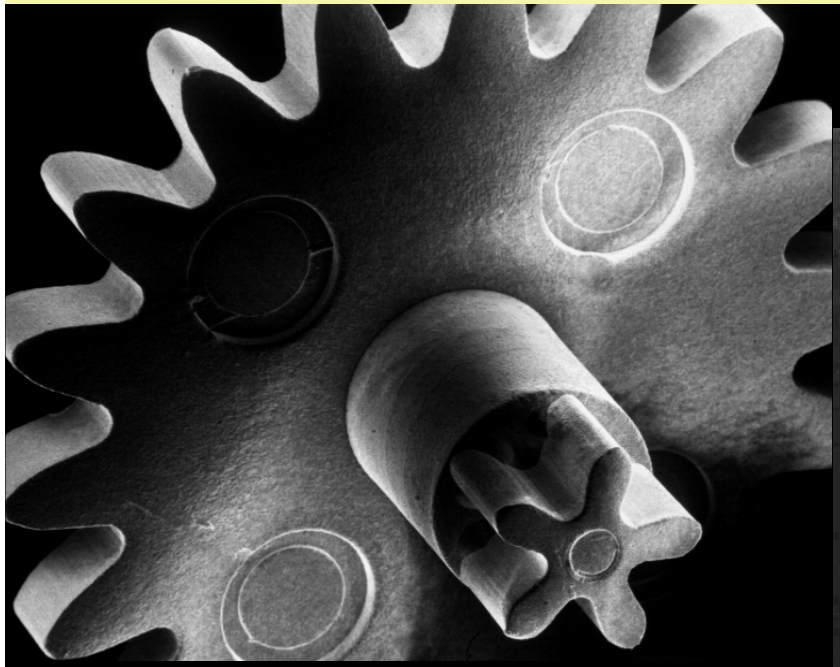
CNT can contribute to the21st century's energy and environment technology !

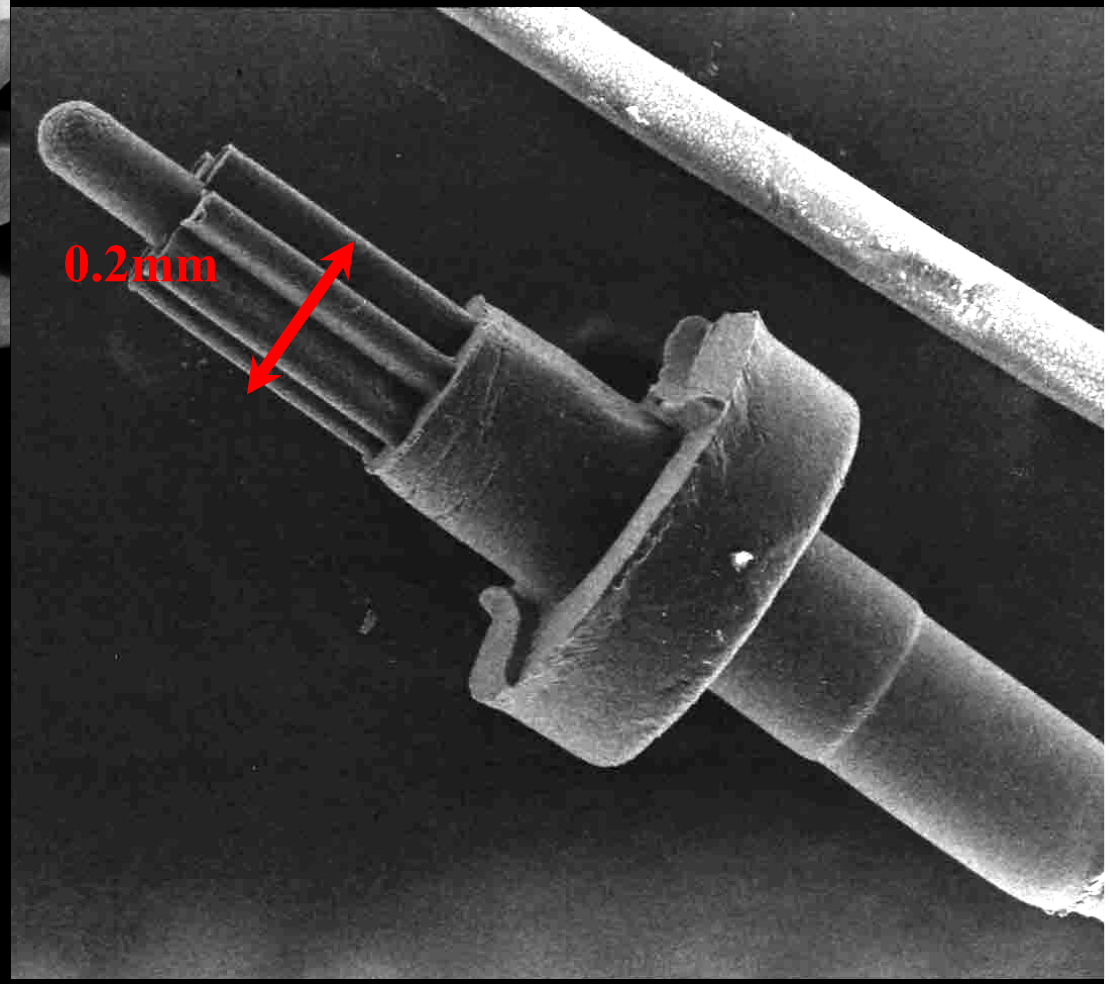
Energy devices have the highest cost performances for NT

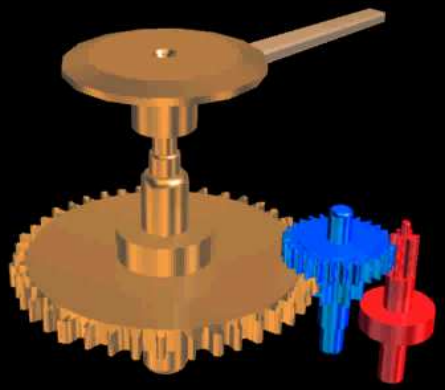
Digital EV
(HEV, EV, Fuel cell V)

M

Micro-gear made by CNT composite







MP-001

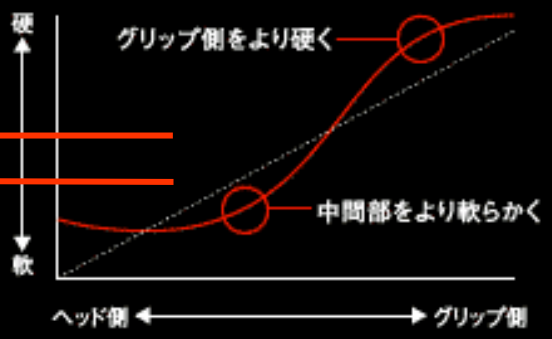
あのMPに、ドライバーデビュー。

最適重心設計によるMP-001専用シャフト。

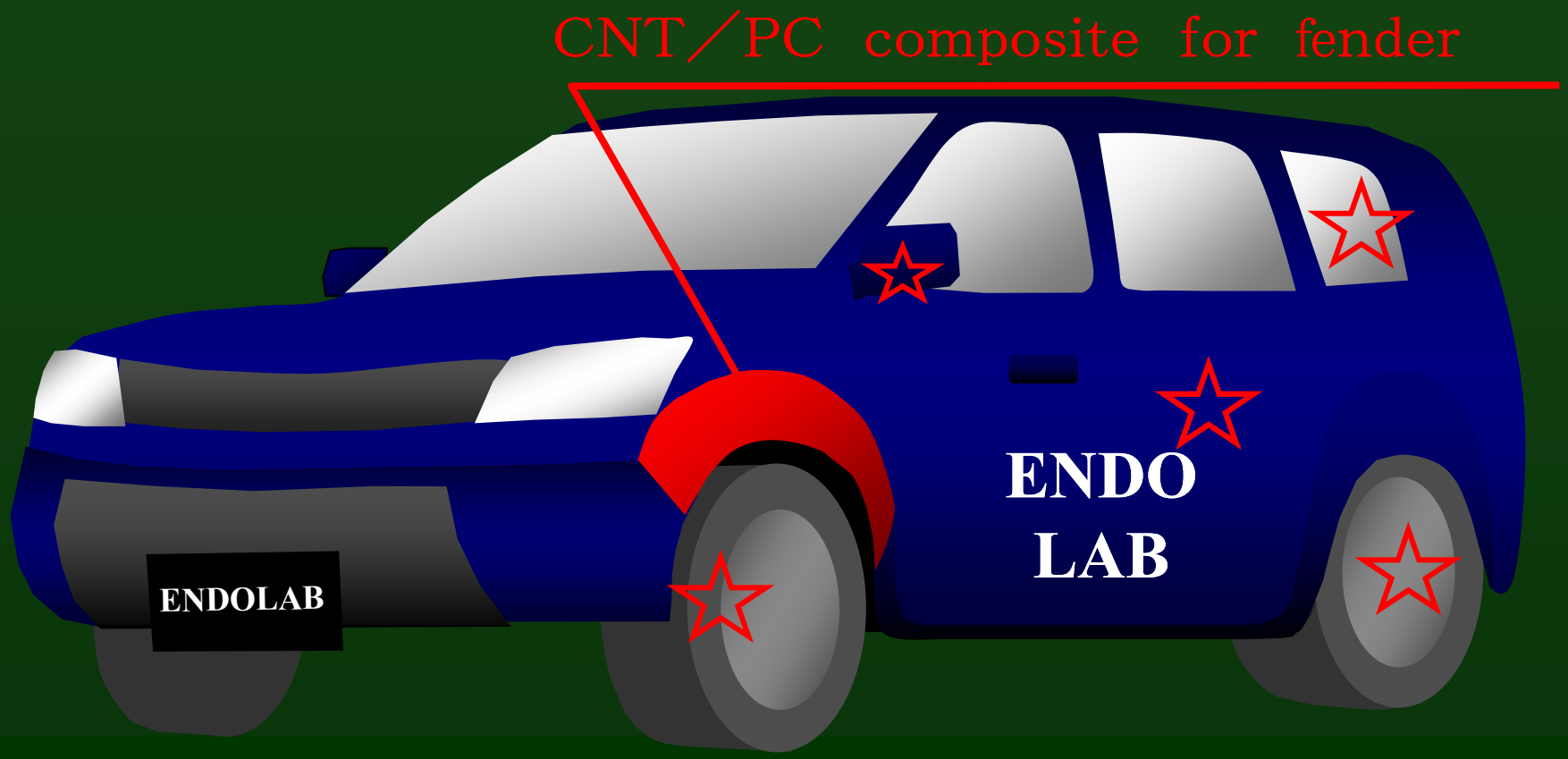
■ツアースピリットMP（400）

Buttスティッフによる弾きのよさ、高弾性カーボンファイバーによるロートルク。さらに、補強層に衝撃強度に優れたカーボンナノチューブ採用で、軽量ながらカウンターバランス設計を実現することでヘッドが利くシャフトとして完成しました。

■MP シャフト硬さ分布



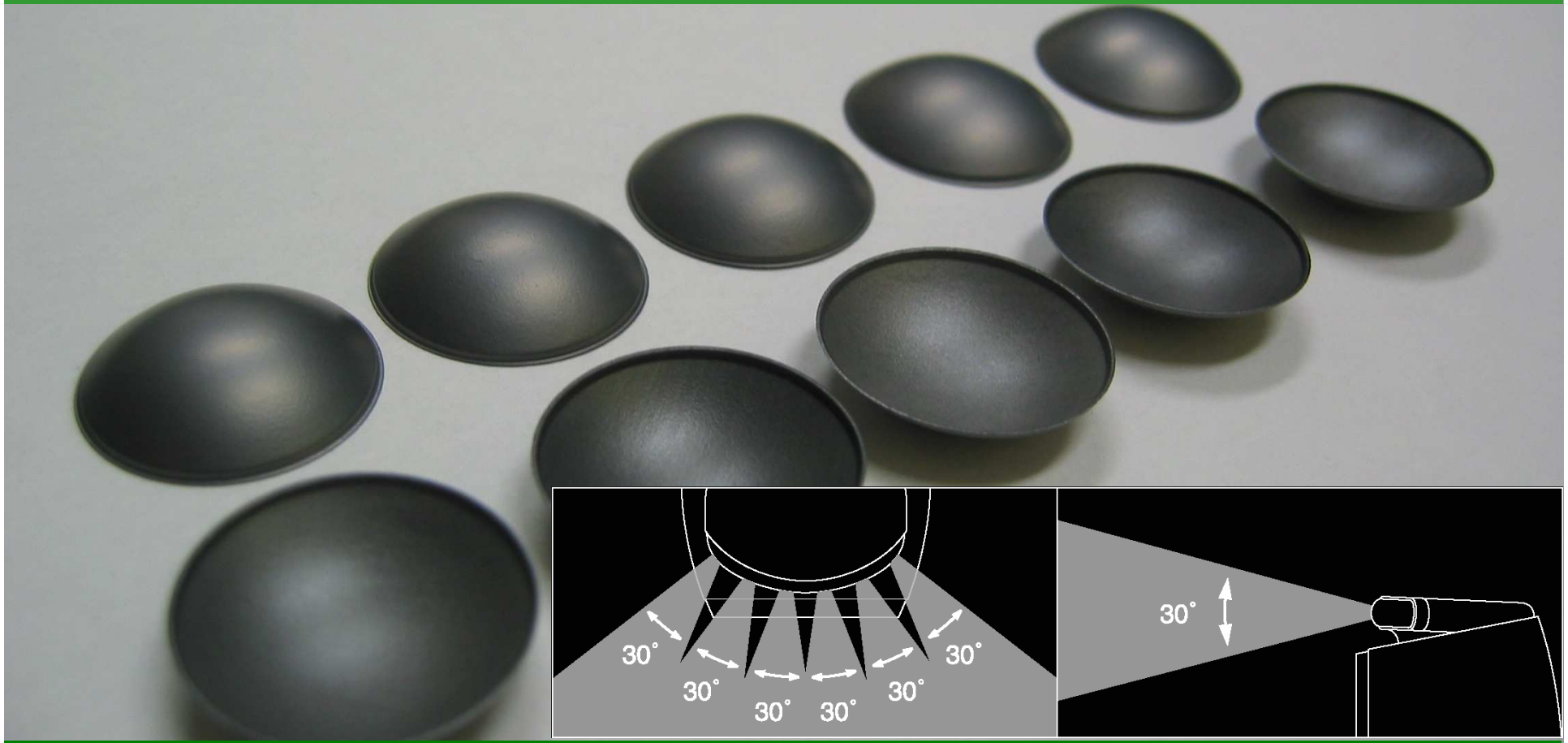
http://www.golfersland.net/mp001/lineup/f_mp001.html



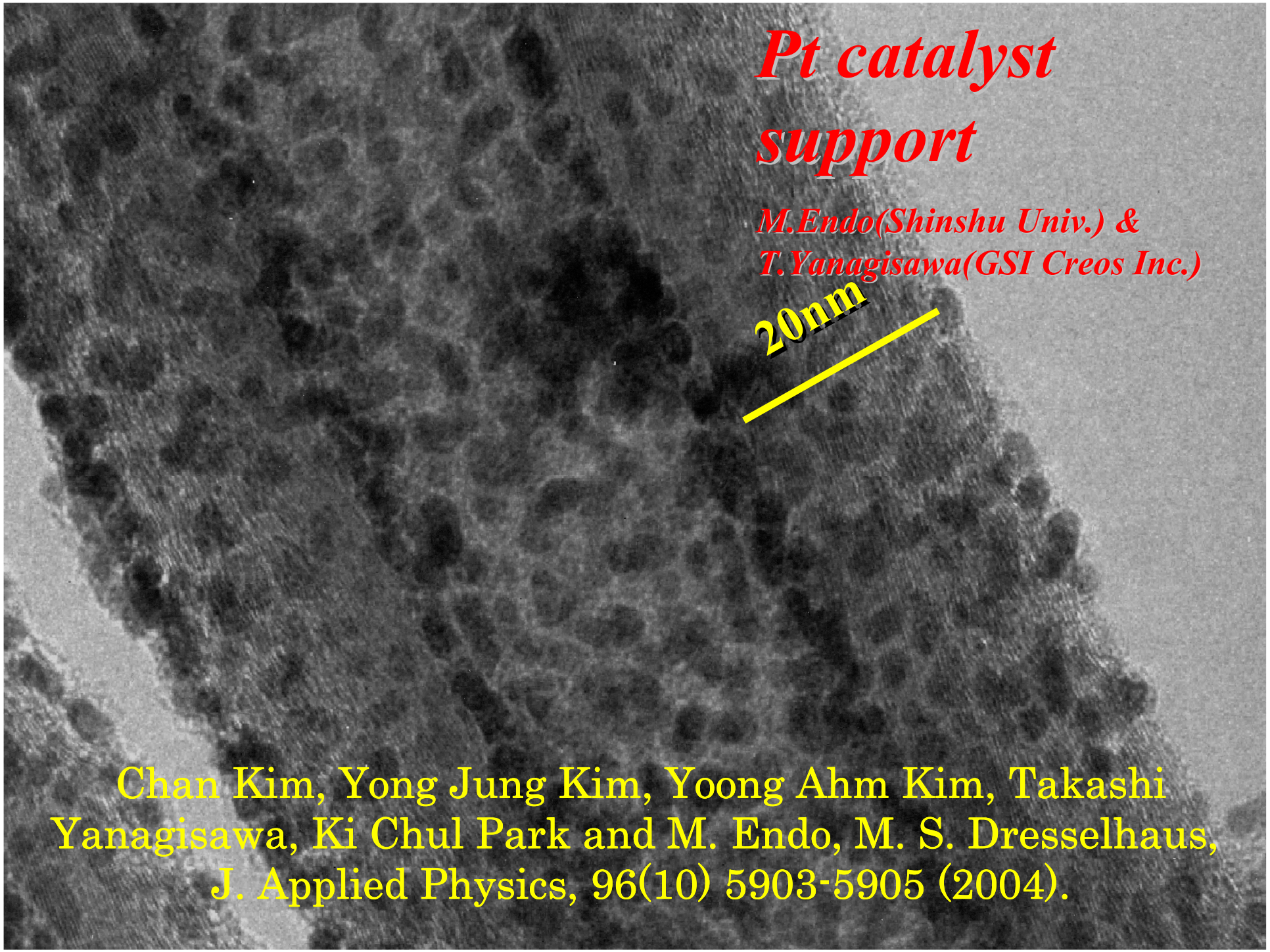
CNT composite (plastics and metals) for promoting the light weighting and recycling in motor vehicle industry

Super tweeter of Carbon NT／C composite

~Realize the feeling of live atmosphere~



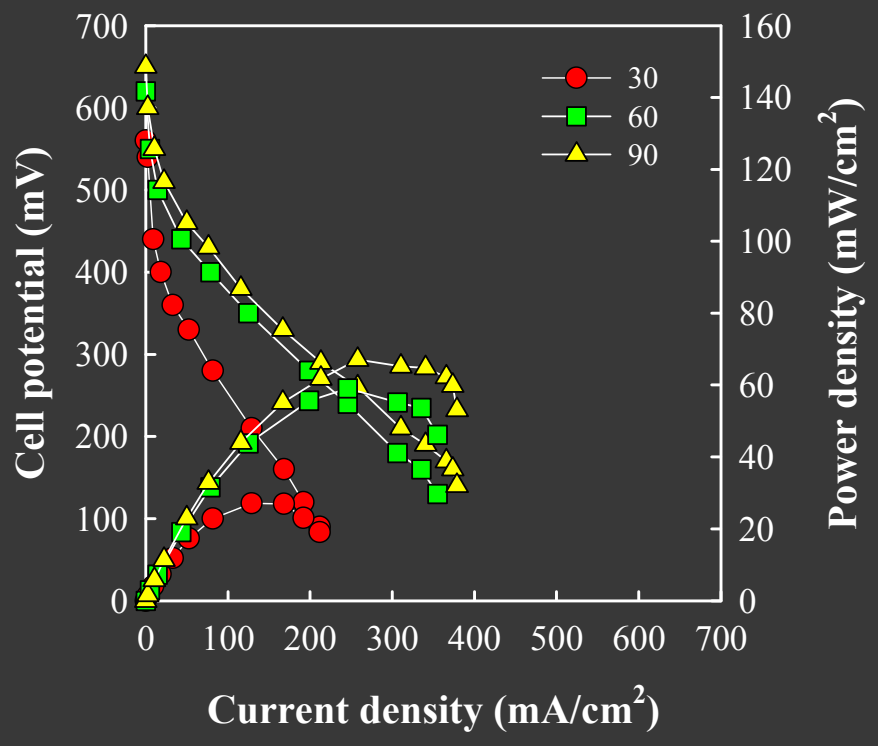
GSI Creos co ltd, Mitubishi pencil co. ltd, M. Endo



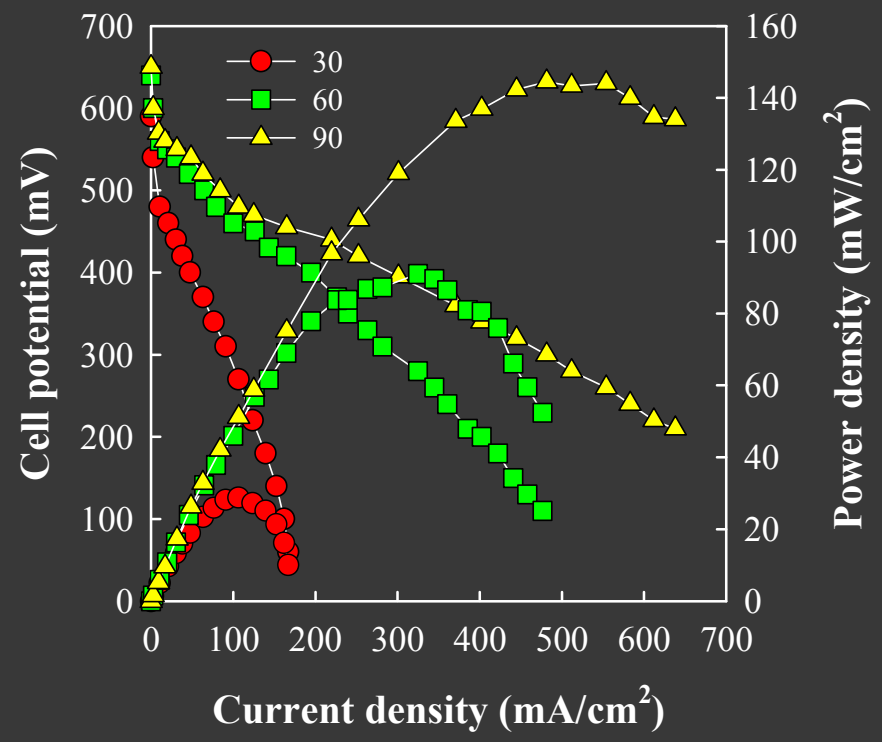
Chan Kim, Yong Jung Kim, Yoong Ahm Kim, Takashi Yanagisawa, Ki Chul Park and M. Endo, M. S. Dresselhaus, J. Applied Physics, 96(10) 5903-5905 (2004).

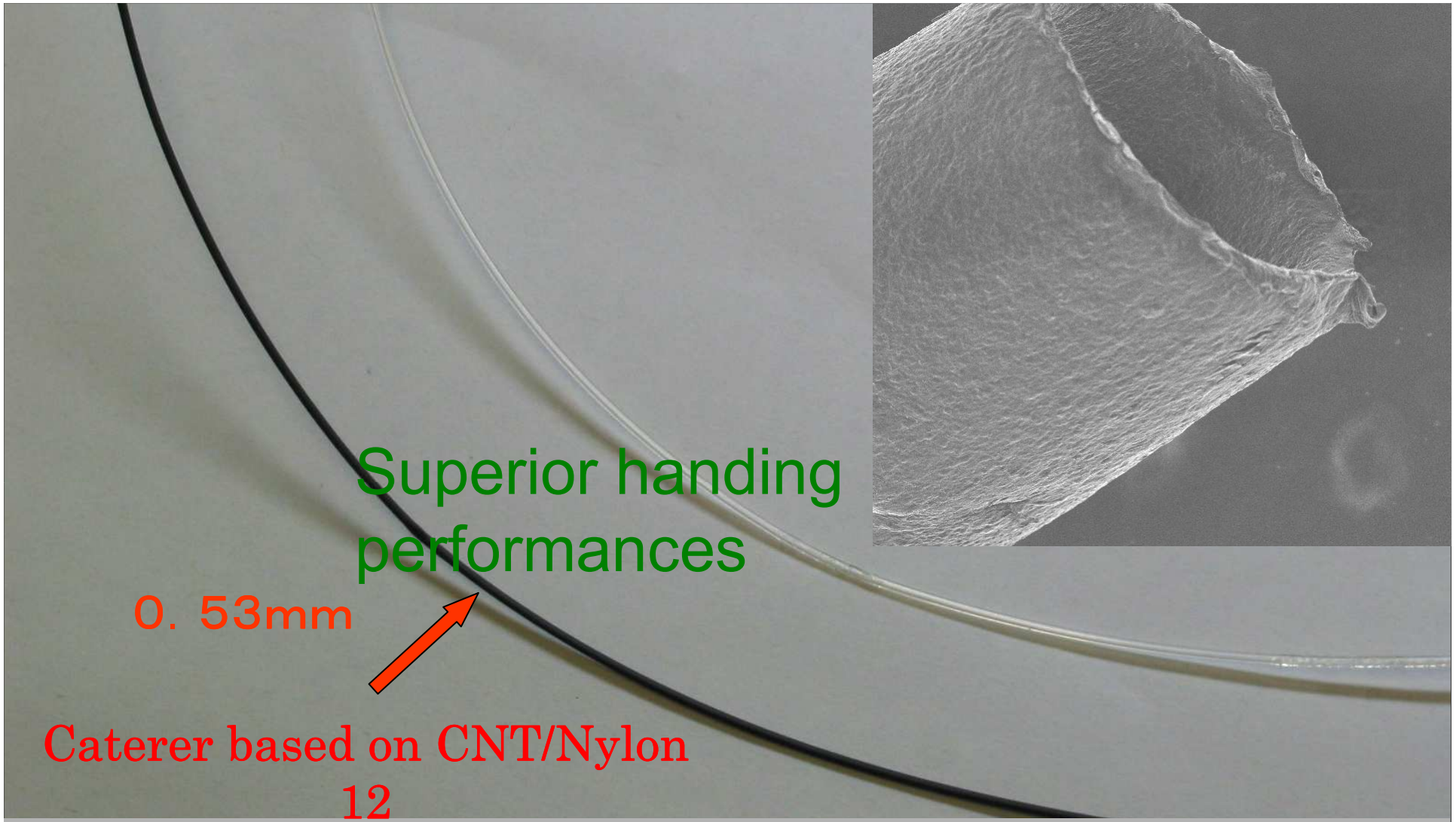
Results of single-cell test

Carbon Black (XG-72)



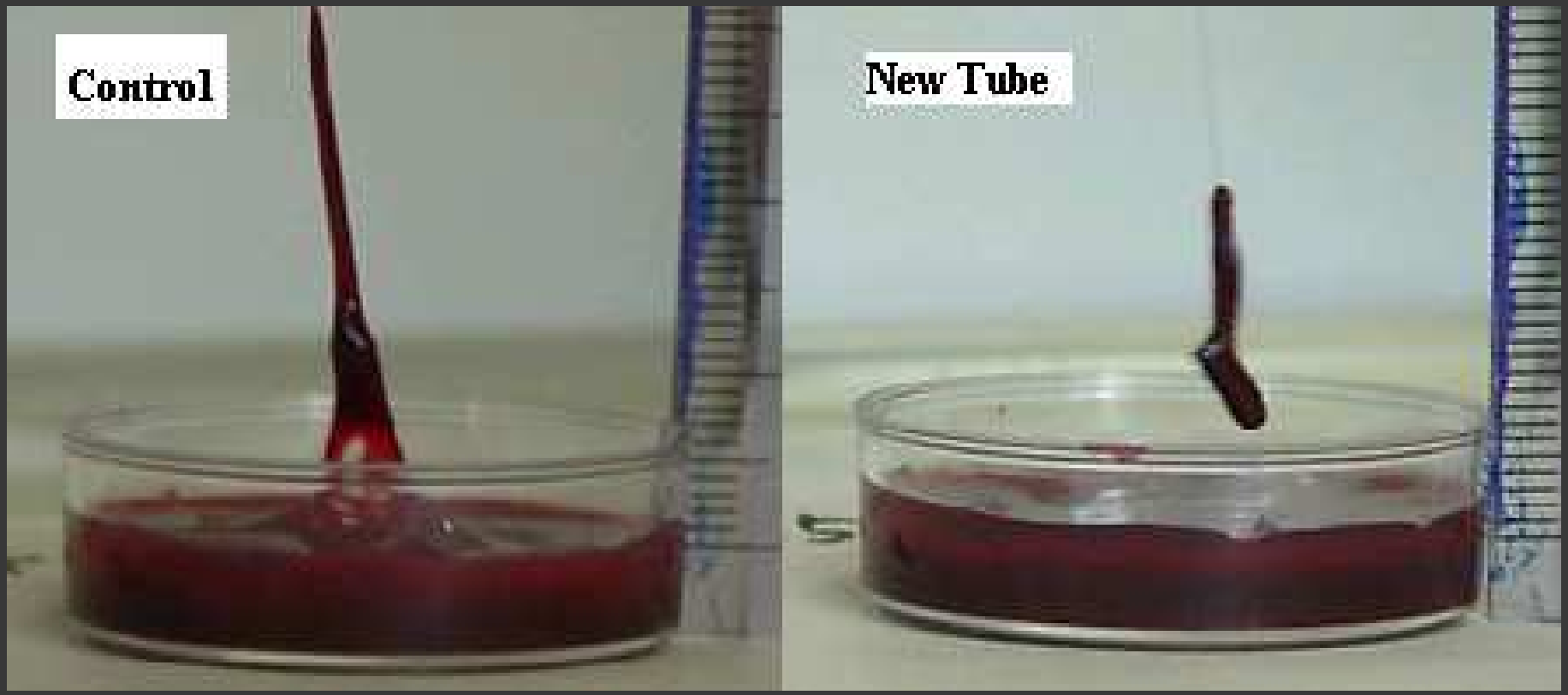
Carbon Nanotube (CUP-Stacked)





M. Endo,et al.: Thrombogenicity and Blood Coagulation of a Micro-Catheter Prepared from Carbon Nanotube-Nylon Based Composite
Nanoletters, 5(1), 101-106 ,2005

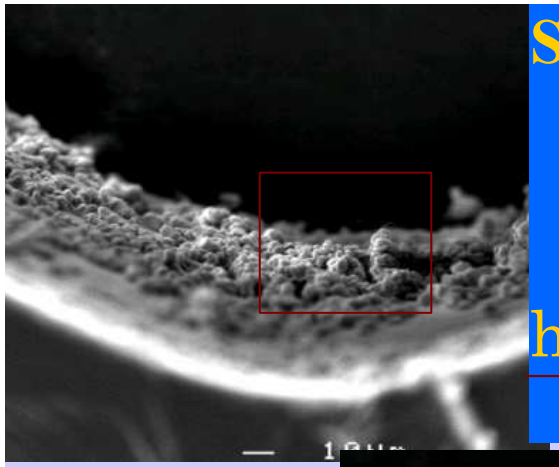
in vitro Experiment

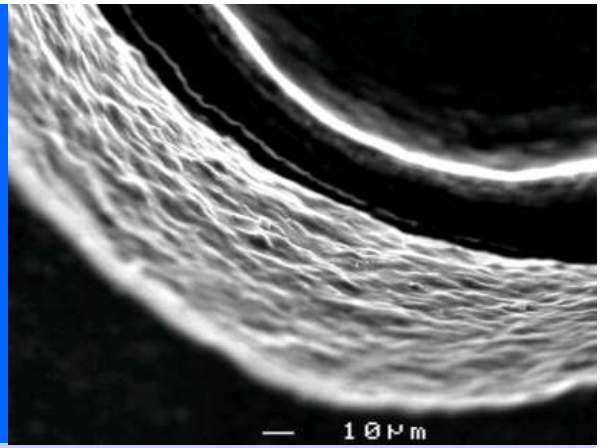


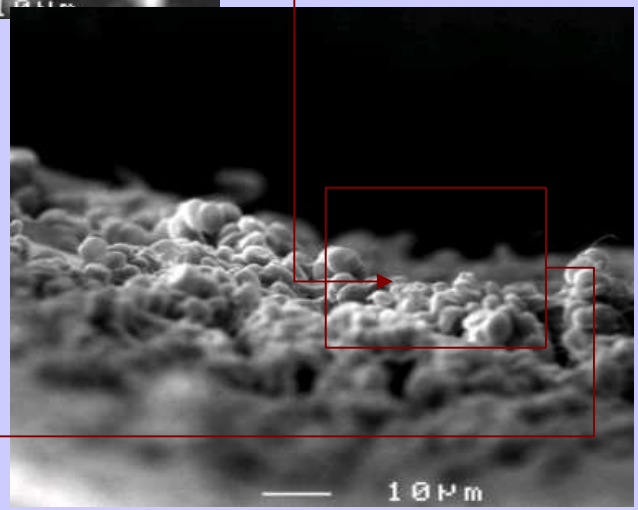
Comparison of blood reaction (coagulability and fibrin deposition) to control tube and new tube, when those were lifted up 60 min after immersion in canine blood.

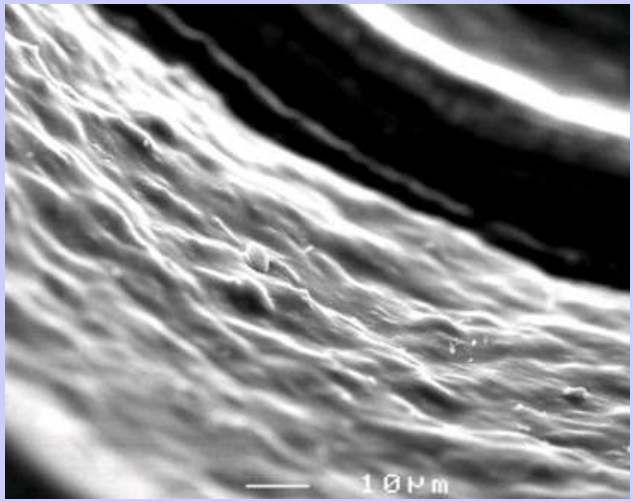
Surface of the catheter observed by SEM

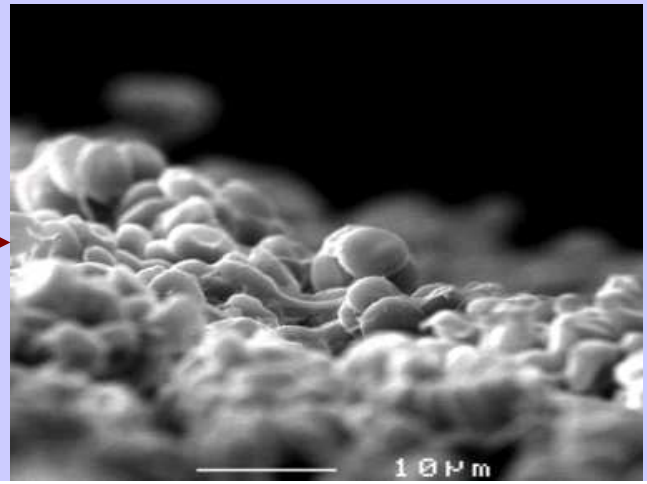
(in canine blood for 1 hour)

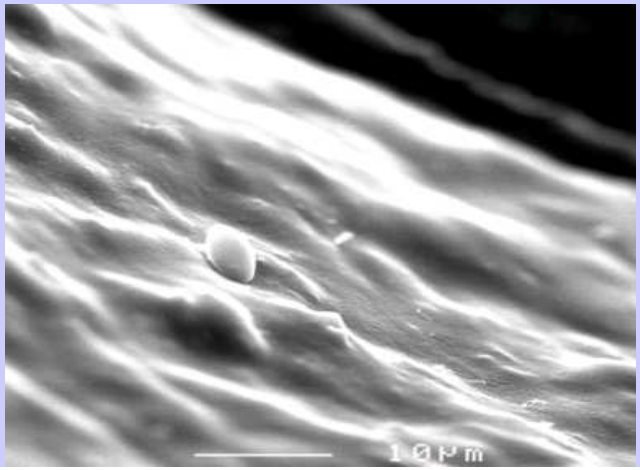


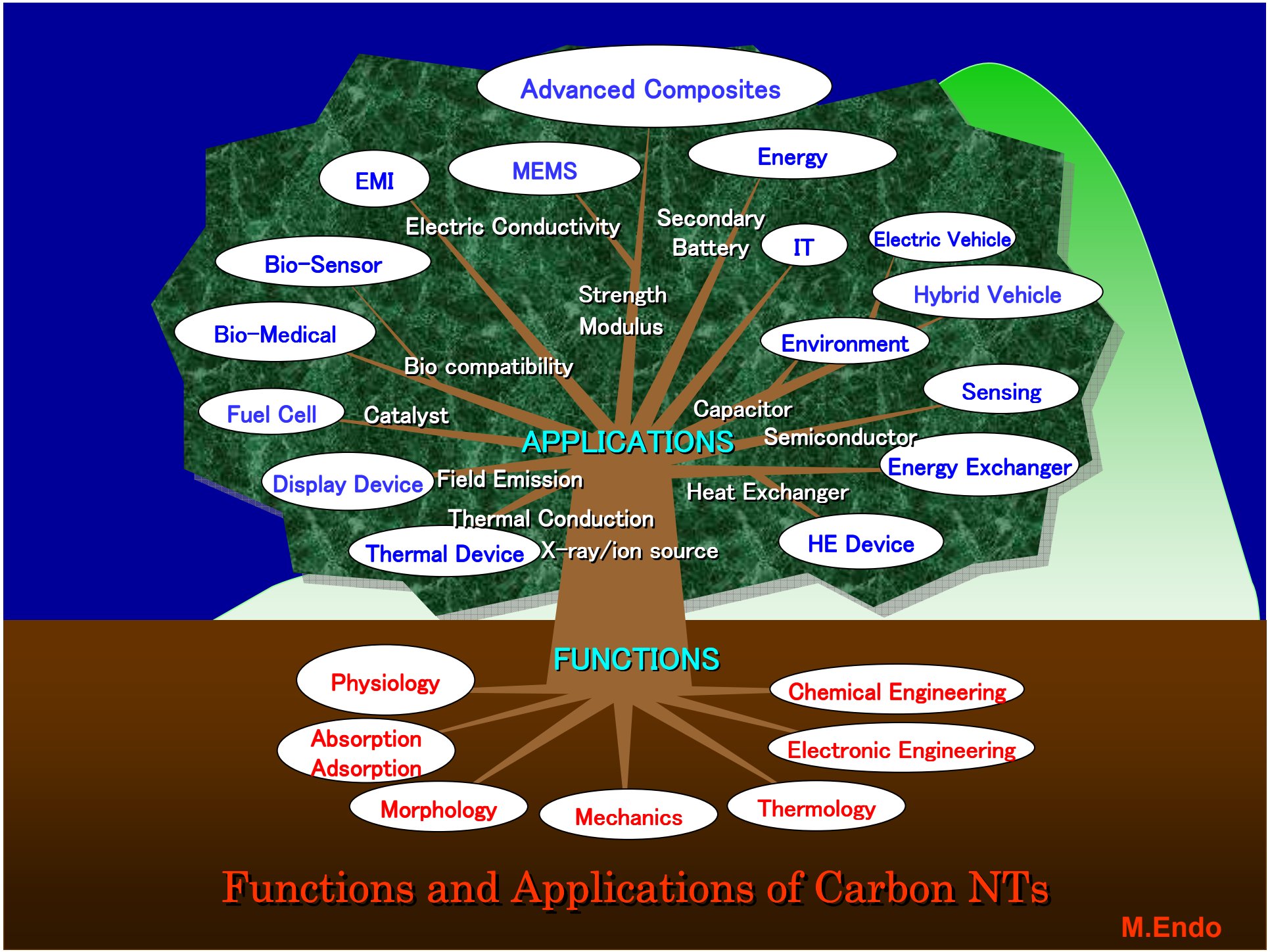












Functions and Applications of Carbon NTs

M.Endo