[After Charles-Amable Lenoir, Wikimedia Commons]

Fibrous Nano and Advanced Materials

Asmus Meyer-Plath

Federal Institute for Occupational Safety and Health (BAuA), Berlin

Unit 4.5 - Particulate Hazardous Substances, Advanced Materials

meyer-plath.asmus@baua.bund.de

baua:

[After Charles-Amable Lenoir, Wikimedia Commons]

Pandora with her box
full of plagues (and hope)

(The plagues were meant to compensate for
Prometheus' intellectual property theft
of heavens' fire science for mankind.)

[Greek Mythology]

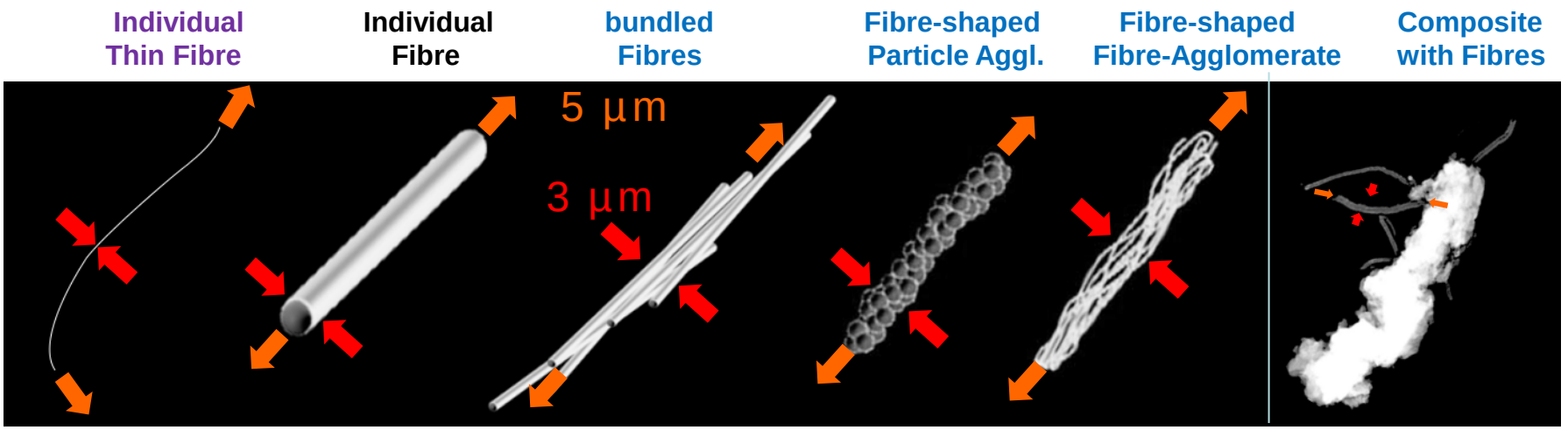
[After Charles-Amable Lenoir, Wikimedia Commons]

Pandora with her box
full of plagues (and hope)

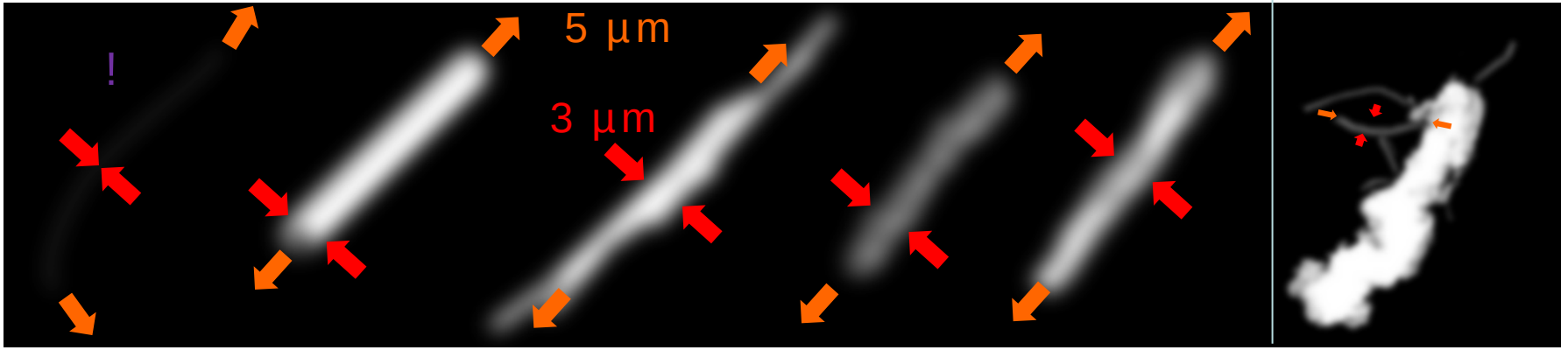
Science is a perpetual source of new hopes and new plagues.

What new plagues will materials science
fill into Pandora's Box?

What is a WHO „Fibre“ ?



A fibre is what looks like a fibre,
so we have to negotiate the image resolution !



Compact and also non-compact objects as well as thin nano fibres (below standard resolution) are to be considered as WHO fibres !

baua:

How big is the world of
nano and advanced fibres types
to be tackled by OSH?

Currently,

Nanofibre Technology Push exceeds Market Pull

Material-inventing developers bear responsibilities!

Technology push

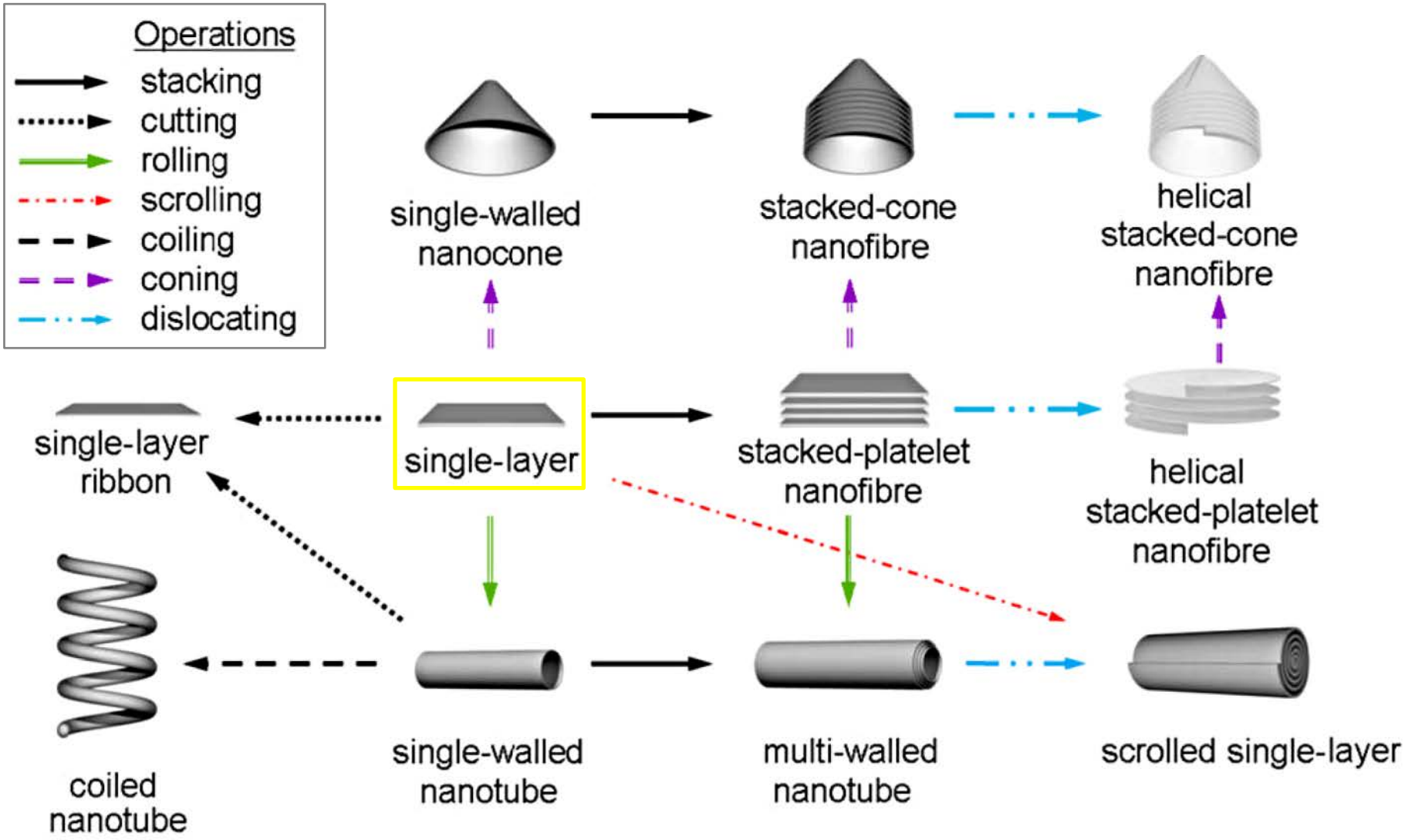
The possibilities of materials scientists to develop new fibres variants are

GIGANTIC!

How big is the nanofibre cosmos already?

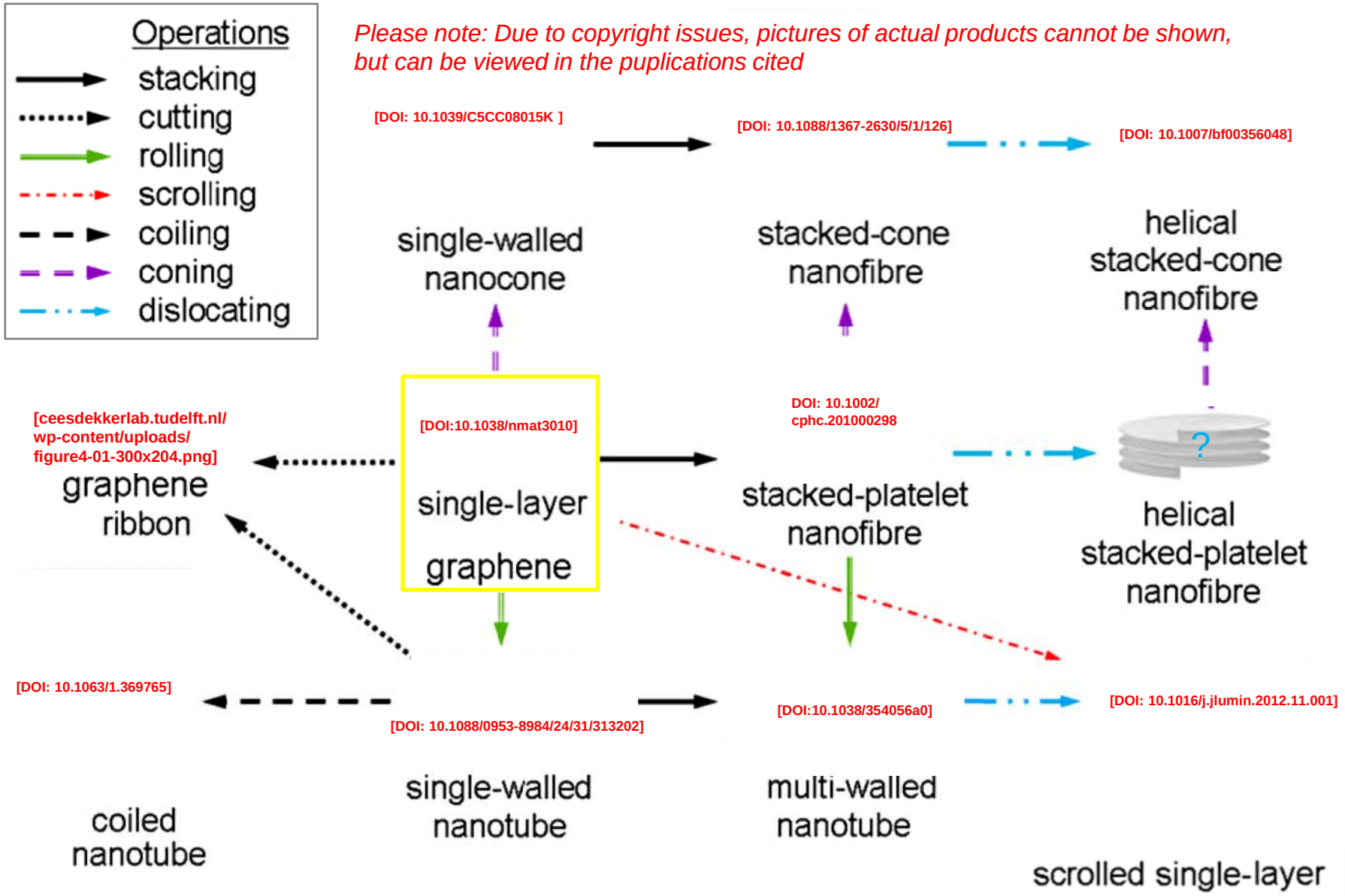
The "Grammar" of Fibrogenesis from Flat Materials

like C, GO, BN, MoS_2, WS_2, $NbSe_2$, ...



Inspired by [I. Suarez-Martinez et al. Nomenclature of sp(2) carbon nanoforms. Carbon 50(3):741-747 (2012). DOI: 10.1016/j.carbon.2011.11.002]

The Products of Fibrogenesis from Carbon



How were these nanoforms synthesized?

5 Major synthesis concepts for new nano and advanced fibre plagues (and hopes) for Pandora’s Box !

[BAuA]

Filling Pandora's Box

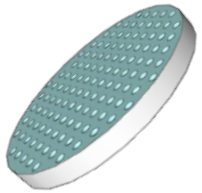
Part 1

Nanofibres from Porous Templates

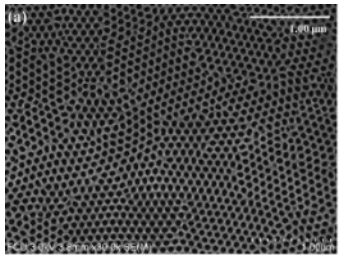
Nanoporous templates shape substances into fibres
(Catalyst-free synthesis)

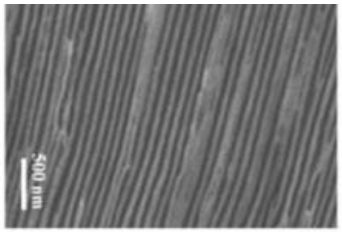
baua:

Nanofibres from Porous Template Filling

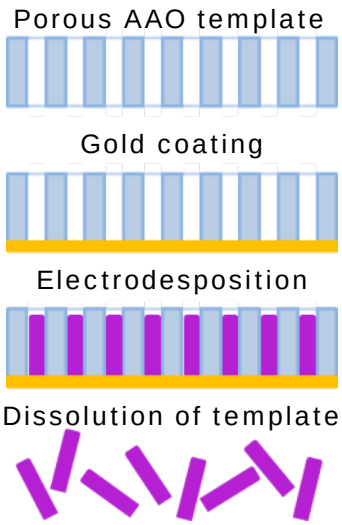


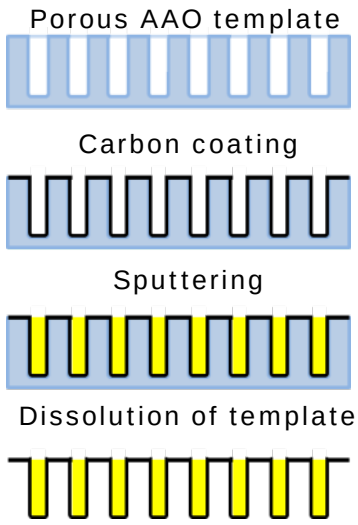
Concept: Electrochemical or PVD filling of AAO nanopores followed by dissolution of the template





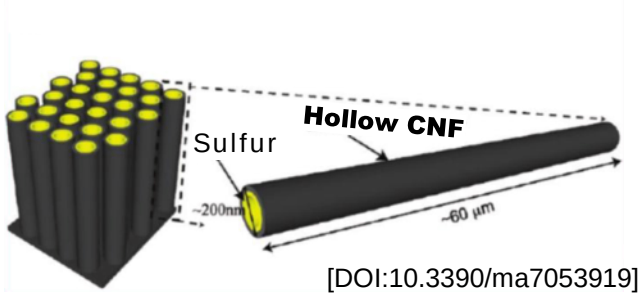
[Xue Y. et al., Sci. Adv. 2015,1(8) e1400198.]





Variants:

- ALL metals possible
- Semiconductors
- Carbon
- Core-shell structures



[DOI:10.3390/ma7053919]

Maturity: R&D level

β-In_2S_3 Nanowires

Fig 1d from [DOI: 10.1007/s11671-009-9357-z]

For picture see [DOI: 10.1039/B614300H]

Applications:

- Catalysis
- Composites
- Energy storage
- Electronics

Potential Hazard	
	• Biopersistence • Respirable fibres • Possible Rigidity • Catalyst impurities • Chemical composition

[BAuA]

Filling Pandora's Box

Part 2

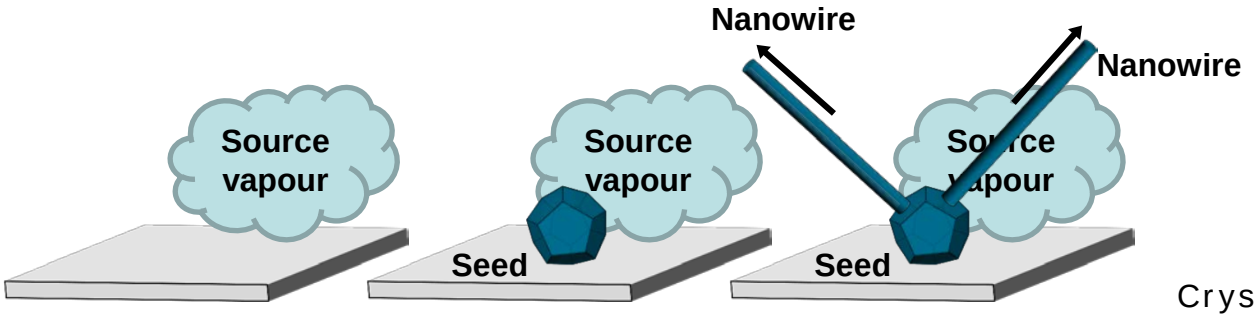
Nanofibres from Crystal Growth

A substance forms crystal seeds that induce fibre formation

baua:

Crystalline Nanowhiskers from Vapour Synthesis

Concept: Synthesis of seeds that induce fibre crystallisation from vapour



Crystalline whiskers of submicron diameter

Maturity: Commercial and R&D

Applications: Catalysis, Composites, Solar cells, Electronics

Variants: Tungsten, Silicon, ZnO, ZnS, GaSe, SiC, SiN, ...

Tungsten

GaSe

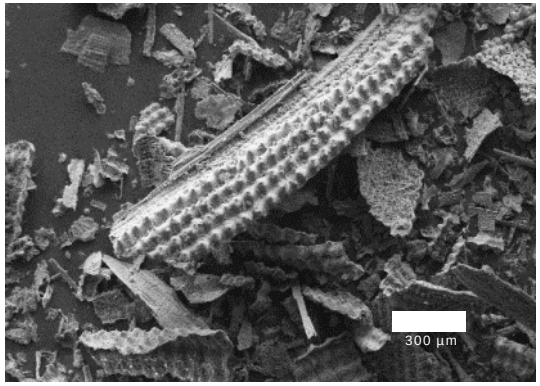
For picture see:
[DOI: 10.1088/0957-4484/18/35/355306]

For picture see:
[Hou L.-Z. et al., Trans. Nonferrous Met. Soc. China 23(2013) 2323-2328.]

Potential Hazard	
	• Biopersistence • Respirable fibres • Rigidity possible • Catalytic activity • Chemical composition • Crystallinity

Highlight:
SiC Whiskers for Composites

Concept: Synthesis by carbo-thermal reduction of SiO_2
Rice husk ash is used as low-cost precursor



[A. Meyer-Plath]

1400°C

See figure 5 from 10.1111/j.1151-2916.1991.tb06856.x

"a very high modulus rigid rod nanotube which is unbreakable at supplied lengths."
[Manufacturer information]

Maturity: Mass production level

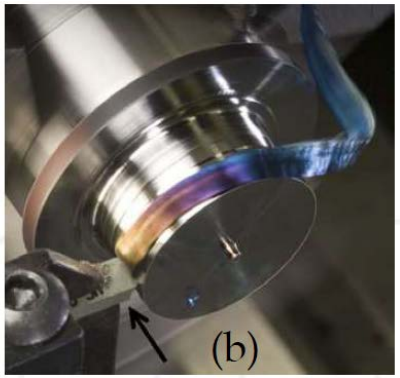
Applications:

High-volume applications as reinforcing agents in composites:

Ceramics (Al_2O_3, ZnO, SiN, ...),
Polymers, Fluoropolymers,
Metals, 3-D-Printing,
Scratch-resistant non-stick Cookware

"SiC whiskers/microfibers are not a hazardous substance according to Regulation (EC) No. 1272/2008 (CLP). […] However, some agencies list SiC whiskers/microfibers as potential carcinogens, based on limited experimental animal data that suggests a carcinogenic effect. Any potential carcinogenicity of SiC whiskers/microfibers is limited to chronic overexposure of dry, respirable dust. No data exists for humans."
[ACM SiC Whisker Microfibre MSDS]

Non-brittle cutting tools made of Al_2O_3 - SiC_w composites



[www.intechopen.com/books/properties-and-applications-of-silicon-carbide/properties-and-applications-of-ceramic-composites-containing-silicon-carbide-whiskers]

[BAuA]

Filling Pandora's Box

Part 3

Nanofibres from Catalytic Growth

Nanoscale catalyst particles
decompose and crystallize precursors into fibre shape

Most prominent

Catalytic CVD for Carbon Nanotube Mass Production

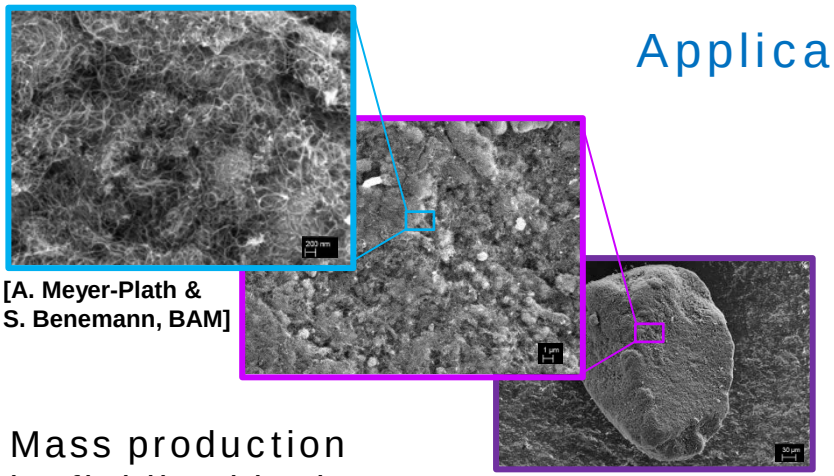
Concept: Catalyst particles decompose the precursor and shape the fibre

See Figure 7 from
[DOI: 10.1021/nl0624824]

[DOI:10.1038/354056a0]

Catalyst → H_xC_y → H_xC_y

Maturity: Mass production level



[A. Meyer-Plath & S. Benemann, BAM]

Mass production by fluidized bed processing

Applications: Catalysis, Composites, Li-Ion-Batteries, Transparent electrodes, Heating, EM Shielding

Variants:
Most industrial MWCNTs are thinner than 20 nm.

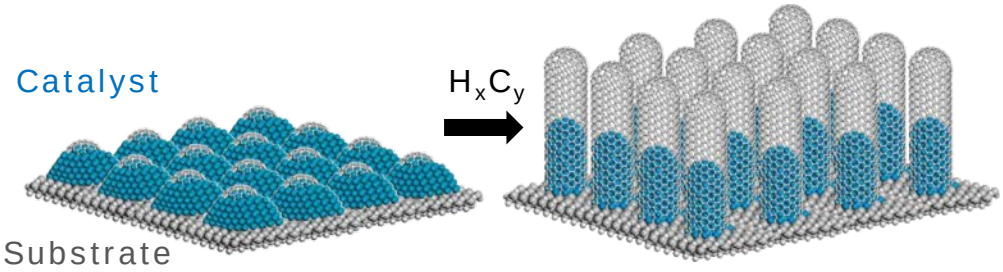
Potential Hazard	
	• Biopersistence • Respirable fibres • Rigidity possible • Catalyst impurities

Better Control

Vertically-aligned Carbon Nanotubes

Inspired by [DOI: 10.1021/nl0624824]

Concept: Catalyst-coated flat substrates



For picture see:
[DOI: 10.1039/C2JM32270F]

Maturity: Commercial production level

Multi-walled CNT carpets

For picture see:
[DOI: 10.1088/0957-4484/23/30/305401]

Single-walled CNT carpets

For picture see:
[Hata K. et al., 2004 Science 306, 1362]

Variants:

Catalyst size and process duration allow controlling wall number and tube length.

Most industrial MWCNTs are thinner than 20 nm.

Application Highlight:
VA-CNTs in nano-enhanced carbon fibre composites

[http://www.n12technologies.com]

$CF_{\perp}$
Prepreg Layer

VA-CNT
Resin

CF_{II}
Prepreg Layer

VA-CNT

[http://hdl.handle.net/1721.1/71233]

VA-CNT transfer
to CF prepreg

[http://hdl.handle.net/1721.1/71233]

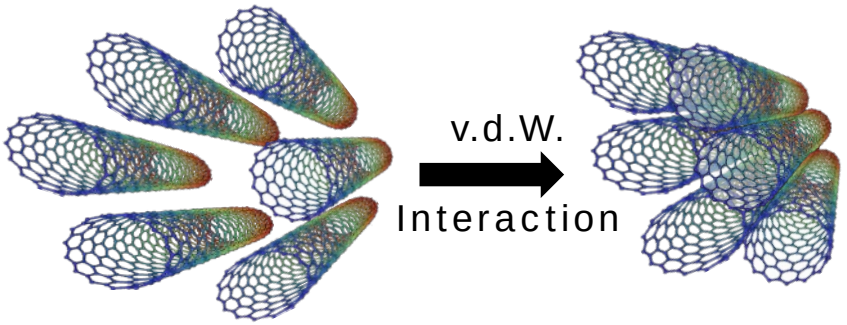
Company claims:

- Industrial-scale production of VA-CNTs
- Improved thermal vertical conductivity
- Interlaminar reinforcement for reduced delamination

... Manufacturing, failure testing and recycling need exposure control expertise

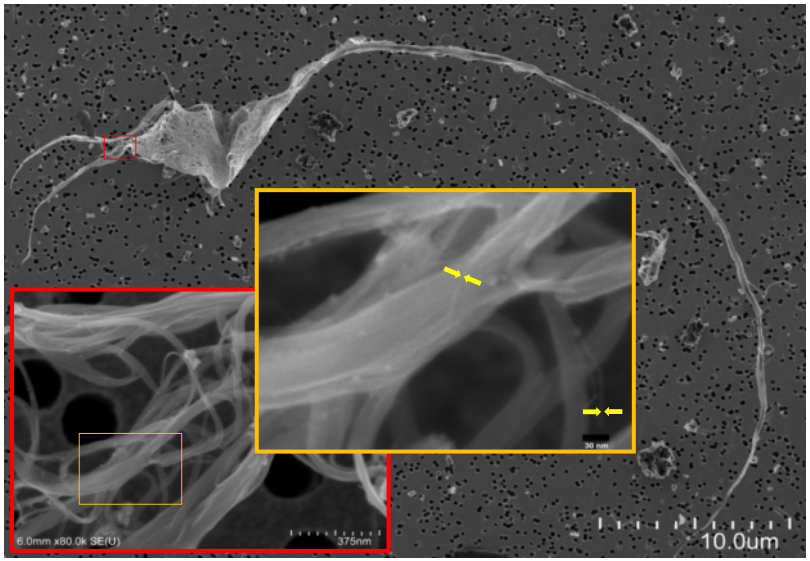
Hierarchic Nanofibres: Bundled Nanofibres

Concept: -1- (Spontaneous) (unintended) bundling of highly flexible NFs
-2- Intentional spinning of NFs



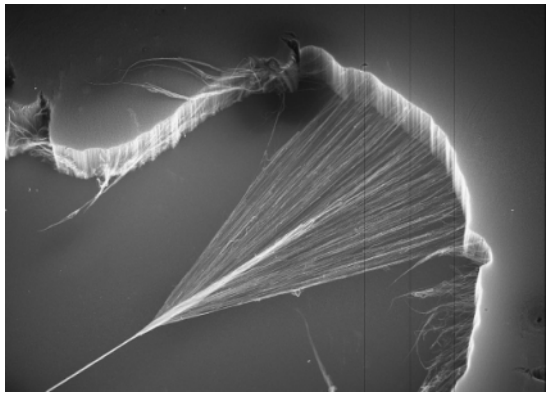
Minimizing
free volume

Maturity: Commercial (unintended) and pilot (yarn and braid) production



[BAuA]

picture see [http://www.photon.t.u-tokyo.ac.jp/~maruyama/ACCVD/TEM1.jpg]



[CSIRO ScienceImage 1074]

Applications: Ultra strong yarns
Light-weight cables

Potential Hazard	
	• Biopersistence
	• Respirable fibres
	• Collective rigidity
	• Catalyst impurities

baua:

[BAuA]

Filling Pandora's Box

Part 4

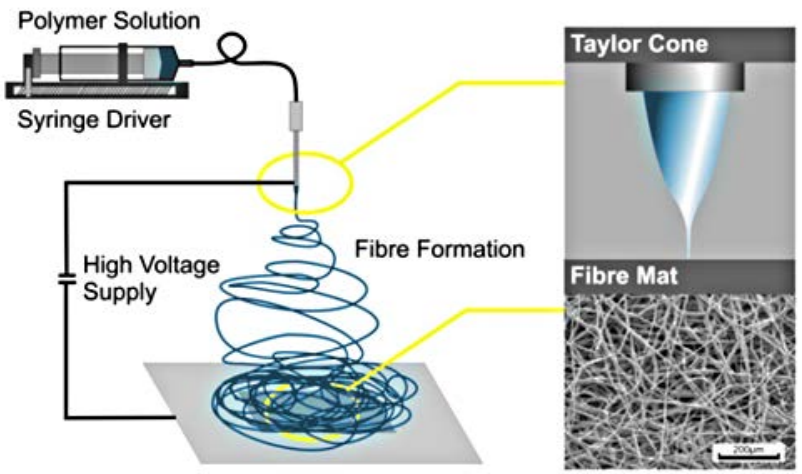
Nanofibres from Electrospinning

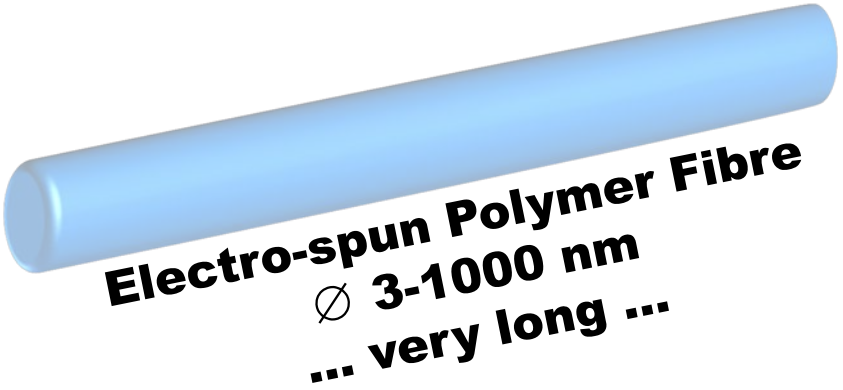
Electric fields shape solutions and melts into fibres

baua:

Electrospun Nanofibres

Concept: Strong electric fields draw solutions or melts into fibres





Maturity: Mass production level

[A. Meyer-Plath]

[Kehren, D., et al. (2014). Polymer 55(9): 2153-2162.]

Variants:

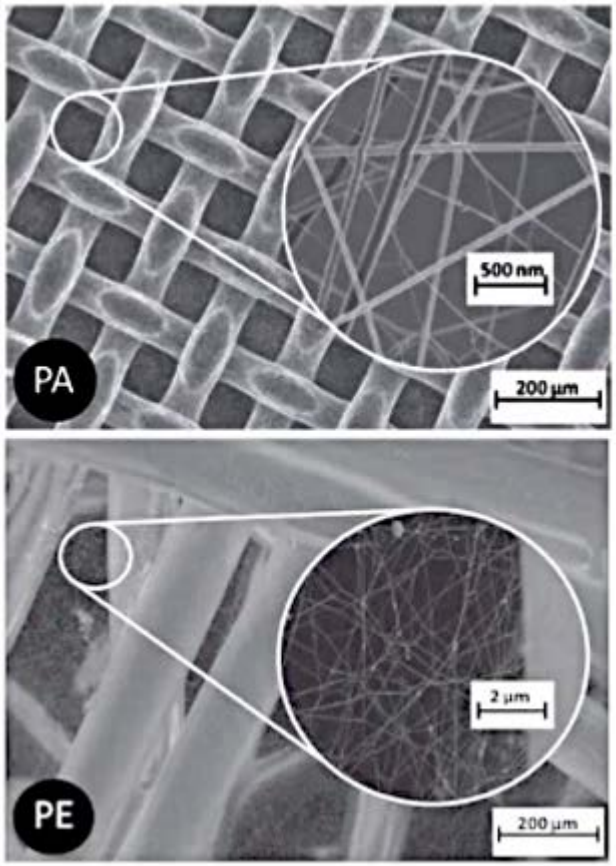
- Many different polymers

Applications:

- Nonwovens
- Filtration
- Composites

Potential Hazard	
	• Biopersistence • Respirable fragments • Rigid fragments • Chemical composition

Application Highlight:
Electrospun Polymer Nanofibres for Filters



[DOI:10.3791/50492]

"An innovative technology redefines for dust removal from welding, cutting and coating processes. Nonwovens with a nanofiber lining assure efficacious filtration of ultra-fine, difficult-to-handle dusts and smokes."

"Filters are highly resistant to chemicals, microbiologically inert and meet all hygiene requirements."

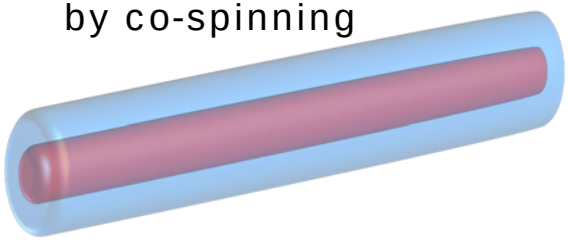
[Company Information]

... Handling and recycling may release respirable fibres

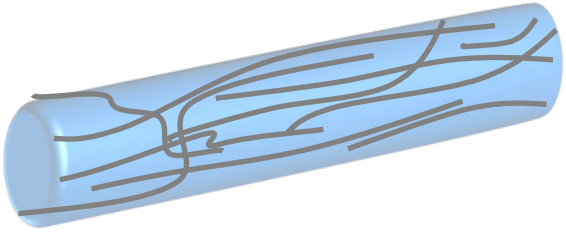
Electrospun Composite Nanofibres

Concept: Spinning of suspensions and co-spinning of polymer solutions

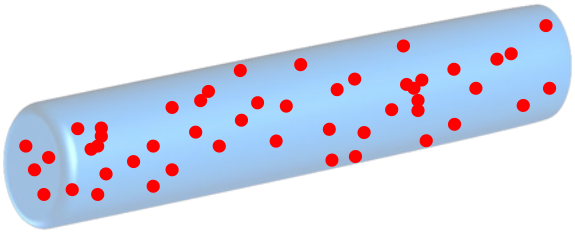
Chemical Filling
by co-spinning



Carbon Nanotube Filling



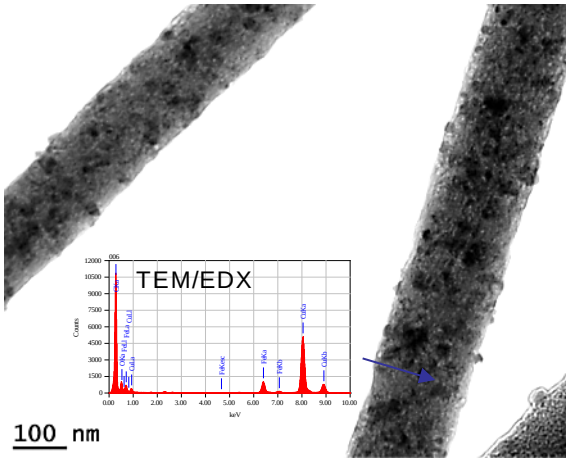
Nanoparticle Filling



Maturity: Research level

[www.nitta.co.jp/en/?post_type=newtech&p=7519]

[Kehren, D., et al. (2014). Polymer 55(9): 2153-2162.]



[A. Meyer-Plath, BAM]

2 µm

Applications:

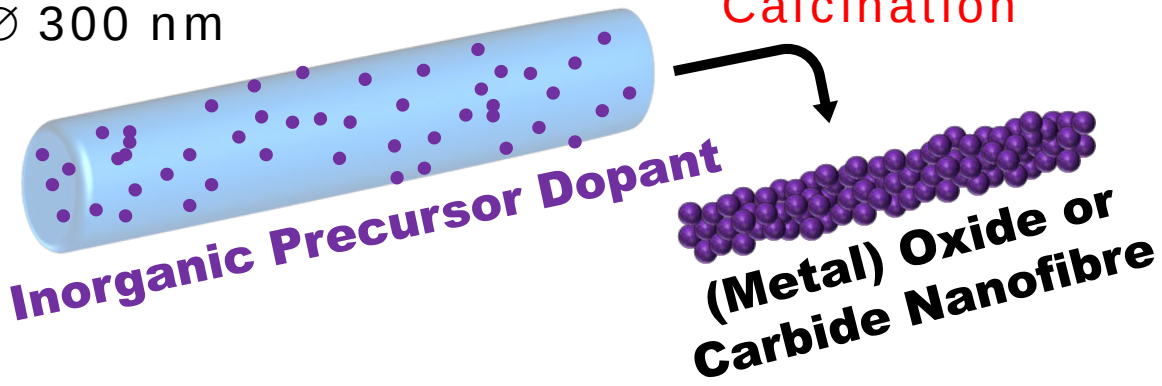
Pheromon loading for biocide application	Conductive polymer High modulus fibres	Catalytically active and precursor fibres ...

Potential Hazard			
	• Biopersistence • Respirable fragments • Rigid fragments • Chemical action	• Biopersistence • Respirable fragments • Rigid fragments	• Biopersistence • Respirable fragments • Rigid fragments • Catalytic action

Doped Polymer-derived Inorganic Nanofibres

Concept: Spinning of doped polymer solutions followed by calcination

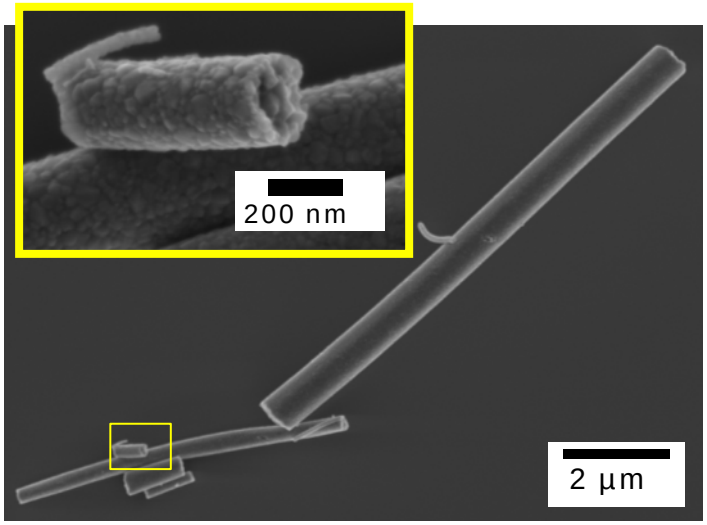
Electro-spun
Polymer Nanofibre
∅ 300 nm



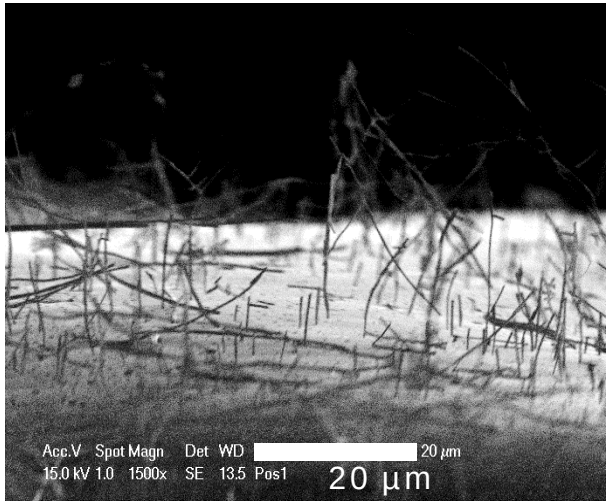
Variants:

- Silicon carbide
- Silicon oxide
- Aluminium oxide
- Titanium oxide

Maturity: Research level



[BAuA]



[BAuA, BAM]

Applications:

- Catalysis
- Composites

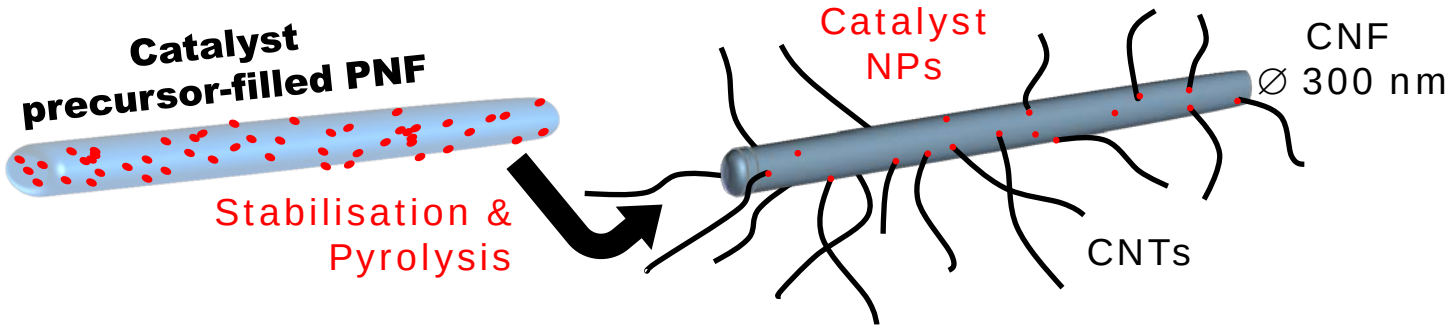
Potential Hazard

- Biopersistence
- Respirable fragments
- Rigid fragments
- Catalytic action

baua:

Hierarchic Fibres – CNT-overgrown CNFs

Concept: Electro-spinning of doped polymers followed by stabilisation, pyrolysis and CVD growth



Variants:

- Microscale CF
- Nanoscale CF

Applications:

- Composites
- Ultrasound

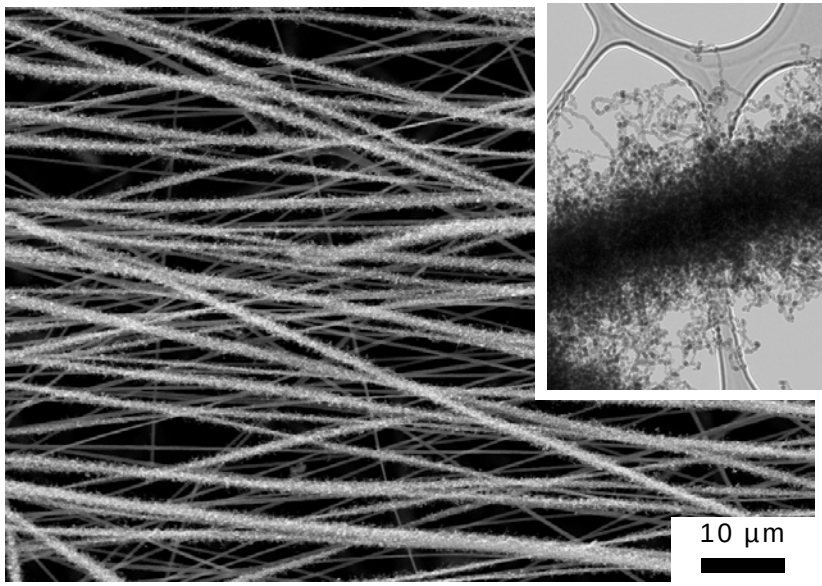
Maturity: Research level

PAN
+
Catalyst Precursor

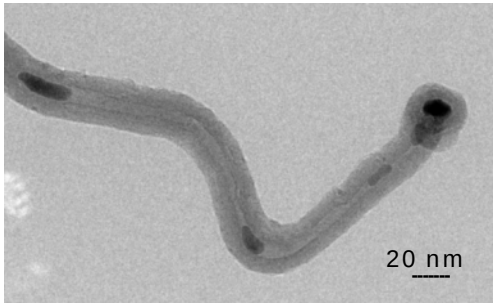
Carboni-zation ↓

CNF
+
C_2H_4

cCVD →



[A. Meyer-Plath, BAM]



[I. Dörfel, BAM]

Potential Hazard

- Biopersistence
- Respirable CNT release
- Nanoparticle release
- Rigid fragments
- Catalytic action

[BAuA/Fox]

Filling Pandora's Box

Part 5

Nanofibres from Self Organisation

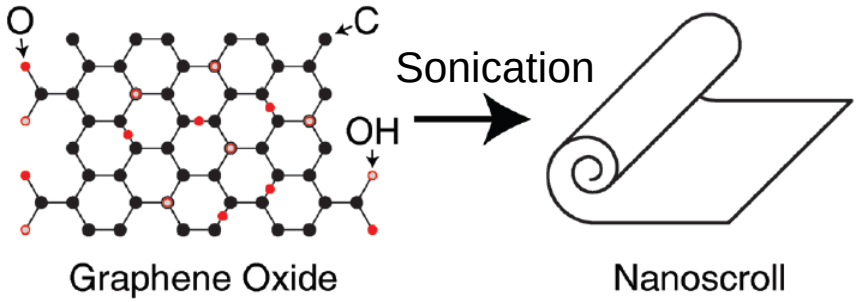
Transformation of flat material to fibres

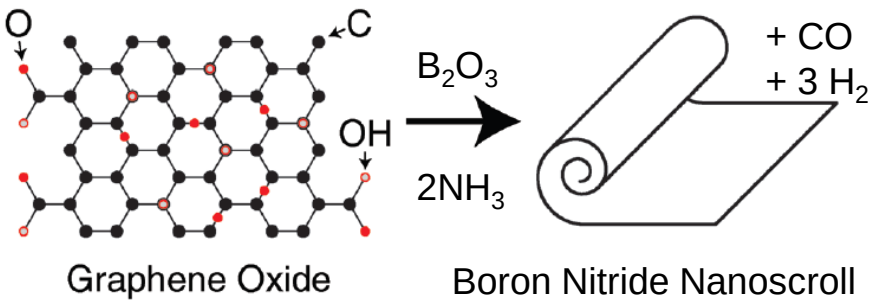
baua:

Similar, but different

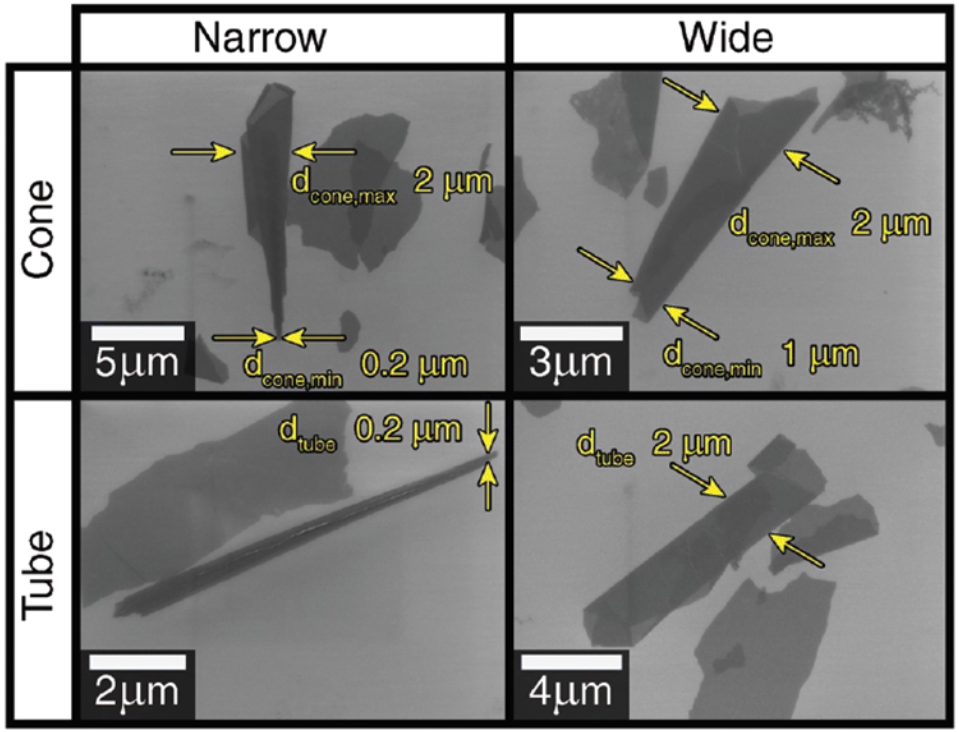
Nanoscrolls, not Nanotubes

Concept: Self-organisation of layered materials to nanoscrolls





Maturity: Advanced research level



[Amadei, C. A., et al. (2016). Nanoscale 8(12): 6783-6791.]

Applications: ???

Ma, C. Y., et al. (2011). Chem Asian J 6(6): 1331-1334.

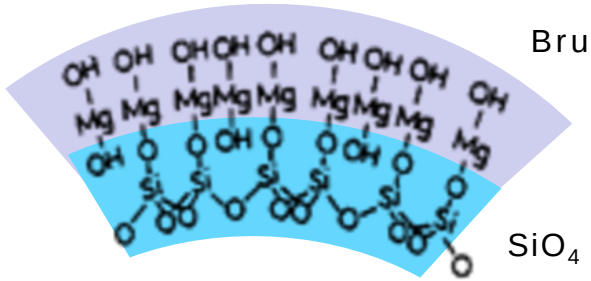
Potential Hazard	
	• Biopersistence • Respirable fibres • Rigidity possible • Reactive surface • Chemical composition

How many hazardous fibre types will OSH experts have to face?

An old Acquaintance

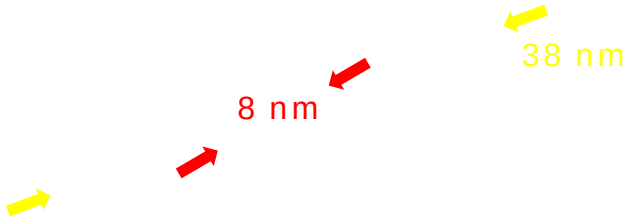
Chrysotile is a (bundled) Nanoscroll

Nature´s Concept:



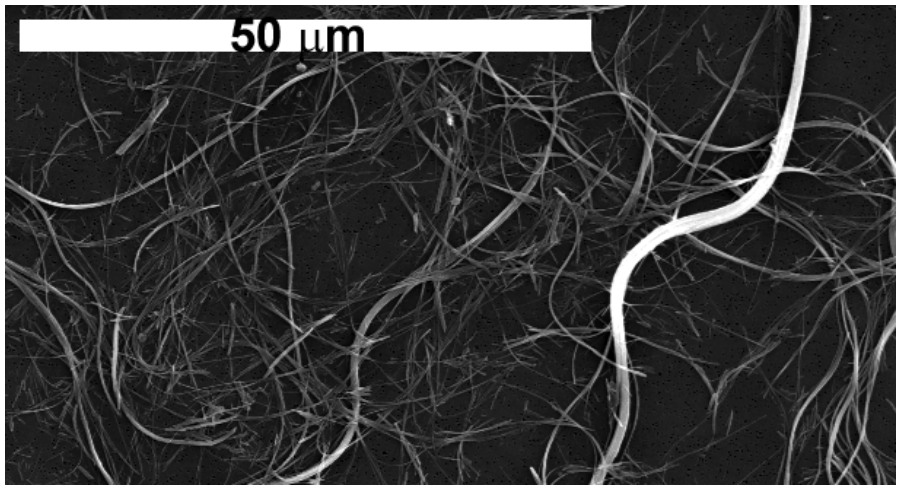
Double layer system
with internal stress but
limited bending elasticity

Realisation:



See Figure 12 from:
[Lotz, B. and S. Z. D. Cheng (2005). Polymer 46(3): 577-610.]

Chrysotile UICC B



[usgsprobe.cr.usgs.gov/picts2.html]

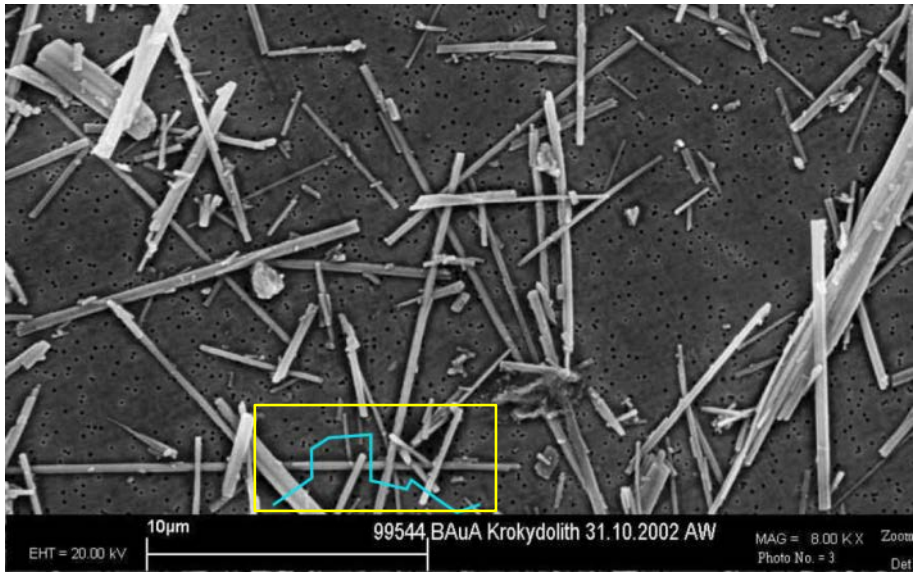
Mean inner diameter ≈ 8 nm
Mean outer diameter ≈ 38 nm
Maximum reported o.d**. ≈ 85 nm**

Chrysotile is a Nanofibre!

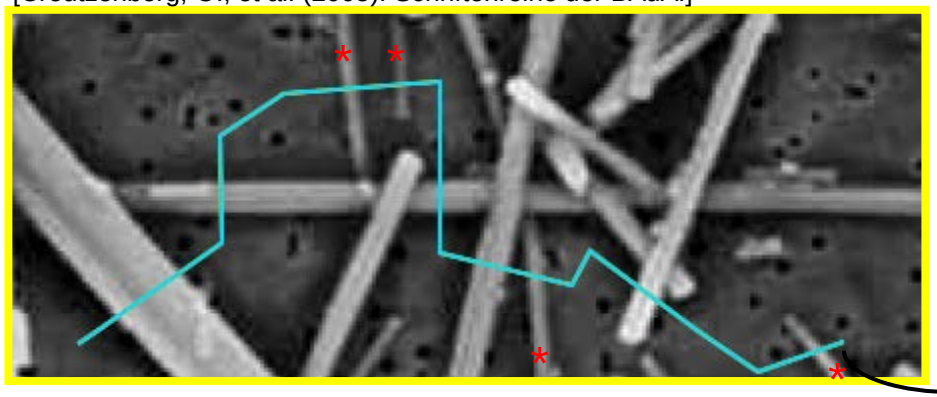
Potential Hazard	
	• Biopersistence • Respirable fibres • Rigidity possible • ROS

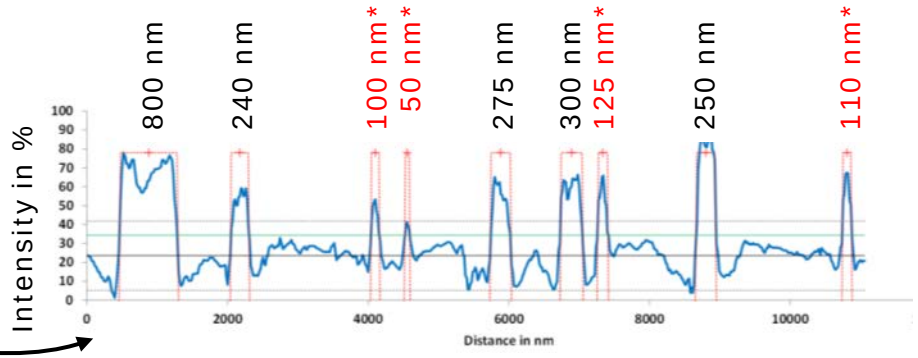
Many Asbestoses contain Nanofibres

thinner than 200 nm which are often not counted



[Creutzenberg, O., et al. (2005). Schriftenreihe der BAuA.]





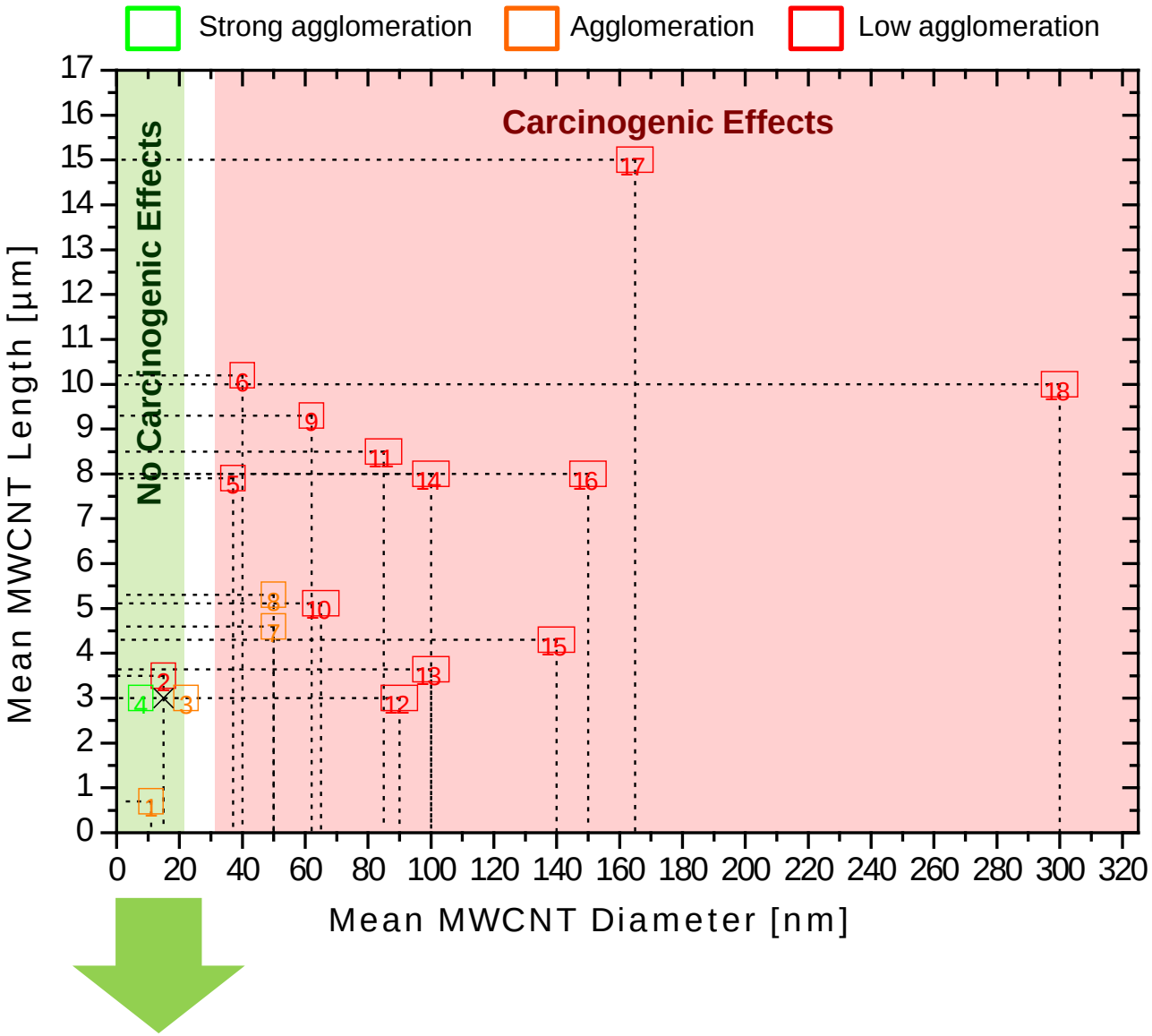
Confirmed for :

- Chrysotile, UICC B
- Amosite, UICC
- Anthophyllite, UICC
- Winchit-Richterit, Libby
- Krokydolith, BAuA

What are the health effects of nanoscale asbestoses?

Asbestosis Potency

Cancerogenic Effects of Carbon Nanofibres
- Literature on Intraperitoneal Testing -



[1] Muller, J., et al. (2009)
Toxicol. Sci. 110(2): 442-448

[2,17] Murphy, F. A., et al. (2011)
Am. J. Pathol. 178(6): 2587-2600

[3,16] Xu, J., et al. (2014)
Cancer Sci. 105(7): 763-769

[4,7-8,15] Nagai, H., et al. (2011)
Proc. Natl. Acad. Sci. USA 108(49)

[5-6,9,11] Rittinghausen, S., et al. (2014)
Part. Fibre Toxicol. 11: 59

[10,13] Xu, J., et al. (2012)
Cancer Sci. 103(12): 2045-2050

[12] Sakamoto, Y., et al. (2009)
J. Toxicol. Sci. 34(1): 65-76

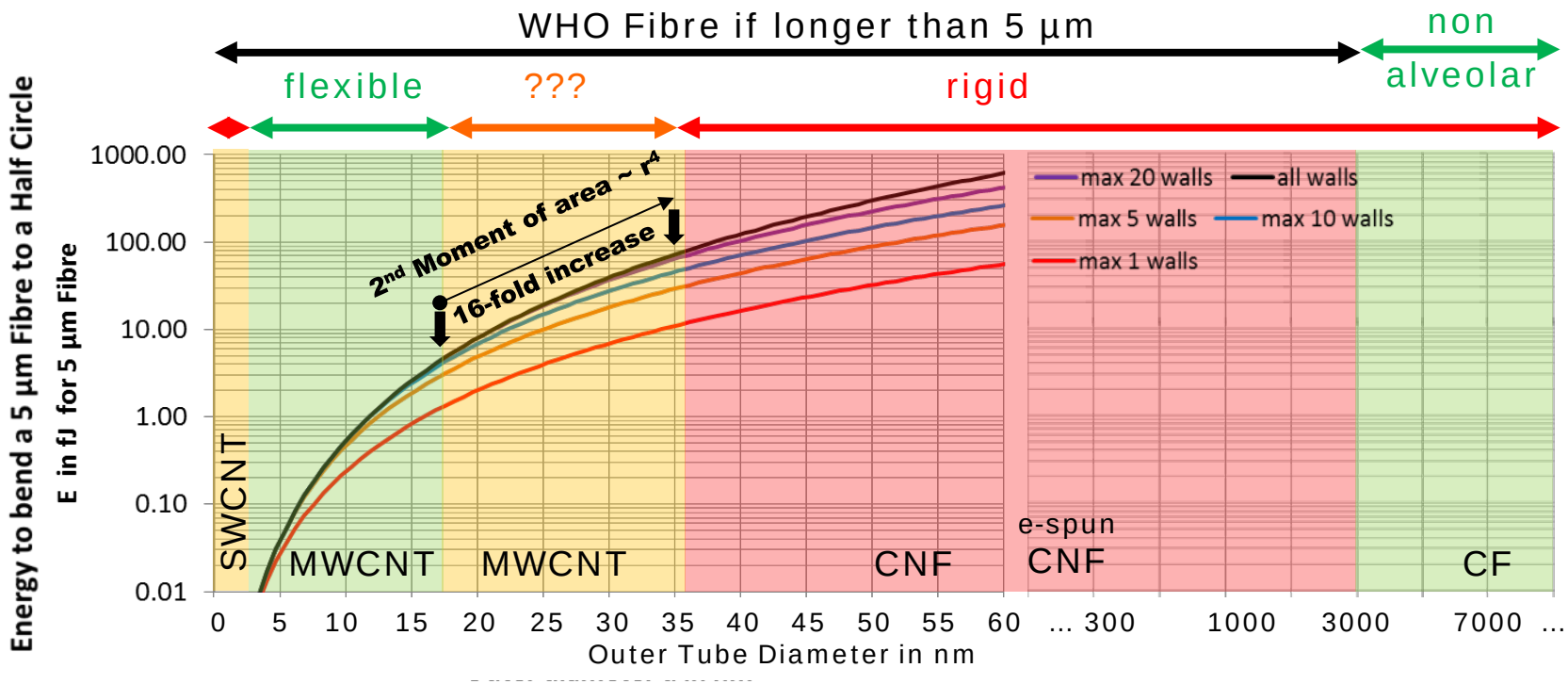
[14] Takagi, A., et al. (2008)
J. Toxicol. Sci. 33(1): 105-116

[18] Sargent, L. M., et al. (2014)
Part. Fibre Toxicol. 11: 3

[F. Herzberg, BfR]

Hypothesis: Nanofibres thinner than 20-30 nm may be safe to use!

Why may thin fibres be safe to use?



[Arias, I. et al. (2008). Phys. Rev. Lett. 100(8): 085503.]

Spontaneous bundling possible ?

Probably flexible. Safe to use ?

Most probably rigid. Must be counted !

Not respi-rable

Open Questions

What is the nanofibre content of asbestoses?

&

Which nano and advanced fibre variants

may have asbestos-like properties?

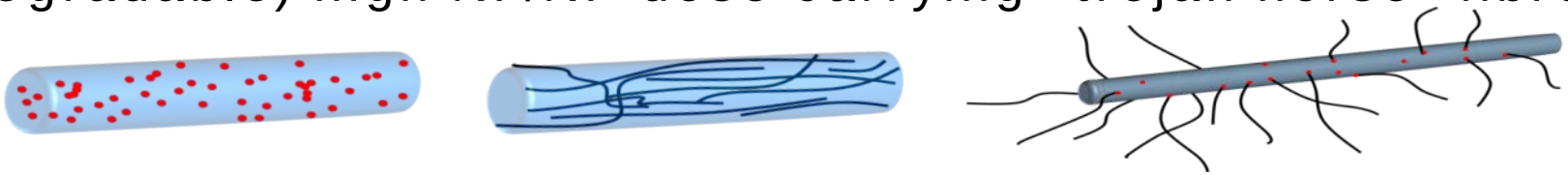
Critical Fibre Morphologies

Respirable, biopersistent and rigid fibres :

- Amorphous or crystalline (semi) metal (oxide) nanofibres

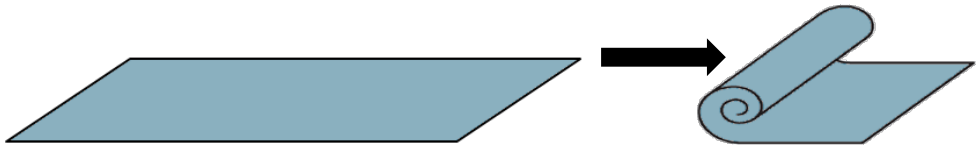
- Respirable electrospun polymer or carbon fibre fragments

- (Degradable) high NF/NP-dose carrying “trojan horse” fibres



- (Unintentionally) formed collectively rigid fibre bundles

- Flat materials (unintentionally) forming nanoscrolls



Conclusions

While asbestos fibres could only be *selected*, nano and advanced fibres can be *designed.*

This should be used to minimize fibre-related hazards!

Material developers thus need:

- Guidance and governance
- Training on fibre hazards and safer-by-design principles.

Sufficiently flexible nanofibres may be safer by design they may behave not like fibres but granular particles.

What means “sufficiently” flexible exactly?

Asbestos-like nano and advanced fibres

like electrospun Polymers, CNTs, Ag-NWs, SiC_w, SiN_w, …

are on the market!

The use of such materials in not exposure-controlled environments like building sites is a matter of serious concern.

More information is needed on:

- Annual production volumes
- Main material variants
- Mass applications
- Life-cycle safety.

For innovative products, such information is hard to obtain.

Sustainable innovations require collaboration with (O)SH experts.

[Photo credit: Tony Rich, www.adorama.com]

Pandora's Box of the 20th century

Thank you !

baua: