NANOTECHNOLOGY BUSINESS CREATION INITIATIVE

The CLH classification of Multi-Walled Carbon Tubes was proposed by Germany.
The ECHA's RAC (Committee for Risk Assessment) has been discussing the CLH classification of Multi-Walled Carbon Tubes.
We can submit comments until September 4, 2022.
The NBCI submitted comments on the German proposal that the carcinogenicity classification is "1B".

NANOTECHNOLOGY BUSINESS CREATION INITIATIVE

8th July 2022

Objective, fair and consistent hazard classification of MWC(N)T to facilitate the safer innovation

Executive summary

There are various methodology for carbon nanotubes (CNTs) production, and the CNTs have diverse morphology and physicochemical properties even if the names are the same. This is the essential issue of nanomaterials management differ from chemicals management. In view of this point, we comment on the CLH report on multi-walled carbon tubes including multi-walled CNTs (MWC(N)T).

- **The stipulation of the length of CNTs entering the lungs requires further discussion, considering the particle size / fiber length entering the lung.**
- **Only MWNT-7 should be classified as Carc.2 of GHS classification in harmony with the International Agency for Research on Cancer (IARC) monograph on CNTs.**
- **We concern a little haste regulatory mandate of MWC(N)T only with diameter, length and aspect ratio ranges.**

We hope the hazard classification of MWC(N)T could facilitate the safer innovation enabling SDGs by taking into consideration specific feature of MWC(N)T objectively.

1. Introduction

To carry out social responsibilities as carbon nanotube (CNT) manufacturers and users, CNT sub-committee of Nanotechnology Business Creation Initiative (NBCI) Japan comments on the CLH report on multi-walled carbon tubes including multi-walled carbon nanotubes (MWC(N)T) defined by BAuA. We hope our knowledge about the MWC(N)T and comments on the CLH report are useful for formulation of better regulatory measures and for enabling Sustainable Development Goals （SDGs）with safer innovation.

2. On intercorrelation between diameter and morphology of MWC(N)T

Chemical Vapor Deposition (CVD) or Chemical Vapor Synthesis (CVS) is known as a methodology for large-scale production of fibril carbon by thermal pyrolysis of hydrocarbons as methane and ethylene at 500 ~ 1000 C. Recently the fibril carbon by the CVD method is called as Carbon Nanotubes, either Single Walled that is SWCNT or Multi Walled that is MWCNT. These CVD-CNTs are widely used as an industrial material, already. For instance, the resin composites reinforced by CNT are applied to several industrial sectors. The CVD-CNTs reinforced resin composites or films are effectively suppressing the CO2 emission thanks to those lightweights. More specifically, some CNTs are synthesized by Methane gas that is much stronger global warming gas than CO2. This means very effective and ideal CH4 fixing method against

global warming.

The Chemical Vapor grown carbon fibril in the diameter range ≥ 1 nm to < 100 nm are called as multi-walled carbon nanotubes (MWCNT) according to the definition of "nano" suggested in the ISO/TC229 Nanotechnologies. MWCT and MWCNT are expressed as MWC(N)T all together in the CLH report.

MWCNT initially appear to grow as ultra-thin graphene tubes with central hollow cores having diameter ca. 2 nm or more [1, 2]. The graphene tubes observed as hollow core may be a single-walled carbon nanotube (SWCNT) judging from those diameters in transmission electron microscope (TEM) images (Fig.1) [3].

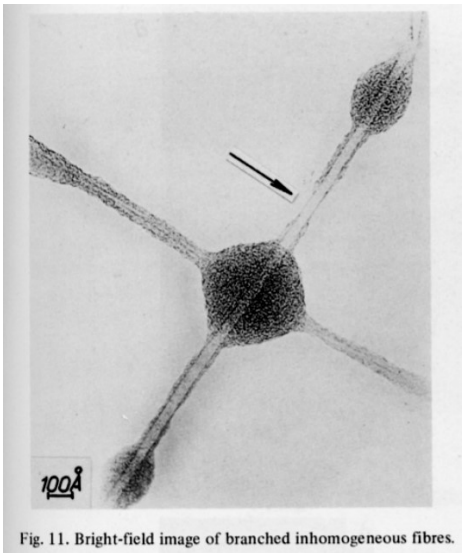


Fig. 11. Bright-field image of branched inhomogeneous fibres.

Fig.1 TEM image of the initial process of CVD-MWCNT [3].
(The arrow in this picture indicates single wall carbon nanotube)

Then the pyrolytic deposition of carbon on the surface of initial SWCNT make hollow core tubes thicker. These stepwise processes were called as axial growth and radial growth, respectively (Fig.2) [4].

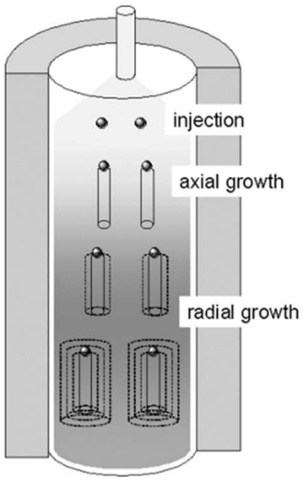


Fig. 9. Proposed reaction mechanism of the MWNTs in the vertical furnace.

Fig.2 Proposal reaction mechanism of the MWNTs in the vertical furnace [4].

The detailed observation of the growth mechanism of CVD grown carbon fibers indicates,

- ✓ All MWC(N)T made by CVD initially grow as SWCNT.
- ✓ The morphology of the MWC(N)T is the same as the morphology of the initial SWCNT.
- ✓ The thickness of MWC(N)T depends on the amount of carbon deposited by thermal pyrolysis of hydrocarbons.

Thus, there is no relation between the diameter of MWC(N)Ts and their shape or morphology. The morphology of the MWC(N)T depends on that of the initial SWCNT. For this reason, we deny the description in the CLH report that the low diameter MWCNT (< 30 nm) are assumed more tangled morphology.
As a general trend of the chemical vapor deposition process under higher temperature results in straighter MWC(N)T due to long-range ordering of graphite structure in tubular shape.

3. Length of MWC(N)T and inhalation exposure

The CLH report advocates MWC(N)T > 5μm as Carc. 1B based on the following toxicokinetic characteristics.

- ✓ MWC(N)T reach and are retained in the deep lung alveoli by inhalation.
- ✓ Then the MWC(N)T slowly relocate to the alveolar interstitium, lung-associated lymph nodes, pleura and other extrapulmonary tissues.
- ✓ MWC(N)T fibres are biopersistent.
- ✓ Rigid MWC(N)T fibres migrate and penetrate the pleura.
- ✓ MWC(N)T fibre retention and disposition depends on time and dose and is related to toxicity.
- ✓ Overall, these toxicokinetic properties support an asbestos like mode of action of rigid MWC(N)T fibers

The CLH report refers the definition of “fiber” by the WHO. The WHO called the particles that are possible to observe using optical microscopes, that is, particles > 5 μm long and < 3 μm diameter and with aspect ratio > 3:1 as “fiber” in 1997. However, the definition of “fiber” by the WHO does not necessarily have direct or specific relation with human health issue.

In particular, we suggest that the lack of a limit on length needs to be reviewed in terms of fibers reaching the lungs.
Below is some reference information.
In the home pages of Ministry of Health, Labour and Welfare (MHLW) of Japan [5] and of the Environmental Protection Agency of United States (US EPA) [6], *particulate materials* (PM) < 10μm and <2.5 μm in diameter are defined as PM 10 and PM 2.5, respectively. The PM > 10 μm can only reach the upper respiratory tract. PM 10 can be transported to the lower respiratory tract and only PM 2.5 are brought directly to alveoli. That’s why both MHLW of Japan and US EPA do not restrict the particulate materials > 10μm [5, 6].

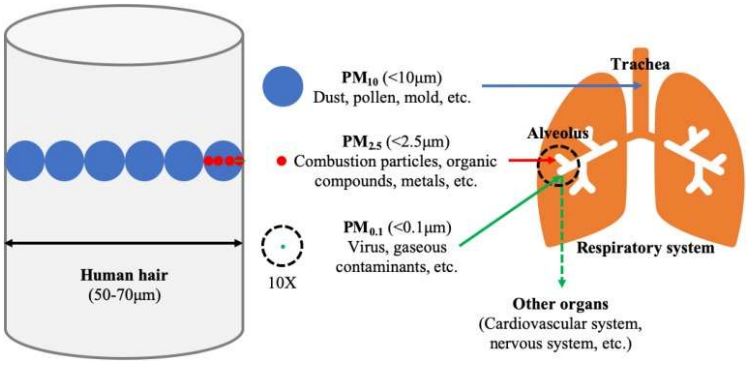


Fig. 3 Human respiratory system and deposit area of particulate materials [7].

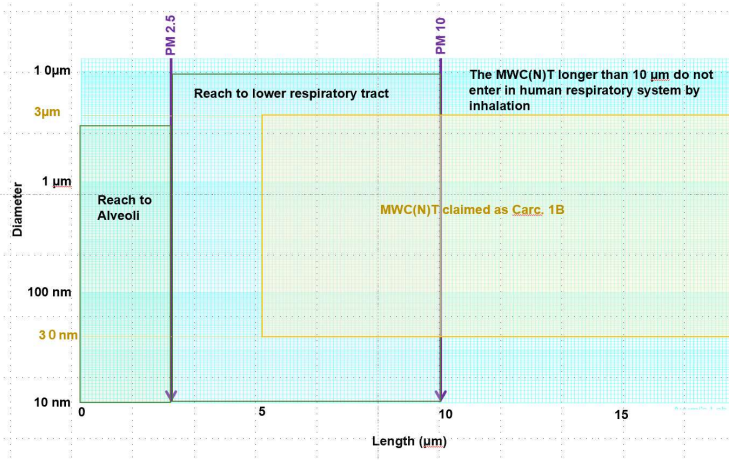


Fig. 4 Deposition area of particulate materials in human respiratory system.

Based on the above, we suggest that further discussion is needed on the stipulation of the length of CNTs entering the lungs.

4. MWC(N)T are not classifiable as Carc. 1B

The International Agency for Research on Cancer (IARC) classified the carcinogenicity of asbestos and CNT in the following way:

- ✓ Asbestos (all forms, including actinolite, amosite, anthophyllite, chrysotile, crocidolite, tremolite) is classified in Group 1: Carcinogenic to humans.
- ✓ Carbon nanotubes, multiwalled of type MWNT-7 are classified in Group 2B: Possibly carcinogenic to humans.
- ✓ Carbon nanotubes, multiwalled, other than MWNT-7, are classified in Group 3: not classifiable as to its carcinogenicity to humans.

As an assessment of carcinogenicity by a public authority, we sincerely take the classification of carcinogenicity [8]. Incidentally, carcinogenicity of carbon black is categorized as 2B, same as MWNT-7 by IARC [9]. In the EU CLP regulation, regarding the CLP Annex I, 3.9.2.8.1. (e), carbon black is not recorded as carcinogen. Thus, the carbon black is not involved in the list of harmonized classification and labelling of

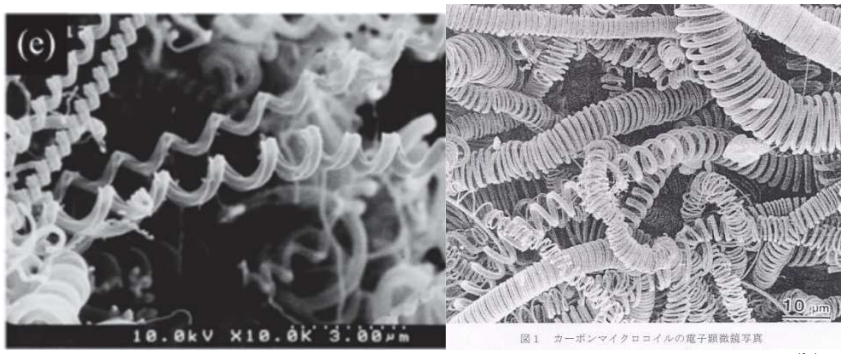
hazardous substances of CLP regulation.
Judging from this situation, MWC(N)T are not classifiable as Carc. 1B.

5. Are MWC(N)T really High Aspect Ratio Materials?

As mentioned above, in 1997, the WHO called “fiber“ all those particles that can be observed using a optical microscope - that is, particles > 5 μm long and < 3 μm diameter and aspect ratio > 3:1. The CLH report claims that the MWC(N)Ts having diameter from 30 nm to 3 μm and with a length ≥ 5 μm and aspect ratio ≥ 3:1 are to be classified as Carc. 1B.

During the process of composite formation, the CNT often (but not always) form an entangled structure like a furball. It’s difficult to find out a reasonable reason to call furballs high aspect ratio materials (HARM). Such furballs do not act like asbestos fibers.

Among MWC(N)Ts, there are coil-shaped structures called ”carbon nano coil” and ”carbon micro coil”. When discussing the influence of these materials on human health, it should be important to think about the aspect ratio of the coils, and to take into consideration their flexibility. For such materials, length and diameter are not the correct parameters to describe them.



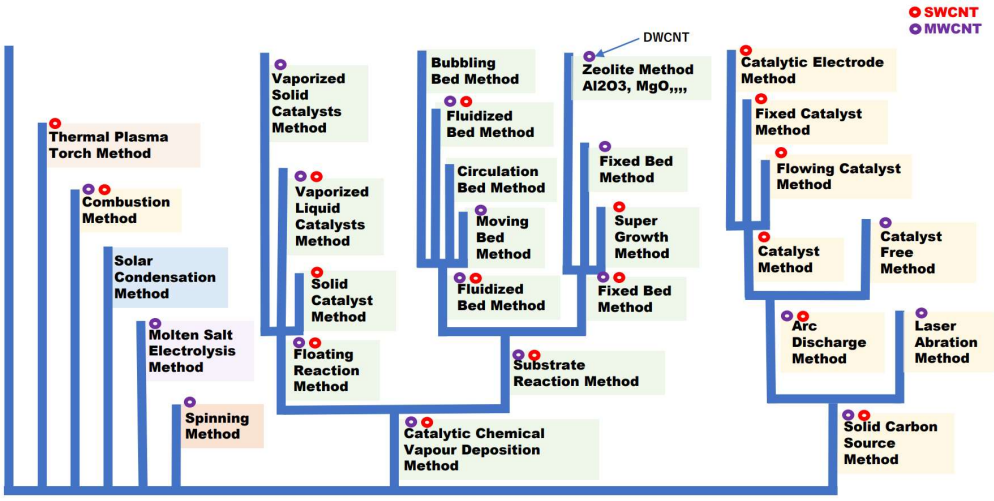
(a) (b)

Fig.5 SEM micrographs of (a) carbon nano coil [10] and (b) carbon micro coil [11]
(note; (a) is altered from Fig.4 (e) of Syntheses and Electronic Applications of Helical Carbon Nanofibers. [10] under (CC BY-NC-SA3.0))

Therefore we suggest,

- ✓ Adoption of “aspect ratio” in the discussion of carcinogenicity of MWC(N)T does not have any meaning, especially for the entangled, curled, and furball like MWC(N)T.
- ✓ We do not agree to classify all of the MWC(N)T in one group. In fact, it is difficult to derive a common and general principle of carcinogenicity for diverse HARM.
- ✓ Also, we point out the fact that there is no suitable equipment to check the diameter and length of MWC(N)T. This is an essential technical problem in the estimation of the aspect ratio of MWC(N)T.

Finally, here we introduce diverse methodology for CNT production.



Referred
https://www.nbci.jp/faq/handling_12.html

Even for the MWC(N)T having same diameter and length, those are quite diverse in morphology as straight and entangles, in elasticity depending on the layer numbers, in surface nature depending on the ordering of graphite structure, and so on.
Some elements within these diversities may correlate with carcinogenicity, but they cannot be uniquely defined by dimensions and aspect ratio, alone.

ABOUT NBCI

NBCI (Nanotechnology Business Creation Initiative) is a Japanese institution established in 2003 to launch and expand the nanotechnology business. NBCI is made up of more than 140 Japanese organizations interested in nanotechnology, promoting the collection and sharing of the latest technical and environmental safety information, and networking with industry, academia and government. Furthermore, we are making recommendations on R & D strategies, environmental safety regulations, and standardization activities in the field of nanotechnology.
Website: https://www.nbci.jp/en/index.html

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