NANOTECHNOLOGY BUSINESS CREATION INITIATIVE

Possibilities and Challenges of CNTs

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CNT Subcommittee

Executive Summary

For a safer innovation approach using carbon nanotubes (CNTs), the socioeconomic impact of the emerging technologies enabled by CNTs is an intrinsic motivation in research and development.

As we have already reported, there are various methodologies for CNTs‘ production, and the CNTs have diverse morphology and physicochemical properties depending on the methodologies even if the names are the same as “Carbon Nanotubes”. This diversity of CNTs characteristics is a competence of the emerging technologies, in the meantime, the diversity makes the management of CNTs difficult.

In this paper, we indicate the scientific and economic impacts in our daily life enabled by using of CNTs. For instance, CNTs have already been used widely as the key component of lithium-ion rechargeable batteries (LIBs) making them efficient and durable. CNTs are essential for reinforcement and electric conductivity of resines as well.

CNTs are being studied intensively as the key material for realizing the space elevator in future. The socioeconomic impacts of these emerging technologies enabled by the use of CNTs should be recognized correctly prior to the discussion on the regulartory framework of nanomaterials.

1. Introduction

Carbon Nanotubes (CNTs) have been known since 1976[1] [2].

Since the start of strategic investment in the “Nanotechnology and Materials” in the 2nd Science and Technology Basic Plan of Japan enforced in FY2001, CNTs have been a key material in the research and development of emerging technologies to realize a sustainable society.

CNTs are excellent in electrical and mechanical properties and are highly durable materials. Those properties bring a drastic change into the properties of various industrial materials by forming the composite even with a minimal amount such as weight and volume of CNTs.

In fact, the number of scientific papers and patents on CNTs has remained at a high level up to the present day as shown in Fig.1.

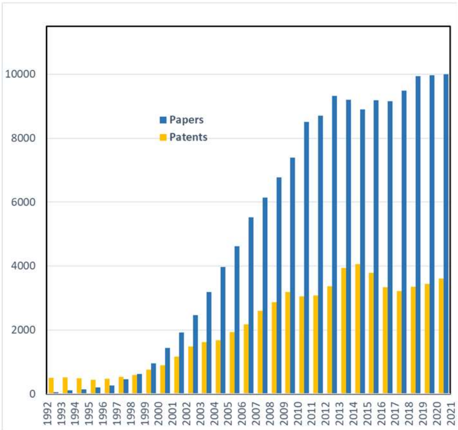

Fig.1 Number of papers and patents on the topic of CNTs

We recognize that scientific and industrial expectation for CNTs is still high and the research targets of CNTs applications are also wide-ranging as electronics and energy devices, industrial materials and so on[3].

Basically, CNTs for industrial usage are produced by Chemical Vapor Deposition (CVD) on a large-scale by thermal pyrolysis of hydrocarbons gas, CxHy at 500 ~ 1000 degrees C. This CVD method has an almost infinite combinations of catalyst source gases, catalysts, reaction temperatures, pressures, a flow rate of feeding gases, etc. By properly adapting the process parameters, we could obtain various types of CNTs having diverse morphologies and properties. For such diverse CNTs, it’s difficult to define the hazard levels univocally as we have published in2022[4]

However, the diversity of morphology and properties of CNTs results in the diverse applications as shown below.

2. Present Typical Applications of CNTs

2.1 Additives for Lithium Ion Battery (LIB)

Since the lithium-ion rechargeable battery (LIB) was launched on to the market in 1991, the performance of LIB has been improved significantly year by year. In particular, LIBs have been supporting the IT/AI society, and now LIB is adopted as the main power source for HEVs and EVs. It is no exaggeration to say that a sustainable future society would not be complete without LIBs. This is because LIBs have the highest energy density compared to existing batteries such as lead-acid batteries (Pb), nickel-cadmium (Ni-Cd), and nickel-hydrogen batteries (NiMH), and provide safer and lighter compact rechargeable batteries.

And it has been found that the addition of CNTs increases the performance of LIBs, since the early stages of LIB development.(Fig.2) [5]

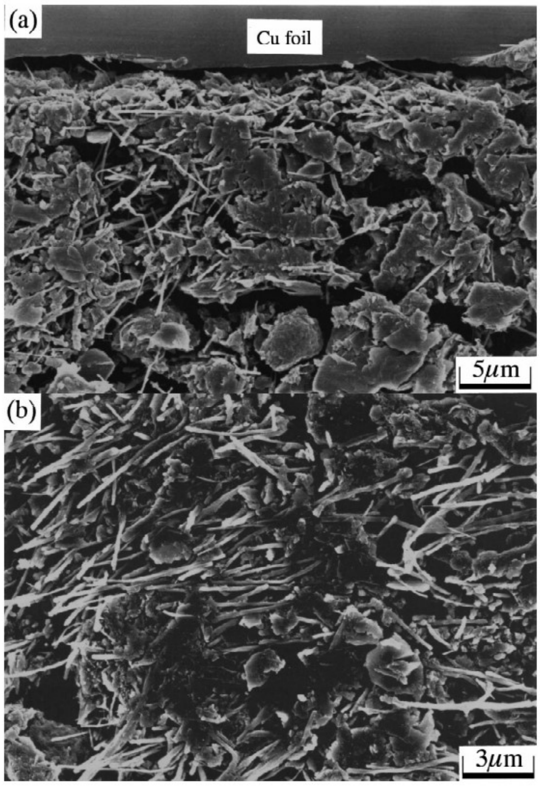

Fig.2 SEM pictures of (a) the carbon anode sheet containing CNTs in a commercial cell and (b) enlarged one.

It is now believed that this tremendous effect of CNTs as additives is due to the following factors.

1) Improvement of energy density:

Fibrous CNTs connect active materials and increase the number of active materials.

2)Reduction of electrical resistance between the active material and external circuit:

CNTs act as a good conductor of electrons and ions, reducing energy loss.

3)Suppression of heat generation in devices:

CNTs having high thermal conductivity thanks to phonon transferring nature reduce heat production between active materials.

Originally, the suitable diameter of CNTs for this application was large such as 100nm or more, but recent report suggests hybrid additives including smaller diameter of CNTs such as 10-50nm and larger diameter of CNTs show the best performance [6].

These excellent effects are achieved through the wonderful properties of CNTs themselves.

(a)the small diameter of CNTs

The small diameter of the CNTs makes it possible to distribute the CNTs homogeneously in the thin electrode material and to introduce a larger surface area to react with the electrolyte.

(b)electrical conductivity

The improved electrical conductivity of the electrode is related to the high electrical conductivity of the fiber itself, and the conductive network formation of the fibers with the graphite particles in the anode to form a fiber-mat.

(c)high intercalation ability

As compared with that of conventional whiskers, the relatively high intercalation ability of CNTs did not lower the capacity of anode materials during charge-discharge cycles.

(d)high flexibility

The electrode is achieved due to the network formation of CNTs in a fiber-mat structure.

(e) high endurance

CNTs absorb the stress in the electrodes caused by the intercalation of Li-ions.

(f) Improvement of penetration of the electrolyte

This effect is due to the homogeneous distribution of CNTs surrounding the anode material.

Through vigorous research and development over 20 years, CNTs in anodes and even in cathodes now contribute significantly to the ultra-long life of LIBs. Currently, the CNTs are inevitable for LIB as mentioned above.

2.2 Electrically Conductive VMQ (Methyl Vinyl Silicone Rubber)

Recently, CNT-filled conductive VMQ composites have been developed, a completely new material that offers high conductivity due to the effective addition of CNTs and can be applied in electrode pads for medical devices for neuromodulation therapy. [6] Figure 3(a)(b).

Highly dispersed high-purity CNTs create a CNT-VMQ composite material with extremely stable and high electrical conductivity, flexibility, and durability compared to other conductive filler materials such as conventional carbon black.

Fig.3(a) Appearance of CNT dispersed VMQ sheet.

(b) Image of CNT-applied device that reduces body tremors

In particular, the use of long CNTs eliminates the falling carbon tiny particle out of the rubber compared to conventional conductive carbon black, and the Biocompatibility test of CNT-filled conductive VMQ was passed and approved by the US Food and Drug Administration(FDA), which was a major trigger for the adoption of CNTs.

This breakthrough material has been implemented in medical wearable devices to improve the quality of life of people suffering from neurological diseases.

2.3 CNTs dispersed Paint system

Metal corrosion has huge economic and safety impacts on social and economic infrastructure. From this viewpoint, the corrosion-protecting polymer coatings have been required, strongly.

Necessary factors for high-performance polymer coatings include strong adhesion between the substrates and polymer layers and physicochemical and mechanical properties of the polymer layer.

These factors depend on the choice of appropriate additives that are CNTs as the strongest element for reinforcing. CNTs dispersed coatings will make the lifetimes of metal products surprisingly long even in chemically and/or mechanically severe environments, thereby greatly reducing their life-cycle costs which means “the environmentally friendly products”.

Fig.4 Nuts & Bolts reinforced by CNT paint in oil field in middle east country

The metallic fasteners such as nuts and bolts which are coated by CNTs dispersed paint are already being expanded for use in chemical plants in middle east countries located under very harsh environments.[7] (Fig.4).

The suitable diameter of CNTs for this application is much larger such as 80 nm and these CNTs reinforce polymer film for tremendous strength and durability against the harsh and severe environment.

3. Applications in the future

3.1 Development of CNT Synthesis Technology as a Strategy for Fixing Global Warming Gases

As mentioned before, CNTs are produced by thermal pyrolysis of hydrocarbons gas, CxHy. And scientists around the world believe that greenhouse gases can be immobilized by using them as raw materials for CNTs and have been vigorously investigating methods and conditions for this purpose [8].

The basic chemical formula for synthesizing CNTs from CO2 is as follows;

Dissolution: CO2(gas) + Li2O(soluble) →Li2CO3(molten)

Electrolysis: Li2CO3(molten) →C(solid)＋Li2O(soluble)+O2(gas)

Net: CO2 (gas) →C(solid) +O2(gas)

Meanwhile, when we think of greenhouse gases, CO2 gas comes to mind, but methane (CH4), which has an even higher global warming potential that has 21 times higher than CO2, is already being used for CNTs synthesis [9].

In the future, it will contribute to a hydrogen society by realizing low-cost hydrogen production as a byproduct, too. (Fig.5) The use of these warming gases will dramatically reduce the cost of CNTs, which will lead to a remarkable expansion of CNT applications in the future.

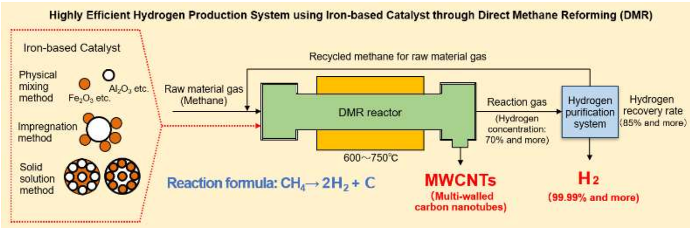

Fig.5 Schematic diagram of H2 production system utilizing CNTs synthesis

3.2 Space Elevator

Half a century of space exploration has diversified the purposes for which humans have ventured into space.

However, in order to further expand the possibilities, economical and mass transportation of people and materials is essential.

The "space elevator," which connects Earth and space via cables and allows people to travel to and from space as easily as taking a train, is expected to be a more efficient, economical, and environmentally friendly means of transportation compared to rockets [10]. (Fig.6(a))

As long as it is built on the earth, there is a limit point at which the construction will break under its own weight. Although a space elevator, a tower that extends into space, was theoretically feasible, it was only a dream because there was no material with

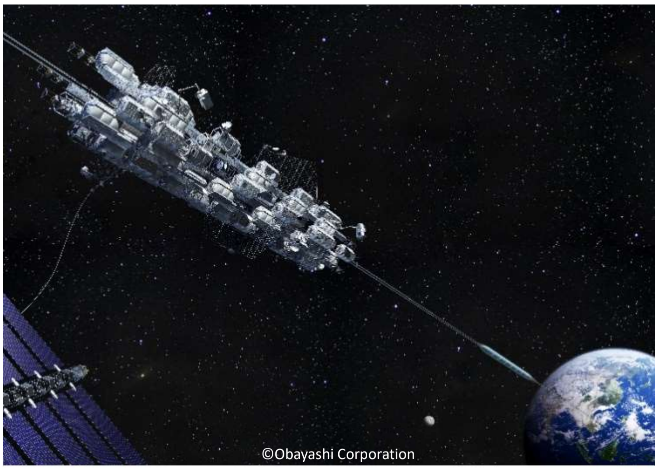

Fig.6(a) Conceptual drawing of a space elevator utilizing CNTs' rope

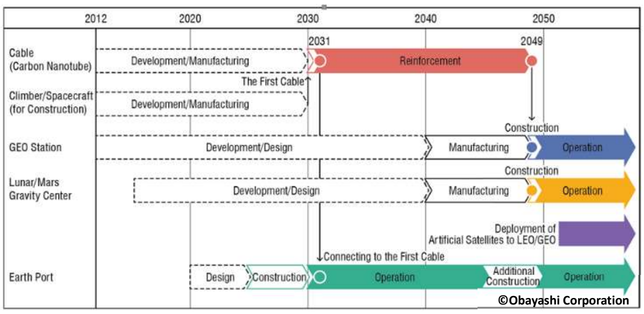

Fig.6(b) Space Elevator Construction Schedule the necessary "lightness" and "strength" for the cable connecting the earth and space.

However, CNTs, a light and strong material opened the gate to the realization of this wonderful space elevator.

The space elevator is planned to be built by the year 2050 with a capacity to carry 100-ton climbers as construction schedule (Fig.6(b)).

It is composed of a 96,000-km CNTs cable, a 400-m diameter floating Earth Port and 12,500-ton counterweight.

Other facilities include Martian/Lunar Gravity Centers, Low Earth Orbit Gate, Geostationary Earth Orbit Station, a Mars Gate and a Solar System Exploration Gate.

CNTs' researchers have to develop continuous and defect-free CNTs having a tensile strength of 150 GPa by 2030 to realize space elevators.

The current technology levels are not yet sufficient to realize the concept, but this plan itself is realistic.

The breakthrough of the CNTs synthesis method is absolutely required to realize this mankind's dream.

4. Conclusion

We have discussed several present applications and expected great applications.

Though the total worldwide production of CNTs is estimated to be about 5,000 tons per year, it is difficult to say that "CNTs have been industrialized", which leaves an undeniable imbalance compared to the number of active papers as pointed out in Fig.1.

We recognize that there are several challenges that need to be addressed in order to make CNTs even more useful and widespread for future grand usage.

(1) Inadequate performances

Size-derived strong aggregates, resulting in difficult dispersion, CNTs lattice defects, resulting in non-uniform quality, fiber-derived orientation and alignment, resulting in anisotropic performance.

(2) Economical efficiency

CNTs are still staying at a high costs.

Economic "causality dilemma" Chicken and Egg Problem unique to new materials exists.

It is calculated that at least several thousand tons per year of demand and production are required to replace carbon black.

(3) Applications

We have unexplored and undiscovered "applications that can only be achieved only with CNTs."

If the current situation is (1) on the above, it is also necessary to develop applications for "applications with a wide range of acceptable performance."

(4) Social Implication

As defined by ISO/IEC GUIDE51, **"Absolute safety does not exist."**

We, CNT Subcommittee take the position that "if CNT is judged to be acceptable in consideration of

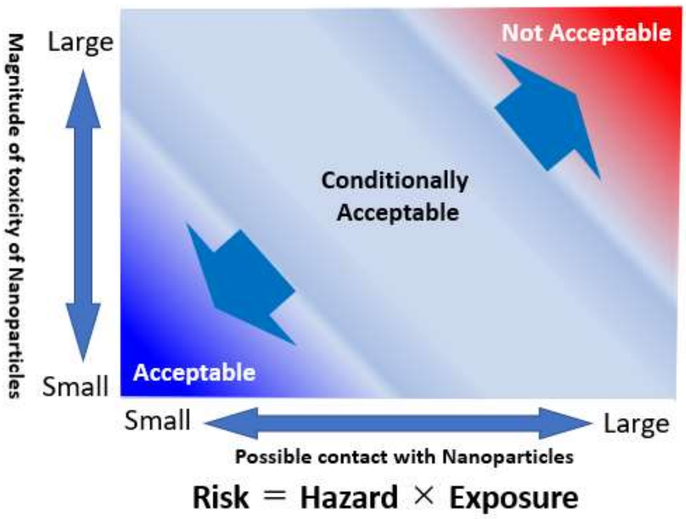

Fig.7 Risk evaluation

its hazard and convenience, risk management is possible by minimizing exposure to CNT, even if the hazard of CNT cannot be quantified". (Fig.7[12])

Risk = Hazard x Exposure (contact between nanoparticles and humans, Exposure)

Even if there is a CNT-specific hazard, if we can reduce and control the possibility of contact, we can minimize the risk to an "acceptable risk," i.e., "deemed safe" as defined by ISO.

LCA (Life Cycle Assessment) are needed, as well, for sustainable development and commercial readiness. LCA should include energy consumption, performance lifetime, degradation or disposal of CNT-based products and their safety.

We hereby propose that the above critical issues be addressed in an international framework.

We believe that this would be a more useful endeavor for humanity than a one-sided and weakly grounded discussion of the dangers of CNTs.

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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