Recent developments on single-walled carbon nanotubes in Japan

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Samenvatting

Cheaper mass production technologies of carbon nanotubes enable new applications like a super capacitor.

Introduction
Japan is one of leading countries in the research and development of carbon nanotubes (CNTs). Since a Japanese scientist, Prof. Sumio Iijma, discovered CNTs in 1991, a lot of research on CNTs have been done in the world. Because CNTs are an interesting material which can be 20 times stronger than steel, half weight of aluminum, and 1000 times as conductive as coppers. CNTs have a potential to influence a wide range of applications such as electronics, automotives, medicine, aerospace, defense, energy, and construction. The global CNT market was € 1.1 billion in 2010 and it estimated to grow € 2.2 billion in 2016 (1). Recently in Japan more focus is on the development of mass production technologies of CNT in order to reduce the production cost. Since a new mass production technology of single-walled carbon nanotube (SWNT, SWCNT) was firstly developed by the Japanese research institute AIST* in 2003, a prototype of manufacturing equipment has been developed in cooperation with Japanese companies, funded by the Japanese governmental R&D funding organization NEDO*. The first application based on this technology is a super capacitor with a CNT-based electrode, which realizes a characteristic of small, high power, and long life time. The Japanese government expects that the manufacturing cost of SWNT will decrease drastically by this development and the SWNT applications will create a new market of € 6 billion and 18,600 new employees in 2030 (2).

Developments of carbon nanotubes (CNTs)
Graphene is a new material consisting of one-atom-thick planar sheets of carbon atoms that are packed in a hexagonal honeycomb lattice. It was the subject of the 2010 Nobel Prize in Physics. A carbon nanotube (CNT) is a hollow-fiber substance made of a cylinder of graphene. There are two main types of CNT, single-walled CNT (SWNT, SWCNT) and multi-walled CNT (MWNT, MWCNT). SWNT consists of a cylinder of graphene. MWNT consists of more than two cylinders of graphene. Especially, the CNT of two cylinders is called double-walled CNT. In principle, SWNT has better characteristics such as conductivity than MWNT. And SWNTs only can have the characterization of a semiconductor when it is produced with diameter less than 4 nm. Actually two-third of the CNTs become semiconducting during the production of less than 4nm in diameter and one-third a rest material of metal. All CNTs become metallic when it is produced with diameter more than 4nm. The production cost of SWNTs is more than 100 times higher than that of MWNTs. SWNTs cost more than € 90 per gram, while MWNTs cost € 0.09 -0.45 per gram. Therefore, MWNTs are much more

produced than SWNTs in the world. One of the current major CNT applications is in batteries. In the world, every year roughly 150- 200 tons of MWNT is manufactured for advanced electrodes of batteries including lithium-ion type. Roughly 50 percent of the CNT market for batteries is shared by two Japanese leading companies, Showa Denko and Hodogaya Chemical. Other leading foreign companies are Bayer MaterialScience (Germany), Arkema (France), SouthWest NanoTechnologies (US), CNano Technology (US), NanoCyl (Belgium), and Hyperion Catalysis (Korea). SouthWest NanoTechnologies produces CNT based on technologies transferred from a Japanese ICT company NEC.

Single-walled carbon nanotubes (SWNTs)
When it comes to applications such as batteries, SWNTs have always been too expensive due to its high cost of production. In Japan the major governmental research institute AIST has been one of main players on CNT research. The Super Growth CNT Team of AIST’ s Nanotube Research Center is one of the main players of the SWNT mass production project in Japan. Dr. Kenji Hata is the project leader at AIST. Dr. Hata’ s group at AIST succeeded in a remarkable result to realize a high speed growth of SWNTs and published it in Science in 2004 (3, 4). Dr. Hata was the first researcher to use water in the CVD process to manufacture SWNTs from ethylene and succeeded in growing them rapidly (1000 times) and purely (99.95 percent) (figure 1).

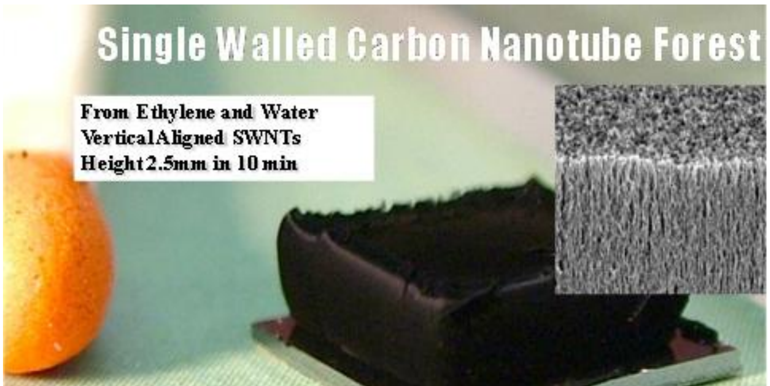

Figure 1. Single-walled carbon nanotube Forest (source: Dr Kenji Hata, AIST).

The Japanese government has promoted SWNT development in cooperation with Japanese companies, Nippon Zeon and Nippon Chemicon. The five-year project “ Carbon Nanotube Super Capacitor” (2006-2011) has been funding AIST and those companies via NEDO (total budget: € 13 million). Nippon Zeon and AIST’ s Nanotube Research Center have been involved in development of mass production of SWNTs, while Nippon Chemicon and AIST’ s Energy Department have been involved in development of the super capacitor using SWNTs. The project was completed in March

2011. Firstly in this project a prototype of a mass production system of SWNTs has been developed and it has a combined system of metal foils and continuous CVD process, in order to contribute to its cost reduction (Figure 2). It produces SWNTs at a rate of 100g per hour. If the market further expands, it might become 100 times cheaper than today. Nippon Zeon will continue to develop a larger mass production system which it will launch into the SWNT market in the near future. Test samples of SWNTs made by this system have been provided to companies such as Toray since May 2011. Nippon Chemicon, a major capacitor producer, will continue to develop it for the advanced capacitor used for hybrid engines in the fields of construction machinery and cars, which need higher performance for charging and discharging.

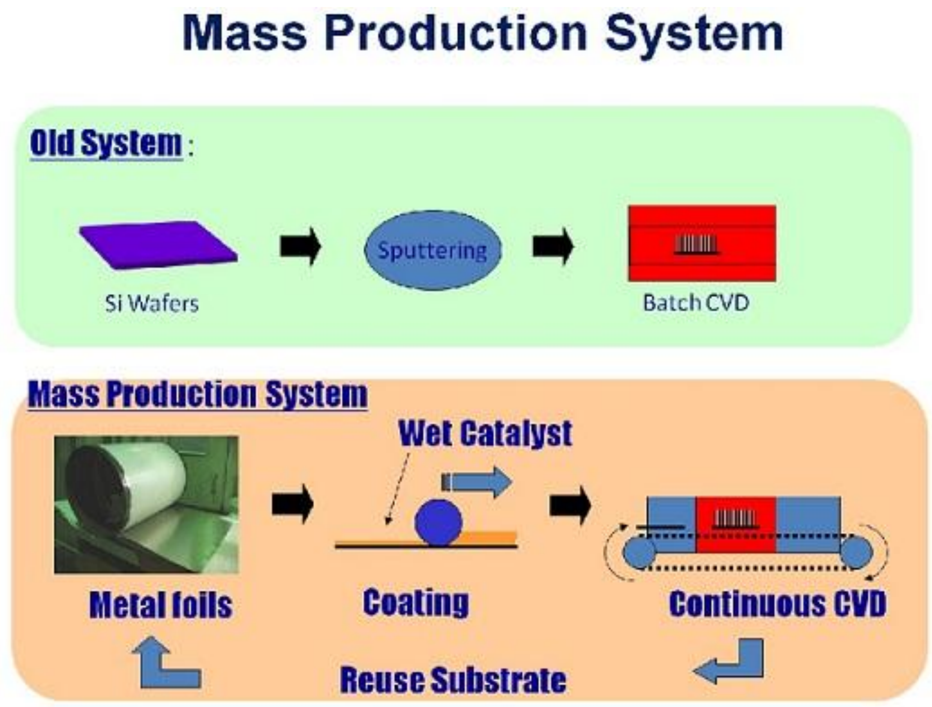

Figure 2. Mass production system of SWNT (source: Dr Kenji Hata, AIST)

TASC to develop SWNT

The Foundation of Technical Research Association of Single Walled Carbon Nanotubes (TASC) has been established by five Japanese major companies (Sumitomo Precision Products, Teijin, Toray, Nippon Zeon, and NEC) and AIST in 2010, funded by Japanese Industry Ministry METI*. TASC is engaging in R&D on ultra-light, super-strength, high performance materials for application development through the establishing of a new industry on CNT composite materials, in order to meet the global demand for building a low-carbon society (5). METI has launched the five-year project " Super light and strong CNT composites for a low carbon community" (2010-2014) which will be executed through TASC and AIST, in cooperation with Nagoya University (Prof. Nori Shinohara) and Kyushu University (Prof. Naotoshi Nakashima) (total budget: € 44 million). This project has a target to achieve by 2014 as follows:

1) More efficient separation technologies (separation rate: 80 percent, metal: 95 percent , semiconductor: 95 percent) to produce 10g/day.
2) Higher thermal conductivity (more than 1000W/mK).
3) Stronger carbon fiber with CNT (strength: 6GPa, tensile: 400GPa).
4) A manual of safety management for workers at CNT manufacturing process, and assessment of safety environment among production, usage, waste and recycle.

At TASC there are two SWNT production technologies. One is the super growth method as the above described. The other is e-DIPS (enhanced direct injection pyrolytic synthesis) method, which has been developed by another group of AIST (6). e-DIPS method is slower on CNT growth than super growth method but it is regarded to be more suitable to separate the semiconductor from the metal. Possible applications from this project are transparent conductive films, heat exchangers, battery electrodes, actuators, electric devices, strong fibers, heat pumps, and capacitor devices. The Japanese government expects that the manufacturing cost of SWNTs will be reduced due to this development and the SWNT applications will create a new market of € 6 billion and new 18,600 employees in 2030.

On the other hand, TASC also targets safety management for workers. It is indicated by experts that nano materials including carbon nanotubes have a potential to damage the human body especially when they are absorbed in the lungs. Therefore, it is very important for companies to assess and evaluate not only safety environment of workers at the manufacturing site, but also of the user side, waste, and recycling. TASC plans to offer ISO (International Standard Organization) standard to be shared with information based on this project.

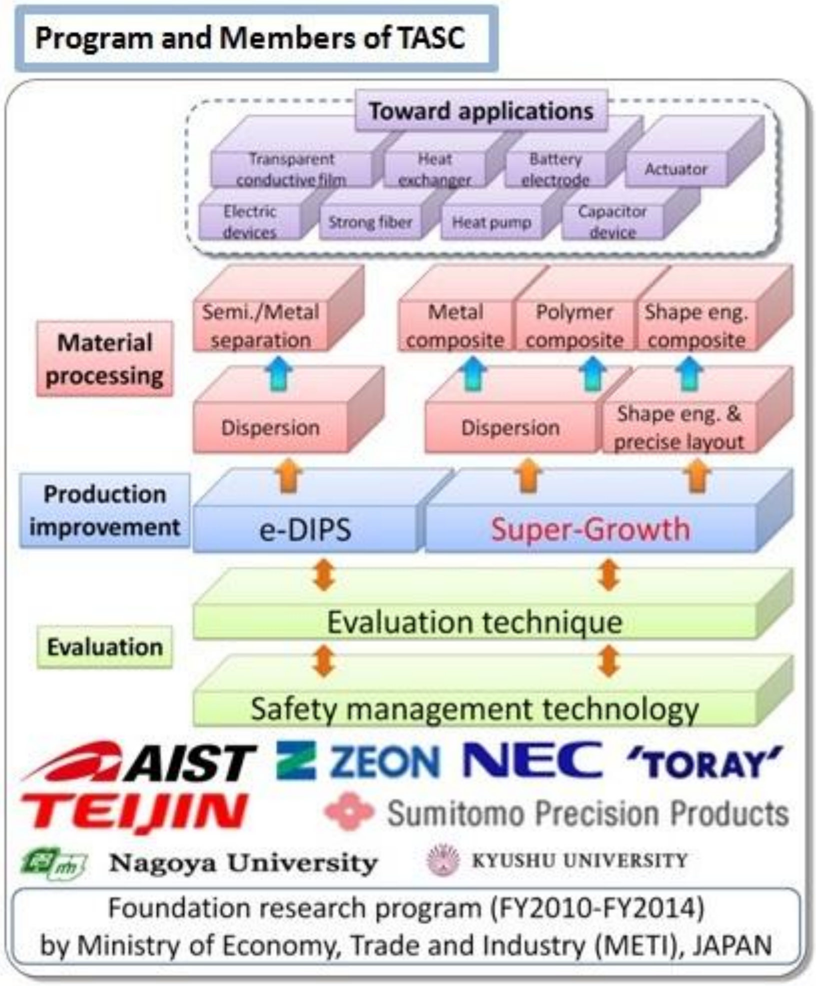

Figure 3. Research program by TASC (Foundation of Technical Research Association of Single Walled Carbon Nanotubes) (source: Dr Kenji Hata, AIST).

Other recent developments of CNT

Among other CNT developments, Japanese major company, Fujitsu has been developing a device of incorporated CNTs on LSI, funded by another governmental project: the MIRAI project (Figure 4). Prof. Takao Someya (Tokyo University) has been developing highly conducting rubber with CNT for stretchable devices and stretchable displays in cooperation with a Japanese printing company DNP (7). In March 2011, AIST (Super Growth CNT Team) succeeded in developing a new stretchable CNT strain sensor which detects human motion (8, 9).

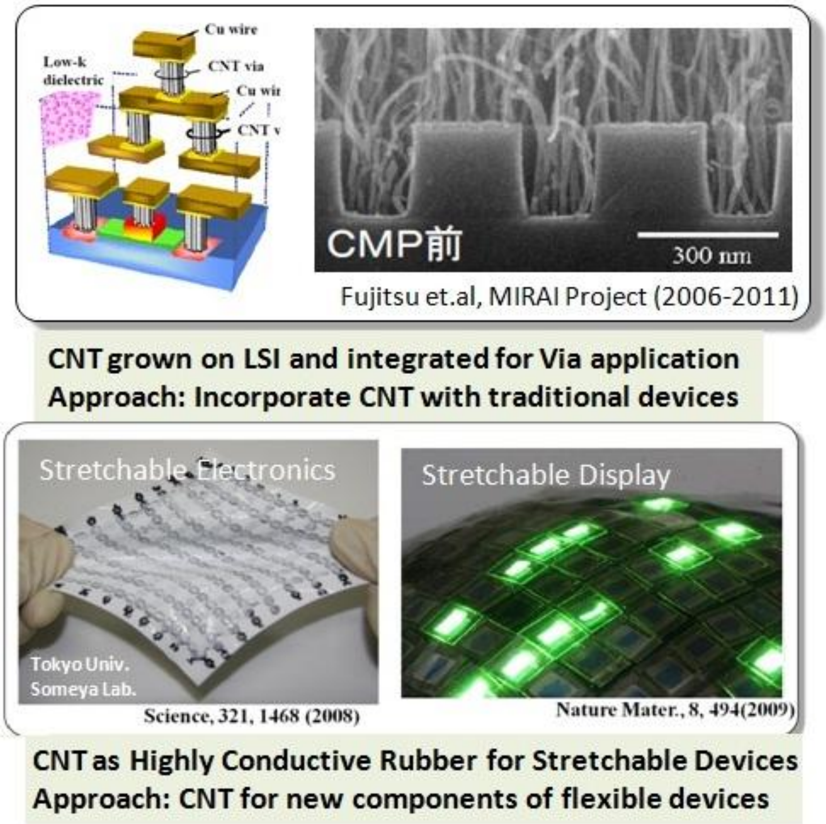

Figure 4. New applications with CNT (source: Dr Kenji Hata, AIST).

*acronym in full:
*AIST - National Institute of Advanced Industrial Science and Technology
*NEDO - New Energy and Industrial Technology Development Organization
*METI – Ministry of Economy, Trade and Industry

Exchange rate of currencies on 29 August 2011
€ 1 = $1.45 (US Dollar)
€ 1 = 111 yen (Japanese Yen)

Sources

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2. Cabinet Secretariat: http://www.kantei.go.jp/.
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