9
Developments in nanofibers for the new millennium

9.1 Background

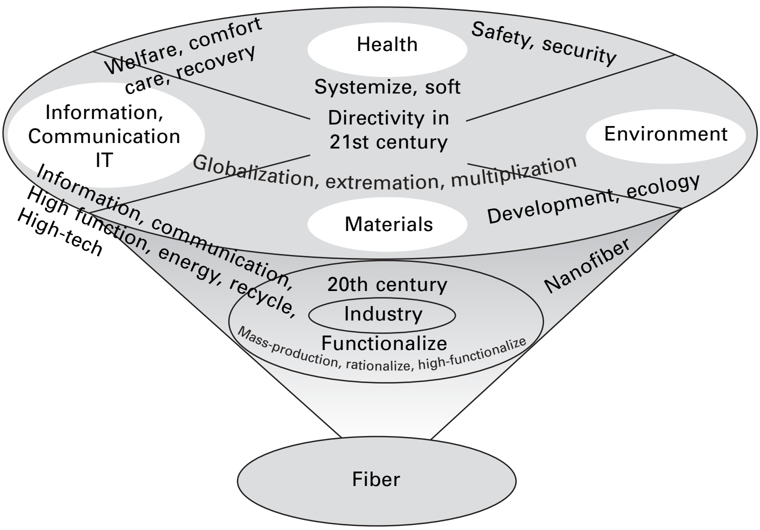
While the history of fibers extends far back in time, developments over the past 100 years have been particularly significant. The Industrial Revolution opened with cotton spinning in Britain in the eighteenth century and brought about a new manufacturing process. Modern chemistry emerged in the nineteenth century and developed in the twentieth century with the growth of the petroleum industry, which led to the emergence of polymer science and three important synthetic fibers.[1] These multipurpose fibers were polyamide fibers (Nylon 66, Nylon 6), poly(ethylene terephthalate) (PET) fibers and acrylic fibers, with spandex fiber appearing in the first half of twentieth century. These fiber materials became the basis of the clothing that consumers wear every day.

The aim of the development of synthetic fibers was imitation and replacement of natural fibers. Developments in engineering from the 1960s followed two directions. One was innovation in processes, improvement in quality and investment of functions in production of the multipurpose fibers. In the 1980s the high performance fibers were developed – a group of carbon fibers and aramid fibers, known as superfibers. The other led to high functional fibers and high sense fibers.[2] In 2004, additional keywords such as environment care, using biodegradable fiber and recyclable fibers, and health, comfort and safety have been added in material development. Life needs have led to multifunctional fibers and attention has moved, over the past ten years, from ecosystem imitation technology (biomimetics) to environment response fibers and intelligent fibers. Nanofiber technology will now be developed for practical needs. Nanofibers of carbon nanotube and GI-type POF have already been produced on an industrial scale. Toray have succeeded in spinning nylon nanofiber where molecular arrangement of polymer chains is controlled in nano-level.[3] Teijin reported a light interference colored fiber, MORPHOTEX® during the 1st International Congress on Nanofiber Science Technology.[4] Professor Y. Atomi *et al*. (The University of Tokyo) have proposed clothes made with nanofiber which activates the body during the 2004 Expo/ Fibers for New Era.[5] This new technology will be applied to multipurpose polymers of polyesters and polypropylene, and polylactic acid. New technology for nanofibers will surely appear continuously in future. These are expected to become the new main trends in fiber science in the twenty-first century.

9.1.1 From biomimetics to super biomimetic

It is not going too far to say that the history of synthetic fibers is that of biomimetics. Many synthetic fibers have evolved out of a desire to produce novel fiber such as silk. Today, mimetic technology develops and produces synthetic fibers excellent in performance and function characteristics, mimicking more elaborate bio-function as well as structures and functions of organizations in nature to enrich our life. We must not forget that we have succeeded in mimicking nature. For example, synthetic fiber mimics the excellent fiber structure of cotton, wool, and silk and in some features improves on nature. Figure 9.1 shows the outlook for developments in fiber technology in the twenty-first century.

From the view of fiber science and technology, the organized structure found in natural fibrous materials (cotton, wool, and silk) ('fiber system') are made up from a hierarchical structure of micro-fiber, or to use the keyword of today, the nanofiber, as the basic unit.



9.1 Directions for development of new frontier fibers in the twenty-first century.

Today, fiber-related fields develop widely in relation to the living body (bio), sugar chains, organs, environment, IT (information). There are a vast number of structural models in nature: the cobweb, iridescence, supra-structures in the skin of tunicates, the flexibility of bamboo, leaves of plants and the structure and functions of bio-organs. Since developments of new functionalized fibers are based on sophisticated biomimetics, the developments lead to second-dimensional functions. Then on to supra-organized fibers or fibers amalgamated in third-dimensional functions to fourth-dimensional functionalized intelligent fibers. These can control environmental changes, and utilize various 'new system' in fiber science and its related fields.[6] These could lead to the creation of ultra-fiber mimicking biosystems and having functions and structures better than those of the original biosystem (super-biomimetics fibers). Here the 'nanofiber' becomes important. Figure 9.2 shows the possible development of fiber technology in the twenty-first century by integrating different fields.

9.2 Nanotechnology, materials and nanofiber[7]

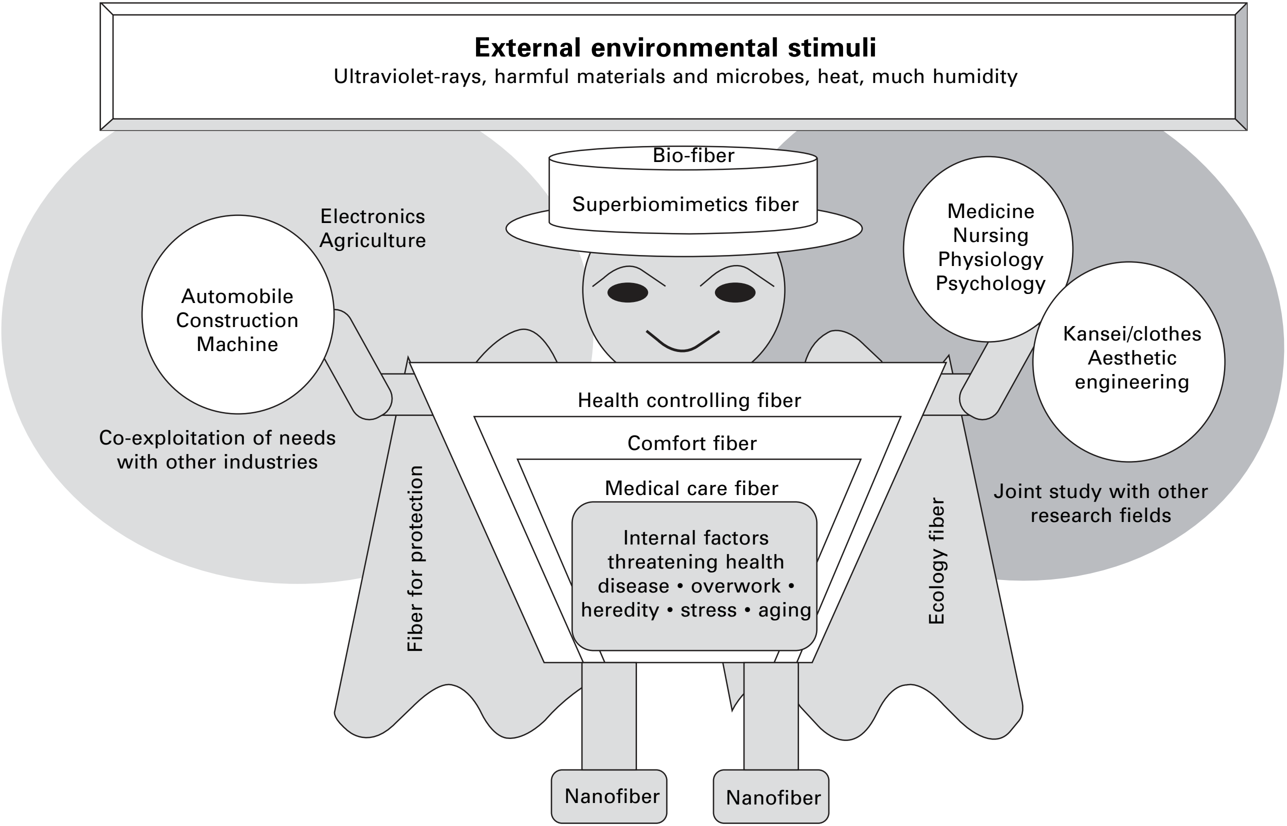
The Japanese government has decided to promote several major projects for improving the economy by developing the following four basic technologies:

(1) life sciences
(2) information and communication
(3) environment and
(4) nanotechnology and materials.

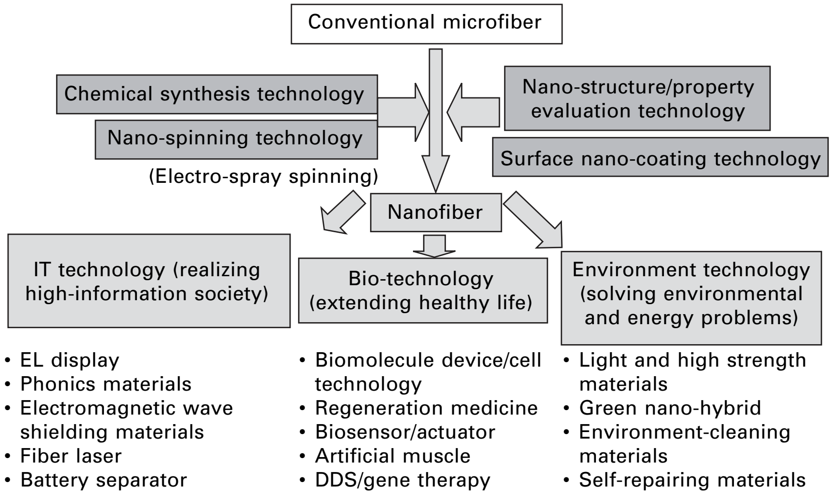
The nanotechnology and materials field can be the basis for extensive science and technology innovation. An example of assimilation technology development with nanofiber is shown in Fig. 9.3.

9.2.1 Generation of innovative technology using nanofibers

A feature of any useful fiber should be characterization and control of its structure at nano-level. Diameters of existing useful fibers are those over 1 μm. With a constant volume, the surface area can increase a few thousand times by decreasing the fiber diameter to an order of nanometers. 'Nanofiber' with its diameter in the other of nanometers would have a huge surface area. Considering the fiber surface as a two-dimensional area film, new characteristics will be found when the structure of the surface and depth direction (radius direction of the fiber) is well controlled. The surface functions can thus increase over 100 times and multi-functions can be set into the system.



9.2 Development of fiber technology in the twenty-first century with integration of different fields.



9.3 Proposal of research project on nanofiber technology development, aiming to create new industries.

9.2.2 Defining characteristics of nanofiber

Although there are various definitions for nanofiber, we select the following.

Nano-size fiber with nanometer order in its dimensions

Nanofiber

In fiber diameters, the range from 0.1 nanometer to 1 nanometer is of angstrom size, that from 1 nanometer to 10 nanometer is nano size, that from 100 nanometer to 1000 nanometer is sub-micron size, and that from 1000 nanometer to 10 000 nanometer is micron size. Fibers with an angstrom size diameter are effectively the molecular chain. Nanometer size and sub-micron size fibers can be classed as nanofiber. A micron size fiber is called a micro-fiber. Fibers with a diameter more than a few micrometers are the conventional fibers, including those with millimeter, centimeter or meter order diameters.

Toray has developed a new technology for the fabrication of multi-filament nanofiber composed of nano-order filament with fiber radius 100 times thinner than that of conventional ultra-thin fiber, with each fiber having a diameter of the order of a few micrometers. This technology achieves thinner radius limits than that attained by any extension of conventional technologies. It can be applied for multi-use fibers such as nylon and polyesters, still using existing facilities.

Today Toray has succeeded in developing nylon nanofiber (44 dtex) composed of over 1 400 000 filaments with radius of a few dozens nanometers. Since this nanofiber has a surface much larger than conventional fibers, special functions are associated with the fiber surface enabling the production of revolutionary new materials. Figure 9.4 shows features of nylon nanofiber.

This new technology gives filament-shaped nanofiber. The nanofiber has easy processing ability. Its orientation and shape are easily controlled. Thus application of the nanofiber to various fields can be expected to accelerate quickly.

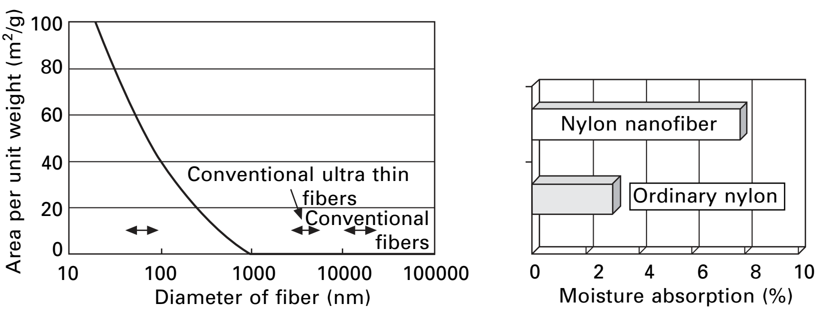
For example, the nylon nanofiber has a high absorbency twice or three times as much as conventional nylon fibers, and as much as cotton. For the conventional nylon fibers, absorbency at the fiber surface is only one-thousandth that for the inside of the fiber, so the absorbency at the surface is negligible. However, the nylon nanofiber has surface area 1000 times as large as the conventional polymer. Thus the absorbency effect of the surface becomes significant.

Hereafter Toray will undertake basic studies for applying this technology to new materials such as polylactic acid and multi-use polymers, such as polyester and polypropylene. In this way merchandise with new functions can be realized, by coupling the produced nanofiber with higher order processing technology.

Fibrous matter containing more than two molecular chains can be regarded as nanofiber. Fibrous matter containing more than two nanofibers becomes micro-fiber or when even more are added it becomes ordinary fiber. So nanofiber is sometimes termed a fibril or microfibril.

Features

1. Diameter of nanofiber 20-100 nm
2. Large surface area
3. High surface activity
4. Fabricability with multi-use polymer (nylon, polyester, polyolephin)
5. Easy processing because of filament (textile, nonwoven fabrics, cotton)



9.4 Features of nylon nanofiber (Toray).

Nanofabric

Two-dimensional structures formed by molecular chains or nanofibers with diameter less than 10 nm are termed nano-coating. Two-dimensional structures formed by fibers with diameter in range from 10 nm to sub-micron are termed nanofabric. Two-dimensional structures formed by micron-fibers are called micro-fabric.

Nanofiber technology

Nanofiber technology has as its objective the control of structure (such as assembling, hierarchy) of the molecular chains and nanofiber. It includes various technologies for producing micro-fiber and ordinary fibers made up of nanofibers.

Figure 9.5 shows relationships in nanofiber, nanofabric and nanotechnology.

Nano structured fiber

'Nano structured fiber' is a fiber given new functions with precise structure designs controlling the inside, outside and surface at nanometer size. These can be:

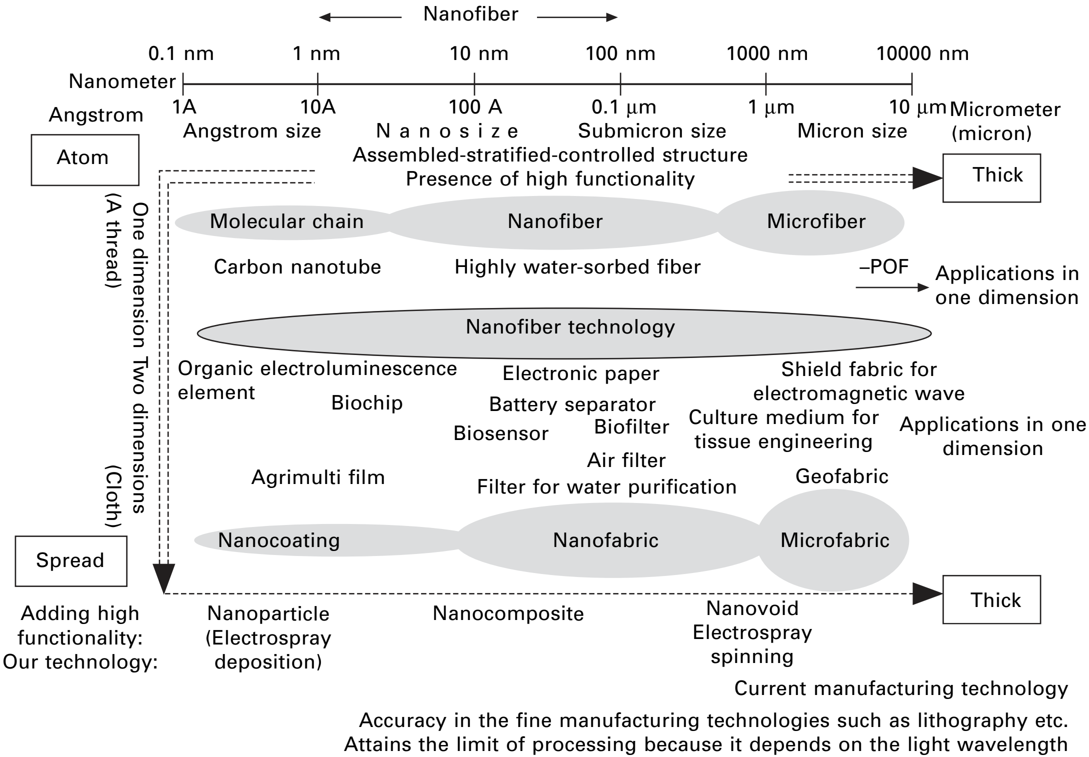
- radial-nano structure: using nano order refined structure in the fiber radius direction
- axial-nano structure: using nano order refined structure in the fiber axis direction
- nano assembly: nano structure formation using copolymerization and organic-inorganic hybrid technology
- nano interface: using nano order refined structure in the fiber surface and interface
- nano design: using nano order refined structure for the inside of the fiber

Figure 9.6 shows nano structure fiber and its uses, Fig. 9.7 shows radial nano structure and axial nano structure, Fig. 9.8 shows nano assembly, and Fig. 9.9 shows nano interface and nano design.

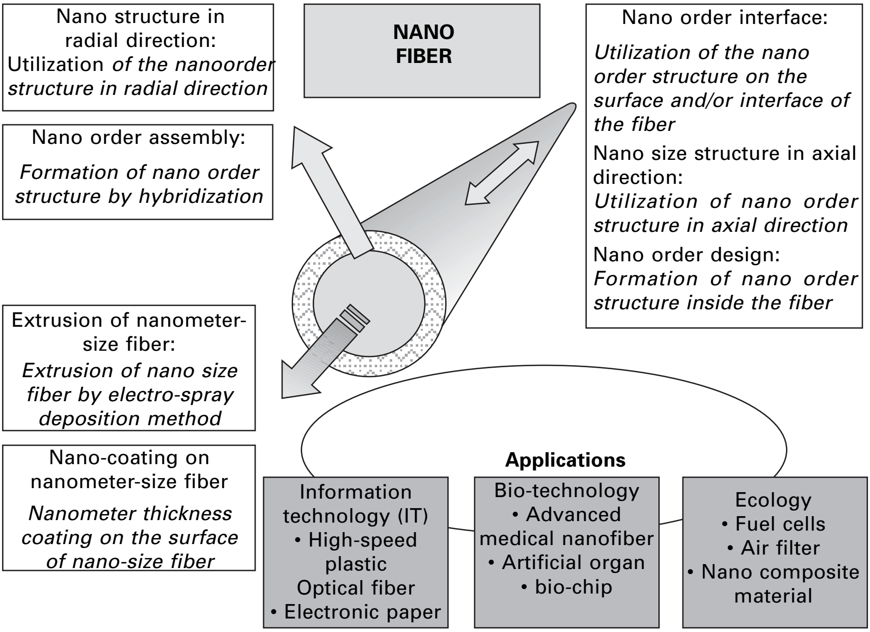
Fabrication of nanofiber

Many researchers in Japanese Institutes now study nanofibers within various fields. These are classified roughly as

(1) gas phase grown nanofiber, such as preparation of carbon nano-tubes,[8]
(2) natural nanofibers such as making self-restorative inductive collagen nanofibers,



9.5 Features, properties, development and usage of nylon nanofiber.



9.6 'Nanofiber' technology.

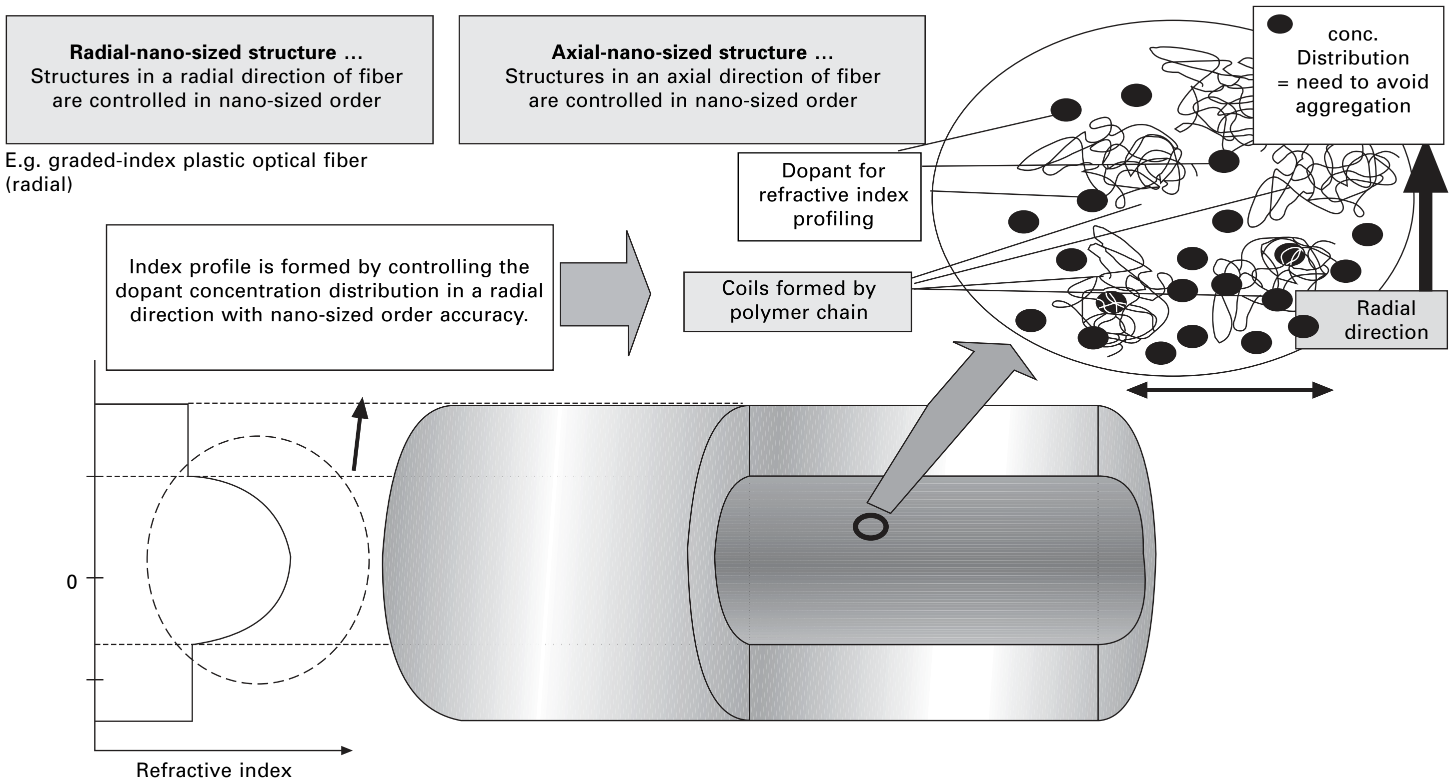
Nanofiber: all the following technologies are designed as 'nono-fiber' technology

(1) Fiber utilizing nano-order structures (highly functional fiber realized by nano order structure design.
(2) Nano size fiber (fiber with the diameter on the order of nanometer).
(3) nanofiber making super molecular nano wire, and
(4) fabricating nano size fiber by spinning[9] (see Fig. 9.10), etc:

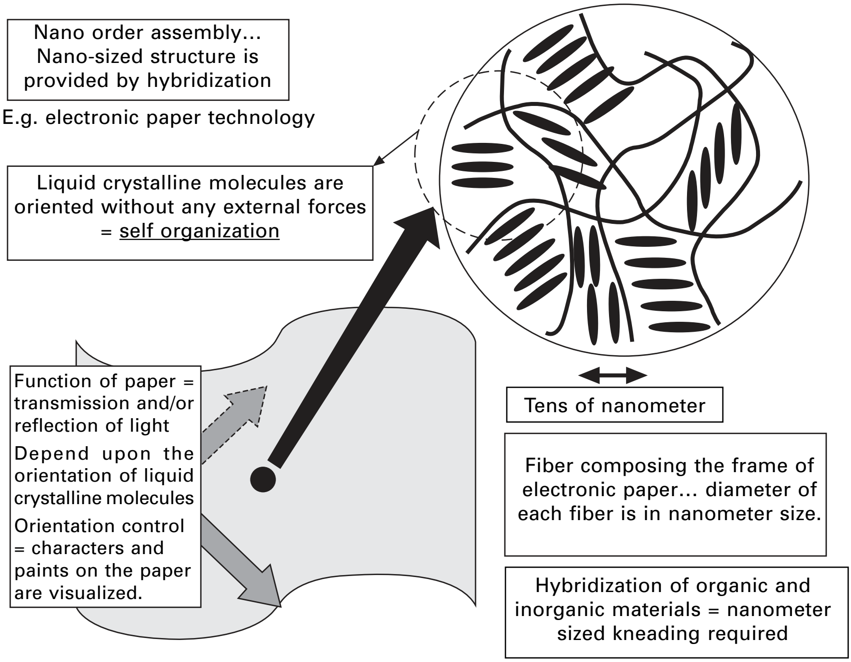
- nano spinning: spinning nanometer size fiber by an electro-spray deposition method
- nano coating: Coating nanometer thickness layers on nanometer order fibers.

Fabrication technologies (conventional process technology, nano-processing and nano-measurement technologies) can control the appearance and function of the final product.

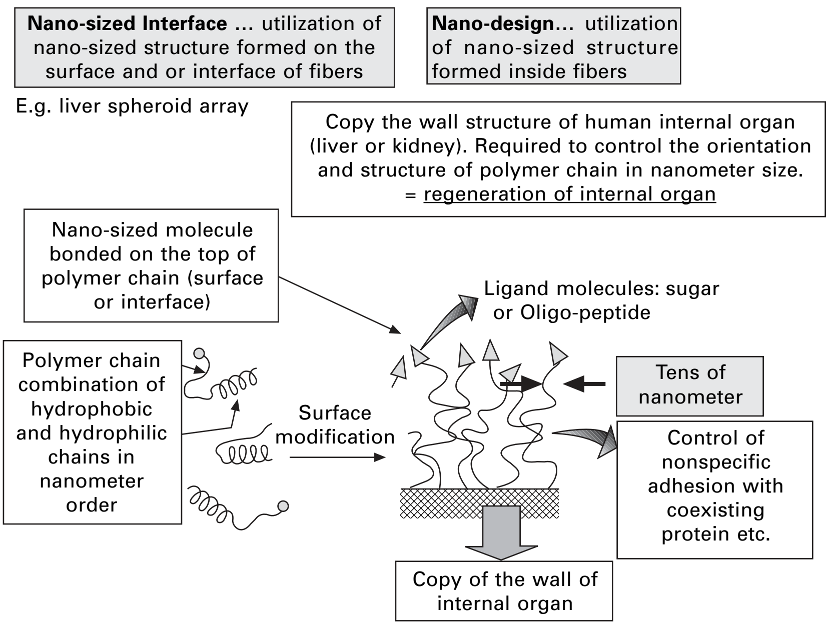
Teijin company developed a structurally colored fiber 'MORPHOTEX®' mimicking the brilliant wing color of a tropical butterfly, *morphinae*. The multiple colors are formed by the interference of light passing through the multiple layers of the wing. Teijin has realized such nano order layered thin film structure on a fiber by means of nanotechnology including ultra precision conjugate spinning and polymer technologies.



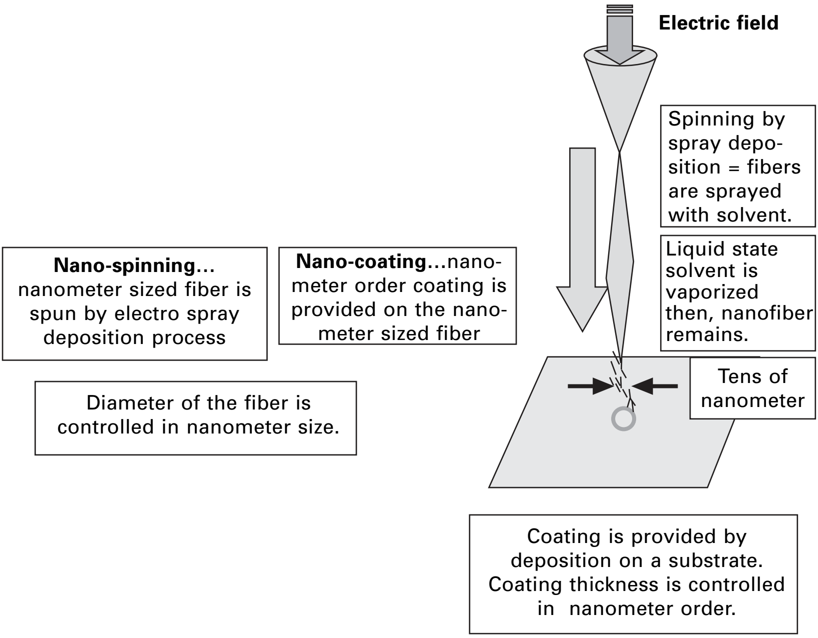
9.7 Radial and axial nano-sized structures.



9.8 Nano order assembly.



9.9 Nano-sized interface and nano design.



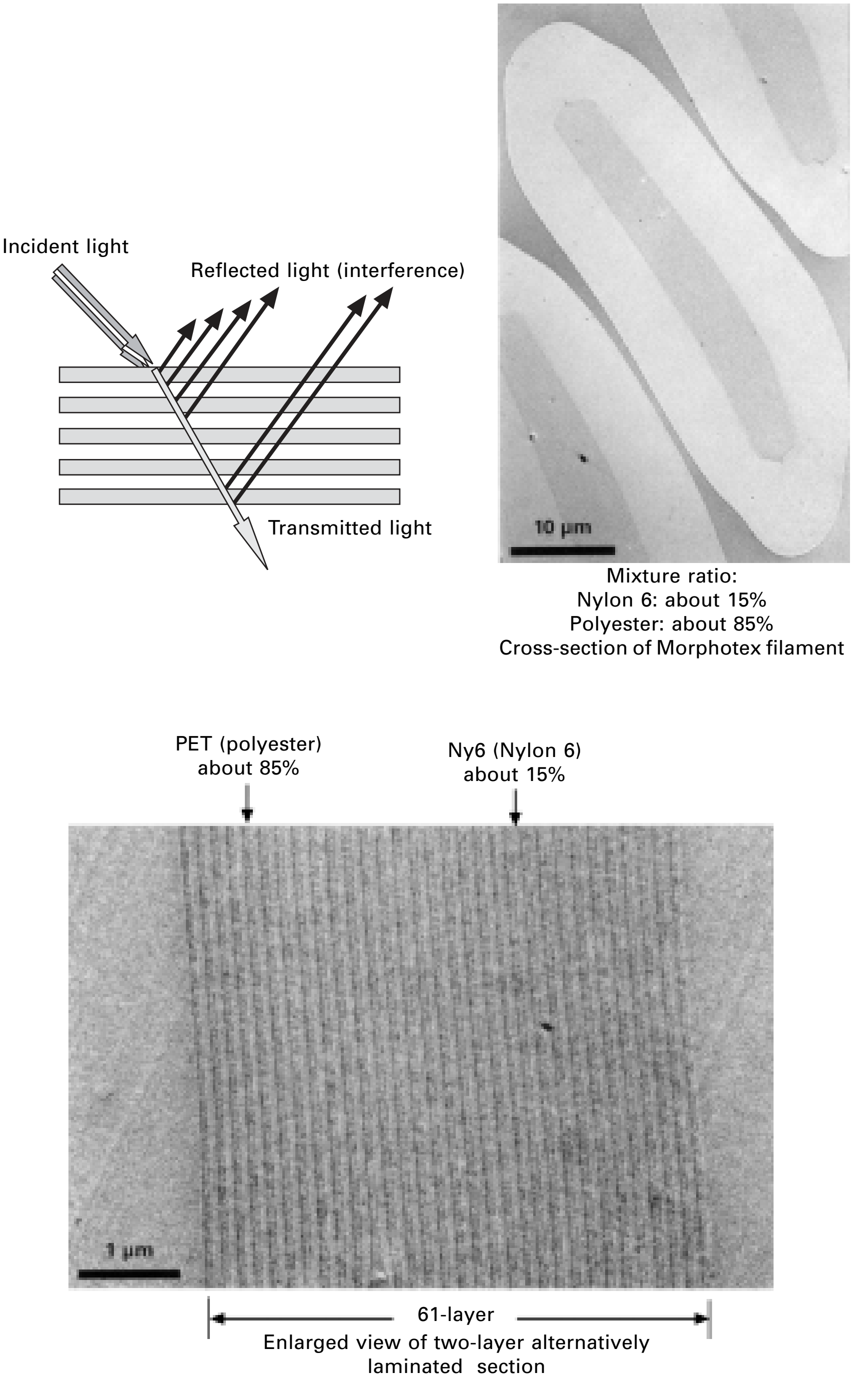
9.10 Nano spinning and nano-coating.

Morphotex® has a 61-layer structure composed of polyester and nylon in alternating layers 70 nm thick. The various colors of Morphotex® are obtained by light interference, depending on the angle or the intensity of the incident light as shown in Fig. 9.11. Teijin expects that the structurally colored fiber in a filament yarn type will be used mainly for women's outer and inner wears, dresses, sportswear, embroidery threads for logos, car seat materials, interior textile materials, etc. Another interesting field is paint materials (Morphotone®), especially automobile paints, cosmetics, and artificial leather coating.

Nanofiber effects which can be produced

Material properties specific to nano-size materials are:

1. size effects (increment in surface area per volume, increment in reactivity and selectivity attributed to decrease in volume)
2. arrangement of super molecules (molecules arranged regularly, self-organized and with new functions and coherence)
3. recognition of cell and biomaterials (nanofiber with unique structure which cells recognize and combine with) and
4. hierarchal structure effect (effects generated from the nano polymer chain level to organized nano hierarchy structure). Seeds and needs of nanofiber are shown in Table 9.1.



9.11 Coloring principle of Morphotex® (Teijin).

Table 9.1 Uses of nanofiber utilizing its properties

	Properties	Various effects	Uses
○	Surface area effect	• Fiber surface area per weight is over 1000 times larger than that of usual fibers. • Very large adsorption.	• Adsorption material • Biochemical hazard prevention material • Ion-exchange material
○	Slip effect	• Flow of molecules changes and pressure loss becomes much smaller.	• Air filter • Biochemical hazard prevention material
	Hole effect	• Sieving by small holes	• Separation material • Sensor
○	Light effect	• Structure color appearance with transparent fiber with diameter less than wavelength of visible light	• Organic EL • Electronic paper • Fashion material • Polarizer
○	Surface tension effect	• Low surface tension force, water repelling of hydrophilic polymer	• Coating material • Paint
	Amalgamation effect	• Amalgamation in nanometer order	• Electromagnetic wave shielding material • High strength structure material
	Void effect	• Giving nano-void to fiber	• Humidity keeping material • Fouling prevention material
○	Three-dimensional effect	• Three-dimensional growth of cells on non-weaved textile	• Reclamation medical
	Sliding effect	• Increment of sliding of materials	• Complex material • Airplane
○	Sub-micron object catching effect	• Catching sub-micron-sized particles	• Biochemical hazard prevention material • Suit • Engine filter • Boiler • Air cleaner • Air conditioner
	Cell, living body, material recognition effect	• Having unique structure for recognition and bond with cell	• Reclamation medical • Bio-tip • Biosensor • Tailor-made medical

○: Important effects

9.2.3 Establishment of the basic technology – construction of nanofiber analysis technology

Nanofiber technology cannot be achieved by conventional spinning technologies. Self organization of molecules is needed in nano spinning technology and further development in usage. For measurement of the structure and properties of nanofiber, conventional analytical methods do not give sufficient sensitivity and resolution. So developments in analytical methods with high sensitivity and high resolution are required. New structure control technology is necessary for the far larger surface of nanofibers. These basic technologies and fabrication technologies are needed for the birth of a new fiber industry. Figure 9.12 shows development of nanofibers and the ripple effects which will be created.

9.3 Creation of new industries

Figure 9.13 shows examples of nanofiber applications in information, bio- and environment technologies.

9.3.1 Information technology materials

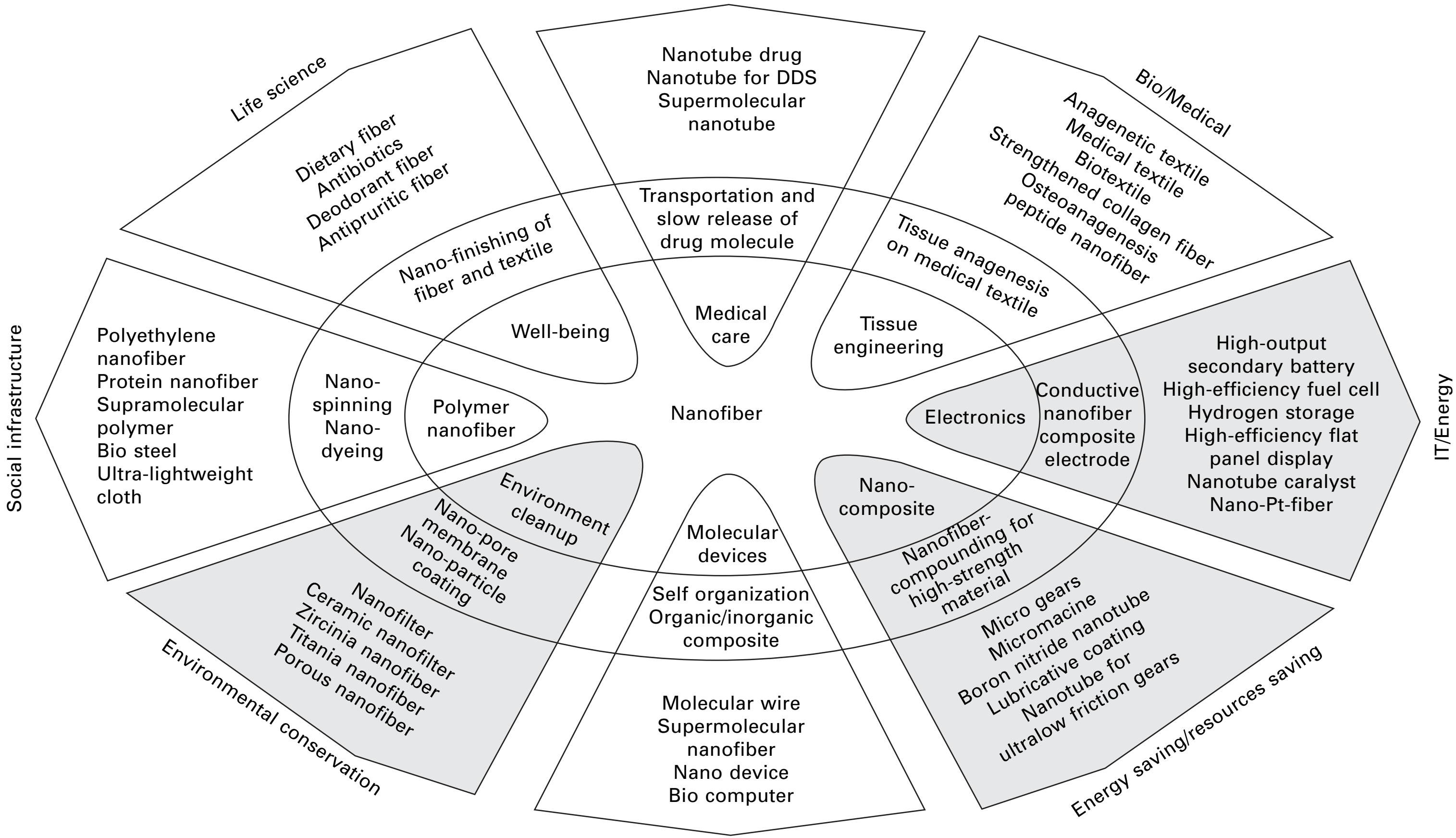
Increments in density and integration in electric devices require materials which can be assembled at nanometer level. High-speed optical information communication and optical computers can be produced using liquid crystalline polymer nanofibers with nonlinear optical properties and metal-covered nanofiber which pass light in one direction only. Nano-ordered distribution control has been realized in plastic optical fiber.[11,12]

9.3.2 Biofiber hybrid material

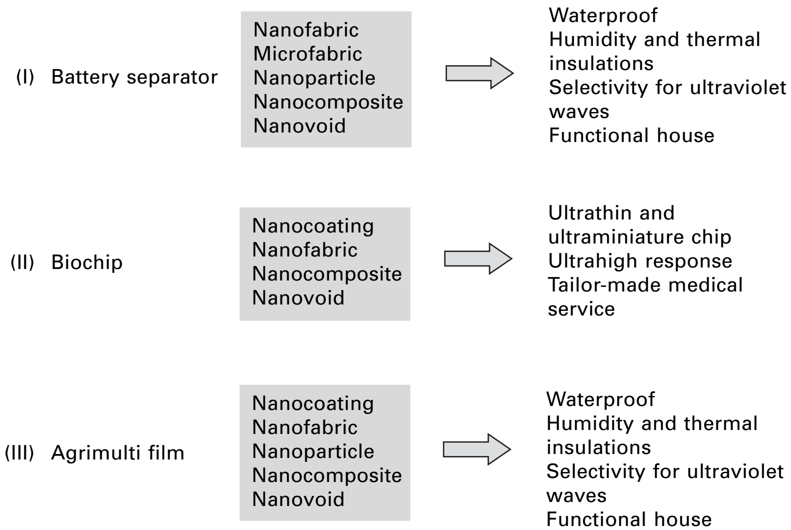
The orientation of biofibers in living materials requires control at nanometer level. High-ordered structures are formed to perform various deformations such as to stretch, compress, bend, and twist. Using three-dimensional assembly technology with nanofibers the growth of nanofibers from the surface of inorganic crystals, such as apatite can be controlled to give high performance materials with new and revolutionary properties.

9.3.3 Biomedical nanofiber

In bio-materials, nanofibers are organized within cells, which transmit communication of substances, energy, and information. For example, cells bound to collagen and fibronectin are recognized as suitable receptors whereby signals are propagated. Nanofibers play a very important role in transmitting



9.12 Development of nanofibers and their ripple effects.



9.13 Nanofiber application examples for IT (I), bio (II) and environmental technologies (III)

cell information in this way. Understanding the function of bio-nanofibers and constructing models will open up new and advanced medical nanofiber technology.[13,14,15]

9.3.4 Bio-nanofiber world – hints for the direction of artificial fibers[5]

The world surrounding humans and the world available to them is made up of nanofibers. Cotton, silk, and polyethylene, skeletal muscles, myofibrils in the human body, and DNA in cells are all composed of nanofibers. Coal, originally derived from plants, is also composed of nanofiber.

Professor Y. Atomi of the University of Tokyo has indicated how clothes from such fibers can have an entirely new function, which can include stimulation of body processes. The effects on the skin can be profound.

9.3.5 Ecology materials

Composites of biodegradable polymers and natural nanofibers of cellulose and imogolite (clay) can give green-nano-hybrid which shows high strength within a short time scale, but can be decomposed by enzymes and microbes over a longer time scale. This material can be applied to a structural material in transplantation medicine.

Hollow nanofiber has an extremely large nanospace. Such nanofiber has many functions, such as electron transfer or encapsulation functions, such as removing pollutants from the environment. Controlled release of drugs retained in the nanospace is another application. Non-weaved clothing with nanofibers has extremely new functions.

Electrical paper processing technology using self-organized nanofiber[16] is also useful in ecology. Characteristics which are necessary or achieved using 'nano-size fiber fabric' for electric paper are:

- Quick response time due to thinness of paper.
- Wavelength of visible light is around 600 nm and diameter of micro-fiber is more than 200–500 nm. Thus electric paper made with micro-fiber is less transparent due to light scattering.
- Since nano-size fibers have diameter less than 100 nm, light propagates without scattering. Thus electric paper with nanofiber fabric is transparent.

9.3.6 High strength ultra light material

Nanofiber with low defects can be fabricated by controlling structures composed of nanofiber. Nanofiber has a very high aspect ratio, so allows development of high strength materials. Ultra light and high strength materials can be fabricated by dispersing high strength nanofibers into polymer and controlling the interface.

Professor T. Kikutani (Tokyo Institute of Technology) has started the development study of such 'high strength fiber'[17] which was adopted as a National Japan project in 2001. The aim of this study is to achieve a strength of multi-use synthesized fibers which approximate the theoretically calculated strength limit. Fiber strength is increased by 2GPa due to the higher orientation of the molecules.

9.4 Researches and global developments of nanofiber

In the United States, the National Science Foundation (NSF), the National Fiber Research Institute (NTC), and the US Army are actively supporting nanofiber research. The US Army alone has provided $50 million ($10 million for five years) to Massachusetts Institute of Technology (MIT) to develop an ultra-lightweight and high functional military. The Institute for Military Nanotechnologies was set up on 1 May 2002, using this money. It is likely that the support to MIT will be provided for a further five years. Additionally non-governmental organizations, such as DuPont, will also participate. In Europe, development of nanofiber is being actively pursued, particularly by Marburg University in Germany. In Asia, China, Taiwan, and South Korea, researchers who have been inspired by the work in the United States are returning to stimulate developments in their own countries. It is an area of fiber technology to keep an eye on in the future.[18]

9.5 Further reading

9.5.1 General

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