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第 37 回本田賞授与式 記念講演（2016 年 11 月 17 日）

「新規セルロースナノファイバーの調製と特性・機能」

東京大学大学院農学生命科学研究科 教授

磯貝 明博士

「植物系ナノ材料の創成」

京都大学生存圏研究所 教授

矢野 浩之博士

Commemorative lectures at the 37th Honda Prize

Award Ceremony on the 17th November 2016

Development of Production Technology of Cellulose Nanofibers and Their Characteristics and Function

Dr. Akira Isogai

Professor of the Graduate School of Agricultural and Life Sciences at The University of Tokyo

Development in Bio-based Materials Inspired by Nano-to Micro-structures in Plants

Dr. Hiroyuki Yano

Professor of the Research Institute for Sustainable Humanosphere at Kyoto University

公益財団法人 本田財団
HONDA FOUNDATION

磯貝 明博士

東京大学大学院農学生命科学研究科 教授

Professor of the Graduate School of Agricultural
and Life Sciences at The University of Tokyo

Dr. Akira Isogai



■生まれ

1954年10月19日

■略 歴

1980年	東京大学 農学部 卒業
1982年	東京大学 大学院農学系研究科修士課程修了
1985年	東京大学 大学院農学系研究科博士課程修了（農学博士）
1985～1986年	米国 Institute of Paper Chemistry（大学院大学）化学科博士研究員
1986～1994年	東京大学 農学部助手
1989～1990年	米国農務省林産物研究所客員研究員
1994～1996年	東京大学 農学部 助教授
1996～2003年	東京大学 大学院農学生命科学研究科 助教授
2003年～現在	東京大学 大学院農学生命科学研究科 教授

■学・協会活動

2013年～現在	セルロース学会会長
2003年～現在	紙パルプ技術協会理事 木材科学委員会委員長
2015年～現在	機能紙研究会副会長
2006年～現在	木材科学アカデミーフェロー
2009年～現在	ナノファイバー学会理事

その他：アメリカ化学会、米国紙パルプ技術協会、
高分子学会、日本木材学会、繊維学会、
キチンキトサン学会、米国紙パルプ技術協会、
会員

■Born

October 19, 1954

■Education and Employment History

1980	Bachelor from Faculty of Agriculture, The University of Tokyo
1982	Master Degree from Graduate School, Division of Agricultural Science, The University of Tokyo
1985	Ph.D from Graduate School, Division of Agricultural Science, The University of Tokyo
1985-1986	Post-doctoral fellow, The Institute of Paper Chemistry, Appleton, WI, USA
1986-1994	Assistant Professor, Faculty of Agriculture, The University of Tokyo
1989-1990	Visiting Scientist, Forest Products Laboratory, United States Department of Agriculture, Madison, WI, USA
1994-1996	Associate Professor, Faculty of Agriculture, The University of Tokyo
1996-2003	Associate Professor, Graduate School of Agricultural and Life Sciences, The University of Tokyo
2003-present	Professor, The University of Tokyo

■Membership

2013-present	The Cellulose Society of Japan: President
2003-present	Japan TAPPI (Technical Association of Pulp and Paper Industry): Board, Chairman of Wood Science Committee
2015-present	High Performance Paper Society of Japan: Vice President
2006-present	Fellow of International Academy of Wood Science
2009-present	The Nanofiber Society: Board

American Chemical Society, TAPPI, Society Polymer Science Japan, etc. : Member

■研究業績・主な出版物

総説および著書：167編

例：セルロースの材料科学、単著、東京大学出版会＜2001年＞、
セルロースの科学、編集、朝倉書店＜2003年＞

出願特許：132件

■受賞歴

2015年 Marcus Wallenberg 賞

2015年 米国化学会 Anselme Payen 賞

2016年 日本農学会賞および読売農学賞

2016年 TAPPI (Technical Association of Pulp and
Paper Industry, USA) Fellow

その他 13件

■Research Achievement and Publications

Review articles, books & book chapters: 167

Patents & patent applications: 132

■Awards

2015 Marcus Wallenberg Award from Sweden

2015 Anselme Payen Award from American Chemical
Society, USA

2016 Japan Prize of Agricultural Science and Yomiuri
Agricultural Science

2016 TAPPI (USA) Fellow and other 13 awards

矢野 浩之博士

京都大学生存圏研究所 教授

Professor of the Research Institute for
Sustainable Humansphere at Kyoto University

Dr. Hiroyuki Yano



■生まれ

1959年2月6日

■略 歴

1982年	京都大学 農学部林産工学科 卒業
1984年	京都大学 大学院農学研究科修士課程 林産工学専攻 修了
1986年	京都大学 大学院博士課程 退学 京都府立大学 農学部 助手
1989年	京都大学 農学博士号 取得
1992年	京都府立大学 講師
1997～1998年	オーストラリア連邦科学産業研究機構 林産物研究所 客員研究者
1998年	京都大学 木質科学研究所 助教授
2002年	秋田県立大学 木材高度加工研究所 客員助教授
2004年～現在	京都大学 生存圏研究所生存圏開発 創成研究系 教授

■学・協会活動

2014年～2016年	ナノセルロースフォーラム会長
2008年～現在	木材科学アカデミーフェロー
2014年～現在	日本木材学会理事

その他：高分子学会、日本材料学会、セルロース学会、
日本成形加工学会、日本ゴム協会、他

■Born

February 6, 1959

■Education and Employment History

1982	Bachelor of Agriculture (Wood Science and Technology), Kyoto University
1984	Master of Agriculture (Wood Science and Technology), Kyoto University
1986	Assistant Professor, Dept. of Forestry, Kyoto Prefectural University
1989	Doctor of Agriculture, Kyoto University
1992	Lecturer, Dept. of Forestry, Kyoto Prefectural University
1997-1998	Visiting Scientist, Forest Products Laboratories, CSIRO, Australia
1998	Associate Professor, Wood Research Institute, Kyoto University
2002	Visiting Associate Professor, Institute of Wood Technology, Akita Prefectural University
2004-present	Professor, Research Institute for Sustainable Humansphere, Kyoto University

■Membership

2014-2016	Nanocellulose Forum: President
2008-present	Fellow of International Academy of Wood Science
2014-present	Japan Wood Research Society: Board

Society of Polymer Science Japan, Society of Materials Science Japan, Cellulose Society of Japan, Japan Society of Polymer Processing, Society of Rubber Science and Technology Japan, etc.: Member

■研究業績・主な出版物

総説および著書：101件

例：A. N. Nakagaito, H. Yano: The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites, Applied Physics A, 78, 547-552 (2004年) .

H. Yano, J. Sugiyama, A. N. Nakagaito, M. Nogi, T. Matsuura, M. Hikita, K. Handa: Optically Transparent Composites Reinforced with Networks of Bacterial Nanofibers, Advanced Materials, 17 (2) , 153-155 (2005年)

A. N. Nakagaito, M. Nogi, H. Yano: Displays from transparent films of natural nanofibers MRS Bulletin, 35 (3) (2010年) 214-218

出願特許：82件

■受賞歴

1989年 日本木材学会奨励賞

2005年 セルロース学会 林治助賞

2009年 日本木材学会賞

■Research Achievement and Publications

Review articles, books & book chapters: 101(A. N. Nakagaito, H. Yano: The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites, Applied Physics A, 78, 547-552(2004).

H. Yano, J. Sugiyama, A. N. Nakagaito, M. Nogi, T. Matsuura, M. Hikita, K. Handa: Optically Transparent Composites Reinforced with Networks of Bacterial Nanofibers, Advanced Materials, 17(2), 153-155(2005)

A. N. Nakagaito, M. Nogi, H. Yano: Displays from transparent films of natural nanofibers MRS Bulletin, 35(3) (2010) 214-218, and others)

Patents & patent applications: 82

■Awards

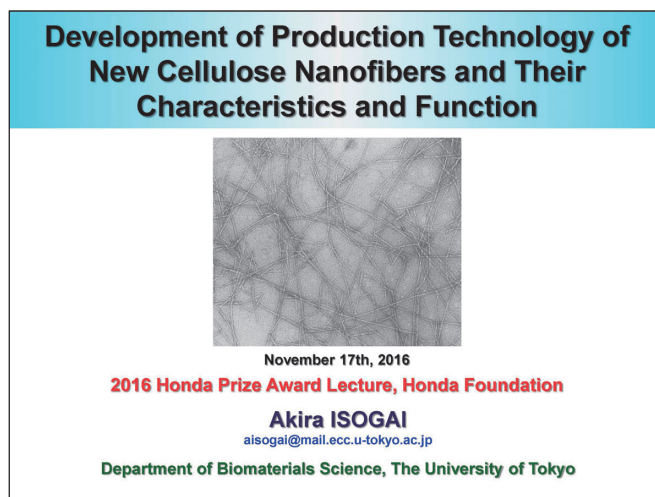
1989 Young Scientist Award, Japan Wood Research Society

2005 Hayashi Jisuke Award, The Cellulose Society of Japan

2009 Japan Wood Research Society Award, Japan Wood Research Society

Development of Production Technology of New Cellulose Nanofibers and Their Characteristics and Function

Akira Isogai



Thank you for your introduction. I would like to give my sincere appreciation to all relevant parties, the selection committee staff, President Ishida, who made a presentation today, and everyone else who congratulated me, for the opportunity to receive the prestigious Honda Prize together with Professor Yano, who also engages in the research and development of nanocellulose. Now, although my presentation is short, please allow me to briefly introduce the content of my research.

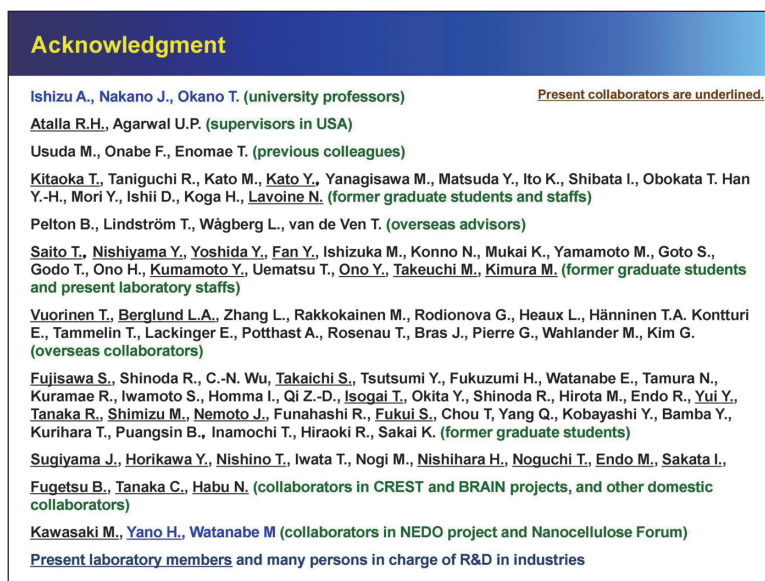


Fig 1

〈Fig 1〉 First, I would like to express my gratitude. I could not have done this work alone.

Through great cooperation from a number of people, somehow I managed to continue my research and achieve some successful results. I would like to give my appreciation to many people, including Professor Ishizu and Professor Okano, who trained me during my university days and are attending this ceremony today; those who helped me during my study in the USA; my postgraduate students; those still engaged in joint research with me (whose names are underlined in the figure); and professors in the field of paper manufacturing chemistry, in which I worked before entering into nanocellulose research.

Furthermore, big outcomes were delivered also by other relevant parties: former postgraduate students involved in this nanocellulose research, including Messrs. Saito and Nishiyama, Saito is now associate professor of this laboratory, and all of the current research staff; and many overseas students and research students from abroad, who stayed and exchanged information in this laboratory, and contributed to further widening of the research area after their return home.

So far, postgraduate students have accumulated substantial results from their research. We still have been working together with a number of professors in some projects, such as the CREST project of the Japan Science and Technology Agency, and the Bio-oriented Technology Research Advancement Institution (BRAIN) project. At the time when this project started, this research field was being exploited by the staff of Nippon Paper Industries Co., Ltd., Professor Yano at Kyoto University, and Mr. Watanabe, a former division chief, at the Paper Industry, Consumer and Recreational Goods Division of the Ministry of Economy, Trade and Industry. To be honest, I think we were lucky to join the stream of nanocellulose research initiated by such forerunners.

We would like to share the honor of this award among the participants: us and our research group (needless to say), and the staff of many companies who are now making efforts aimed at the practical application of nanocellulose. In addition, we are connected with hundreds of people through a network, relaying through everyone whom I have greeted today. I would appreciate it most if many people would receive any delight from this award and that it would lead to further research and development activities in the future.



Fig 2

〈Fig 2〉 This is a commemorative photo taken at an international conference in which I participated in my younger days (28 years ago). In the photo, I am with Professor Ishizu, who is attending this ceremony today, and Professor Atalla, who helped me in my research in the USA.

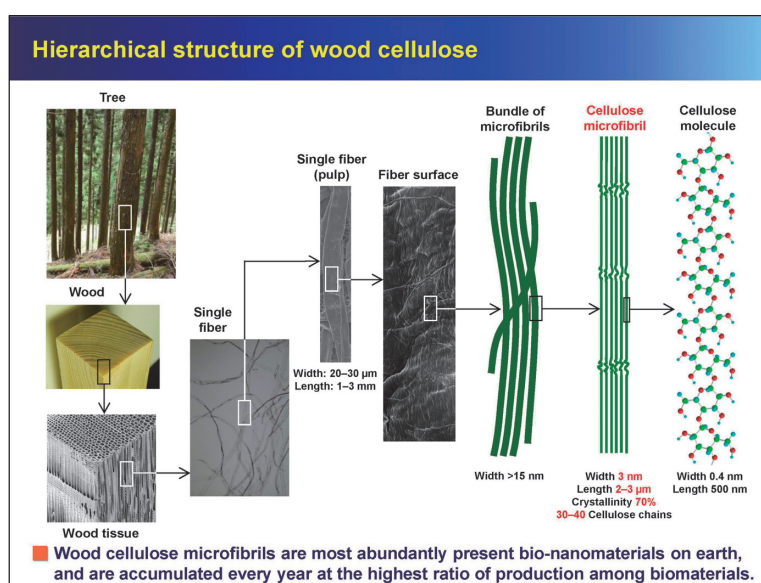


Fig 3

〈Fig 3〉 Trees grow upward against gravity and resist the damage from weather events and microorganisms. They have a hydrophobic nature, which enables pulling water to their top leaves against gravity, through the inside of their cell tissues, which resemble an assembly of pipes in structure. Those pipe-shaped aggregates of fibers preserve the body and life of a tree.

Pulp, the basic component of paper, is made by separating these wood cell tissues into individual fibers. Furthermore, when enlarging the surface of the pulp fibers, we can see that their minimum unit is a cellulose molecule, a straight-chained polysaccharide. The

second minimum unit is a cellulose microfibril, which is a bio-based nanofiber with a width of 3 nanometers, with a regular array of $6 \times 6 = 36$ straight long cellulose molecules.

In other words, cellulose microfibril is the most abundant bio-based nanofiber on earth. It is being produced and accumulated every year at the highest rate of production among all bio-based nanofibers. However, as those microfibrils are inseparably bound to each other by a significant number of hydrogen bonds, it was impossible to separate those microfibrils into undamaged individual nanofibers in order to make use of them as bio-based nano materials.

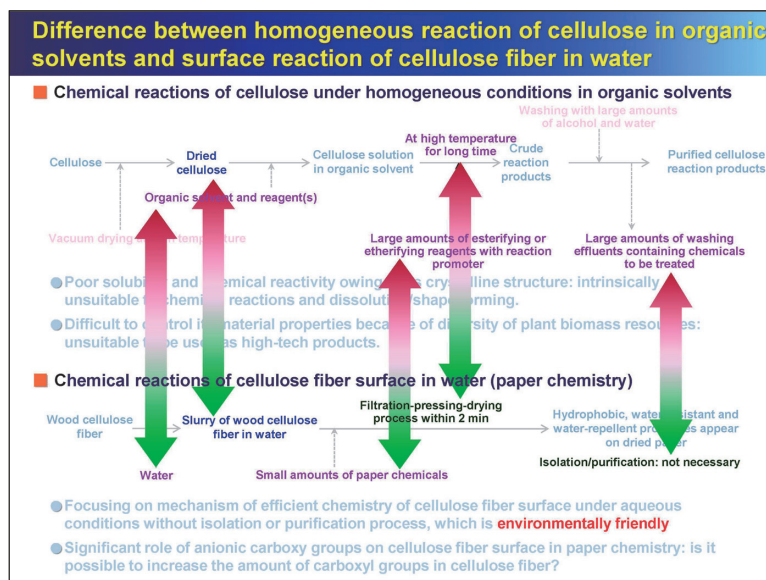
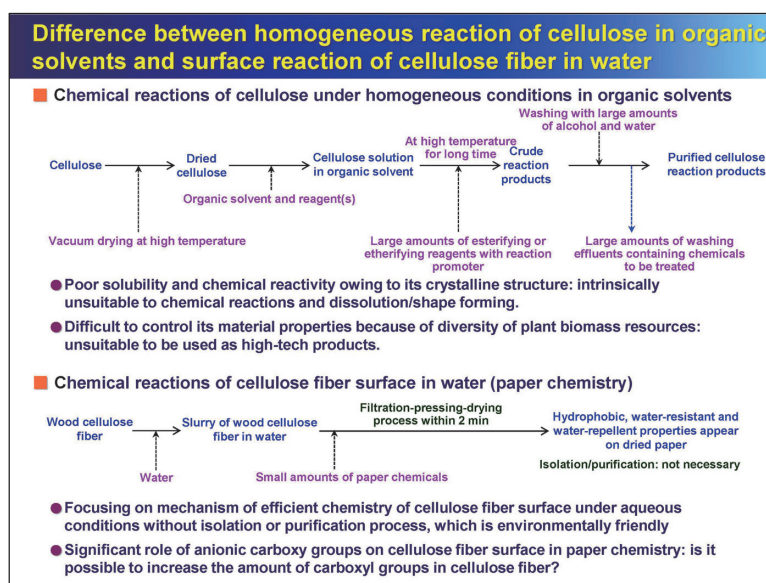


Fig 4 and Fig 5

〈Fig 4 and Fig 5〉 During my undergraduate and postgraduate days, I was engaged in the research on various chemical reactions of cellulose under the direction of Professor

Ishizu. In the research process, I dried a piece of cellulose, added an organic solvent into it, did the same with a large quantity of reagent, and stirred them at high temperature for a long time. After that, when cleansing the treated cellulose by a mass of alcohol and water in its isolation/purification process, a volume of waste liquid, which had to be treated, was produced in the course of obtaining a slight amount of cellulose reactant. Although the disposal of the waste liquid into the sewer was previously permitted (subject to pre-mixing with a large amount of water), currently, it must be recovered and treated in an appropriate manner. Since those days, I have thought that some treatment methods, such as chemical reactions and dissolution, will hardly work for cellulose because of its chemical stability. Also, since biomass-derived materials, such as cellulose, have a wide range of structures and characteristics due to biodiversity, it was difficult to control the qualities of cellulose (characteristic, structure, and physicality) constantly within a certain definite range, for the purpose of applying it to cutting-edge materials.

Then, in my assistant days, I conducted research for chemical treatments applied to the surface of cellulose fibers, specifically those employed in the field of paper manufacturing chemistry. In the field, paper is produced through the following 3-step process: dispersing wood cellulose fibers into water, applying a bit of additive to them, and finally making paper within 2 minutes through a sequence of screening, pressing, and drying. The resulting paper is effectively provided with water resistance and repellency, which cellulose does not have initially, and it is used as a convenient low-price material in our surroundings.

When comparing the 2 improvement processes of cellulose—improving it by organic chemical reactions and improving the surface of its fibers by the paper manufacturing chemical process—the former needs a complete desiccation, the addition of much reagent, and a long period of reaction at high temperature, resulting in mass generation of waste liquid in its isolation/purification process. On the other hand, the latter needs only a slight addition of reagent and no desiccation, completing in a short time without an isolation/purification process. That is to say, the latter is an outstanding improvement process of cellulose, in terms of its environmental friendliness and high reaction efficiency. With that, I tried to find out more about the mechanisms of this efficient improvement process.

In the course of this research, recognizing the importance of negatively charged carboxyl groups, which exist on the surface of cellulose fibers, I came to feel a strong need to increase the amount of carboxyl groups inside cellulose.

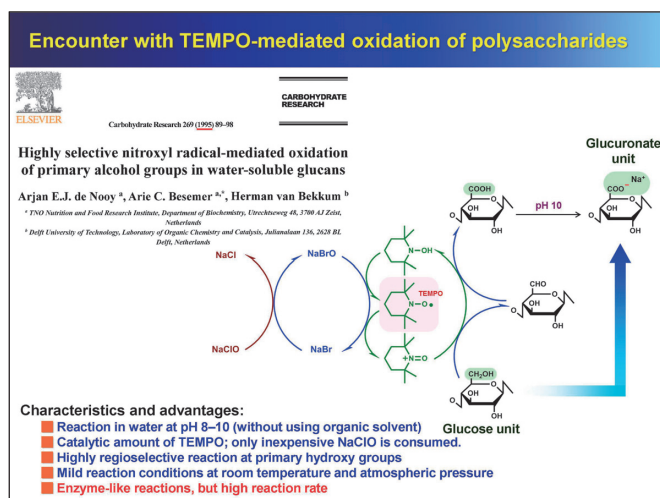


Fig 6

⟨Fig 6⟩ In 1995, a research group in the Netherlands applied TEMPO catalytic oxidation to starch, which is a polysaccharide and similar to cellulose. TEMPO functions as a catalyzer and selectively oxidizes and changes polysaccharide primary hydroxyl groups into sodium salt (carboxyl group) during the course of the reaction in which inexpensive sodium hypochlorite changes into sodium chloride.

Compared to the chemical reaction of cellulose using organic solvents, this reaction is water-based and catalytic, contributing to a reduction in the amount of chemical additives used. In addition, this is an extremely regioselective reaction, which is similar to biological and enzyme reactions occurring inside our body. Inside our body, at normal temperature and pressure, water-based and selective material conversion and energy production are possible. One of the reasons why biotechnology is currently drawing much attention is the fact that water-based selective material conversion and energy production through catalytic reactions are possible at normal temperature and pressure. From such a point of view, we worked on TEMPO catalytic oxidation of polysaccharides including cellulose.

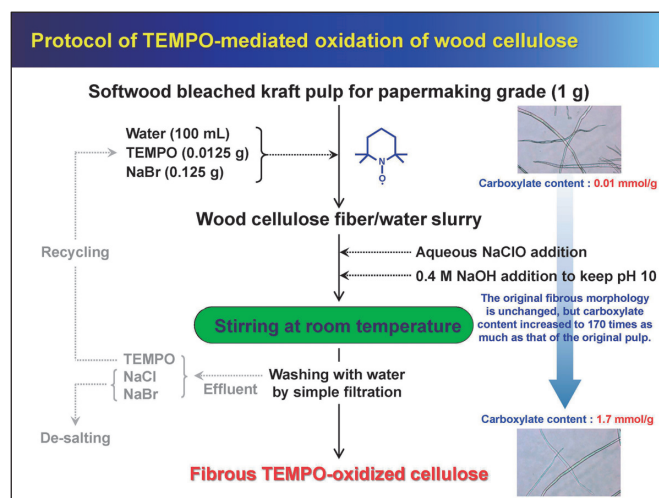


Fig 7

〈Fig 7〉 The actual treatment process is quite simple. Since cellulose fiber does not dissolve into water, the only things you have to do are to disperse it into water, add a small amount of TEMPO, and stir it at normal temperature. As a result, carboxyl groups that have a negative charge are produced 170 times more as compared to the initial amount contained in cellulose fiber and while maintaining their fiber form. At the initial stage of our research, we aimed to modify cellulose fiber, which does not dissolve into water, in order to enable it to dissolve into water through the TEMPO catalytic oxidation reaction. However, cellulose fiber did not either dissolve into water or change its fiber form even after TEMPO catalytic oxidation. Thus, it was no longer in our interest and we halted the research. However, from the subsequent research, we figured out that even though the fiber form does not change, carboxyl groups that provide a negative charge are produced 170 times more when compared to the initial amount.

Afterwards, R&D staff at Nippon Paper Industries have established a technology for collection and reuse of TEMPO from the waste washing liquid.

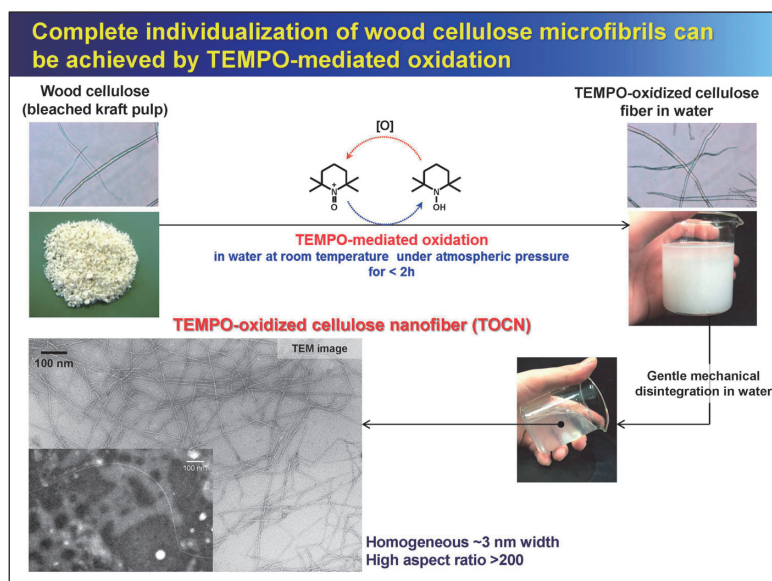


Fig 8

〈Fig 8〉 Here is a slide showing the process sequence. Through the TEMPO catalytic oxidation reaction of wood cellulose, primary hydroxyl groups on the surface of crystalline cellulose microfibril are selectively oxidized, therefore, a negative charge (shown as the yellow dots) can be introduced. At this stage, the fiber form remains the same. When this TEMPO-oxidized cellulose fiber is dispersed into water and goes through a simple stirring process, a transparent gel can be produced.

At first glance, I thought it dissolved into water. However, when observed with a transmission electron microscope, the fiber was completely separated into individual nanofibers of 3 nanometers in width, which is the second smallest unit after the plant-biosynthesized cellulose molecule. No one in the world had ever discovered this phenomenon before. In this slide, you can also see some nanofibers bent sharply. Those were produced during the course of a preparation of observation samples. As a result, we realized the development of a novel bio-based nanofiber whose width is 3 nanometers and length is at a micron level.

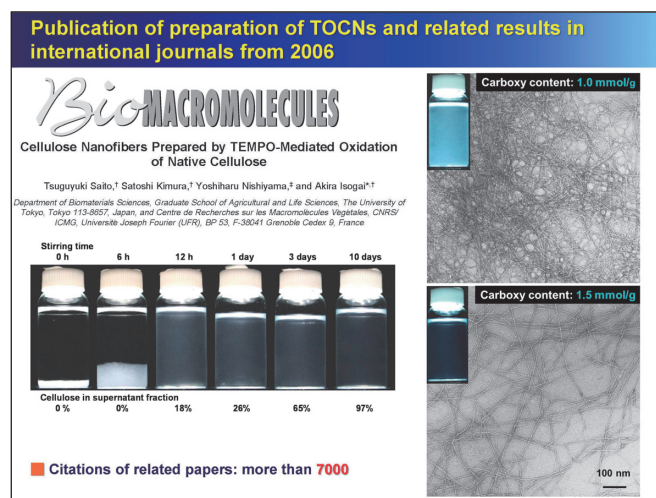


Fig 9

〈Fig 9〉 In regards to our discovery of preparation conditions for the new bio-based nanofiber, we did not consider its practical application or related matters. However, first, we wrote a research article and contributed to international journals. The reason is we had no idea what to do with such a new fiber. Actually, we did not give any thought to it. As this photo shows, fibrous TEMPO-oxidized cellulose sinks to the bottom of water. However, if one continues stirring it, it gradually swells and, in the end, it becomes a transparent gel. Then, nanofiber is individually separated and dispersed into the water. When the amount of carboxyl groups is small, the water remains cloudy and there will be some visible light-sized aggregate left if performed under the same conditions. Thus, the amount of carboxyl groups to be introduced is considered to be the important factor and a necessary condition when producing nanofibers from cellulose.

Since we did not know what applications we had for this new material, we first contributed an article to the American Chemical Society and published our findings. The article was cited by many researchers and further experiments ensued. An easy preparation method of intuitively interesting bio-based nanofiber was reported and consideration of its possible fields of application went far beyond our imagination. As a result, the number of citations to our article rapidly increased. Who could have imagined this?

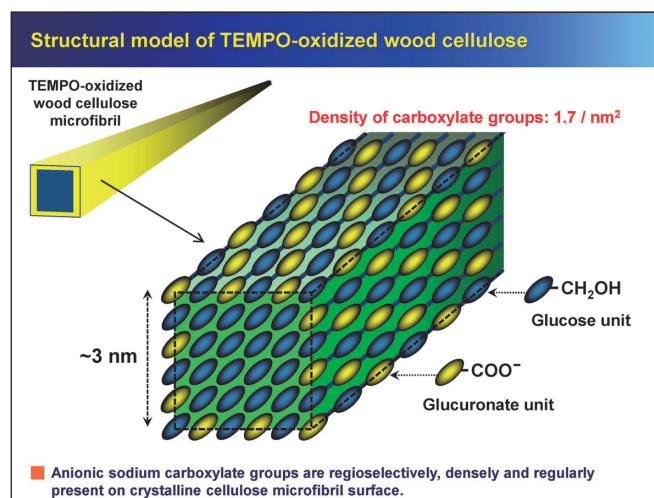


Fig 10

〈Fig 10〉 As stated previously, the main component of plant's cell walls are comprised of cellulose microfibrils constituted by bundling $6 \times 6 = 36$ straight-chain cellulose molecules. $4 \times 4 = 16$ celluloses inside the crystal will not be oxidized at all by the TEMPO catalytic oxidation reaction of plant cellulose. However, carboxyl groups, each of which has a negative charge, will be systematically introduced to alternate cellulose molecules exposed on the surface of cellulose microfibril. This is an extremely specific and regioselective reaction. If the findings were obtained through research specifically aiming to unveil the mechanism of such a selective reaction, I would be proud of myself to some extent. However, that was discovered by accident.

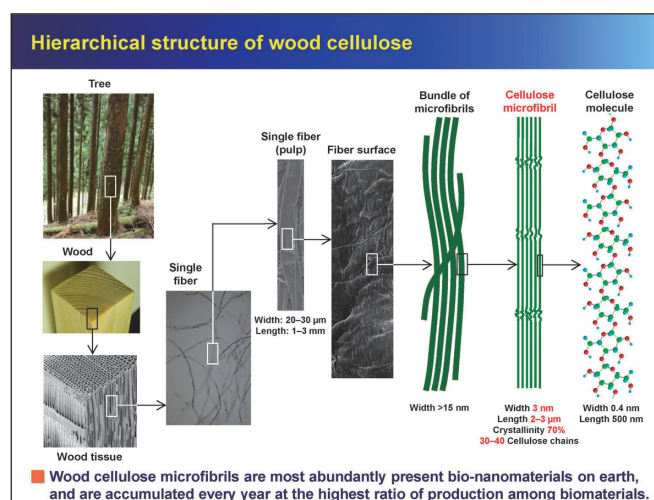


Fig 11

〈Fig 11〉 It was previously impossible to individually separate nanofiber by breaking all the hydrogen bonds between cellulose microfibrils of 3 nanometers in width—the second smallest unit after the cellulose molecule among the layered structures of plant cellulose and comprised of $6 \times 6 = 36$ straight-chain cellulose molecules.

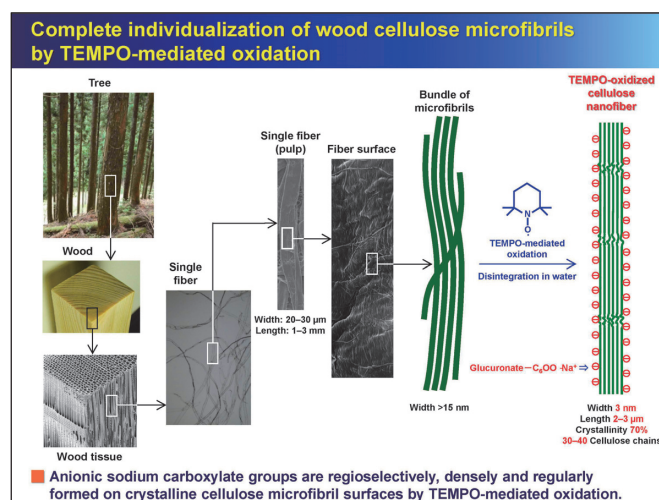


Fig 12

〈Fig 12〉 However, through the TEMPO catalytic oxidization treatment of plant cellulose fiber, a negative charge can be regularly and densely introduced on the surface without oxidizing inside the cellulose microfibril. This induces a strong osmotic pressure effect and charge repulsion. As a result, individually separated TEMPO-oxidized cellulose nanofiber (TOCN) can be produced.

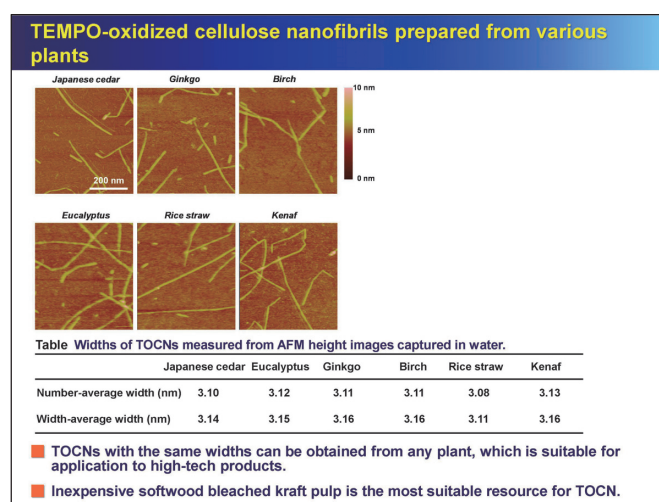


Fig 13

〈Fig 13〉 Characteristics of plant-derived materials may differ according to tree species and their growing locations. This is also a part of biodiversity. Broad-leaved trees are suitable as raw material for printing/communication paper while needle-leaved trees, which have long fiber length, are suitable for packaging paper such as cardboard and milk cartons. However, a characteristic unique to cellulose microfibrils that exist inside the cell walls supporting plants is that they have exactly the same size and structure although they may have been procured from any kind of tree species. TEMPO-oxidized cellulose nanofiber that is a uniformly sized material of 3 nanometers in width can be produced from different

plant species such as needle-leaved trees like Japanese cedars; broad-leaved trees like eucalyptuses and birches; gymnosperms like ginkgo trees; and herbaceous plants like rice plants and kenafs.

Unfortunately, the average length and length distributions of TEMPO-oxidized cellulose nanofiber cannot be controlled perfectly. However, as mentioned above, to produce nanofiber materials that have uniform width from any tree species and any plant raw materials is an essential factor when considering application to advanced materials. If applicable nanofiber can be produced only from specific tree species, raw material availability and scope of its application will be limited. Thus, being able to produce nanofiber, such as TEMPO-oxidized cellulose nanofiber whose width is uniformly nanosized, from any plant materials brings about a superior advantage.

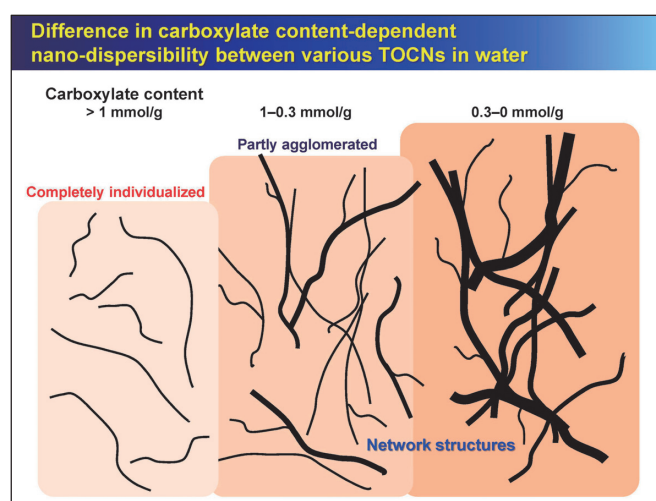


Fig 14

〈Fig 14〉 Probably, even in Japan, there are more than 100 kinds of cellulose nanofiber that are currently accessible. However, as this slide shows, most of the cellulose nanofiber prepared solely through the machine fibrillation process often became non-uniformly-sized or split while forming inconsistent aggregation/network structures. Such a network type cellulose nanofiber has superiority since it can be efficiently dehydrated and sheeted through filtration on a wire mesh, which are processes performed in paper production.

However, it is currently impossible to accurately and scientifically measure and evaluate shapes and structures of such inconsistently structured nanocellulose. You can sometimes measure them through microscopic images, but what you are observing is only a small part of a whole.

On the other hand, the TEMPO-oxidized nanofiber that we developed is completely individually separated. Since its width is 3 nanometers and uniform, we can apply some analytic and scientific methods we have theoretically and experimentally accumulated in the field of polymer science. There are some differences when compared to polymers. For

example, nanofiber has a slightly larger width and it consists of an aggregate of 10 polymer chains. As cellulose nanofiber is a new nano material discovered very recently, there are substantial academic challenges to be fundamentally investigated. Since TEMPO-oxidized cellulose nanofiber is extremely small, although an aqueous dispersion solution is applied on a wire mesh as performed in a paper making method, no films or sheets will be made because nanofiber goes through the wire mesh and falls into a drain port. Thus, films and sheets made from TEMPO-oxidized cellulose nanofiber cannot be produced through a paper making process. However, considering from the fact that the nanofiber is completely individually separated, characteristic analysis can be performed easily, in other words, it is relatively easy to conduct analysis or structure investigation to define a necessary condition where this nano material can be utilized as an advanced material.

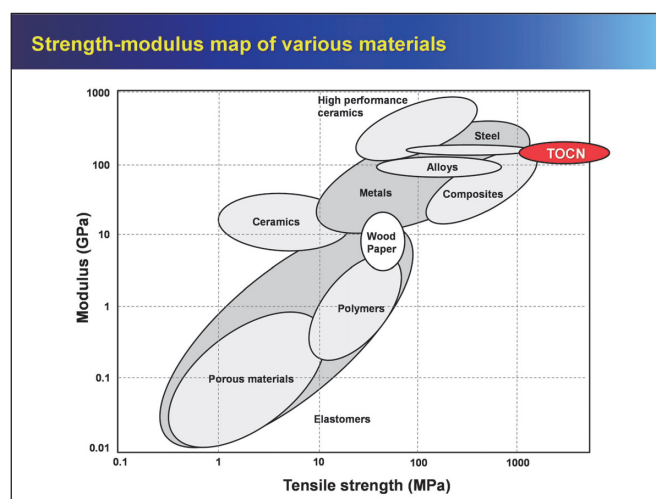


Fig 15

〈Fig 15〉 This is a strength-modulus map. The Y-axis indicates elastic modulus and hardness while X-axis indicates a tensile strength at break. As this map is logarithmically displayed, there are huge differences in strength between each material. As TEMPO-oxidized cellulose nanofiber is considered to be a material that is harder and stronger than steel, its application to high strength material would be possible if we could leverage such characteristics.

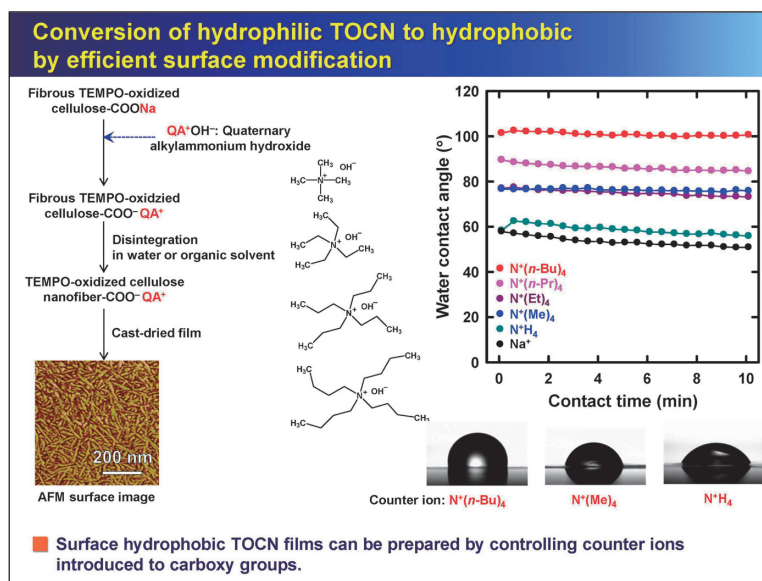


Fig 16

〈 Fig 16 〉 TEMPO-oxidized cellulose nanofiber demonstrates an extremely high hydrophilic property, since sodium salt of the hydrophilic carboxyl group is present on its surface in a regular manner at high density. On the other hand, many of those involved in research and development are more likely to think about the possibility of taking advantage of the high strength and high elastic modulus of nanocellulose to produce light and strong plastic composite material and also utilizing that biomass-derived lightweight high-strength material for cars or the like as an alternative for glass fiber reinforced materials. However, while TEMPO-oxidized cellulose nanofiber is extremely hydrophilic, plastic is a hydrophobic material, so they cannot be sufficiently uniformly mixed in a manner similar to oil and water. Therefore, even a starting material with a width of 3 nanometers clumps together in a plastic substrate; thus, in many cases, we face a problem in which a nano-composite effect cannot be expressed.

In that case, you can easily switch the surface of TEMPO-oxidized cellulose nanofiber from hydrophilic to hydrophobic, by performing ion-exchanging on sodium salt of hydrophilic carboxyl group that is present at high density on its surface so as to change the sodium salt into hydrophobic quaternary alkylammonium salt. This hydrophobization treatment is difficult to implement when a chemical reaction requires the treatment to be conducted in a high temperature organic solvent for a long period of time. However, this ion exchange reaction is water-based and can proceed stoichiometrically at a ratio of one to one. Thus, the feature of this ion exchange reaction is that it enables you to efficiently switch the surface of cellulose nanofiber from hydrophilic to hydrophobic, without adding excessive chemicals.

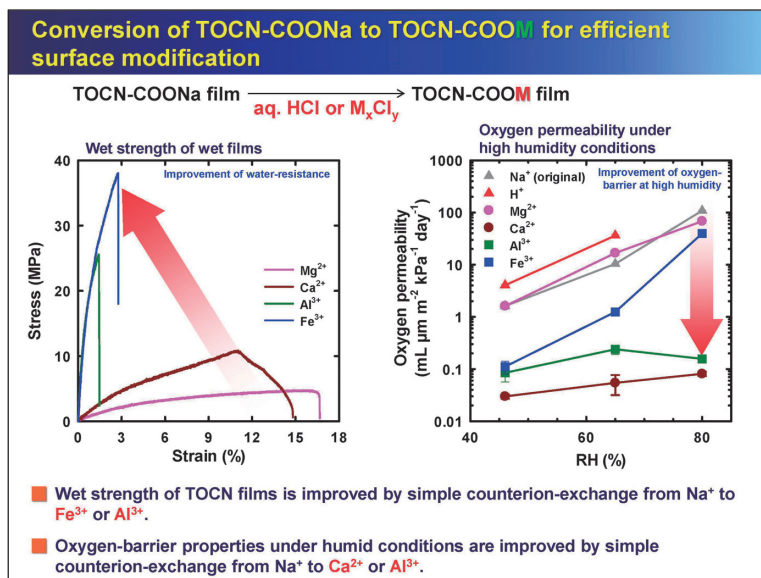


Fig 17

〈Fig 17〉 This figure shows more interesting research findings. The previous figure showed that sodium salt of the carboxyl group on the surface of TEMPO-oxidized cellulose nanofiber was changed into hydrophobic alkylammonium salt. This figure shows the change in characteristics when a sodium ion is exchanged with another type of ion such as one of aluminum or iron. The original sodium salt-type TEMPO-oxidized cellulose nanofiber film is not water-resistant enough, so the shape of a film disintegrates instantly when soaked in water. However, by performing ion-exchanging to change a counter ion of carboxyl group into an iron ion or an aluminum ion, water resistance clearly develops, which leads to a remarkable increase in elastic modulus and breaking strength of the film in water.

Also, films for wrapping pharmaceutical products, foods, and electronic parts are required to have an oxygen barrier property, that is, those films have to prevent oxygen penetration. The sodium salt-type TEMPO-oxidized cellulose nanofiber film exhibits an extremely high oxygen barrier property under dry conditions, however, in an under high-humidity environment close to normal conditions, its oxygen barrier property remarkably decreases, that is, oxygen permeation rate markedly increases. This property also stems from the low water resistance of sodium salt-type TEMPO-oxidized cellulose nanofiber. Meanwhile, by performing ion-exchanging to change counter ions from sodium salt to calcium salt or aluminum salt, the film came to exhibit a sufficiently high oxygen barrier property, that is, a sufficiently low oxygen permeation rate, even under high-humidity conditions. You can achieve the exchange of the counter ion of TEMPO-oxidized cellulose nanofiber film from sodium salt to calcium salt simply by a process of immersing the film in a calcium chloride aqueous solution and drying it. As such, by exchanging counter ions of the carboxyl group on the surface of TEMPO-oxidized cellulose nanofiber into other metal ions, new functions

can be added under a water-based condition, giving it an advantage.

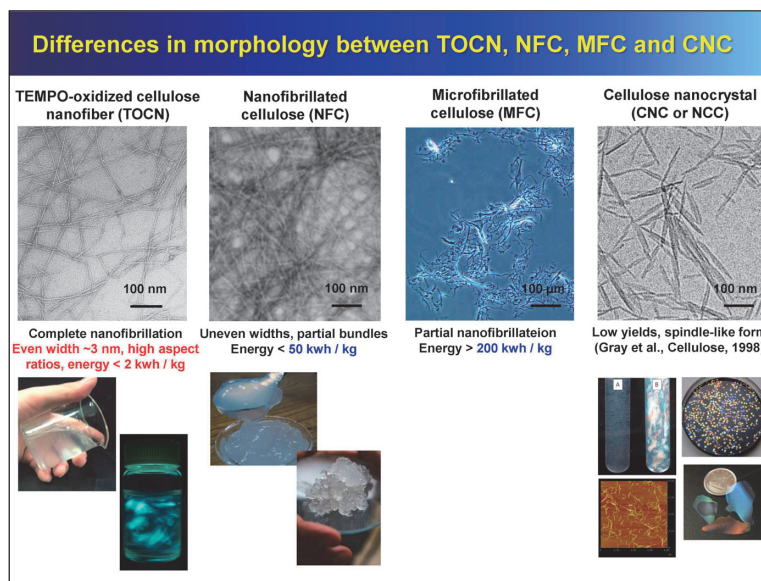


Fig 18

〈Fig 18〉 We classified various types of representative nano cellulose that have been discovered according to shape. The far right is a photo of a cellulose nanocrystal, upon which Canada and America are focusing their attention; it is spindle-shaped and short-length nanocellulose produced by using 64% sulfuric acid. The second from the right is microfibrillated cellulose (MFC), which has already been available in the domestic market since the 1980s. In the photo of this MFC, the length scale is 100-micrometer long, which is 1,000 times the length of a nanometer; therefore, thick and wide fibers at a micron level are mixed. As shown in the second from the left, when cellulose is dispersed in water and subject to defibration performed only by mechanical treatment, the width of nanocellulose becomes about 10 to 20 nanometers. However, the nanofiber partly clumps together or forms network structures. In the case of TEMPO-oxidized nanofiber, since fibers, each of which is characterized by a uniform width of 3 nanometers, are completely separated from each other, it is possible to drastically reduce defibration energy required for nanofiberization.

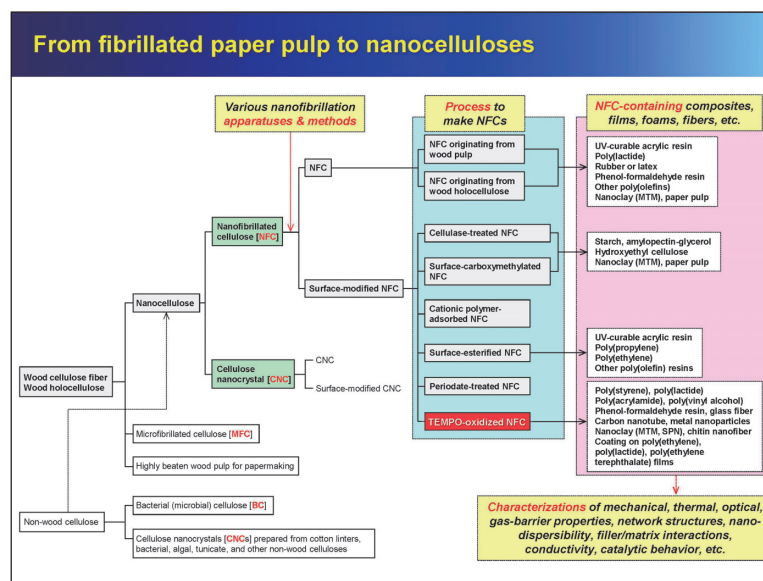


Fig 19

〈Fig 19〉 Since the beginning of the 21st century, there has been a boom of research and development on nanocellulose materials. One of the factors behind the boom is the trend in which, with the rise of information technology and population decrease, demand for printing paper and communication paper has declined, and, in response, the paper industry has sought new uses of pulp fiber instead of using it for paper. Additionally, as mentioned before, in Japan, Professor Yano at Kyoto University and the Ministry of Economy, Trade and Industry have made concerted efforts in explaining the features and advantages of nanocellulose widely across various fields in order to promote understanding for nanocellulose, which has also contributed to driving the boom.

Before gaining public recognition for research on nanocellulose materials, it seems that there has been a four-step breakthrough as shown here. One of the steps involves the development of a new device that improves nano-defibrillation efficiency. Still, since the defibrillation process required a large amount of power consumption, quality improvement through a pulp pretreatment process was considered. Examples of such pretreatments involve treatment to increase hemicellulose content, and minor pretreatment by means of cellulase, which is a cellulose-degrading enzyme. TEMPO catalytic oxidation reaction used by us was also involved in those pretreatments of pulp fiber.

After this breakthrough method was made public through papers, presentation meetings, or other occasions, nanocellulose came to receive increasing attention as new bio-based nanomaterial. Furthermore, researchers in engineering and science except those in agriculture, as well as people from business enterprises have been considering the possibility of creating various types of composite materials and their practical application. Simply combining materials may mostly produce only a mediocre result like “1 + 1 = 2,” however, in some cases, “1 + 1” can result in 3, 5 or 10.

As a result of conducting a study on how to create nanocellulose-based composite materials, it was found that the composite materials are light and strong, optically transparent, heat-resistant, and have an oxygen barrier property, that prevents oxygen penetration, a conductive property, and a high-activity catalyst function. Thus, they were found to have many excellent properties as an advanced material. These research findings raised the expectation for the possibility of utilizing pulp fiber for a variety of advanced materials as well as for conventional paper or paper board, which led to the research and development of nanocellulose in this century having been rapidly driven forward by the four-step breakthrough.

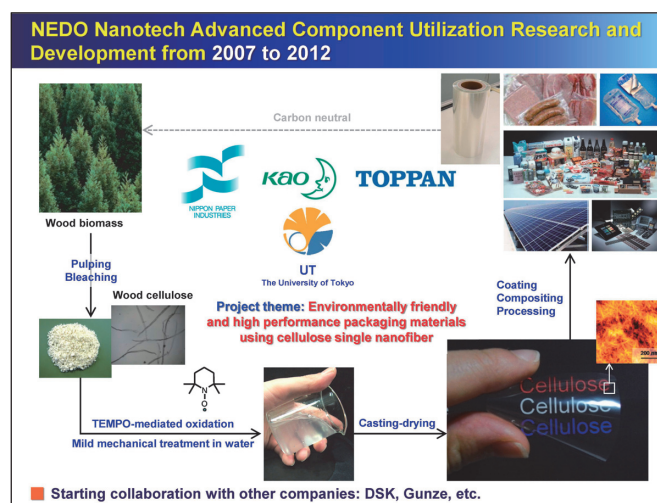


Fig 20

〈Fig 20〉 In the course of study on TEMPO catalytic oxidation reaction of polysaccharide, without any intent to develop a new production method of nanocellulose, we incidentally discovered how to prepare novel nanocellulose, which has a specific structure. However, we did not have even the faintest idea of in which fields our nanocellulose would be able to be used. Researchers engaged in fields related to agriculture are usually interested in plant structure and biosynthesis, but they do not necessarily put up their antenna towards the utilization of our findings for advanced materials or other practical applications. Basically, we are engaged in a scientific field that is related to biology, chemistry, physics, and mathematics concerning plants and animals. Therefore, not many faculty members nor graduate students in our field are cut out for or actively engaged in making things. Accordingly, when we discovered this new nanocellulose, we openly introduced it to people in business enterprises for consultation, and asked them to conduct basic collaborative research towards its practical application. Initially, we received a cold reaction from many business enterprises; however, some of the representatives from Nippon Paper Industries, Kao, Toppan Printing, DKS, and Gunze showed interest in nanocellulose. We have been proceeding with collaborative research and exchange of information with these companies

for more than 10 years.

Supported by Nippon Paper Industries, Kao, and Toppan Printing, our research proposal presented to the Nanotech Advanced Component Utilization Research and Development was adopted by the New Energy and Industrial Technology Development Organization (NEDO), and we proceeded with a collaborative project under the theme of the Development of Environment-Friendly High-Performance Packing Members Using Cellulose Single Nanofiber from 2007 to 2012. This project was intended to utilize a high oxygen barrier property, that is, a property that prevents oxygen penetration, of a TEMPO-oxidized cellulose nanofiber film for environment-friendly high-performance, transparent packaging materials. Most of the packaging films for food, medicine, and electronic devices are discarded and incinerated after use. Packaging films in current use are derived from petroleum, so incineration of such film results in atmospheric CO₂ increase and contributes to global warming. So, we expect that utilizing bio-based nanofiber as a substitute for some share of petroleum-based packaging films will contribute to the reduction of CO₂ emissions.

We learned a lot from this collaborative research with those companies. Through network and information exchange with professionals experienced in practical application and commercialization who have skills and knowledge beyond our reach, we can learn many lessons. For example, when we exchange some information with one person from one company, through him or her, we can develop a human network with dozens or hundreds of people behind that person, all of whom have their own business contacts, who again have their own compartmentalized network. Thus, we will further develop a human network into various fields.

We realized that without borrowing skills, wisdom, and experience from many people, it would be impossible to find a suitable application of novel nanocellulose, which was incidentally discovered without being aware of its potential usage.

With that, we began to engage in collaborative research projects with people from business enterprises, while placing a special emphasis on fundamental research, as a university laboratory. I am truly grateful that now many people are conducting research on this material with great interest.

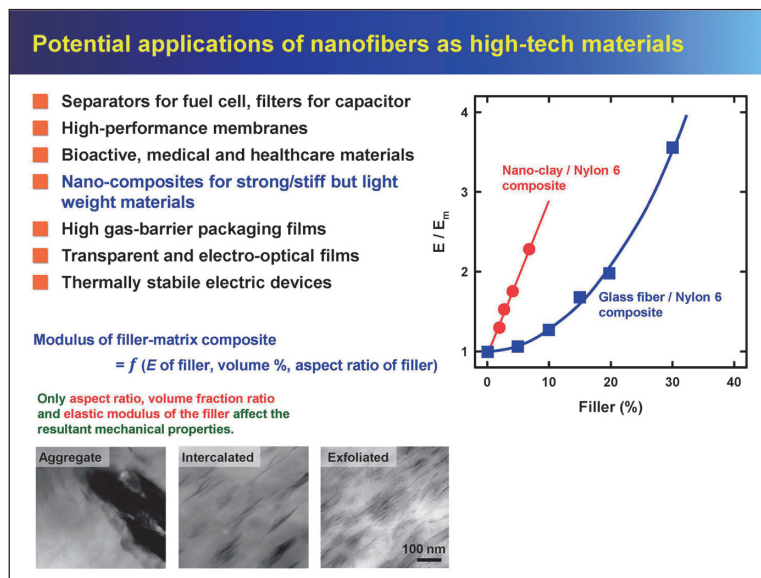


Fig 21

〈Fig 21〉 The figure shows a list of possible nanofiber applications. Among them, the application to lightweight high-strength composite materials is attracting the attention of many people as the most promising use. If a nanofiber is thinner than a glass fiber, even a smaller additive amount of nanofiber can provide the same degree of strength that a larger additive amount of glass fiber can do. To make this possible, however, it is necessary for each one of nanofibers to be completely nano-dispersed in a plastic substrate at that time. Success depends on whether it is possible to nano-disperse fibers that originally are in nano size without allowing them to clump together. It is difficult for us, a group of beginners in a university laboratory, to learn a method of engineering nano-dispersion in a substrate in a short period of time, from the viewpoint of skill and safety which require know-how. Therefore, we depend on business enterprises relating to this compounding technology.

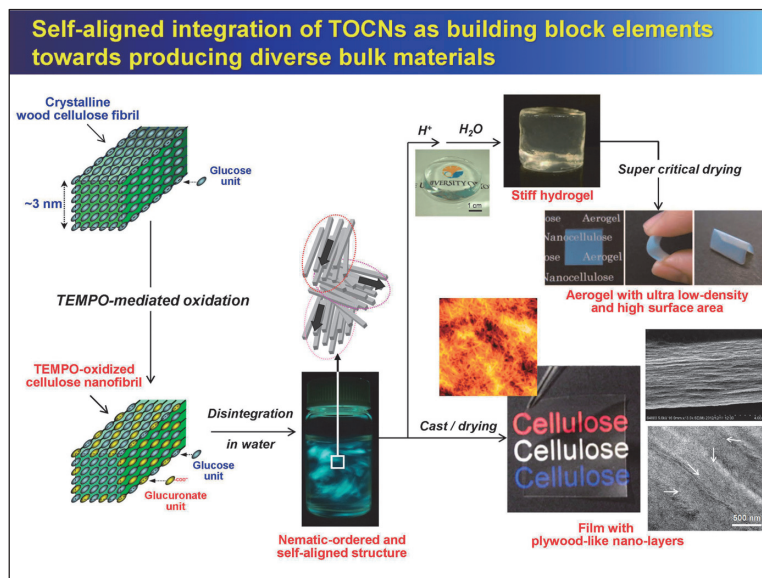


Fig 22

〈Fig 22〉 TEMPO-oxidized cellulose nanofiber is characterized by the regular presence of sodium salt of a carboxyl group that is highly condensed and negatively charged on its surface.

Due to this characteristic, it is subject to self-organization in water and comes to have a liquid crystal structure of a nematic state. This liquid crystal structure constitutes a factor leading to the development of a cast-dry film that is transparent, has a dense nano multilayer structure and exhibits a property which prevents oxygen penetration. At the same time, this nanofiber is also characterized by its convertibility that allows you to convert it by changing the molding process into a spiderweb-like network structure and aerogel that has transparency, high-strength, and high heat insulation properties.

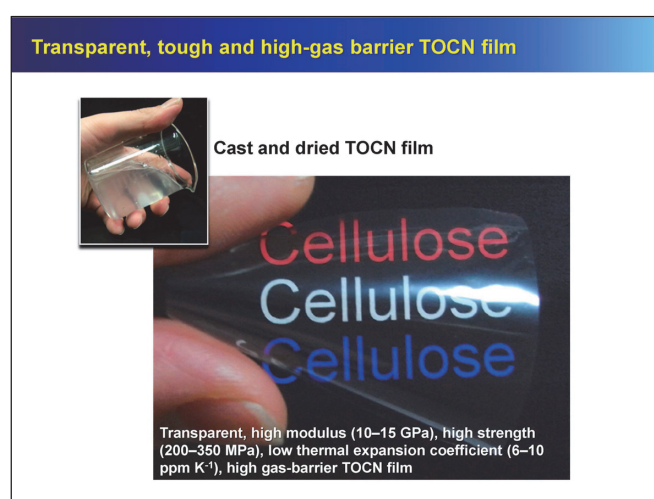


Fig 23

〈Fig 23〉 As I have explained, the film that is obtained by applying a casting-drying

process to an aqueous dispersion of TEMPO-oxidized cellulose nanofiber exhibits transparency, high elastic modulus, high strength, low coefficient of linear thermal expansion, high oxygen barrier property, and hydrogen gas permselectivity. These are properties that only this nanofiber can exhibit.

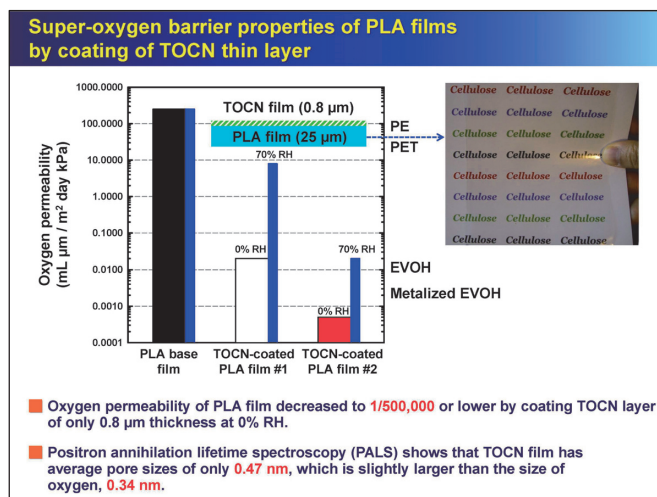


Fig 24

〈Fig 24〉 As shown in the figure, a polylactic acid film and a polyester film show a high oxygen permeation rate, since they easily allow oxygen penetration. When a thin TEMPO-oxidized cellulose nanofiber film with a thickness of a little less than one micron is combined with the surface of those films, the oxygen permeation rate remarkably decreases and a high oxygen barrier property develops; their oxygen permeation rate is reduced to less than 1/500 thousandth of their original rate under dry conditions. On the other hand, under high-humidity conditions, the oxygen permeation rate increases and the oxygen barrier property decreases due to the hydrophilic property of nanofiber; however, they still have a higher oxygen barrier property than conventional petroleum-based films. To find out the reason for this phenomenon, we carried out a study by using a positron annihilation technique, which is a technique for measuring the size of small pores. By using the film with an oxygen barrier property, we can drastically extend the shelf life of foods, pharmaceutical products, medicines, etc. and since it is made from biomass-derived carbon-neutral materials, incineration disposal after use will not result in atmospheric CO₂ increase.

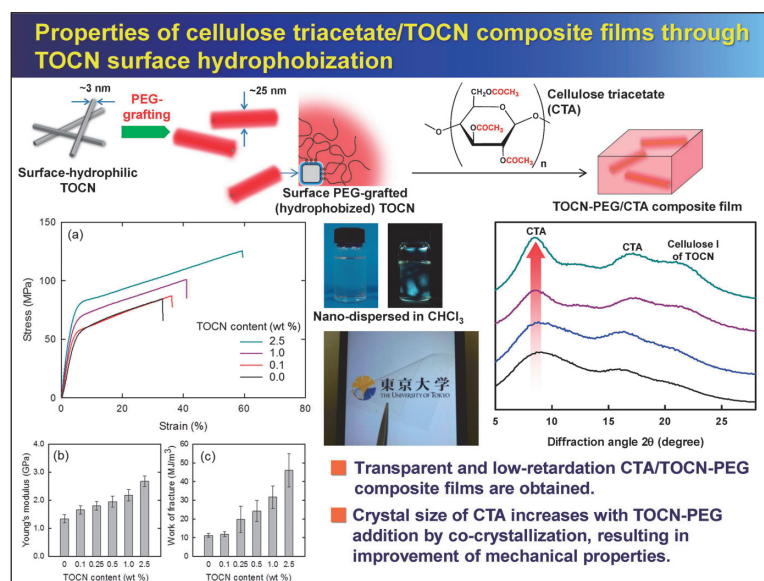


Fig 25

〈Fig 25〉 This figure shows an example of composite material development based on cellulose triacetate, which is used for liquid crystal displays. By simply combining cellulose triacetate with several percent cellulose nanofiber, a high level of strength and toughness will be expressed. The effect resulting from combining a polymeric substrate with cellulose nanofiber depends on the nano-dispersibility of the nanofiber in the substrate.

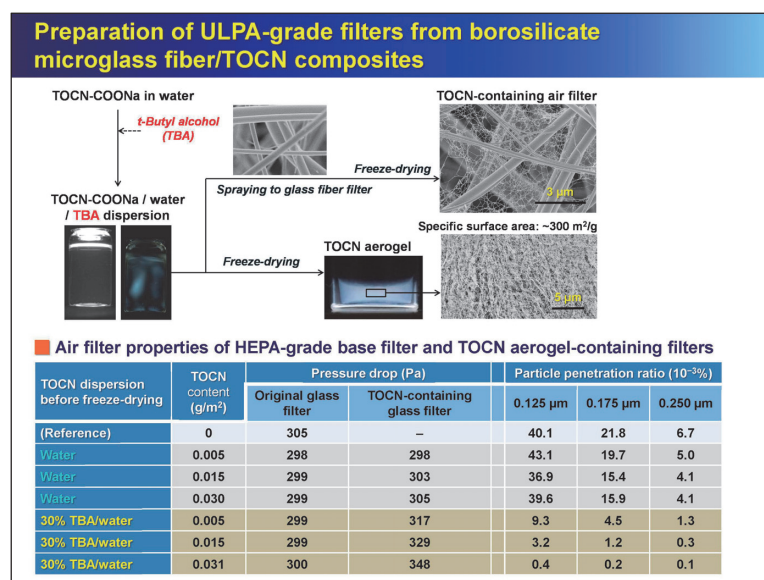


Fig 26

〈Fig 26〉 This slide shows the manufacturing method and characteristics of a spiderweb-like air filter using nanofiber. By converting TEMPO-oxidized cellulose nanofiber dispersion liquid into a spiderweb-like nano-network structure, an air filter will exhibit impressive characteristics; it can efficiently trap fine particles at a size of PM2.5, while exhibiting low pressure loss.

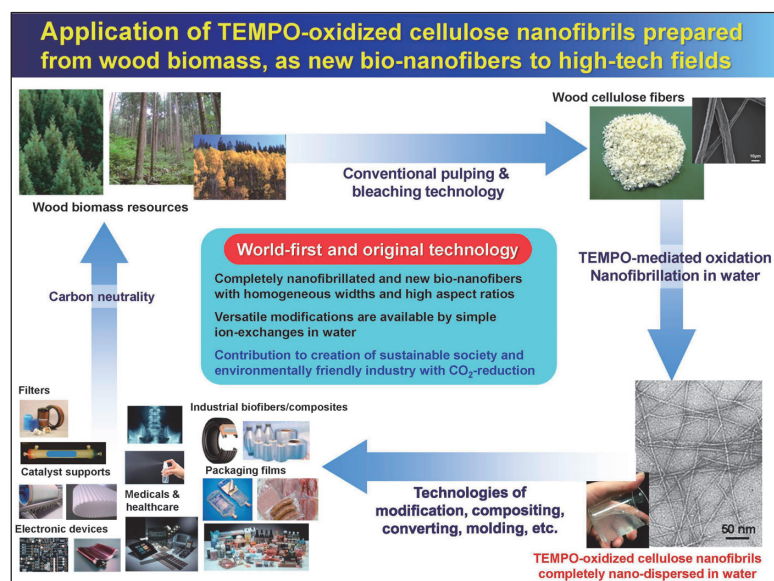


Fig 27

〈Fig 27〉 From the above findings, it is expected that forestry biomass will be utilized in a circulative manner as the figure shows. More specifically, we can utilize existing pulping and bleaching technologies in order to obtain both electric energy and high-purity cellulose by exploiting abundant unutilized forestry biomass in the country as starting material.

Exploiting the accumulated technologies of a paper manufacturing company makes it possible to obtain inexpensive cellulose material that is about 60 yen per 1 kg in dry weight. Until now, this cellulose material has been used as raw material for paper and paper board. However, we expect that by converting some part of this cellulose material into nanocellulose and further promoting the cycle to apply it to new advanced materials that have not used this material until now, we will be able to contribute to the revitalization of the forest industry. The creation of new industries in which integration of different industries in different fields is promoted, and global issues including creating the sustainable society social infrastructure, the reduction of carbon dioxide in the atmosphere, and the prevention of global warming will follow.

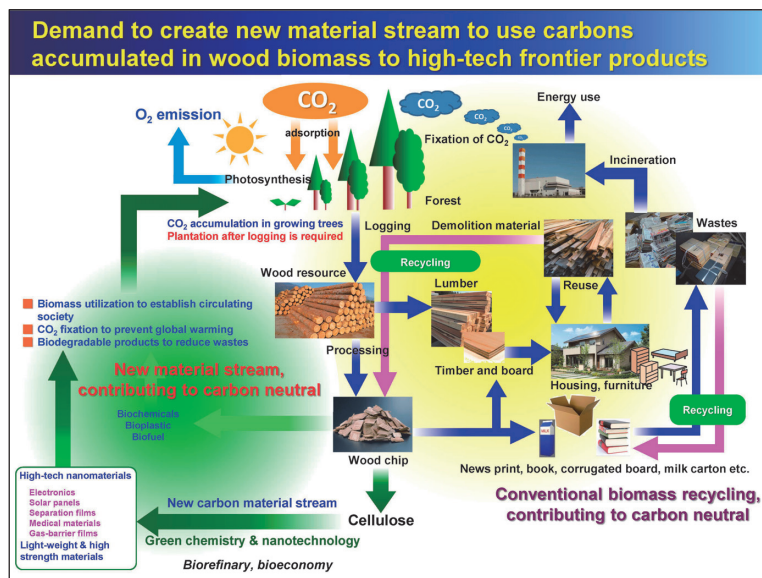


Fig 28

〈Fig 28〉 Until about 20 years ago, people had a misconception that use of forest resources would lead to environmental destruction. It is only plants in the growing stage that absorb and fix CO₂ in the atmosphere and release oxygen. Since trees that are fully grown do not need to further develop their tree bodies, they will no longer absorb and fix CO₂ much, emitting greater amounts of CO₂ in their respiratory process. Therefore, in order to reduce atmospheric CO₂, it is important to promote efforts to cut down full-grown trees and utilize them as materials in which CO₂ is stored and fixed without burning them. After logging operations, we need to plant new trees and grow them, which is a typical method of reducing CO₂. However, due to population decrease and information technology development, the demand for wooden houses and paper has been decreasing, which hampers the smooth operation of this circulating loop. This results in a vicious circle in which neither tree planting nor reduction of CO₂ can make progress.

On the other hand, however, if it becomes possible to utilize cellulose, which accounts for half the weight of wood chips, for advanced materials in an environmentally friendly manner, we will be able to make these two circulating loops work smoothly, which will pave the way for the possibility where forest biomass resources can be used in unprecedented new industries or for the creation of new materials. Activating these two circulating loops will promote tree planting in deforested areas and lead to growing trees. Additionally, while these trees are growing, they will absorb CO₂ and take it into their tree bodies, which can potentially contribute to the prevention of global warming. In the face of this global challenge, Japan, a country with plentiful forest biomass resources and with accumulated scientific knowledge and skills on cellulose nanofiber, is ready to take the lead in making efforts towards a resolution, and I sincerely hope that Japan will develop a social infrastructure that can serve as a model ahead of the rest of the world.

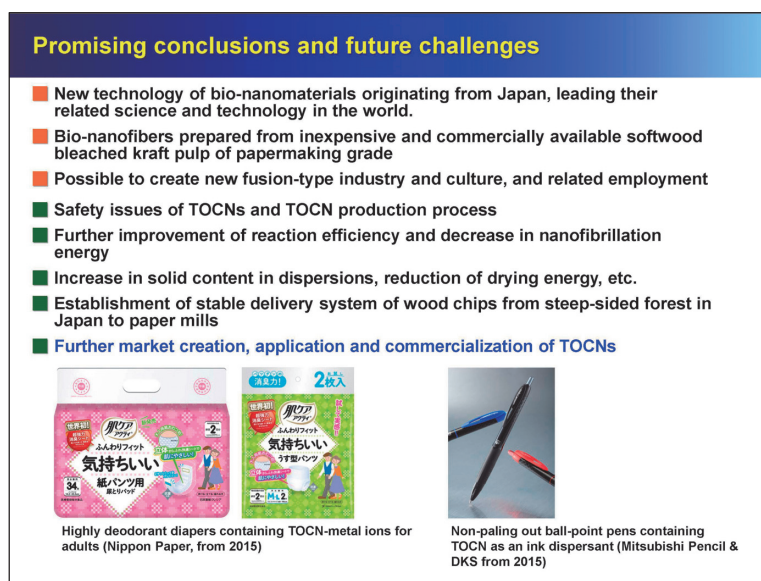


Fig 29

〈Fig 29〉 What we expect of cellulose nanofiber is shown in the three points displayed in the upper part of the figure. However, there are some challenges. At the production and utilization steps, safety confirmation has to be conducted. More efforts have to be made to improve production efficiency and to impart water resistance efficiently. Also, it is important to consider how to carry wood chips from Japanese forests on steep slopes in order to provide a stable source for advanced materials. It is necessary to build a system and a method for the distribution. Of course, it is required to promote the commercialization, market formation, and practical application of cellulose nanofiber. Nippon Paper Industries, which kindly delivered a congratulatory message today, achieved the practical use of cellulose nanofiber by combining it to disposable diapers for adults with a deodorizing function designed to alleviate the burden on caregivers. In addition, Mitsubishi Pencil and DKS have been promoting the practical use of cellulose nanofiber by producing ballpoint ink that does not cause blurring of characters and graphics. We sincerely appreciate these businesses for taking the lead in promoting practical application.



Fig 30

〈Fig 30〉 It has already been 20 years since we started research on TEMPO catalytic oxidation reaction to polysaccharide in 1996. We are extremely grateful for the support that the Japan Society for the Promotion of Science has provided for the past 20 years. We owe our past achievements to such continuous support. Their support resulted in the discovery of a new cellulose nanofiber in 2006, after 10 years of research, and presently, we are continuing basic research with various supports. Associate Professor Tsuguyuki Saito in our research laboratory has made the greatest contribution to the discovery of TEMPO-oxidized cellulose nanofiber. This photo shows the current members of our laboratory.

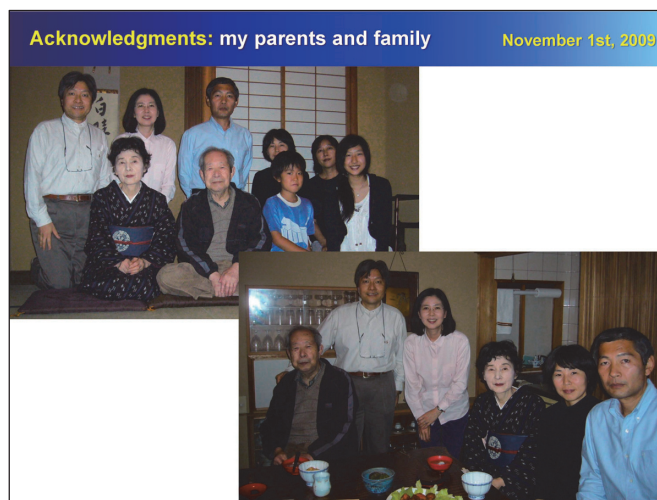


Fig 31

〈Fig 31〉 Lastly, I would like to express my appreciation to my parents who raised me in a very healthy way. This has allowed me to promote research and educational and social activities up to now. The photo above was taken at my father's 88-year old celebration (*beiju* (米寿)). He himself was an engineer who wanted to be a researcher, so I believe he is

delighted to know about this in heaven. My brother and his wife also supported me. Thankfully, my mother is blessed with good health. Also, I would like to express my thanks to Chiaki, my wife, who has always supported me and taken care of my health by paying attention to my diet. I would like to thank you all for your attention.

Development in Bio-based Materials Inspired by Nano-to Micro-structures in Plants

Hiroyuki Yano



First, I would like to express my deepest gratitude to Honda Foundation; Mr. Ishida, the president of Honda Foundation; Mr. Yamamoto, managing director; Honda Foundation staff including Ms. Norie Yamamoto; as well as the selection committee member for selecting me as the 37th Honda Prize laureate. Likewise, I also would like to give my sincere appreciation to everyone attending today's ceremony despite your busy schedule, including Mr. Fumio Manoshiro, chairman of Japan Paper Association who kindly presented the congratulatory address; Mr. Masahiro Samejima, chairman of The Japan Wood Research Society and professor at The University of Tokyo; Mr. Takahiro Hachigo, president and representative director of Honda Motor Co., Ltd. Receiving such a prestigious prize absolutely came out of the blue. I don't think I compare with past renowned Honda Prize laureates, but I am truly honored to be a part of them.

I believe that my former teachers, seniors, and colleagues who have been engaged in our research together will be very grateful for the fact that research in wood physics, relatively considered as a minor academic field, has been recognized as an award-deserving field of research from the perspective of ecotechnology.

Today, as you can see, we have a number of people kindly attending the ceremony and many congratulatory addresses were presented. This reminds me of my wedding, exactly 25 years ago. This November, my wife and I celebrated our silver wedding. Receiving the Honda Prize at the same time as Professor Isogai, whom I greatly respect, is truly a great honor and I genuinely appreciate that our "*mariage*" between his research and my research was appreciated in leading the development of Honda Foundation's philosophy—ecotechnology.



Fig 1

〈Fig 1〉 Today, I would like to talk about how I encountered cellulose nanofiber (CNF) and how I have been engaged in this research in terms of its application. Before starting, let me note that, unlike Professor Isogai's work, my research in cellulose nanofiber has not been applied to actual products yet and thus is still under development.

I was born in Nagano Prefecture. When I was in elementary school, I lived in Azumino city where there are beautiful mountains and clean bodies of water. On a day off, I used to go outside and play around in this lovely nature for the whole day.

When I started my degree, I moved to Kyoto. Kyoto had been the capital of Japan since the Heian period and there are many old temples and shrines. The temple you can see in the figure is Houkaiji-temple, located 10 minutes away by foot from my house. As such, wooden architecture built 1,000 years ago during the Fujiwara period can be still found from place to place in the city.

I had lived in an environment of rich natural beauty and lush woods (with epic wooden architecture) during my university years, and then, I transferred to the Wood Research Institute in Uji, Kyoto for my postgraduate courses. It is the predecessor of the present Research Institute for Sustainable Humanosphere.

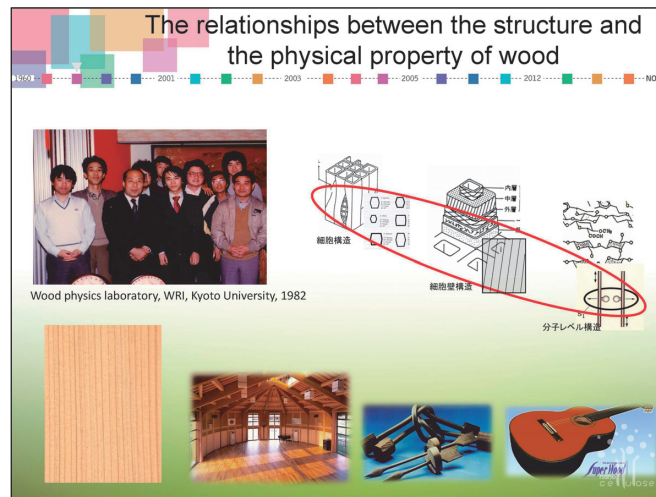


Fig 2

〈Fig 2〉 I studied wood physics in my postgraduate studies. Woods are obviously widely used in our daily life, such as for architectural and furniture material.

Many of you present today would wonder “is studying wood physics still necessary?” However, there are still many elements which remain unknown regarding the material produced by plants.

Wood has an extremely complex structure developed through its long history of evolution in order to pass genes onto next generations. At the Wood Physics Laboratory, which I belonged to, the relationships between the structure and the physical property at the wood’s molecule level, cell level, and cellular structure level had been studied.

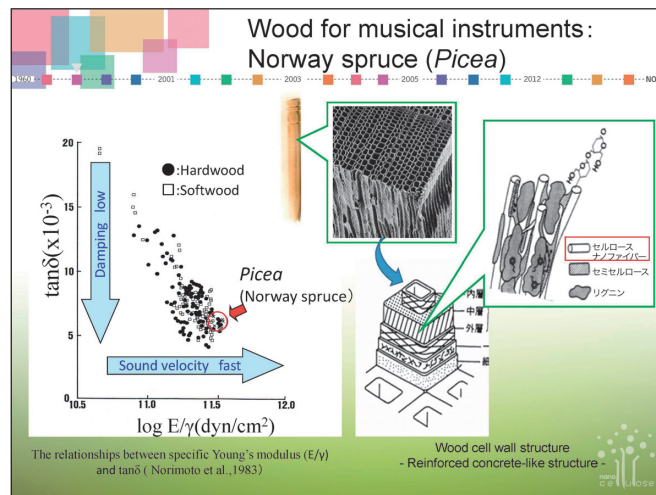


Fig 3

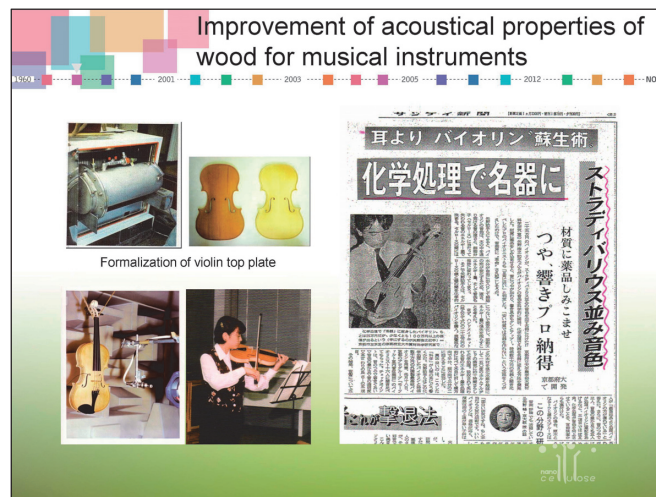


Fig 4

〈Fig 3 and 4〉 I engaged in research in identifying the acoustical properties of woods used for musical instruments and its modification using chemical treatment under the direction of Professor Tadashi Yamada and Professor Misato Norimoto.

Professor Norimoto has been engaged in research in cellulose nanofibers, called microfibril in other words, the relationship between wood properties and layered structures such as cellulose nanofiber's crystalline structure and its orientation inside the cell wall. At that time, he had published his study arguing that Norway spruce, often used as a material for the violin and piano, has a property that transmits sound faster among woods because cellulose nanofiber is horizontally oriented to the grain inside the cell walls. On the contrary, in the case of woods that are easy to bend, cellulose nanofiber is vertically oriented to the grain.

After meeting Professor Norimoto, I found the research very interesting and fascinating. Then, after 2 months from my first encounter with him, I decided to join doctoral programs. He gave me the idea of analyzing wood properties from the aspect of cellulose nanofiber.

At postgraduate school, I discovered that chemical modifications such as acetylation and formalization can improve the acoustic properties of wood materials for musical instruments. I actually built a violin using wood materials that were chemically treated and tested how much improvement could be identified. I summarized the findings and results into my doctoral thesis.

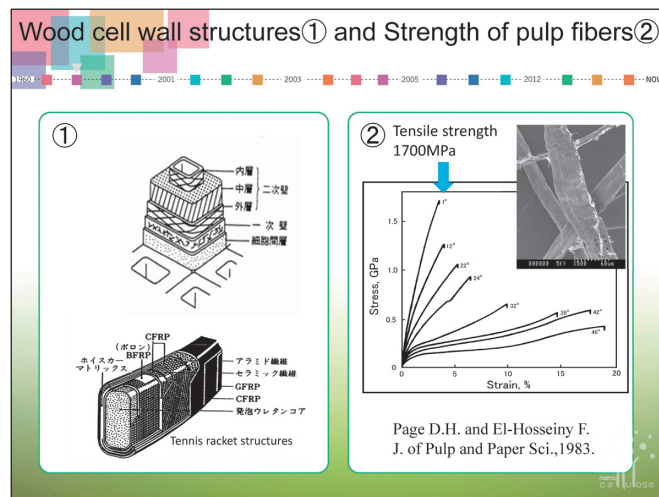


Fig 5

〈Fig 5〉 After that, I got a position at Kyoto Prefectural University and continued my research in wood materials for musical instruments. Then, there was a turning point.

This picture shows a comparison between cell wall structures and tennis racket structures. I realized that the structures of a tennis racket frame, which aims to be light and strong, and the cell wall of wood material are very similar. In addition, I happened to know that pulp is 3 to 4 times stronger than steel.

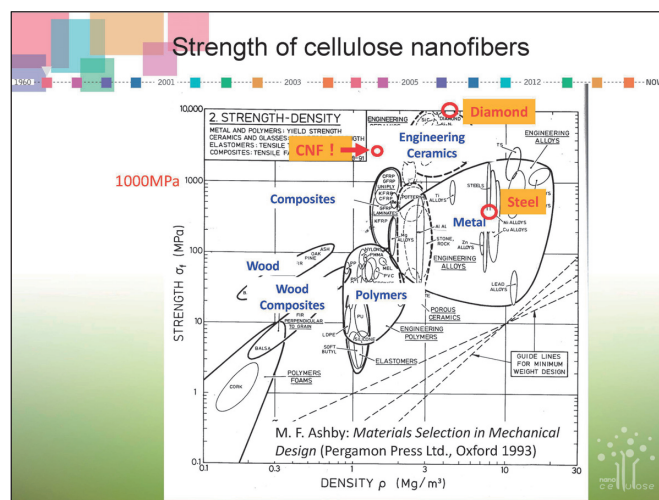


Fig 6

〈Fig 6〉 Based on the data on pulp strength, I calculated the strength of cellulose nanofiber and made comparisons with other materials. Surprisingly, I found that its weight is 1/5 that of steel while its strength is at least 5 times stronger.

These findings were not widely recognized by the researchers in cellulose and wood material fields. However, to me who, at that time, was wondering whether I should continue research in musical instruments, it was definitely an impressive result.

I came to realize that cellulose nanofiber in other words, microfibril are essential factors developed through the process of plant evolution in order to establish a light and strong structure. Then, I started thinking about developing a material based on cellulose nanofiber. That was about 20 years ago.



Fig 7

〈Fig 7〉 These are the materials we have developed using cellulose nanofiber. I will introduce some of them now.

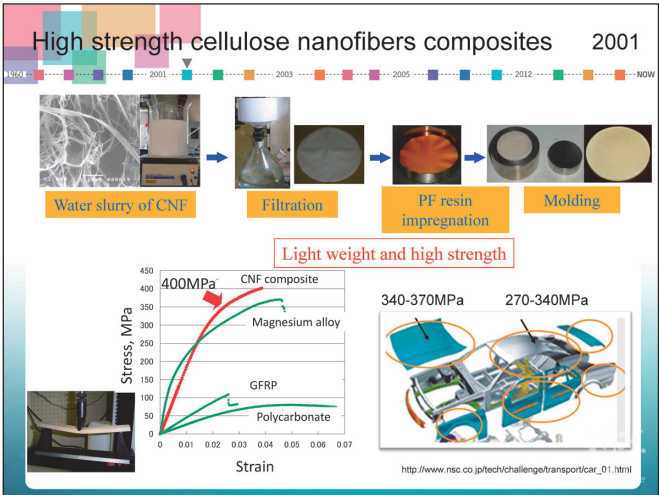


Fig 8

〈Fig 8〉 The first material we produced in 2001 was a high-strength material made by applying cellulose nanofiber's strength properties of lightness and strength. In its production process, cellulose nanofiber was dispersed in water and then filtered to be made into sheets, which were finally solidified by resin impregnation.

For the first time in the world, we succeeded in showing that materials as strong as steel could be made from plants. They are 1/5 the weight of steel.

2001 was the year in which global warming caused by increased atmospheric CO₂ began to be recognized. The change from fossil to sustainable resources began to be discussed, and, as well, the potential of cellulose nanofiber, as a sustainable high-quality nanofiber, which is synthesized by absorbing and fixing CO₂, began to draw my strong awareness.

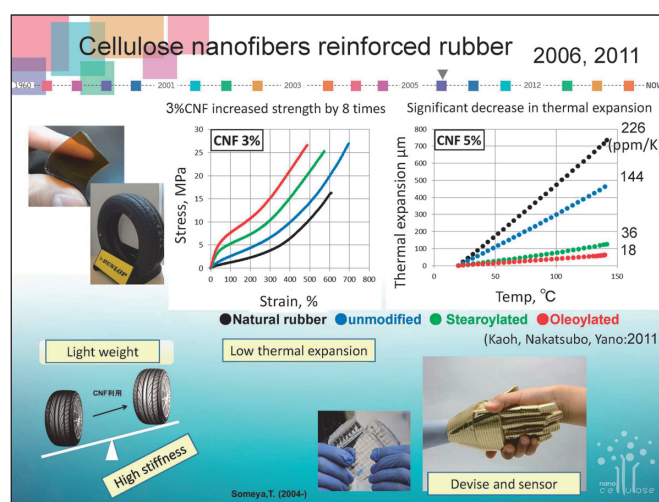


Fig 9

〈Fig 9〉 Reinforcing rubber by applying cellulose nanofiber is a very interesting theme. Carbon black accounts for approx. 30% of existing tire rubbers, and when tires are worn down, carbon black becomes particles and released into the environment.

Since 2006, we have been engaged in the reinforcement of tire rubber by applying cellulose nanofiber, together with Sumitomo Rubber Industries, Ltd. We prototyped CNF-containing rubber tires and confirmed the effect during actual driving tests.

Further, chemical modification of cellulose nanofiber made it possible to reduce the amount to be added to attain a great reinforcement effect for the rubber.

For example, if the cellulose nanofiber is added into the rubber at a rate of only 3%, it becomes 8 times harder to deform than non-reinforced rubbers.

Also, it can greatly reduce the thermal expansion of rubber, so that it is expected to be applied to soft devices and sensors like these (lower right).

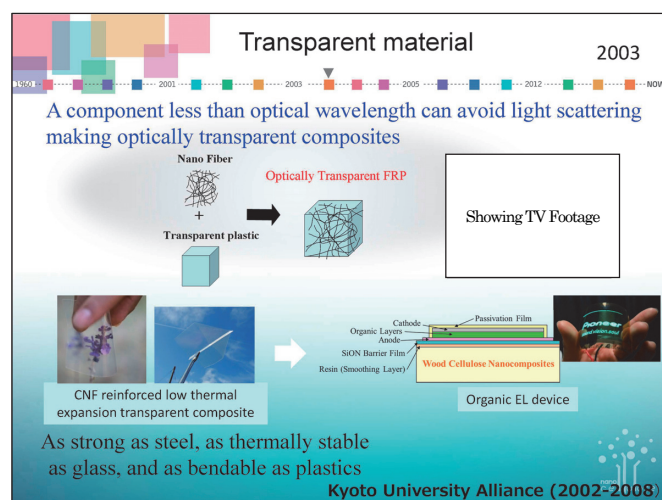


Fig 10

〈Fig 10〉 Now for the transparent material. Please watch this video (showing TV pictures). The light we are seeing is composed of electromagnetic waves with a wavelength of 400 to 800 nanometers. Within the range of the wavelength, fine fibers such as cellulose nanofiber do not produce a scattering of light.

Therefore, if cellulose nanofiber is mixed into transparent resin at a rate of 50 to 60%, its transparency remains equal.

By using cellulose nanofiber as reinforcing fibers, it becomes possible to produce a transparent material which is as strong as steel, as flexible as plastic, and has a low thermal expansion of glass.

We developed this material in a comprehensive academic-industrial alliance regarding the organic electronic device development activities carried out by Kyoto University jointly with Mitsubishi Chemical, NTT, Pioneer, etc., based on some pieces of advice from the companies which participated in the alliance. That was in 2003.

Further, we could produce organic EL (LED) and organic transistors by using this transparent material instead of glass. It was with the help of an alliance framework of cross-sectoral vertical cooperation, which is even now innovative as ever, that a wood material researcher could be involved in cutting-edge electronic devices. That was when I began to strongly feel the possibility of cellulose nanofiber as a leading material.



Fig 11

〈Fig 11〉 Cellulose nanofiber is a basic substance of all plant cells. Sprouts and lettuce are also composed of cellulose nanofiber. In other words, we eat cellulose nanofiber every day. We tried to mix it into a soft-served ice cream at a rate of only 0.1%. On the left is an average soft-served ice cream, and on the right is a soft-served ice cream which contains cellulose nanofiber at a rate of only 0.1%. We put them in a box at 35 degrees Celsius, which is as high as being in the hot midsummer sun. Please watch at fast speed. The cellulose nanofiber-containing ice cream did not drip out, even after sitting in a room at 35 degrees Celsius for nearly 20 minutes. Imagine, young children enjoying their ice cream on a hot day without staining their clothes.

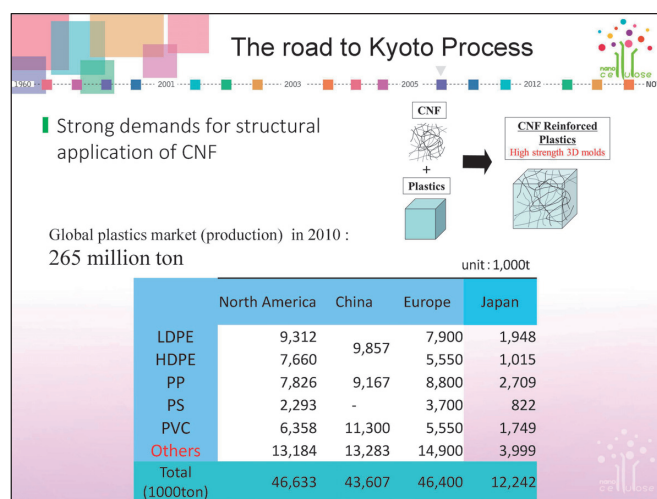


Fig 12

〈Fig 12〉 Besides high-strength materials and transparent materials, cellulose nanofiber is being applied into various uses, such as foods, cosmetics, ink, etc. Among them, the most expected use is in the reinforcement of structural plastics like this. Recently, 3 hundred million tons of plastics are produced every year around the world. Reinforcing 20 to 30% of

this amount by applying cellulose nanofiber would result in exploiting a 10 to 20 trillion-yen global market.

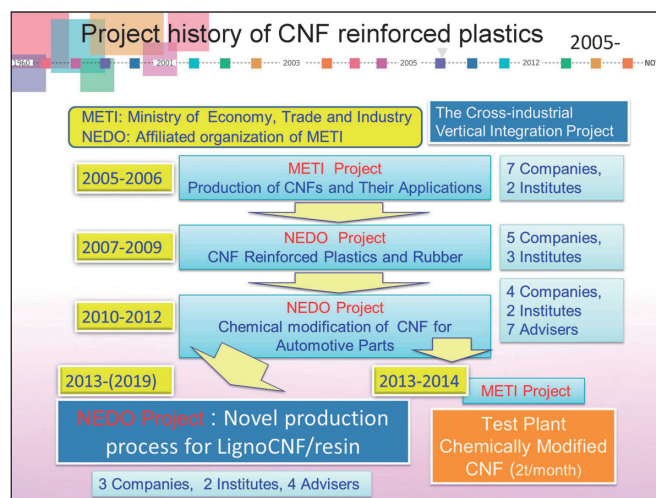


Fig 13

〈Fig 13〉 We have been engaged in reinforcement of structural plastics jointly with Kyoto Municipal Institute of Industrial Technology and Culture, and with a lot of relevant companies. The first big project was a Ministry of Economy, Trade and Industry program, which we started 12 years ago with Dr. Kazuo Kitagawa of the same institute. Dr. Kitagawa is still an important research partner for us in development of cellulose nanofiber materials.

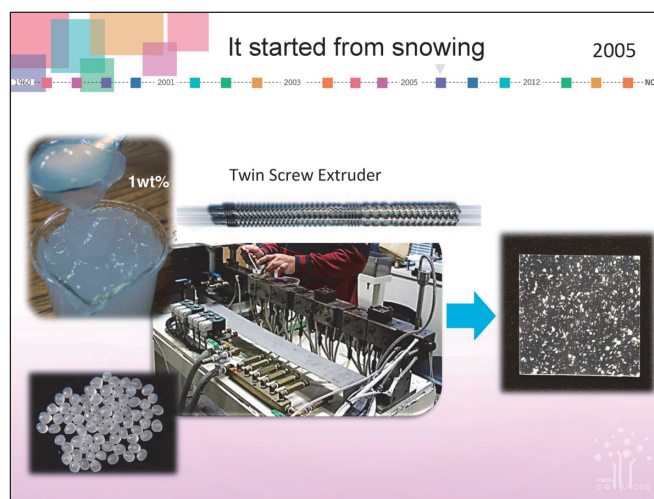


Fig 14

〈Fig 14〉 Since cellulose nanofiber is fiber that is at least 5 times as strong as steel, we thought that we could easily create strong plastic by mixing it with plastic. However, that was a much harder task than we expected. Cellulose nanofiber has an affinity for water while, on the other hand, plastic, which is made from petroleum, has oil-like properties. Therefore, they simply will not blend, becoming just like salad dressing. Also, when moisture escapes,

only cellulose nanofiber solidifies, turning into white grains as the figure shows. This cannot be used for reinforcing resin at all. We called this condition “*yukiguni* (snow country).”

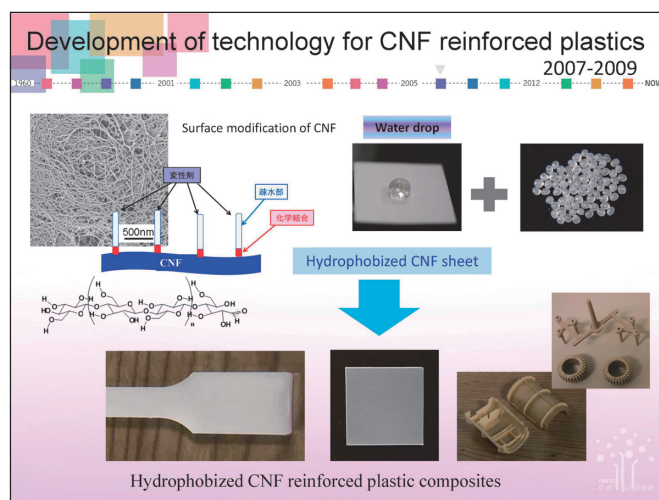


Fig 15

〈Fig 15〉 The snow country condition was improved by using powdered resin and by modifying the surface of CNF with a modifying agent in order to make it have oil-like properties to the best degree possible. However, the CNF did not demonstrate sufficient reinforcing performance.

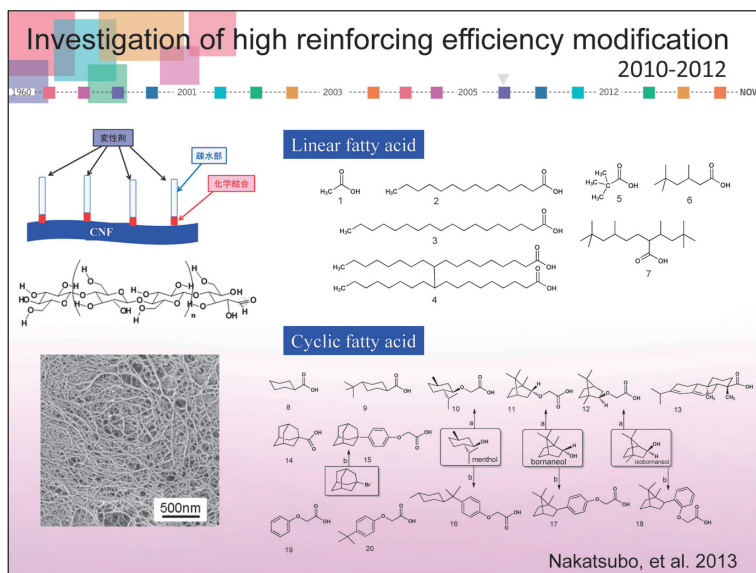


Fig 16

〈Fig 16〉 With that, we asked Professor Nakatsubo to apply various types of chemical structures like these only to the surface of cellulose nanofiber, and then, we mixed it with resins such as polyethylene and polypropylene to examine its reinforcing performance. Professor Nakatsubo is a very prominent chemist who has succeeded in creating cellulose

from glucose by using organic synthesis for the first time in the world.

Thanks to the assist from Professor Nakatsubo, we were able to introduce these many types of chemical structures into the surface of cellulose nanofiber and examine its reinforcing performance in a systematic manner.

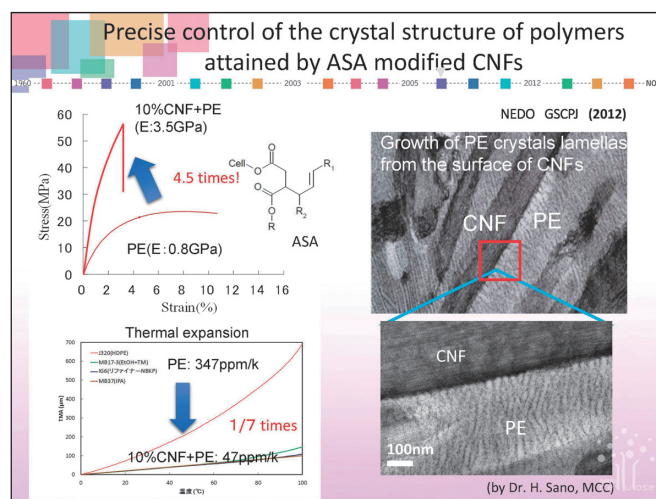


Fig 17

〈Fig 17〉 Through trying many types of chemical modification, we gradually came to understand what chemical structure exhibits excellent reinforcing performance. On the basis of the finding, a chemical called ASA was selected from a practical viewpoint.

Mixing ASA is commonly used to increase the strength of paper, but mixing polyethylene with cellulose nanofiber, weighing only 10% of the total weight of the polyethylene, makes it 4.5 times more resistant to deformity and greatly reduces expansion and contraction due to heat.

Also, as shown in the figure, the crystal structure of polyethylene has also been controlled. The figure also shows that ASA treatment has allowed the crystals of polyethylene, which has oil-like properties, to grow properly on the surface of cellulose nanofiber.

I think that the control of crystal structure of plastics by cellulose nanofiber will become an important research area in polymer science in the future.

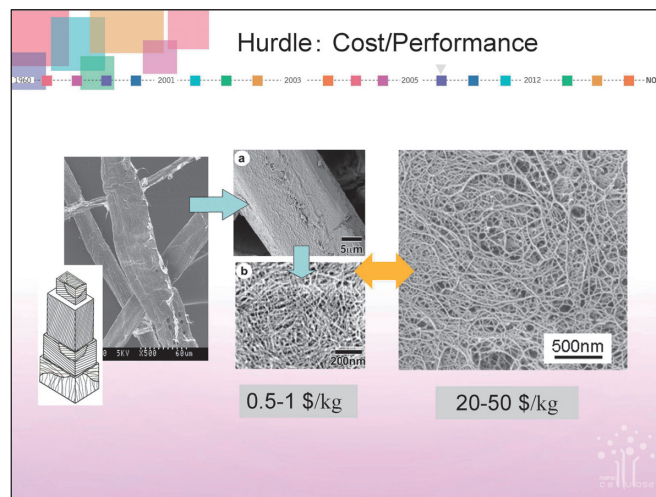


Fig 18

〈Fig 18〉 Proper chemical modification of cellulose nanofiber enhances performance in reinforcing resins, but there was a huge barrier to overcome before putting it to practical use. The issue of cost for producing modified CNF had to be solved.

1 kg of pulp, which is a collection of cellulose nanofiber, can be purchased only for 50 yen, so the material cost is very low; however, it costs 2,000 yen to 5,000 yen to produce nanofiber by disintegrating it. Modifying it costs the same amount, making the total cost twice as much.

Even if cellulose nanofiber demonstrates superior performance, if it costs 5,000 to 10,000 yen to produce 1 kg of cellulose nanofiber, nobody will use it for reinforcing resin. With that, we explored various possibilities with the aim of reducing the production cost.

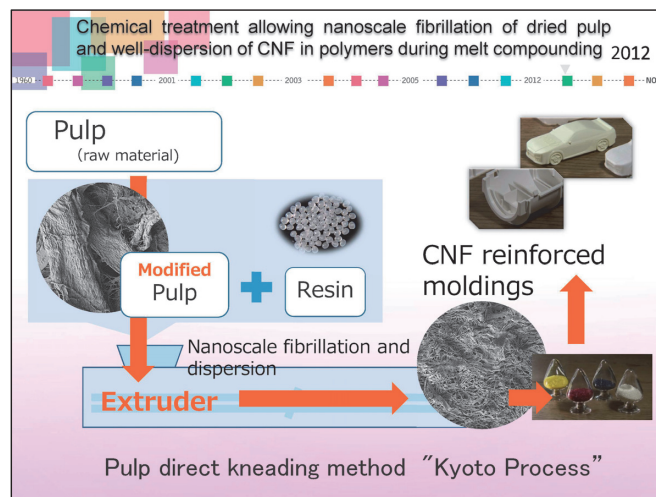


Fig 19

〈Fig 19〉 As a result of proceeding with the examination on raw materials and chemical treatments, we developed a method of simultaneously realizing nanoscale fibrillation of pulp fiber and its uniform dispersion into resin. That was five years ago. This made it unnecessary to produce nanofiber from pulp beforehand.

Integrating two processes, (1) the production of cellulose nanofiber and (2) the production of composite of cellulose nanofiber and resin, into a single process realized a considerable reduction in time and cost.

Later, we named this method the “Pulp Direct-Kneading Method (Kyoto Process),” because we viewed the process as a fruit of no less than 10 years of collaborative research by Kyoto University and Kyoto Municipal Institute of Industrial Technology and Culture.

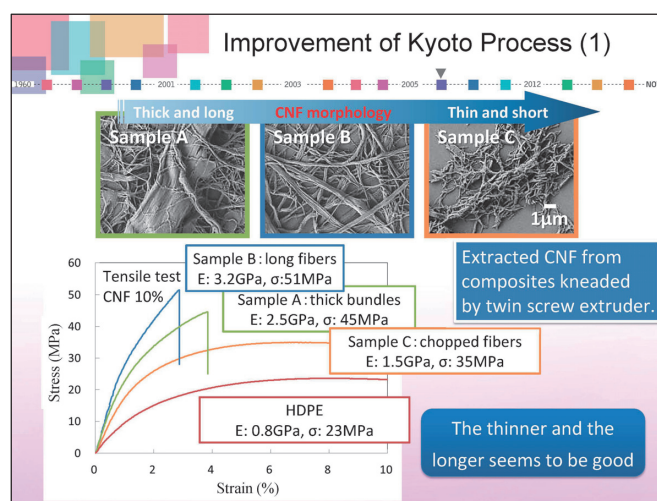


Fig 20

〈Fig 20〉 However, initially, we were able to apply the Kyoto Process only to general-purpose plastics processed at temperatures of 200 degrees Celsius or lower, due to the limited heat resistance of cellulose nanofiber.

Furthermore, when cellulose nanofiber was applied with strong force when kneading it with resin, the cellulose nanofiber was chopped, leading to a large decline in reinforcing performance.

In order to solve this problem, we reviewed all the elemental technologies employed in the Kyoto Process from scratch.



Fig 21

〈Fig 21〉 All the processes from 1 to 5, including the selection of raw materials such as wood, bamboo, and rice straw, the method to produce pulp, chemicals used for chemical processing, and molding process technology, were thoroughly reviewed with the aim of increasing disintegration performance and heat resistance of pulp. As a result, it became possible to reinforce plastics, such as Nylon6, that are processed at temperatures of 230 to 250 degrees Celsius.

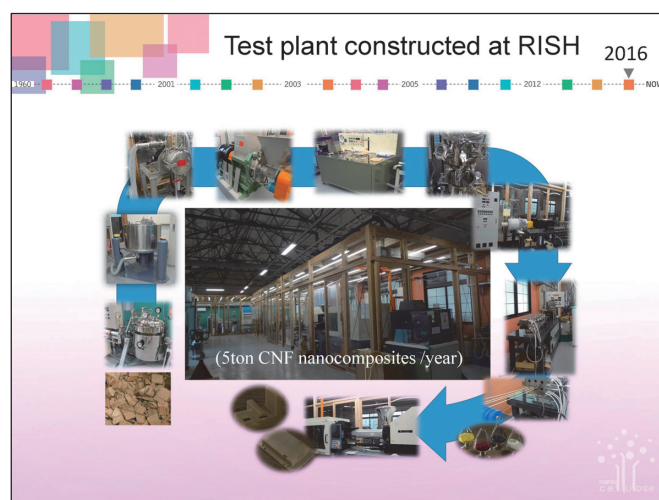


Fig 22

〈Fig 22〉 On the basis of the latest version of the Kyoto Process, we completed a test plant that is able to seamlessly produce resin molded products from raw materials at Kyoto University in March of this year.

We took a giant step towards the practical use of cellulose nanofiber composite materials and the manufacture of large industrial materials for the next generation.



Fig 23

〈Fig 23〉 Recently, a large-scale verification project by the Ministry of the Environment, in which cars are made by using reinforced plastic or other materials produced in this test plant, became operational with participation of 20 organizations.

Now my dream is to see an eco-friendly car that uses a lot of cellulose nanofiber, thus being lighter in weight, higher in fuel economy, and lower in CO₂ emissions, being driven in the city of Tokyo as the lead car for the marathon race at the upcoming 2020 Tokyo Olympics and Paralympics.



Fig 24

〈Fig 24〉 Last, I would like to talk about the Nanocellulose Forum in Japan, which researchers working on the study of nanocellulose all over the world look at with awe.

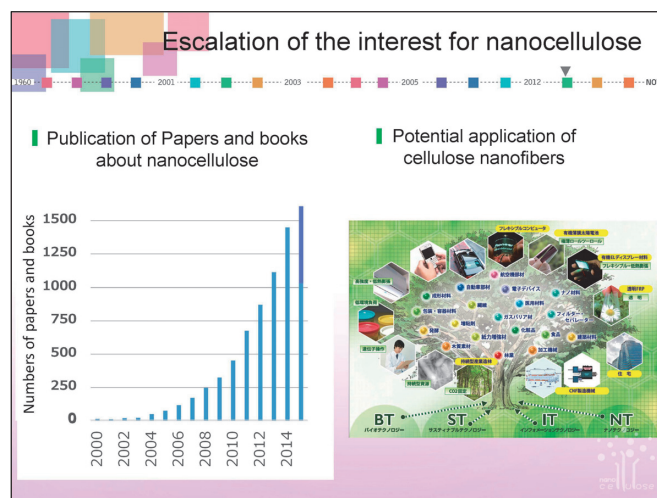


Fig 25

〈Fig 25〉 It was about three and a half years ago that cellulose nanofiber first came under the spotlight. Numbers of papers regarding cellulose nanofiber surged.

Also, since it was expected to be used for various purposes, we received inquiries relating to CNF from many companies as often as every week.

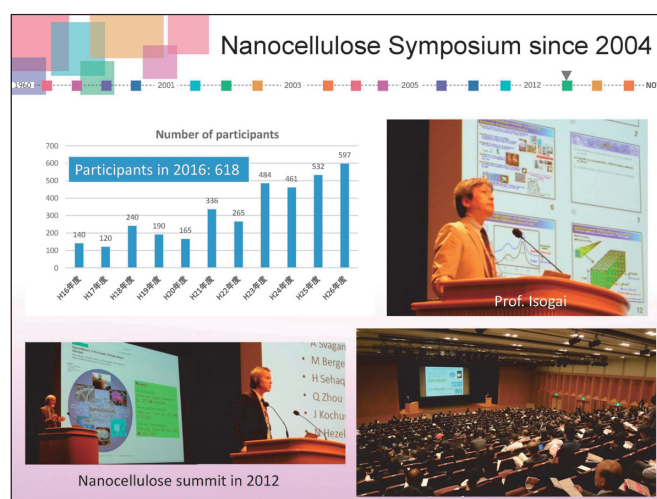


Fig 26

〈Fig 26〉 Enthusiasm that participants showed at the Cellulose Nanofiber Symposium, which has been hosted by my research group since FY 2004, also demonstrated the high level of interest in CNF.

At the beginning, there were only 140 participants at the symposium, but in FY 2013, there were more than 500 participants, so we had difficulty in finding a suitable venue.

I felt an urgent need to make further efforts to share information on cellulose nanofiber with a lot of people so as to rapidly accelerate the research on cellulose nanofiber in Japan.

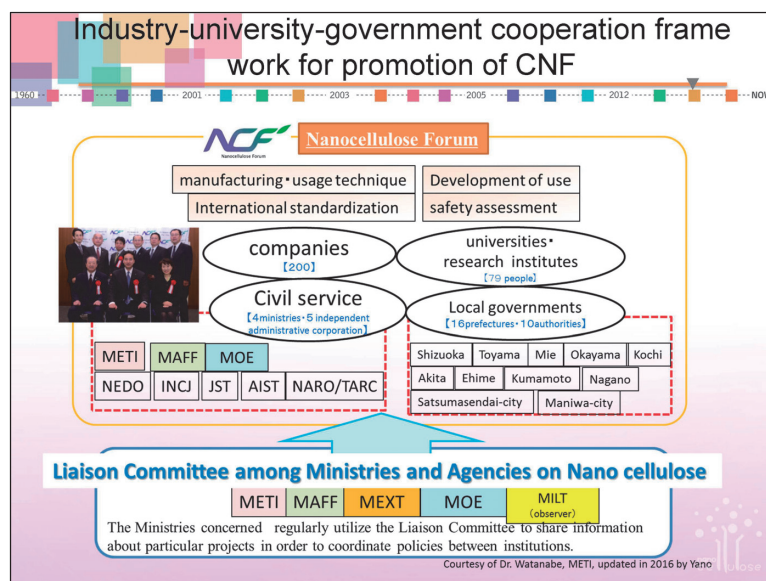


Fig 27

〈Fig 27〉 To that end, I visited the Paper Industry, Consumer and Recreational Goods Division of the Ministry of Economy, Trade and Industry to see Dr. Watanabe, a division chief, in July 2013, to ask him to help us with the establishment of a forum for exchanging information on cellulose nanofiber and the activation of cellulose nanofiber research in local public research and development institutes.

Dr. Watanabe immediately took action, and the Nanocellulose Forum, the world's first forum on cellulose nanofiber, was launched in June in the following year. Currently, nearly 200 companies participate in the forum.

Responding to a call from Dr. Watanabe, the Liaison Conference of Relevant Ministries and Agencies Concerned with Nanocellulose was established as an organization to support the forum through cooperation among government ministries and agencies.

Since then, construction of plants for producing cellulose nanofiber has progressed all over Japan, and, presently, cellulose nanofiber is being provided from 12 organizations.

In addition, projects featuring regional resources and industrial characteristics were launched throughout Japan under the initiative of universities and public research and development institutes.

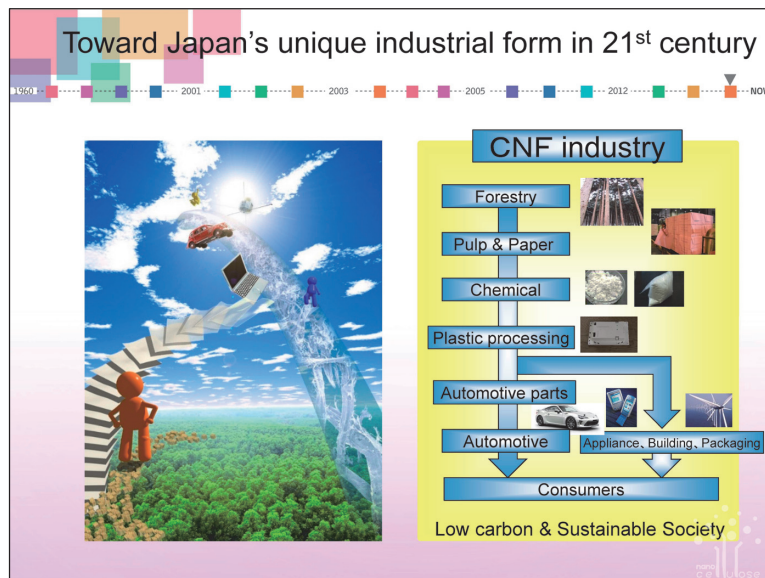


Fig 28

〈Fig 28〉 The launching of the forum accelerated cooperation among industries that had not been closely connected with each other, promoting a large trend towards the formulation of a society based on sustainable resources.

Under this trend, for example, the forest industry and the car industry are deepening their relationship in the figure. It is expected that Japan's unique industrial form will thus be developed.

In conclusion, I would like to summarize my speech and talk about the outlook of 21st century development based on ecotechnology.

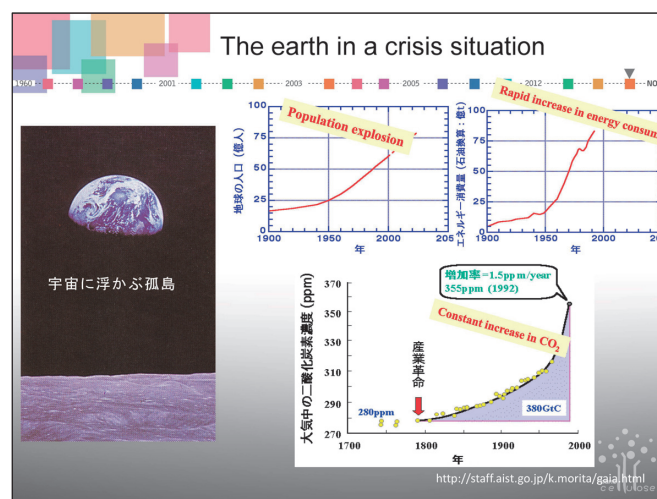


Fig 29

〈Fig 29〉 The earth is now in a crisis situation. The world is facing the issues of population explosion and rapid increase in energy consumption, particularly fossil-fuels, due to improvement in living standards, which are accompanied by constant increase in CO₂. As the earth is in a closed environment and resources now available will not be available unlimitedly,

people will compete over resources such as crude oil and iron ore, leading to an inevitable rise in resource prices in the future.

Then, is there any way to enrich our lives by utilizing limited natural resources? One of the answers to that question is the realization of a sustainable society through the utilization of plant biomass.

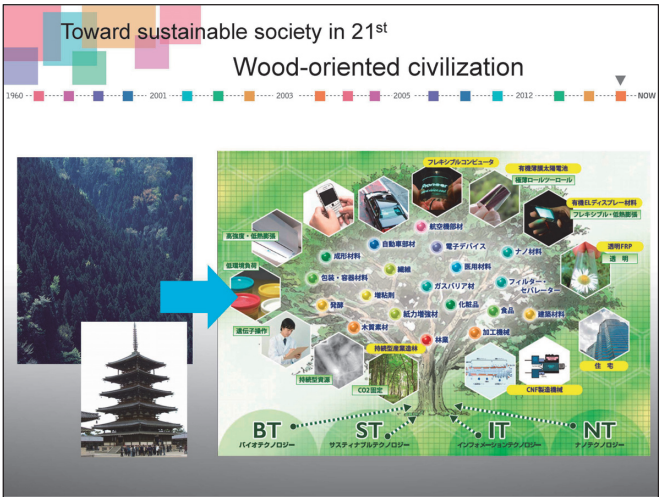


Fig 30

〈Fig 30〉 I believe that the time will come when a variety of materials like these can be created from sustainable plant biomass in the future, which is absolutely necessary for the survival of mankind.

Nothing would be a greater pleasure to me than seeing that people are enjoying their lives in an affluent society dependent on sustainable plant resources and finding such a wood-oriented civilization started from the research on cellulose nanofiber, which is what Professor Isogai's group and our group are now working on in Japan, when we turn back the pages of history 50 years or 100 years from now.



Fig 31

〈Fig 31〉 There are still many more cellulose nanofiber materials that I must create. One of those, for example, is a material made from 100% cellulose nanofiber that allows sheet-metal processing like steel does.

To overcome many challenges, I believe it is necessary for us to understand how trees, the producer of cellulose nanofiber, have developed and evolved and proceed with our research accordingly. To develop plant-based materials, it is important to know how best we can approach plants to learn from them.

To learn from plants, which are the producer, we have to consider how and for what purpose it came to acquire its structure, and what functions are displayed in such a structure.

For a person who was brought up in the natural environment and culture of Japan and has been living here in Japan, it may be natural to accept the concept that the Buddha's spirit of nature dwells in all living things.

Such an outlook on nature unique to Japan made it possible to promote the research contributing to the construction of a sustainable society, and such an approach is adherent to what the prospectus of Honda Foundation states, which is "creating a truly humane civilization," which is what I am also aspiring to realize.

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山田 正 京都大学名誉教授
則元 京 京都大学名誉教授
中坪文明 京都大学名誉教授
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Fig 32

〈Fig 32〉 At the end of today's speech, there is one more important thing I have to do. I would like to take this opportunity to express my sincere gratitude to all the people and organizations who have worked on the research together with me in the course of the development of the Kyoto Process and all the people who have supported our venture. There are so many people who have helped us that I cannot introduce all of their individual names here. Please forgive me for limiting the mention of their names in this way.

I would like to close my speech by expressing my appreciation to my parents living in Shinshu, who have enriched all my life, and my wife and two children present at the ceremony today.

Thank you for your kind attention.



公益財団法人 本田財団
HONDA FOUNDATION

発行責任者 山 本 雅 貴
Editor in chief Masataka Yamamoto

104-0028 東京都中央区八重洲 2-6-20 ホンダ八重洲ビル

Tel. 03-3274-5125 Fax. 03-3274-5103

6-20, Yaesu 2-chome, Chuo-ku, Tokyo 104-0028 Japan

Tel. +81 3 3274-5125 Fax. +81 3 3274-5103

<http://www.hondafoundation.jp>