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## Introduction

In the beginning of 2008, the research program "Nihon University Strategic Projects for Academic Research" was announced. In the program, researchers from different Colleges of Nihon University, geographically separated, were expected to work together. I believe that this was an ambitious program which tried to address issues along the national science and technology policy and meet the society needs, and can have impact, increasing the University's competitiveness.

We started to make a team to apply to the program. There was a group led by Itoh in the College of Science and Technology that I work for, which had worked together in application to the COE and global COE programs by the MEXT (Japanese government). There was also a group members in the College of Science and Technology for the High-Tech Research Center Project on nanomaterials supported by the MEXT to be over in 2008. We made a team mainly from these groups and recruited new members from the College of Humanities and Sciences and the School of Medicine. We had meetings, made a research proposal, and applied to the "feasibility research" in May 2008. Our proposal was selected as one of the five feasibility researches after screening and hearing processes. The team was further improved joined by new members from the College of Bioresource Sciences and the School of Pharmacy. After further presentation, paperwork, and hearing, our proposal was approved as the only one designated research in October 2008. I remember that we held a research retreat in Atami Onsen (hot spring) in February 2009 and discussed our project all day long to jump start the Project.

## **Research Proposal**

The submitted research proposal was as follows.

This project addresses three major issues that needs technological innovations:

- 1. Information technology: Ultrahigh speed, ultrahigh density recording and quantum information processing

- 2. Energy technology: Solar energy harvesting with nanostructures

- 3. Medical technology: Nanobiotechnologies for medical applications

on the basis of our photonic, quantum, and bio technologies through collaborative research across different Colleges of Nihon University.

To establish a common basis for the research on the three subjects, this project also explores sciences and technologies in

- Photonics and quantum aspects of nanomaterials.

Nanomaterials will be fabricated both from bottom-up approaches and top-down approaches as well as by reactions controlled at the nanometer level. The experimental approaches are complemented by quantum theoretical and computational studies on the interaction of light with matter at the nanometer scale. Nanomaterials will be developed through these approaches for the applications in the above mentioned three areas.

Thus this project aims at providing innovative technologies to contribute to realizing a highlydeveloped sustainable society. We also put an emphasis on education for young generations through the interdisciplinary cutting-edge research.

The areas of research were determined from a point of view that the members had already established backgrounds and were likely to further develop significantly. We also decided to address

important issues, rather than niche issues, to contribute to solving problems facing society. On the basis of these considerations, we decided to address issues in the most important areas, i.e., information, energy, and medicine. These appear, and are, too broad a theme. From a technological point of view, properties of substances and materials relevant to each one of these areas are determined by the microscopic structures and properties such as the arrangement of atoms and the way they interact with light. Therefore, we need to get insights into the microscopic world and to devise technologies based on the insights. There came a common theme of sciences and technologies on the nanometer scale that is the dimension of assemblies of atoms and molecules. A nanometer (nm) is: 1 nm =  $0.000\ 000\ 001\ m$ .



Figure. The goals of this research project.

**Information Technologies.** A new methodology is required to meet the demand of information explosion to record and read more information on smaller regions, faster. Safety must be assured for the large-volume data transfer. This project aims at faster, smaller, and safer information technologies.

**Energy Technologies.** Only the people in the last 100 years enjoy lives which depends on massive fossil fuels as shown in the figure. The Fukushima disaster happened on March 11, 2011, which was beyond our imagination at the start of this project. Although shale gas is being developed, it is certain that the Sun is the only sustainable source of energy. This project aims at better use of solar energy and hydrogen as an energy carrier.



Figure. Energy consumption of humans. The unit of the ordinate is megaton oil equivalent, the abscissa represents the year. Data from the United Nations, BP, and WEO.

**Medical Technologies.** Cancer accounts for a third of Japanese death. Cancer is a disease in which cell proliferation is out of control due to abnormal gene expression. Therefore, if one can control the gene expression, the cure may be within our reach. Doctors in the School of Medicine had been working on synthetic compounds called pyrrole-imidazole polyamides which can recognize the base sequence of DNAs. This project aims at developing drugs based on this class of compounds.

**Nanomaterials Research.** Every one of the above mentioned researches needs nanomaterial-based science and technology. Information needs to be written into an ever smaller area of nanodimension; photovoltaic efficiency depends on the properties of nanointerface where photon-to-electron conversion occurs; the DNA binding compounds recognize the shape and properties of DNA at the nanoscale. We studied these specific aspects of nanoscience and nanotechnology as well as those from broader perspectives.

To fabricate nanomaterials, there are two approaches. One is the top-down approach which is wellknown in the semiconductor industry and the other is the bottom-up approach relying on self-assembly which is adopted by living organisms. Both approaches, depending on the background of the individual researchers, are jointly employed in this project. Theoretical studies and numerical simulations were also performed along with the experimental works, because theoretical understanding is indispensible on the interaction of light and nanomaterials.

### **Research Progress and Achievements**

The scientific impact, novelty, and significance are demonstrated by papers published in reputed journals such as Nature and its sister journals, Nature Communications, Nature Photonics, Nature Materials as well as J. Am. Chem. Soc., etc. On the other hand, the technological novelty is seen from 31 patent applications. Thirty five awards were granted from scientific communities; many of which were presentation and poster awards to young researchers, showing the effectiveness of the training and development for young researchers of the project.

The overview of the research achievement is described in the following. Please see the group reports and individual reports that follow for details.

**Information Technologies: Ultrafast, Ultrahigh Density Recording.** The hard disk has an array of tiny magnets, called magnetizations, on the surface. Digital information comprising zero's and one's is recorded as an up or a down of each magnetization. Therefore, the magnetization must be flipped over to write information. In the present technology, the flip-over of magnetization is achieved by magnetic field, which is a slow process on the order of 0.25 Gbit (250 000 000 zero's or one's) per second.

Before this project started, Tsukamoto and Itoh, in collaboration with a Netherlands team, had found a physically new phenomenon. The electric field of passing waves of light can change direction as it passes, which is called circularly polarized light. The new phenomenon Tsukamoto and Itoh found is that a pulse of circularly polarized light on their material flips the magnetization.<sup>123</sup> They named the phenomenon "light-induced ultrahigh speed magnetization inversion." This is a new

<sup>&</sup>lt;sup>1</sup> Tsukamoto and Itoh et al., *Phys. Rev. Lett.* **2007**, 99, 217204.

<sup>&</sup>lt;sup>2</sup> Tsukamoto and Itoh et al., *Phys. Rev. Lett.* **2007**, *99*, 047601.

<sup>&</sup>lt;sup>3</sup> Tsukamoto and Itoh et al., *Phys. Rev. Lett.* **2007**, *98*, 207401.

method for inverting magnetization completely different from conventional methods. The recording in this new method can be 100 000 times faster than the present method, in principle.

The mechanism had not been known because the phenomenon was unprecedented. They attempted to obtain insight into the mechanism of the magnetization reversal, with faster recording in mind. They successfully demonstrated fast writing by destroying and flipping the magnetization with the first pulse and reading with the second pulse.<sup>4</sup> The whole process took only 30 ps (0.000 000 000 03 seconds), which was already much faster than the status quo. This result was highlighted in the Spotlighting Exceptional Research in *Physics* (**2009**, *2*, 73) published by the American Physical Society, in Research Highlights in *Nature* (**2009**, *461*, 318), and in Research Highlights in *Nature Photonics* (**2009**, *3*, 606).



Figure. "*N*." (Nihon University icon) written by the light-induced ultrahigh speed magnetization inversion.

They then were successful in probing the behavior of magnetization reversal with an extremely short time.<sup>5</sup> Upon irradiation by laser pulse on the material containing iron and gadolinium, the magnetization of iron flips in 300 fs (0.000 000 000 000 3 seconds), while that of gadolinium flips slower in 1.5 ps (0.000 000 000 001 5 seconds). Little had been known about what happens in this time scale and this work marked a milestone in the magnetic materials research. Further, they newly discovered another mechanism for magnetization reversal by ultrafast heating with laser pulse.<sup>6</sup>

In yet another work, they obtained insights not only in a short time domain but also in a small spatial domain by observing magnetization reversal by X-ray laser.<sup>7</sup> The data showed that magnetic interaction between iron-rich domain and gadolinium-rich domain affects the magnetization dynamics. These results suggest that the nanostructure of the magnetic material can be engineered to control the magnetization reversal behavior, possibly leading to faster recording.

Light can be fast but on the other hand cannot be concentrated smaller than its wavelength scale due to its nature as waves. With visible light, with the wavelength around 500 nm, one can write a bit of information in an area of  $500 \times 500$  nm, which determines the information density. Nakagawa and Ohnuki et al. addressed this problem with near-field light. Upon light irradiation on a nano-sized metal, the light apparently resides near the metal. This state of light, which is called near-field light, has the effect of concentrated light around the nanoregion and thus may be used for ultrahigh density recording. They approach the issue from both experiments and simulation, culminating in a minimum 62 nm  $\times$  67 nm recording area at present.

**Information Technologies: Key Technologies for Quantum Information.** The amount of information trafficking is increasing exponentially as well as the information stored. The safety of information transfer is assured by cryptography. The present cryptography relies on the

<sup>&</sup>lt;sup>4</sup> Tsukamoto and Itoh et al., *Phys. Rev. Lett.* **2009**, *103*, 17201.

<sup>&</sup>lt;sup>5</sup> Tsukamoto and Itoh et al., *Nature* **2011**, *472*, 205.

<sup>&</sup>lt;sup>6</sup> Tsukamoto and Itoh et al., *Nat. Commun.* **2012**, *3*, 666.

<sup>&</sup>lt;sup>7</sup> Tsukamoto et al., *Nat. Mater.* **2013**, *12*, 293.

fact that computers are not good at integer factorization or prime factorization, meaning that it takes too much time to do it. Recently, integer factorization of numbers over 200 digits was reported (NTT, 2010) and the safety concerns are increasing.

Quantum cryptography is attracting attention because it is impossible, on the basis of its principle, to do eavesdropping or decoding. There remains a number of technological problems to bring the quantum cryptography into reality, however. Namekata and Inoue had cutting-edge achievements including

- First cryptography demonstration in Japan using existing local area network (LAN) lines,<sup>8</sup>
- A single-photon detector with the highest repetition rate for optical communication band,<sup>9</sup>
- Quantum key distribution with the highest repetition frequency.<sup>10</sup>

In this project, they further developed key devices and demonstrated their performances.



Figure. The first quantum cryptography experiment in Japan using the LAN.

The most important device for quantum information technology is the single-photon detector. Light is a wave on the one hand but a particle called a photon on the other and is counted as one, two, and so on. The quantum cryptography utilizes this property of light. Therefore, the individual photons must be detected when they arrived, and quickly. Namekata and Inoue have developed a single-photon detector with a repetition frequency of 2 GHz (2 000 000 000 times per second) by a custom-operated avalanche photodiode photodetector. <sup>11</sup> They also developed a high-quality photon-number discriminator that can tell how many photons arrived with a repetition rate of 80 MHz (80 000 000 times per second), orders of magnitude faster than conventional devices (100 kHz, 100 000 times per second). They were successfully demonstrated a quantum operation called non-Gaussian operation.<sup>12</sup>

They performed quantum key distribution experiments using their own devices and achieved longdistance distribution (160 km) and high-rate distribution (1 Mbps =  $1000\ 000$  times per second).<sup>13</sup>

Further extension of the distribution distance requires quantum relays. One of the key technologies for quantum relay is the generation of entangled photon pairs and entanglement swapping. They obtained entangled photon pairs with a high purity of ~0.9 compared with conventional ~0.75 for the optical communication band (1550 nm). They also developed a quantum receiver beyond the standard

<sup>&</sup>lt;sup>8</sup> Namekata, Inoue et al., Opt. Express 2005, 13, 9961.

<sup>&</sup>lt;sup>9</sup> Namekata, Inoue et al., Opt. Express 2006, 14, 10043.

<sup>&</sup>lt;sup>10</sup> Namekata, Inoue et al., *Appl. Phys. Lett.* **2007**, *91*, 011112.

<sup>&</sup>lt;sup>11</sup> Namekata, Inoue et al., *IEEE Photo. Tech. Lett.* **2010**, *22*, 529.

<sup>&</sup>lt;sup>12</sup> Namekata, Inoue et al., *Nat. Photon.* **2010**, *4*, 655.

<sup>&</sup>lt;sup>13</sup> Namekata, Inoue et al., *Opt. Express* **2011**, *19*, 10632.

quantum limit of coherent optical communication.<sup>14</sup>

These achievements attracted great attention from industry and were highlighted in many specialized periodicals.

- Nikkan Kogyo Shinbun, February 12, 2010.
- Nikkan Kogyo Shinbun, July 8, 2010.
- Laser Focus World, June 28, 2011.
- Fuji Sankei Business i, June 28, 2011.
- Nikkan Kogyo Shinbun, May 16, 2011.
- Denkei Shinbun, February 27, 2012.
- Denpa Times, March 5, 2012.

For the quantum relay, a quantum memory is required in addition to the entanglement exchange mentioned above. Relevant paper by Kuwamoto on the Bose-Einstein condensates was selected in the Highlights of 2011 of *J. Phys. B*.<sup>15</sup>

**Energy Technologies: Solar Energy and Hydrogen.** In the energy technology area, we put focus on systems that utilize solar light energy. We studied each of the technologies that comprise the solar utilization cycle shown in the figure below, i.e., solar photovoltaics, photodriven hydrogen generation, hydrogen storage, and fuel cells that generate electricity from hydrogen.



Figure. Solar energy utility cycle and technologies we addressed.

Dye-sensitized solar cells are one of the promising candidates for the next-generation solar cells. This has an advantage that the absorption wavelength and electrochemical potentials can be tuned by chemical design because light absorbing materials are molecules unlike silicon solar cells. To take advantage of this property, Otsuki examined a class of compounds named "perylenedicarboxylic imdies" systematically and revealed the structure–performance correlation. The maximum efficiency obtained through the study was 3.1%.

Matsushita attempted to increase the efficiency by using photonic crystals to confine the light on the cell. She obtained data that confirmed that the near-field light produced by the photonic crystals indeed increases the light-to-current conversion efficiency per dye molecule.

The sun light may be converted to chemical energy such as in the form of hydrogen molecule, instead of producing electricity. Hydrogen generation using synthetic molecules and photosynthetic bacteria was both examined. Otsuki designed supramolecular catalysts that self-assemble to form

<sup>&</sup>lt;sup>14</sup> Inoue et al, *Phys. Rev. Lett.* **2011**, *106*, 250503.

<sup>&</sup>lt;sup>15</sup> Kuwamoto et al., *J. Phys. B* **2011**, *44*, 075302.

catalytic sites spontaneously just upon mixing in solution and found that the turn-over number of hydrogen generation was twice as much as a system without self-assembly.<sup>16</sup>

Asada and Nishimiya found that the hydrogen generation was increased by placing a hydrogenstorage alloy in the hydrogen-generation chamber containing photosynthetic bacteria.<sup>17</sup> This was made possible by a water- and moisture-resistant treatment of the hydrogen-storage alloy developed by Nishimiya.

Fuel cells are used for the generation of electricity from hydrogen. There are several types of fuel cells, among which the solid oxide fuel cells are attracting attention as a highly efficient device. For the commercialization of the solid oxide fuel cells, the operation temperature must be lowered from the present 800–1000 °C to 600–800 °C. New materials are needed to achieve the low temperature operation, which was addressed in the project.

Hashimoto systematically searched for materials prepared by the Pechini method that can mix the starting materials at the nanoscale and found materials that achieved the required properties. Fuel cells require the air electrode and the proton conductive material. He found that the optimal air electrode material is LaNi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>3- $\delta$ <sup>18</sup></sub> and the optimal proton conductive material is Ba<sub>1-x</sub>Sr<sub>x</sub>Zr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3- $\delta$ <sup>19</sup></sup> He is now at the stage of preparation of prototypes of fuel cells.</sub>

**Medical Technologies: DNA Recognition Drug Development.** Genetic information is stored as the sequence of four types of bases in DNAs, which are giant molecules. It was known that distamycin, which has pyrrole groups, pentagonal units containing a nitrogen atom, binds DNA. Around 1990, Dervan found that synthetic molecules in which imidazole, a pentagonal unit containing two nitrogen atoms, is introduced into the distamycin framework bind DNA in a sequence-selective manner. He termed the molecules pyrrole–imidazole polyamides (PI polyamides hereafter).

The researchers of the Schools of Medicine had been working on the PI polyamide when the project started. They have advanced the studies aiming at drug development in this Project.



Figure. Distamycin (left) and an example of PI polyamides (right).

They confirmed suppression effects of PI polyamides on gene expression and cell proliferation in experiments using an osteosarcoma cell line, a hepatoblastoma cell line, Wilm's tumor cell line, and a

<sup>&</sup>lt;sup>16</sup> Otsuki et al., *Chem. Commun.* **2010**, *46*, 8466.

<sup>&</sup>lt;sup>17</sup> Asada, Nishimiya et al., Patent Application 2011-124597.

<sup>&</sup>lt;sup>18</sup> Hashimoto et al., *Solid State Ionics*, **2010**, *181*, 1771.

<sup>&</sup>lt;sup>19</sup> Hashimoto et al., Solid State Ionics 2012, 206, 91.

human prostate cancer cell line. Some PI polyamides were also found effective in mice experiments. Pharmacokinetic behaviors of PI polyamides were also evaluated. A paper by Soma, Fukuda, and Matsumoto on PI polyamides was selected as the excellent paper in *Biol. Pharm. Bull.* published by the Pharmaceutical Society of Japan in 2012.<sup>20</sup>

The transforming growth factor (TGF) is a class of proteins that bind DNA and regulate its expression. TGF is categorized into two subdivisions, TGF- $\alpha$  and TGF- $\beta$ . The TGF- $\beta$  are proteins which are produced in various tissues and are involved in cell growth, production of extracellular matrices, and regulation of immunity. Fukuda et al. designed multiple PI polyamides that bind to the sequences in the binding site of TGF- $\beta$ 1 and found a lead compound that inhibited the expression of TGF- $\beta$ 1 mRNA (the template for TGF- $\beta$ 1) in human- and marmoset-derived fibroblasts. To facilitate drug development, while continuing studies aiming at treating cancer, evaluation of the compounds for a simpler symptom was performed on mammalian marmoset. They made the PI polyamide into ointment and applied to fibrotic scar on marmosets and confirmed the inhibition of the skin scar. The results were highlighted in Nihon Keizai Shinbun (October 18, 2013, for a full image, see appendix).



Figure. Less scar after surgical operation. Clinical trial expected next year.

Other than on PI polyamides, studies on dedifferentiated fat cells (DFAT) found by Kano and the Stabilon, a 16-peptide motif that stabilizes proteins, found by Masuhiro have advanced. Further, Kano et al. clarified the relationship between the dynamics of cell shape and gene expression during cellular differentiation of fat cells.<sup>21</sup> Photodynamic effects were evaluated for newly synthesized porphyrin and chlorophyll derivatives by Otsuki, Fujiwara, and Nagase. Asai and Fukuda are working on plasma for applications in medicine.

Another topic is that Nagase et al. in the Balmain group have analyzed genetic network structures related to skin inflammation and tumor susceptibility, the results of which were published in *Nature*.<sup>22</sup>.

**Nanomaterials Research.** Each member of the project has his/her own expertise in various area of nanoscience and nanotechnology. This project aims at facilitating communication among them thereby advancing collaborative studies and providing their expertise, materials, and techniques to the

<sup>&</sup>lt;sup>20</sup> Soma, Fukuda, Matsumoto et al., *Biol. Pharm. Bull.* **2012**, *35*, 2028.

<sup>&</sup>lt;sup>21</sup> Kano et al., *Nat. Commun.* **2014**, in press.

<sup>&</sup>lt;sup>22</sup> Nagase, Balmain et al., *Nature* **2009**, *458*, 505.

areas of information, energy, and medical technologies.

The following three groups were organized.

• **Supramolecules and Self-Assembly Group.** Preparation and characterization of nanomaterials and nanostructures from the bottom-up approach.

• **Nanomaterials and Nanotechnology Group.** Preparation and characterization of nanomaterials and nanostructures from the top-down approach.

• Quantum Theory and Computation Group. Quantum mechanics and simulation on the interaction of nanomaterials and light.

Advances in these groups will be described in the following sections. There I present various nanostructures and their properties obtained in the Project, which include examples with significance in their own right and those promising for applications to information, energy, and medical technologies.

**Nanostructures through Supramolecules and Self-Assembly.** Otsuki et al. had been working on construction of molecular assemblies and characterization of them at the molecular scale. The examples shown below are arrays of compounds called porphyrins. The molecular structures are custom-designed such that intermolecular interaction moieties (hydrogen bonding sites) are introduced in the molecules. They found that, by design of the molecular structure, molecules can be arranged, for example, into double-rows (left) and into a zigzag pattern (right).<sup>23</sup> In this Project, the self-assembly has been further examined including three-dimensional architecture.



Figure. Porphyrin molecules arranged in double rows (left) and in a zigzag pattern depending on the molecular structure.

In natural photosynthesis, chlorophyll molecules assemble into organized arrays and function as light-harvesting antenna. Otsuki et al. investigated self-assembly structures with synthetically modified chlorophyll molecules. One of them was found to form double helices, reminiscent of the double helices of DNA, in the crystal state.<sup>24</sup> It is significant that a molecule was organized into a three-dimensional structure of this complexity (and beauty). The result also offers a hint to construct artificial antennae for light-harvesting.

<sup>&</sup>lt;sup>23</sup> Otsuki et al., J. Am. Chem. Soc. 2005, 127, 10400.

<sup>&</sup>lt;sup>24</sup> Otsuki et al., J. Am. Chem. Soc. 2013, 135, 5262.



Figure. Double helices of a modified chlorophyll molecule.

Otsuki et al. prepared a double-decker porphyrin complex to observe molecular dynamics at the single molecule level. It was anticipated that this molecule rotates around a cerium atom residing at the center of the molecule. The molecules were made into array on a substrate surface and were observed with a scanning tunneling microscope. They obtained images showing that some molecules have changed their orientation, which was the first successful visualization of this type of molecular motion.<sup>25</sup>



Figure. Visualization of molecular motion at the single molecule level.

Itoh and Tsukamoto succeeded in preparing magnetic nanoparticle arrays for ultrahigh-density magnetic recording. Their method took advantage of the self-assembly of 5-nm sized silica nanoparticles and nanopores. The particle density was 5.4 T (5 400 000 000 000) particles per square inch, which was beyond the original goal. Matsushita et al. prepared star-shaped and ring-shaped nano-objects by a newly developed method combining a bottom-up approach and local heating.<sup>26</sup> Ikake et al. found that polylactic acid, a polymer derived from plants, forms highly transparent films by preparation of complexes of the stereoisomers.



Figure. Nanopore array (left) and nano stars (right).

<sup>&</sup>lt;sup>25</sup> Otsuki et al., J. Am. Chem. Soc. 2010, 132, 6870.

<sup>&</sup>lt;sup>26</sup> Matsushita et al., *Chem. Commun.* **2012**, *48*, 1668.

# Preparation and Characterization of Nanomaterials and Nanodevices.

The members of the Project have various backgrounds in specialized methods and materials. The methods include precision electron and X-ray diffraction analysis, characterization of superconductivity, single photon detection, and control over plasma; the materials include superconductive two-dimensional layered materials, metal oxide nanoparticles, carbon nanotubes, carbon nanorods, and hetero-structured semiconductors.

In this Project, the following materials, systems, and properties were studied.

- Carbon nanotubes containing ferromagnetic metal (magnet) inside
- Diodes made from carbon nanotubes (nanorods) and diamond-like carbon
- Thin films of hydrogen storage alloy
- Highly crystalline zinc oxide thin films
- Iron-based superconductors, particularly 1111- and 111-types
- Ultrahigh-density target prepared with the Pechini method
- Superlattice prepared using the ultrahigh-density target
- Chirality-controlled single-walled carbon nanotubes via irradiation of free-electron laser
- Photonic crystals for efficiency improvement of dye-sensitized solar cells
- Nano ribbons of silver tolylacetylide
- Photoluminescence of oxygen storage materials

The following devices and methods have been developed.

- Plasma irradiation device for sterilizing periodontal disease bacteria
- Nano bubble producing device<sup>27</sup>
- Atmospheric plasma device for cancer treatment
- Single photon detector for terahertz bands
- Characterization of molecular motion in muscle and ATP hydrolysis at the molecular level
- Scanning electron microscopic method for live cells

**Quantum Theory and Simulation of Electromagnetic Field over Nanostructures.** Theorists, in collaboration with experimental teams, studied quantum theory and made simulations on the nanoscale. Materials in nano-scale regions behave in accordance with quantum mechanics. Therefore, it is important to address unresolved problems in quantum mechanics as well as to develop computational methods to predict what happens when light hit a nanomaterial. This Project addressed these issues.

There remains unresolved issues in quantum mechanics. One of them is Hund's rule. The rule states that, in a situation where two electrons reside in different orbitals, the state in which electron spins are oriented in the same way is more stable than the state in which electron spins are oriented in the opposite ways. The puzzle was why. Sako found that there is a domain in space where two electron spins in the opposite directions cannot exist, which raises the energy of the spins in the opposite directions.<sup>28</sup> This analysis solved the long-standing puzzle in quantum mechanics. The work was chosen as the IOP select by the Institute of Physics (UK) and highlighted in the Europhysics News published by the European Physical Society.

Solid surfaces are important for device applications. The surface is nanoscale in essence and hence the properties are determined by quantum mechanics. Ishida et al. revealed properties of the following

<sup>&</sup>lt;sup>27</sup> Suzuki et al., Patent Application 2012-204982.

<sup>&</sup>lt;sup>28</sup> Sako et al., *Phys. Rev. A* **2011**, *83*, 032511.

surface systems quantum mechanically.

- Interface between metal and Mott insulator
- A single molecule between metal electrodes
- Surface of metal crystals

The information technology group of this Project has investigated near-field light as a means of information recording. Ohnuki and Nakagawa approached the problem from simulation. They developed a high-precision computation method more than 100-fold faster than conventional methods.<sup>29</sup>

Simulation of a variety of nanostructured photonic crystals were also performed to analyze the light confinement effects.

Ohnuki and Sako have developed a new code that simultaneously solves the Maxwell equations, which describes how electromagnetic waves behave, and the Shrödinger equation, which describes how nanomaterials behave, to simulate the interaction between light and nanomaterials.<sup>30</sup> Only the newly developed method afforded the correct solution to a situation where light is irradiated onto a nano-sized plate, while conventional methods failed to give the correct solution.

## **Publication Summary**

**Initial Goals and Final Achievments.** The tables below list the initial goals and the final achievements for each group.

Items	Status quo	Original technologies	Target
(1) writing speed	0.25 Gbits/s	photoinduced magnetization	25000 Gbits/s
(2) recording density	0.2 Tbits/inch <sup>2</sup>	nanomagnetic material through self-assembly	2 Tbits/inch <sup>2</sup>
(3) writing density	0.6 µm²/bit	near-field thermally assisted recording	0.003 µm²/bit

#### Table. Information Technology: Ultrahigh Speed/Density Recording

(1) Magnetization reversal was proven with a single 40 fs pulse, corresponding to 250000 Gbits/s. Continuous recording is to be addressed.

(2) Particle density of 5.4 Tbits/inch<sup>2</sup> (2.7-fold greater than the goal) was achieved. Homogeneous preparation in sizes and properties is to be addressed.

(3) 0.004 mm<sup>2</sup>/bit was achieved. Further miniaturization is ongoing.

<sup>&</sup>lt;sup>29</sup> Ohnuki, Nakawaga et al., J. Electromagn. Waves Appl. 2012, 26, 997.

<sup>&</sup>lt;sup>30</sup> Ohunuki, Sako, Nakawaga et al., Int. J. Numer. Model. 2013, 26, 533.

Items Status quo		Original technologies	Target
(1) single photon	<10%	quantum dots	30%
(2) single photon detector	1%, dark count~ $10^{-8}$	superconducting thin wire	50%, 10 <sup>-8</sup>
(3) photon number resolving detector	0.2 eV, 100 kHz	superconducting transition edge sensor	0.2 eV, 1 MHz
(4) entanglement exchange	fidelity<0.7	High fidelity exchange	>0.9
(5) quantum memory 1 ms, low temp		Bose condensates	10 ms
(6) quantum bit device $\sim 1\%$ , <0.3 K		THz plasmonic quantum bit	>5%, rt–1.8 K

**Table. Information Technology: Quantum Information** 

(1) Single photon emission was confirmed.

(2) Detection with 6% efficiency with dark count ~ $10^{-8}$  was achieved with a InGaAs/InP-APD.

(3) Efficiency >80%, resolution 0.2 eV, repetition >80 MHz (80-fold greater than the goal) were achieved.

(4) Fidelity ~0.9 was achieved.

(5) ~0.3 ms Storage and 100% efficiency were achieved.

(6) Results suggesting >1.1 K operation. Sensitivity of the detector increases by an order of magnitude.

Items	Status quo	Original technologies	Target
(1) water photolysis with supramolecules	not exist	self-assembly of sensitizer and redox catalysts	to realize
(2) light assisted hydrogen storage	a new concept	light triggered desorption that we have found	yield >0.1 >6 wt%
(3) high strength fuel cell	60 МРа, 900 °С	a new preparation process from micro/nano particles	2–5 fold, 600 °C
(4) DSSC with inexpensive dyes	3%	light confinement effect of nano structure	5%
(5) bioreaction of photo- synthetic organisms	rate 34 nmol/h/mg	genetically engineered photosynthetic organisms	an order of magnitude increase

 Table. Energy Technologies: Harnessing Solar Energy with Nanostructures

(1) Supramolecular system produced twice as much H<sub>2</sub>. Complete water photolysis is yet achieved.

(2) Quantum yield ~0.01. Doubling capacity with 2wt% alloy achieved. 3wt% alloy being tested.

(3) Promising cathode and electrolyte materials found. Test cell has been completed to be tested.

(4) 1.7-fold increase confirmed due to light confinement effect.

(5) Anabaena/ZrVFe system recorded 7-fold increase in H<sub>2</sub> production.

(1) probe compounds for	under investigation	cancer specific compounds identified	to realize	
cancer				
(2) luminescent compounds	safety, sensitivity	safe, long wavelength luminescent compounds	detection of cancer marker with compounds	
(3) ex vivo diagnosis	low diagnosis rate	highly sensitive and specific diagnosis	diagnosis rate >80% small error <10%	
(4) in vivo image	early detection of	improvement and low-cost	candidate compounds for	
diagnosis	cancer is difficult	detection system	in vivo use	
(5) treatment of	affecting normal	cancer-specific drugs and	preclinical trial	
cancer and other	region	new treatment		
diseases				

Table, Medical	<b>Technologies:</b>	Nanobiotechnologies (	for Medical	Applications
I upici micuicui	reemotogiest	1 unobiotechnologies	tor miculcul	applications

(1), (2) in progress.

(3) Telomere labeling method established by coworkers. Applications being tested.

(4) Fluorescence tumor labeling achieved in animal experiments. Diagnostic application needs further studies.

(5) Data obtained in preclinical trials in animal experiments. Clinical trials to be done. As a scar treatment drug, the compound was made into ointment and effect confirmed for mammalian experiments.

**Publication Data.** The following table presents the numbers of papers, books, patent applications, conference presentations, awards, and external funding. The first numbers in the parentheses are for collaboration among members and the second numbers for collaboration among members across Colleges. The network showing collaboration is also shown.

ruole. ruolleutions.					
	2009	2010	2011	2012	2013
Paper	117(20,6)	108(15,4)	121(20,3)	112(22,5)	128(18,11)
Patent application	8(1,0)	9(4,1)	8(2,0)	3(2,0)	3(1,0)
Invited lecture	80	45 66		29(5,2)	68(6,2)
Conference					
presentation	323	327(51,10)	281(57,6)	277(126,16)	391(104,29)
Book	17	11	19	5	17
Award	4	4	5	9	13
External funding	30(11,0)	33(13,2)	27(10,2)	27(7,1)	30(3,0)

Table. Publications.



Figure. Collaboration network of individual members in the Project. The lines represent collaboration with the width indicating the number. Black lines are for joint papers and grey lines are for other forms of publication.

**Awards Granted.** Twelve awards were granted to members for their research and 23 poster and presentation awards were granted to researchers and students under the supervision of a member.

## **Project Activities**

Twice a year, all members got together to semiannual meetings to report and discuss about progresses. Once a year we organized a symposium, co-organized a young forum with the Advanced Materials Science Center (AMSC) of the College of Science and Technology (CST), and organized a special session in the CST symposium. Seminars were also organized on a non regular basis. Other activities for dissemination purposes will be described later.

	0	
AY 2008	Feb 27	Semiannual Meeting (retreat, Atami)
AY 2009	Sep 7	Semiannual Meeting (CST)
	Sep 18	The First Symposium (SM)
	Oct 31	Science Agora (Odaiba)
	Nov 28	CST symposium special session (CST)
	Jan 15	Semiannual Meeting (CST)
	Feb 13	AMSC young forum (CST)
AY2010	May 10	Semiannual Meeting (CST)
	Sep 8	Second Symposium (CST)
	Jan 8	Semiannual Meeting (CST)
	Feb 5	AMSC young forum (CST)
AY 2011	May 27	Semiannual Meeting (CST)
	Aug 24	Semiannual Meeting (CST)
	Nov 26	CST symposium special session (CST)
	Jan 7	Semiannual Meeting (CST)
	Jan 28	AMSC young forum (CST)

Table. Events facilitating collaboration and dissemination.

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	Feb 20	Third Symposium (HQ)
AY 2012	May 26	Semiannual Meeting (CST)
	Sep 15	Fourth Symposium (CHS)
	Nov 28	CST symposium special session (CST)
	Jan 12	Semiannual Meeting (CST)
	Feb 9	AMSC young forum (CST)
AY 2013	May 18	Semiannual Meeting (CST)
	Jun 11	JST New Technology Presentation Meeting (JST)
	Dec 21	Fifth Symposium (HQ)
	Feb 15	AMSC young forum (CST)

CST: College of Science and Technology, SM: School of Medicine, AMSC: Advanced Materials Science Center, HQ: Headquarters of Nihon University, CHS: College of Humanities and Sciences, JST: Japan Science and Technology Agency.

**Support to Young Researchers.** We hired (post-doctoral) research fellows for their support as well as for advancing research. We also hired research assistants for their works in the PhD courses, taking in consideration that many Japanese universities now discount the fees for the graduate school. Two of the research assistants were granted the DC scholarship by the Japan Society for the Promotion of Science.

ruble. Research felle wis and research assistants						
	2009	2010	2011	2012	2013	
(PD) research fellow	3	7	9	10	10	
research assistant	5	5	3	4	5	

Table. Research fellows and research assistants

Former fellows are now working in universities, industry, and medical institutions in the world:

Gandhigram Rural Institute (India), Chisso, physician, Akiru Municipal Medical Center, CHS of Nihon University, Masukawa Institute of Science and Culture, CHS of Nihon University, Chiba Cancer Center, Tsukuba University, Keio University, Alcaliber (Spain)

### **Dissemination: For Academics and Industry**

**Symposium.** Symposiums were organized annually. The first one in 2009 was on an international basis in English language, the second one in 2010 was organized for young researchers, and the fourth one was jointly organized with the MEXT project of the College of Humanities and Sciences. We organized the final symposium including a cross talk show with high-school students (see Dissemination: General Public).



Figure. Posters for the symposiums (2009–2013).

**JST New Technology Presentation Meeting.** Japan Science and Technology Agency organizes New Technology Presentation Meetings for the promotion of commercialization of technology seeds held by universities and public institutes. On June 11, 2013, we jointly organized this meeting for the promotion of our technology seeds and presented six inventions for which the patents are applied.

We greatly acknowledge the Research Promotion Department, the Intellectual Property Departments, and the Nihon University Business, Research and Intellectual Property Center (Nubic) of Nihon University.



Figure. JST New Technology Presentation Meeting (2013).

Journal of Research Institute of Science and Technology. Review articles were published in the *Journal of Research Institute of Science and Technology*, published by the College of Science and Technology, Nihon University. This journal is available free of charge on line through J-Stage.

• Tsukamoto, Itoh, "Ultrafast Manipulation and Measurements of Magnetization by Ultra Short Pulsed Laser", 2011, No. 122, p. 25.

• Inoue, Namekata, "Development of Single-photon Detectors for Practical Quantum Cryptography", 2011, No. 123, p. 1.

• Otsuki, "Fiddling with Electrons and Photons Using Metal Complexes at the Molecular Scale" 2011, No. 124, p. 26.

**Special Sessions in the Annual Meeting of the Chemical Society of Japan.** The Chemical Society of Japan organizes special sessions for communications among industry, public, and academic sectors, development of new fields, and interdisciplinary researches. Two such special session were

organized by members of this Project.

- March 27, 2009, Special session in the 89th Annual Meeting; organized by Nishimiya "Chemistry as central science: building up sustainable healthy society"
- March 27, 2014, Special session in the 94th Annual Meeting; organized by Otsuki (planned) "Interaction of Light and Matter: From Basics to Photonic Materials and Devices"

## **Dissemination: For General Public**

**Website.** We made our website that was linked from the top page of Nihon University. News of publications in top journals and awards granted and announcements for symposium were publicized.

**Science Agora.** Science Agora is one of the largest scientific events in Japan for general public annually held in Odaiba in the Tokyo bay area. We presented a panel designed by Prof. Kimura of the College of Art.



Figure. Science Agora (2009).

**Cross Talk Show with High School Students.** As part of the final symposium held on December 21, 2013, a cross talk show "great science and job as a scientist." Some researchers from the Project (Otsuki, Tsukamoto, and Matsushita) and high school students talked about science on the stage. Twenty three high school students joined the show. This event was planned by Prof. Kimura of the College of Art and Owada of the Research Promotion Department. Ms. Kuwabara, a student of the College of Art, emceed the show.

**Publication of Book.** An easy-to-read book about the researches and researchers' thoughts in this Project will be published written by science writers who interviewed some of the members. The book is entitled "Six Promises in the Future – Stories of Nihon University *N*. Research Project –" and is to be published in March 2014 by Leave-A-Nest Publication.

**Media.** Our Project was highlighted in several media for general public. Most of them was mediated by the Research Promotion Department, Intellectual Property Department, and the (Nihon University Business, Research and Instinctual Property Center (Nubic).

- · 2009, Nikkan Kogyo Shinbun, April 17
- · 2009, Toyo Keizai, June 27
- · 2010, 2011 Takuetsu-suru Daigaku, Daigaku Tsushin
- · 2013, Daigaku no Yakusoku, Recruit



Figure. Our Project highlighted in media.

**Dissemination in the University.** Five issues of Nihon University Press covered our Project and published articles on various aspects of the Project. Nichidai Koho and many other College brochures also highlighted our Project.



Figure. Nihon University Press, April to August, 2010.

### **Prospects**

One of our goals was to acquire another funding when the Project is over based on our achievements during the five years. In this sense, we were able to start a new large-scale project this year, the MEXT strategic project for private universities "Search and Creation of New Materials, Properties, and Devices through Understanding and Control of Ultrafast Interaction between Light and Matter", led by Tsukamoto, which we hope will be a successor locomotive for further research

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activities.

Some of the members will join large-scale projects which are listed below.

the MEXT strategic project for private universities
Institute: Nihon University, AY 2013 to 2017
Search and Creation of New Materials, Properties, and Devices through Understanding and Control
of Ultrafast Interaction between Light and Matter" led by Tsukamoto
Grant-in-Aid for Scientific Research on Innovative Areas
AY 2013 to 2017
Molecular Architectonics: Orchestration of Single Molecules for Novel Functions
Ishida, Sako
METI Technology for renewable energy storage and transport (energy carrier project)
AY 2013 to 2017
Electrochemical Ammonia Synthesis from Water and Nitrogen in Molten Salt
Nishimiya