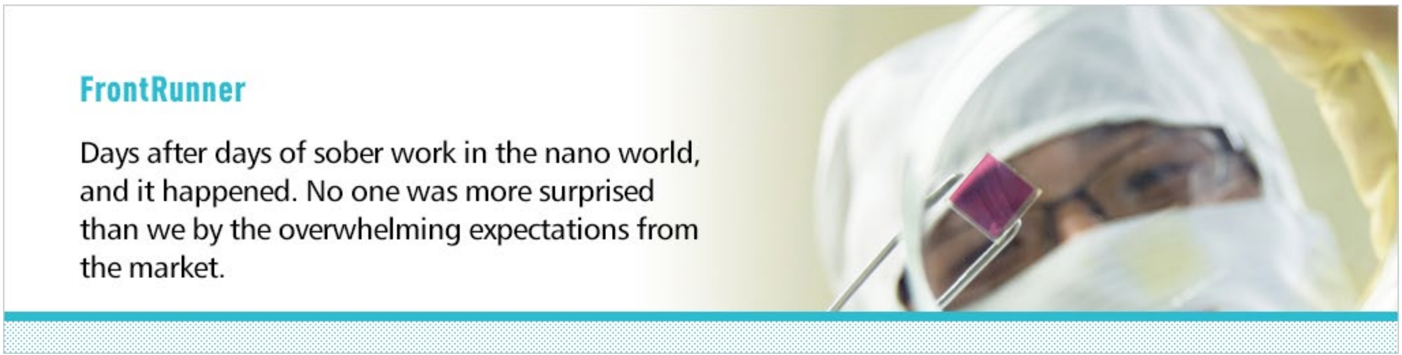
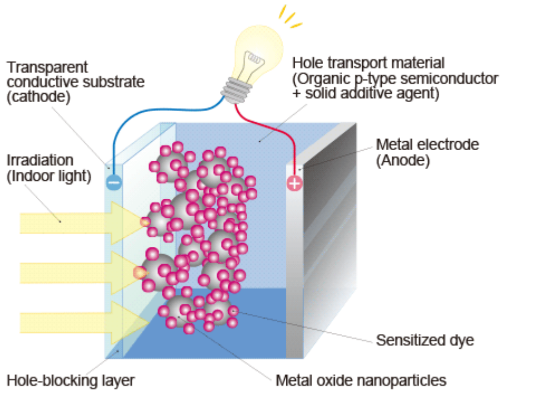
SPECIAL “Round-table talk” Complete Solid-State Dye-Sensitized Solar Cell



Energy harvesting is a key factor of the Internet of Things (IoT) because an IoT-based society will require ubiquitous power supply. Much is expected from solar cells, which convert optical energy into electric energy. Efforts on solar cells, however, have centered on outdoor use. While progress has been seen with the dissemination and technological innovation of outdoor solar cells, little has been done with those used indoors or under weak light. For instance, amorphous silicon solar cells, which are mainstream for indoor use, have limited applications because they generate low power and must be used in combination with button batteries.

The situation totally changed in June 2014, when Ricoh announced its solid-state dye-sensitized solar cell (solid-state DSSC(*1)). Soon after the announcement, inquiries rushed in from a range of manufacturers developing IoT technologies. The solid-state DSSC generates 13.6μW/cm^2, which is twice as powerful as the amorphous silicon solar cell. Further, the new solid-state DSSC has excellent properties for harvesting energy, including safety and durability. Past DSSCs were liquid-based and were not put into practical use; they had issues with power generation performance and safety as they were filled with a liquid electrolyte. The solid-state DSSC has brought about true innovation in energy harvesting technologies.

Principle of the Solid-State DSSC



① Light hits a transparent conductive substrate (cathode, or negatively charged electrode) → ② Sensitized dye absorbs the light and excites electrons → ③ Excited electrons penetrate the conduction band (metal oxide nanoparticles) → ④ Electrons flow through the hole-blocking layer to the transparent conductive substrate (cathode), which includes a hole-blocking layer that prevents electrons from flowing to the hole transport layer → ⑤ Electrons travel through an external circuit to a metal electrode (anode, or positively-charged electrode). → ⑥ The electrons reach the dye via the hole transport layer. Light is converted into electrical energy through this circuitry.

How did Ricoh engineers overturn common sense and make this spectacular achievement a reality? Central members of the development team reveal the secret.

*1 DSSC: Dye-Sensitized Solar Cell. The principles of photosynthesis are used but no silicon is used. This type of solar cell is inexpensive and can be manufactured without large-scale equipment. Most DSSCs are based on the oxidation-reduction reaction of an electrolyte (liquid-state), but Ricoh developed the world’s first practical solid-state DSSC.

PROFILE

Tetsuya Tanaka, Leader

Majored in Precision Machine Engineering, joined Ricoh in 1992.

Group Leader, 2nd NT Development Section, NT Development Department, Functional Material Development Center (since April 2014). Past responsibilities include development of production technologies based on numeric simulation. Develops applications and manages themes for creating new energy-related business.

Yuji Tanaka

Majored in Functional Polymer Science, Engineering Research, joined Ricoh in 2002.

Leader, Solid-State DSSC Development Themes (since April 2014). Past responsibilities include development of OPC material technologies, and application of nanotechnology to electronic photographs.

Ryota Arai

Majored in Material Creation Engineering and Applied Chemistry, Faculty of Engineering, joined Ricoh in 2008.

Develops materials (primarily dyes) for organic solar cells, including solid-state DSSC (since April 2012). Past responsibilities include developing OPC material technologies and new materials.

Naomichi Kanei

Majored in Industrial Chemistry, Technical Studies, joined Ricoh in 2013.

Develops element technologies (primarily modularization) for increasing the efficiency and durability of solid-state DSSC.

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01. Ricoh's technological resources were effectively used to develop the new material

Tetsuya:

If I remember correctly, development of the solid-state dye-sensitized solar cell (solid-state DSSC) started two years before the announcement (June 2014).

Yuji:

Yes. Originally, we decided in 2011 to develop a novel material using Ricoh's organic photo conductor (OPC) technology. Developing a next-generation technology was the theme. We had several candidates, and chose to go for the solid-state DSSC.

Tetsuya:

DSSCs are generally liquid-based. What made you go for the solid state?

Yuji:

Ricoh already had a technology using supercritical fluid carbon dioxide(*2) and I anticipated I would be able to use that technology to make a solid-state hole transport layer, which was conventionally a liquid electrolyte, and densely pack the porous photoelectrode layer. Yet I was not the first in this area. Since 2008 or so, an internal staff member had been studying and developing a solid-state DSSC under a national project. The concept was to combine the OPC technology and the supercritical technology to produce a never-before-seen device.

Tetsuya:

So the theme you presented in 2012 was not at all sudden?

Yuji:

Before the theme was presented, I had checked the principles with the person who had been studying and developing it. I then conceptualized the theme in the first half of 2012. Development started in the second half of 2012, with Ryota and me at the center. Ryota developed the materials, particularly the sensitized dye, and I developed the device in general. I am thankful for my supervisor at that time, who gave me the development opportunity.

Tetsuya:

Ryota, at that time, you were synthesizing materials for a different type of solar cell, weren't you?

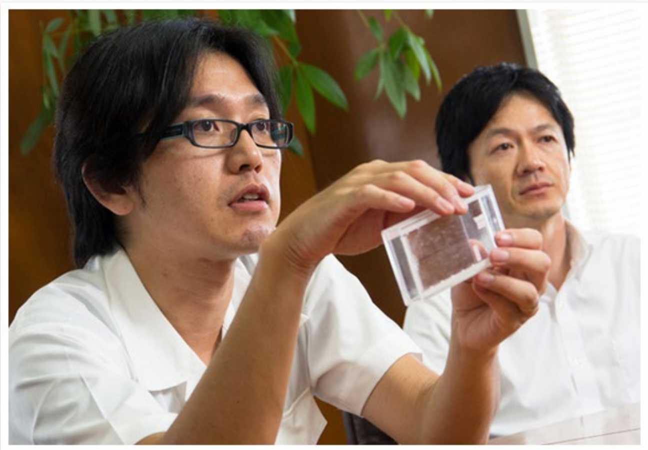
Ryota:

Well, in fact, the other type was the main thing. I was developing an organic thin-film solar cell(*3), and began to be involved with the solid-state DSSC primarily on dyes. But the special dyes for super-criticality differed greatly from what I had been doing. It wasn't exactly in my line.

*2 Supercritical carbon dioxide: Carbon dioxide is gaseous at room temperature, but becomes a highly functional solvent (supercritical fluid) at a critical temperature (31℃ or higher) under a critical pressure (73 atmospheres or higher). Supercritical carbon dioxide has properties of both gas and liquid, and enables various substances to be extracted, be separated, and permeate.

*3 Organic thin-film solar cell: A solar cell consisting of a thin substrate of plastic film or metal and an organic semiconductor material formed on it (pn junction).

02.One day, a turning point comes suddenly



Tetsuya:

The development was first intended for sunlight, that is, outdoors, right? I heard that the project was accidentally steered to indoor light.

Yuji:

Well, you can say that now, but I wish you could keep it between you and me (grin). For nearly a year, the outdoor power generation performance was not satisfactory. So we decided to add a highly basic(*4) material in order to raise the voltage, and chose a solid material. It eventually led to the successful development, but that was not what we had in mind then. We just considered that the conventional liquid additives were not durable enough when combined with a solid organic material (p-type semiconductor), which was the main material for the hole transport layer. That is why we chose a solid material.

Tetsuya:

You addressed the durability issue and decided to use a basic material. You came up with the idea because you had experience of OPC development, didn't you?

Yuji:
Exactly. We knew that basic materials are effective for controlling charges on the OPC surface and for improving image quality. We had had enough trouble with liquid materials placed inside solid materials; they escape and seep out.
Tetsuya:
That made the material completely solid-state to the letter. Did the solid additive increase the power generation performance?
Yuji:
Not at all (grin). Yet the voltage got higher, and I had a hunch. I had the material tested under indoor light. Then, voila!
Tetsuya:
You made it.
Yuji:
I immediately changed the course of the development. We had been aiming at a sufficient performance level in shadows outdoors. However, if indoor light would work, we would have a lot more applications. Well, that's another story that should be kept between you and me, but I wasn't really thinking much about the applications of the device or its potential markets. My thoughts on how to use the device were just vague...I wasn't sure if it could be commercialized. Yet I found that the device might be useable under indoor light, and I began to visualize its specific applications.
Tetsuya:
The idea of using it in the IoT market—was that conceived after that?
Yuji:
Somebody may have come up with the idea earlier. For my part, the idea first came to my mind when I saw a rise in performance under indoor light.

*4 Basic: Property to neutralize acid. Alkaline.

03.Triple and quadruple hurdles on the way

Tetsuya:
The project was steered to indoor light in the middle of 2013. Naomichi, you had joined the company by then, hadn't you?
Naomichi:
Yes. The first assignment I was given was modularization. Making panels, that is. As a newbie, I wasn't sure if I was qualified to be assigned such an important task (grin).
Yuji:
That's what this company is all about (grin).
Naomichi:
I was to make a test device with a supercritical fluid device. At that time, the quality of the manufactured devices tended to vary, and testing them was not easy. Then Yuji gave me some advice. He told me to try spin-coat application(*5). The changeover to the application method turned out good later when we sought a business use.

Yuji:
The supercritical method produces a homogenous film, but the spin-coat application method is superior in terms of equipment cost when it comes to scaling up for business. Ricoh has ample know-how on application methods, so related projects can be quickly started when the company starts to examine the possibility of commercialization. The changeover to the application method, however, took place

sooner than originally intended, because of the shift toward the indoor light and the tests by Naomichi.

Tetsuya:

Meanwhile, Ryota suffered much. The wavelengths changed from sunlight to indoor light, the prescriptions for the hole transport layer were changed, and even the engineering method changed.

Ryota:

I was at a loss on what to do (grin). The solid-state DSSC, in the first place, has limitations in terms of the amount of dye that can be packed. This is because you need to make the titanium oxide layer thinner than that of the liquid-state DSSC. That means you have to increase the amount of light absorbed by each dye molecule. This was one reason why the solid-state DSSC was difficult to develop. As the intended applications were indoors, there were restrictions on the color of the dye. The device would be often seen by people, so the color had to look good. That would in turn limit the wavelengths. The conditions got more and more severe.

Tetsuya:

Further, you had been developing dyes for supercriticality for about a year, but you had to change them to those suitable for application. It sounds as if you suddenly encountered triple and quadruple hurdles in front of you.

Ryota:

The conclusion is that I was not able to develop the dyes in time for the announcement. I haven't even found clear enough principles of dyes optimal for the solid-state DSSC. I'm abashed as an engineer. But I will not give up. I will use this disappointment as a springboard and develop special dyes for the completely solid-state DSSC, which no one has ever seen.

*5 Spin-coat application: A method of forming a thin film with centrifugal force by applying base material on the center of the substrate and then rotating the substrate at high speed.

04.During development, nothing was readily available

Tetsuya:

The tasks of modularization were also hard, weren't they?

Naomichi:

I sympathize with Ryota, who dealt with the dyes. Few technical materials, not even papers, were available regarding serial modules of DSSC for indoor light. Technology had not been accumulated internally. It was almost as if starting with a blank sheet of paper. In a test module, you can use big electrodes in the gaps between the cells. A marketable device, however, has to have narrow gaps between the cells so that the power-generating area (opening ratio) is large. I repeated trial-and-error processes day by day, trying to maintain the performance with many cells and large areas. We need to continue to increase efficiency of the serial modules, which will greatly influence the possibility of commercial production. I feel great responsibility.

Yuji:

You mentioned starting with a blank sheet of paper. When you joined the project, the test environment had not been organized yet, had it?

Naomichi:

Indeed. We didn't even have a measuring instrument for indoor light. Nor a black curtain. For a while, I confined myself to a room that had no windows. You wouldn't be able to imagine such an environment today. Yet the company had an academic atmosphere. In June 2014, it was my second year at Ricoh; Yuji had a technical presentation at the Imaging Society of Japan. In July of the same year, he again had a presentation at a social gathering with Professor Grätzel(*6), the inventor of the DSSC. I myself joined Yuji and made a technical presentation at the Electrochemical Society of Japan in October 2014. That was quite different from the image of development I had for a company before joining Ricoh.

Yuji:

The technical presentation in front of Professor Grätzel was hard. I was also nervous when I was invited and made a presentation at the Chemical Society of Japan later (March 2015), but the gathering with Professor was an event I will remember for the rest of my life. I suspect I will never be as nervous again. I am thankful for the valuable opportunity. As you can see, development of the solid-state DSSC is very interdisciplinary today. The development of a DSSC device involves a variety of technologies that are harmonized: the OPC technology mentioned earlier, microprocessing technology for semiconductors, liquid crystal manufacturing technology for sticking substrates together, and organic EL technology for forming metal electrode films. You can experience all of them, so working on the DSSC makes you quickly grow as an engineer.

Naomichi:

I spend most of my days in the clean room. I never imagined it before I joined Ricoh.

*6 Michael Grätzel: Professor at Swiss Federal Institute of Technology Lausanne. In 1991, he invented a liquid-state DSSC consisting of electrodes of titanium dioxide particles adsorbing organic dyes, OTL of an iodine electrolyte, and counter electrodes of platinum.

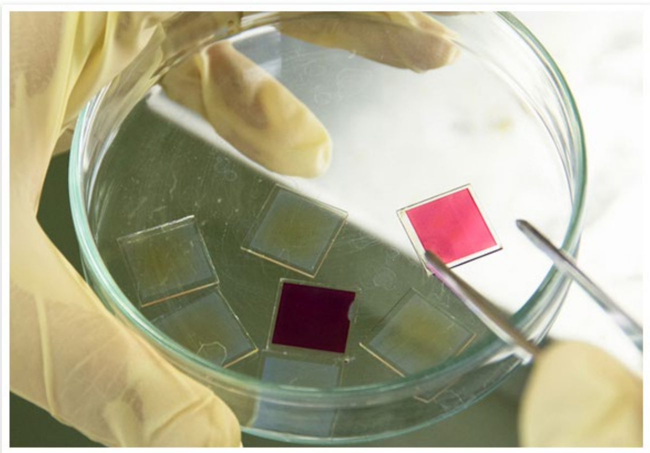
05. Extraordinary power generation performance

Tetsuya:

It was not until April 2014 that I joined this development group(*7). At that time, the DSSC already had a power generation performance more than double that of the amorphous silicon solar cell. In the latest announcement, the stakeholders were most surprised by the figures of the output: 13.6 microwatts (μW) per square centimeter.

Yuji:

We confirmed sufficient performance under indoor light in the middle of 2013. However, since then, the output had stayed around 7 $\mu W/cm^2$ for about six months. That was a little higher than the amorphous silicon solar cell, but was not impressive. We definitely wanted to exceed 10 $\mu W/cm^2$. We thought double digits would be convincing enough to change the way people look at the device.



Tetsuya:

It was then that the specific ideas arose for the IoT as an indoor light application. To make the device practical, exceeding 10 $\mu W/cm^2$ was a must. When was that performance reached?

Yuji:

End of 2013. The number began to improve at one point, and then rapidly increased—7, 8, 9, and 10 μW/cm². Things were quick afterwards. When Tetsuya joined the group, the performance had already exceeded the amorphous silicon solar cell, easily more than double. Naomichi was half in doubt, saying "Shall we measure it again?" (grin).

Naomichi:

To be honest, I couldn't believe it in the beginning. I studied the DSSC in college, and I thought that such a rapid increase in performance was impossible in this area. Double the amorphous silicon was just "shady" (grin).

Tetsuya:

Yet it was real. It stunned the people of the field. Internally, people thought "That will make it." It looked promising as a key device for the IoT society, and drew attention inside the company.

Naomichi:

It took some more time for me. I realized I had done something great after hearing external reputations after the announcement.

Yuji:

(Nodding profoundly) The reaction was beyond what we expected, wasn't it? For over a decade, the DSSC market was modest, with nothing new in particular. We had no idea how much attention we could get until it actually happened.

*7 Joined this development group: Tetsuya was in another department, developing nanoparticle control technology, particularly even distribution of electrode films.

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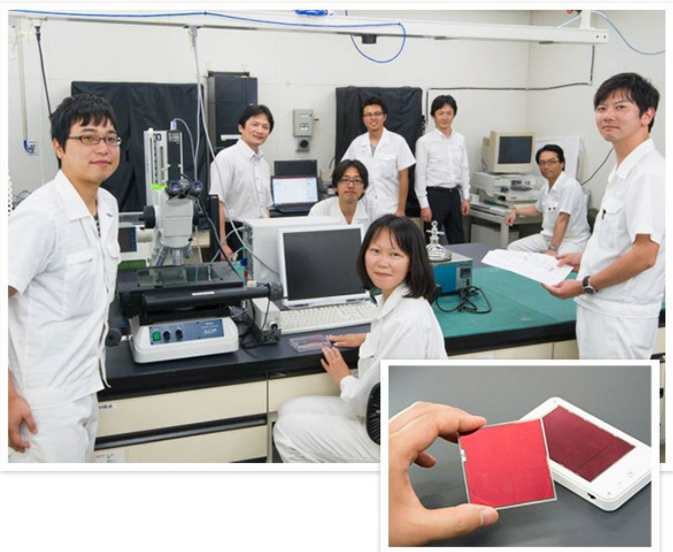
06. Creating a new energy harvesting market



Tetsuya:

We had been very busy until the press release, hoping to take some rest afterward. Well, we are still getting busier and busier. We had a good response at the exhibition, and inquiries came one after another.

Naomichi:

I said "academic" earlier, but I have had more opportunities to talk with customers after the announcement. Another thing I never imagined as a student. Following the presentation at the Society last year (2014), I explained the technology to customers at various exhibitions this year (2015). Through direct interaction with the customers, I realize my responsibility for making the device commercial as soon as possible.

Ryota:

I too have more opportunities to talk with customers than before. I feel the demands from the customers are more familiar to me now, which makes me think about what I should do in the future.

Tetsuya:

After the announcement, I often hear from people in the industry that they "feel the commitment of Ricoh." In the solar cell market, movements were getting a little dull in the past few years, including the DSSC. Then, suddenly, an indoor light solar cell appeared, with a power generation performance double that of the amorphous silicon. It was not a mere technical announcement; spectators viewed the device at a practical level, and expectations are rising.

Yuji:

I'm very aware of it. We have already started to deliver samples for practical applications (EH-Terminal(*8): thin photovoltaic wireless sensor network terminals), and people are moving to bring the devices to business use. We still have a lot of issues to solve, including module efficiency. Yet I believe it will not be so long before we can start actual business.

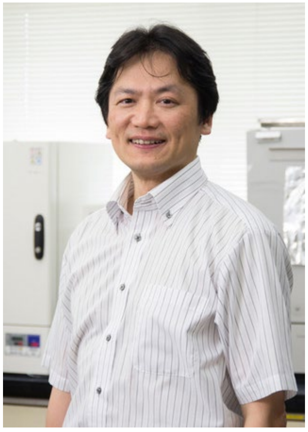
Ryota:
I agree. In my idea, the key to practical use is the dyes. Now more than 20% of the current is left unabsorbed by the dyes. To sustain and develop the business, we need to develop dyes with better properties. By my own hands, I definitely want to produce new dyes that can make the solid-state DSSC exhibit its full performance.

Tetsuya:
In the favorable wind of the IoT, the power supply for sensors is just a first exit for us. As I recognize it, the applications of the solid-state DSSC mostly remain undiscovered. We shouldn't just consider it a new business for Ricoh. Beyond that, we should keep committed to creating a new energy harvesting market.

*8 EH-Terminal: In May 2015, Altima adopted Ricoh's solid-state DSSC (with a generating performance of approximately 340 μW under a white LED light source of 200 lx) as a standalone power supply for wireless sensor terminals for information such as the temperature, humidity, and illumination of the room. The objective is to disseminate the IoT under indoor light.

Pioneering devices come from counterintuitive thinking

Shinji Otani
Manager, NT Development Department, Functional Material Development Center



"I want to use the organic photo conductor technology to develop dye-sensitized solar cells," said Yuji Tanaka. Honestly, my first impression was "That again, how boring." I was unfair and just thought he took an easy way of conceptualizing an organic solar cell, whose configuration was similar to the photo conductor.

I allowed him to start, under one condition—have a clear exit. Then, in just one year, the proposal led to a marvelous result: a solar cell that cannot be called a solar cell. It is a solar cell, but sunlight is put aside. Yuji's conclusion was truly counterintuitive. The wise decision enabled a magnificent achievement—an overwhelming power generation performance under indoor light, more than double the conventional amorphous silicon solar cell. Just at that moment, the concept of the IoT (Internet of Things) began to be widespread. People began to recognize the great value of standalone power sources, regardless of the weakness of their output.

Thus, we have successfully pioneered in the area of energy-harvesting devices for the IoT. We are already in the position of the pursued. In solidarity as a team, we need to keep seeking ingenious technologies to maintain the overwhelming performance difference. I am immensely proud to work with the development members fighting on the front lines of the world.

Comments from other central members

Tsuyoshi Matsuyama

Majored in System Science, joined Ricoh in 2011 after careers at other places including a device manufacturer

"I joined development of the solid-state DSSC in February 2015. Until then, I had worked on several tasks, such as starting up business with energy conservation in offices. In the previous company, I was a project leader for the development of LCD backlighting for smart terminals, handling a wide range of responsibilities from development to commercialization. I consider that fully using the experience and commercializing the solid-state DSSC is a theme under which I should work. When commercializing something, you need to meet the specifications the market demands while considering profitability. Further, you need to open up a market strategically. For that purpose, you need to forecast customer needs and things beyond them, and widely publicize the advantages of using the technology and collaborating with Ricoh. I believe that Japanese manufacturers should develop services related to things. We should address the peripheral tasks surrounding the main business of the customer, and eventually develop services for the main business. Developing services for the main business will make Ricoh a real partner to the customer, making our business sustainable. The ideal business for Ricoh is to be strong on things and to ensure customer satisfaction through the development of services using the strengths fully. I hope our solid-state DSSC has strengths as a thing, and the strengths be fully used in our development of services."

Shigeyo Suzuki

Majored in Electronics and Physics Engineering, joined Ricoh in 2007

"I joined development of the solid-state DSSC in October 2014. For about five years before that, I had been developing titanium oxide films (TiO2 paste) for the DSSC in a different department. I am still working on it after moving to the current department—the development theme is packed with the thoughts of many engineers. The TiO2 paste is used to support the dyes contributing to power generation and to form an electron transport layer that carries the generated electrons without a loss. To obtain a good conversion efficiency and stable properties, you need to vary the manufacturing conditions and prescriptions for dispersed elements. The development of the solid-state DSSC technology is still under way, and you need to focus on important factors out of a range of knowledge—knowledge on necessary materials, knowledge on analysis and evaluation, and knowledge on electrochemistry, for instance. No matter how hard I try, I have to keep filling what I don't have. My colleagues help me move forward. The device is packed with the thoughts of many engineers, so I want it to be on the market and evolve into products that are useful for customers. I will go forward, solving the technical issues in front of me, one issue at a time."

Tokushige Kino

Majored in Electronic Information Systems, joined Ricoh in 2014 after working for a manufacturer of electric appliances

"I joined the solid-state DSSC development team in December 2014, and have been working mainly on inspection technologies and production technologies. In inspection technologies, my focus of examination is on the inspection takt time (unit working time for each process) and how the inspection results influence the final products. In production technologies, my focus of examination is on material losses and takt time. As I make an actual sample and evaluate it, I often stumble on the unique properties of the solid-state DSSC. I am mostly free to choose the methods of making and evaluating the samples, so I feel the examinations have a very important role. Actually, I was quite optimistic in the beginning—I thought I would be able to use the know-how I gained in my previous work (designing and evaluating crystal silicon solar cells and providing technical instructions in each process). The product was different, though. The production and evaluation methods totally changed, and I had to learn new knowledge and skills. I keep learning day by day. The greatest joy as an engineer comes when the customer is delighted with a product I have made. At present, we are ready to start delivering samples. I will soon be able to hear from customers about the samples. Taking their voices into account, I would like to improve the device and make it better and better as a product."

(October 2015)