Artificial Photosynthesis Technology for Solving Environmental and Energy Issues

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To create a sustainable society that is friendly to the global environment for the future, decreasing the amount of greenhouse gases such as CO_2 is an urgent matter, and also producing storable clean energy that does not depend on fossil fuels is demanded. Artificial photosynthesis consisting of a light reaction dependent on a light source and dark reaction not related to it is technology with which oxygen, hydrogen, and organic products are produced artificially by using solar energy, water, and CO_2. Recently, this has come to be regarded as an important technology for solving both the environmental and energy issues we face, as described above. Fujitsu has researched this technology as one of the important basic technologies relating to energy and the environment in order to achieve a sustainable human-centric society for the future. This paper introduces basic research regarding materials and devices applied to the light reaction and dark reaction that we are currently investigating in order to develop a highly efficient artificial photosynthesis system producing storable energy by using CO_2, water molecules, and electrons generated from a photocatalyst irradiated with solar light.

1. Introduction

The issues relating to global warming, natural resource depletion, and radioactive contamination caused by nuclear power plant accidents demand the development of next-generation technology that can produce storable clean energy, while decreasing the emissions of greenhouse gases such as CO_2, for a future sustainable society. There are expectations that a hydrogen society and methanol society using hydrogen and methanol as an energy source, respectively, can be feasible examples. Producing storable clean energy sources with a small environmental load is important for building a green smart city utilizing information and communications technology (ICT), and it can be useful in a situation where social infrastructure fails to function due to a natural disaster such as an earthquake.

It is well known that plants produce organic products such as starch from solar light, water, and carbon dioxide, store the products and consume them for growing, in the natural world. The photosynthesis of plants is the ideal energy creation technology which meets all of the requirements relating to our current social issues. Therefore, creating artificial photosynthesis that performs better than the photosynthesis of plants would solve our environmental and energy problems.

This paper introduces the basic concept and fundamental material research regarding artificial photosynthesis technology that Fujitsu is working on as environmental and energy R&D.

2. Artificial photosynthesis technology

Technology that produces storable energy sources such as hydrogen, methanol, and methane by irradiating solar light on a photocatalyst is called artificial photosynthesis, and there are high expectations that it will be remarkable environmental and energy technology.[1] An artificial photosynthesis reaction system is shown in **Figure 1**. An anode coated with a photocatalyst and a cathode for producing organic reaction products are installed in water containing CO_2 gas. By irradiating solar light on a photocatalyst formed on the anode, the light energy is converted to high-energy electrons and simultaneously a hole with high oxidation capability is formed.

When light energy more than the band gap between the conduction band composed of electrons in

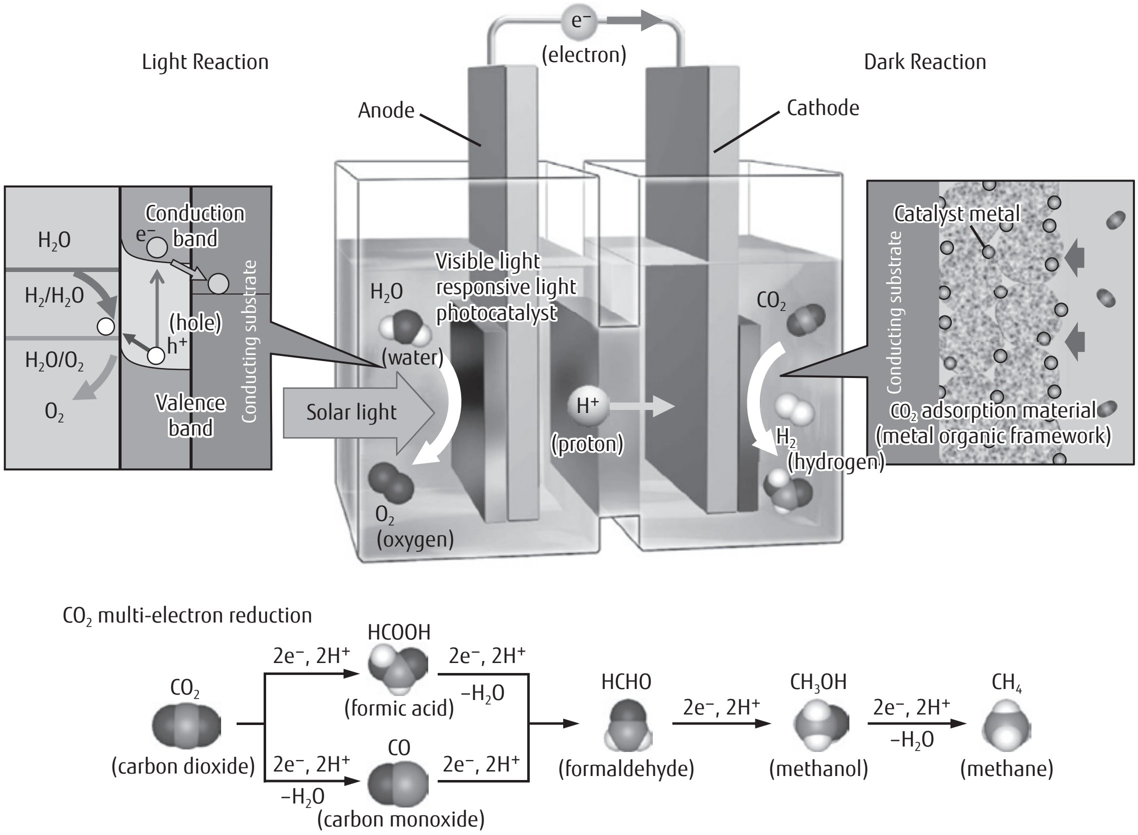


Figure 1
Concept of artificial photosynthesis.

the outermost electron shell, and the valence band composed of highest energy orbitals in which all electrons are occupied is supplied, the electrons in the valence band are excited to a conduction band, and a hole is formed in the valence band. The formed hole reacts with water, and then oxygen is formed on the anode. The electrons formed by light energy are transmitted to the cathode through conductive wiring. By reacting protons (H^+), electrons, and carbon dioxide on the cathode, organic products such as hydrogen, methanol, and methane are synthesized. In order to generate oxygen on the anode, the hole energy potential in the photocatalyst material should be higher than the oxidation-reduction potential of water. And to synthesize hydrogen, methanol, and methane, electrons having a higher reduction potential than the oxidation-reduction potential of carbon dioxide should be supplied. Artificial photosynthesis is technology that combines a light-dependent reaction on an anode with a dark reaction, which is not related to solar light. The next section describes research regarding the light reaction and the dark reaction, in detail.

3. Development of light reaction

Figure 2 shows the wavelength distribution of solar light spectrum. It consists of light with continuously different wavelengths. Since TiO_2, which is widely used as a photocatalyst, has a wide band gap, higher energy light with a short wavelength (e.g., ultra-violet light) is needed for exciting electrons. Therefore, only about 5% of all solar light energy power is used.[2] A photocatalyst with a shorter bandgap is required in a light reaction so that longer solar light wavelengths can be used. In addition, to provide holes and electrons needed for the reaction in artificial photosynthesis, the oxidation-reduction potential of water and hydrogen or carbon dioxide should be located between the valence band maximum (VBM) and the conduction band minimum (CBM). However, no materials that satisfy the two above requirements exist, generally. For this reason, there has recently been active R&D on materials that can contribute to photosynthesis in the range of visible light.[3)]

To increase the reaction efficiency in a light reaction, it is imperative to use a photocatalyst that satisfies the requirements described above for the anode. Besides that, producing a nanoparticulated structure with a large surface area is required to promote the reaction with solar light and water. In addition, to transport the electrons excited by solar light, it is necessary to form a film and interface structure indicating excellent electron conductivity on an electrode substrate. However, meeting these demands simultaneously is difficult using conventional methods.

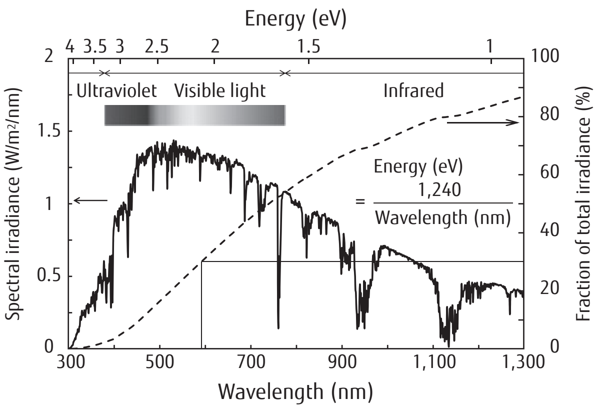


Figure 2
Wavelength distribution of solar light spectrum.

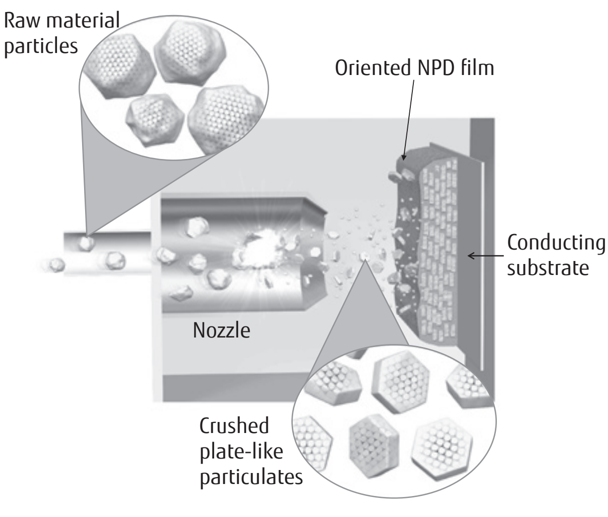
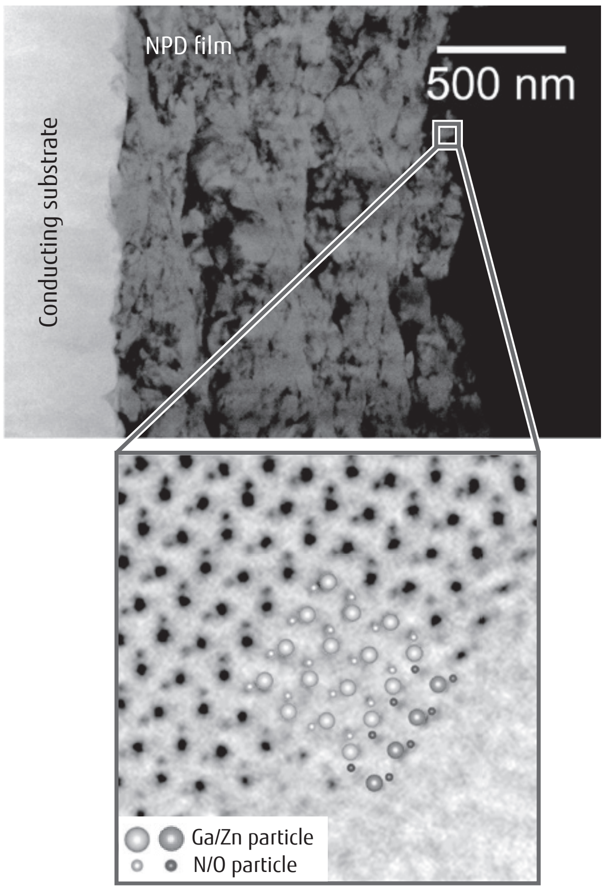


Figure 3
Concept of deposition of photocatalyst film by NPD.

Fujitsu succeed in forming a nanoparticulated structure consisting of a narrow-band-gap photocatalyst and strongly adhered it to a conducting substrate by making use of original technology called nanoparticle deposition (NPD)[4)] originally developed as a deposition method for electronic ceramics in microelectronics packaging. The particles consisting of a visible-light response photocatalyst—a GaN-ZnO solid solution—and gas are mixed, and then the nanoparticles that are strained and pulverized during the deposition process are sprayed on a substrate using a nozzle. Finally, a nanoparticulated photocatalyst film can be formed on a conducting substrate (**Figure 3**).

Figure 4 shows a cross-sectional view of a photocatalyst film formed on a conducting anode substrate observed with a transmission electron microscope. In this figure, a lamellar structure indicating accumulated nanoparticles can be observed. Around the top of the



TEM photograph: Ikuhara lab., the University of Tokyo

Figure 4
Atomic structure of photocatalyst film with a transmission electron microscope (TEM) observation.

film, a fluctuation in atomic distance in crystals due to atomic misalignment can be observed. We clarified that electron orbitals are expanded and the band gap of the photocatalyst film can be reduced finally by introducing a strain in crystals and forming disordered atomic arrangements in the NPD process (the detailed mechanism will be described later).

In the example of **Figure 5**, the bandgap of 2.53 eV of the raw material is successfully lowered to a band gap of less than 2.0 eV by applying the NPD process. As a result, we found that the covering wavelength region can be expanded by more than 25% by using a modified GaN-ZnO film with our NPD process.[5)]

To clarify the phenomenon of how the band gap, which is inherent to material primary, is reduced after the NPD process, the characteristics of the NPD film and raw powder were analyzed in detail using X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) and hard-X-ray photoelectron spectroscopy (HAXPES) in the SPring-8 synchrotron radiation facility, Hyogo, Japan. From these analysis results, we found that no difference was detected between the NPD film and raw powder in terms of crystal structure, but the atomic distance between metals (Ga and Zn) in crystals deviated in the NPD film. In contrast, it was found that the atomic distance between metal (Ga and Zn) and non-metal (N and O) in crystals was not changed, comparing the NPD film and raw powder.

To investigate the correlation between the deviation of atomic position in the crystal structure and decrement of band gap, a simulation was carried out with a first-principles calculation using density functional theory (DFT) applying pseudopotential.

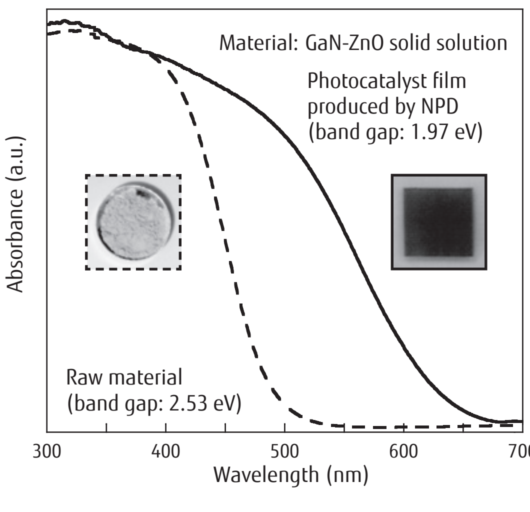


Figure 5
Reflection/absorption properties of photocatalyst film developed for light reaction.

GaN-ZnO has a hexagonal wurtzite structure, and metal atoms are bonded to non-metal atoms alternately. The metal atoms are located in the center of a tetrahedron consisting of four apexes of non-metal atoms. Ga or Zn in the metal sites and N or O in the non-metal sites are randomly occupied respectively [**Figure 6 (a)**].[6)] Every atom is bonded in a zigzag manner in a crystal structure, as shown in **Figure 6 (b)**. The angles between the center atom of the tetrahedron and the atoms of the apex are about 110 degrees in raw material. In a film, as shown in **Figure 6 (c)** although the distance between directly bonded metal atoms and non-metal atoms is kept constant, the distance between metal atoms deviates. In the model where the distance between metal atoms deviates while there is a constant distance between metal atoms and non-metal atoms, it is found from a simulation that the bandwidths are expanded and band gap is narrower. **Figure 6 (d)** shows an example of the density of state (DOS) separated in every orbital forming GaN-ZnO.

In a metal oxide and a metal nitride, a valence band and a conduction band is formed by a metal-oxygen bond and metal-nitrogen bond, and as a result, a band gap is generated. It is considered that in the film deposited by NPD, the partial mutual interaction between metal atoms caused by the deviation of metal atom distance results in expanding the bandwidth of the valence band and conduction band, and the band gap of an NPD film is narrower [**Figure 6 (e)**].[7)]

4. Development of dark reaction

In the dark reaction, organic products such as methanol and methane are generated on a cathode by making use of the electrons produced by a light reaction and protons. When a proton is directly reduced, hydrogen is generated. When carbon dioxide is supplied and a higher-level reduction reaction occurs, like the photosynthesis of a plant, storable organic products can be generated. In the latter case, carbon dioxide is reduced by the reaction of two electrons and two protons to an organic product. The reduction proceeds in succession from carbon dioxide to formic acid or carbon monoxide, formaldehyde, methanol, and

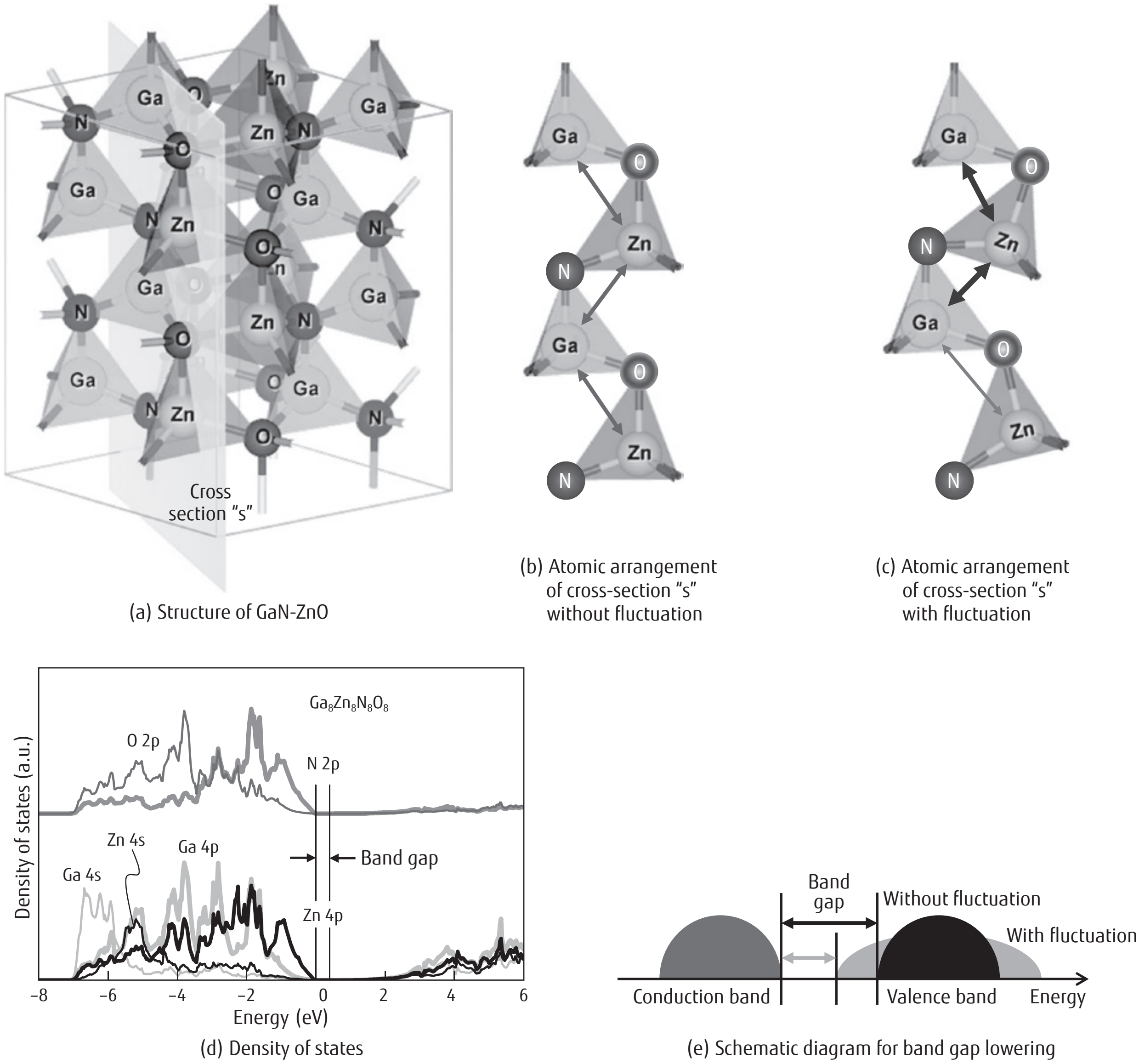


Figure 6
DFT simulation.

methane (Figure 1). We researched the cathode material for use in a dark reaction for effectively carrying out multi-electron reduction. Conventionally, preferentially forming organic products except formic acid and carbon monoxide has been difficult in terms of carbon dioxide reduction. This is because adequate multi-electron reduction cannot be controlled, since it is not easy to hold carbon dioxide on the surface of the metal catalyst on a cathode. We try to generate a reaction on a site which is suitable for multi-electron reduction by maintaining and holding carbon dioxide with an adsorbed material shown in **Figure 7**.

The following four conditions regarding the material for a dark reaction need to be met to increase the efficiency of multi-electron reduction on a cathode.

1) High adsorbed amount of carbon dioxide and selectivity
2) Formation of the active point of catalyst (inside and near pores)
3) High electric conductivity
4) High protonic conductivity

It is well known that a porous material is suitable for carbon dioxide adsorption. We researched a porous metal organic framework (MOF) or porous coordination

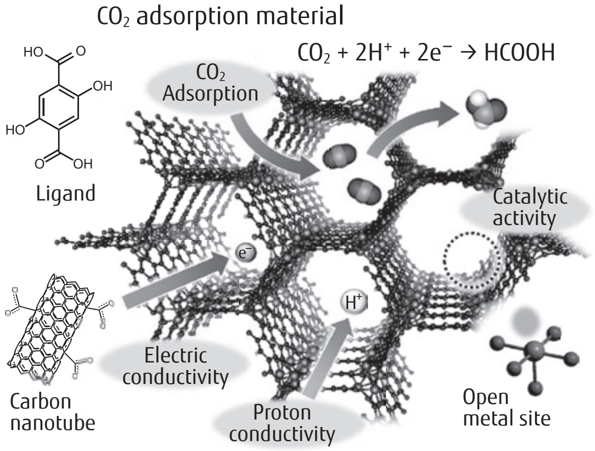


Figure 7
Concept of development for cathode materials.

polymer (PCP), upon which very high expectations have been placed recently. To add a catalytic active point, there are two methods: one is to support fine metal particles on the adsorbed material surface, and the other is to make use of coordinated unsaturated sites (open metal sites).

The M_2(dobdc) using 2,5-Dihydroxyterephthalic acid for ligand[8)] possesses open-site metal, which adsorbs a large amount of carbon dioxide preferentially, but expresses insulated properties. The electrons are supplied from the electrode-side in our photosynthesis system. For the reduction process in the pore of an adsorption material, high electric conductivity is needed inside of the material. Currently, we are trying to increase the electric conductivity by combining a carbon nanotube with MOF.

We confirmed that an effective way to achieve high electric conductivity in hydrothermal synthesis is to add to M_2(dobdc) a carbon nanotube having a surface that has been modified with a carboxyl group.

Research on proton conductivity is being done with the development of a total system. Since the cathode is immersed in an electrolyte in the current system, protons can be moved easily. However, collecting the dissolved reaction product is difficult. For this reason, a system that does not use an electrolyte, a method for forming a proton conductivity path in the pore of MOF, and a non-aqueous system cell are also being developed.

5. Future perspective

In this paper, research on artificial photosynthesis was introduced, focusing on material for use in artificial photosynthesis. To apply this material to the environmental and energy technology of an ICT society, it is imperative to develop a reaction unit at an industrial level. We are trying to obtain high efficiency for a total reaction unit by controlling electrons and atoms in a material, controlling the nanostructure of a film, and controlling micro- and macro-scale electrode structures. We are researching key material for a high performance, and we will study new material, structural modification, and improvement of reaction property and functionality by examining the simulation results produced with a supercomputer.

6. Conclusion

Artificial photosynthesis is the ultimate technology for solving the issue of global warming and depletion of fossil fuel resources. By using this technology, even in an emergency situation when a power-supply grid cannot be used due to a natural disaster such as an earthquake, a secure society that can maintain an energy source can be acquired.

Fujitsu will help to realize a sustainable society using renewable energy by combining practical technologies and will develop basic technology for use in the environmental and energy field.

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