

Peer Review File

Manuscript Title: Photocatalytic solar hydrogen production from water on a 100 m²-scale

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

The paper discusses the demonstration of a 100 m² solar water splitting system based on a photocatalyst sheet of SrTiO₃:Al that includes a commercial H₂/O₂-separation membrane system.

While this is one of the first scaled demonstration of a photocatalyst sheet-based water splitting, which is an important achievement, I have troubles identifying the (scientific) novelty of this contribution (especially in the light of a similar publication by Goto et al., Joule, 2018, where the same material and similar scaling approach was used). What is the novelty here? The addition of a (commercial) separation unit seems – in my opinion – not a justification for publication. The two videos showing some explosion tests and that are used to argue the safety of this co-evolution approach, are confusing and not well explained (what do we see, what experiment was conducted, what pressures/temperatures/concentration were applied/measured, how many times was the experiment conducted, etc.). The abstract and the paper in general are missing scientific precision and quantitative description (for example, line 101: "...were more active and durable...", abstract is missing average production rates [ideally in kg/day]). The engineering design is not motivated (what are the reasons for the dimensions of the panels, their thickness, what is the design process behind the design of the panels, etc.). Humidity of the O₂/H₂ combined and separated gas streams is not consistently indicated, the molar fraction of hydrogen and oxygen is indicated as 2.0, without proof or indication of potential variation. Generally, the experimental data is not indicating the experimental error/reproducibility (i.e. error bars). In my opinion, every experimental data point (efficiency, rates, stoichiometric ratios, separation efficiency, etc.) requires an error bar.

It seems that this demonstration has been operating over multiple months. However, only a small subset of data is actually shown in this manuscript. Which is a pity. Such data is extremely valuable, difficult to obtain and a tremendous achievement! It would be interesting to see the performance over multiple months to get an understanding of the dynamics and durability of the system, and to support economic arguments.

Scaling description in the manuscript are purely based on area (is a "mega-scale solar plant" based on MW, i.e. power? "Mega-scale" as such seems not a very scientific description of a system). Representing scaling only based on area seems an incomplete view. A same area system but 10x more efficient is more valuable. It seems output power or production rates might be a more reasonable "scaling" argument or comparison (or need to be considered equally). Correspondingly, clear indication of the produced mass of pure (after separation) hydrogen and oxygen should be given per day (not only peak rates) for the different seasons and should be clearly stated in the abstract.

Additional comments:

- Techno-economic study of Pinaud et al. For their type 1 and type 2 system (photocatalytic system) cannot be used to justify this photocatalyst sheet based demonstration. Additionally, the cost number of Pinaud et al are outdated.
- Generally, here we discuss a photocatalyst sheet approach, but arguments are mixed with photocatalytic slurry systems (for example the cost numbers from Pinaud et al. paper) and even

separate PV-driven electrolysis (for example the PV-driven, two-electrolyzer in-series approach by Jia et al. with 30% efficiency). I believe it is confusing and unreasonable to directly compare these three approaches, i.e. they should be compared with care and clear identification and mentioning of their differences.

- The photocatalyst sheet layers seem rather non-uniform (Extended data Fig. 2), especially for the manually sprayed type. Can you comment on the effect of this? The thickness in the text is indicated as 4-10 μm , a significant variation, as well. What would be the optimal thickness?
- UV transparent glass is used for the system. This seems economically a disadvantage. Can you comment on the availability/economics/technical details of such glass?
- Is supplementary movie 1 in real time? The evolution rates seem high.
- It is claimed that "the activation period for this system is evidently a result of the relocation of impregnated chromium...". However, I cannot find evidence for this, for example elemental analysis or so.
- What is the scientific reason for the difference in frosted versus non-frosted glass? Optical? Mechanical?
- STH efficiency under natural and simulated light are compared (it seems they vary between 0.48% and 0.76%) and it is argued by the spectral variation of the solar irradiation. It seems almost a doubling of the UV/violet is required to almost double the efficiency, which seems quite extreme. Is this indeed only a result of the spectrum? Also, what is the thermodynamic limit of this material, and what are the losses that results in an efficiency $<1\%$? This should be discussed.
- Generally: I assume not only production rates are measured in the system, but also temperatures and pressures, which are important information to report and should also be given (in addition or humidity, etc.). For example, what is the pressure in the panels/tubes/etc.?
- Minor: the figure number of the uploaded extended data do not match the provided figure legend (fig 2 corresponds to figure 10 legend, and figure 3 corresponds to figure 2 legend etc.).

Referee #2 (Remarks to the Author):

This submission by Nishiyama et al. is the first description of a practical photocatalytic solar hydrogen fuel generation system based on overall water splitting. In addition to the detailed device configuration, its input, output and energy conversion parameters, the authors also provide long term operation data and an experimental assessment of the reactor safety with regard to spontaneous combustion of the fuel. The latter point is important because previous concerns over the safe co-evolution of hydrogen and oxygen in the same reactor space have created obstacles to research and development of photocatalysis technology. This report shows for the first time that these problems can be overcome with engineering controls, incl. the use of thin PVC tubes for gas transport and by reducing the water film on the catalyst to sub millimeter dimensions. Other notable aspects of the work are the description of the impact of water freezing on device performance and the implementation of a gas separation system for the production of nearly pure hydrogen at standard pressure. The energy efficiency of the photocatalysis device is lower than that of complementary photovoltaic and photoelectrochemical systems, but as the authors point out, their device can be scaled up without expected losses in efficiency. Higher efficiency is possible by optimizing the gas separation unit and by using photocatalyst particles with improved visible light activity. Overall, the design provides a blueprint for future solar hydrogen production systems based on photocatalysis technology. The work is the crowning conclusion of over 40 years of overall water splitting research, a very significant part of which was conducted by the authors. The publication comes at a time when demand for scalable technologies for solar fuel generation has never been higher. The impact of the work is expected to go well beyond that of the photocatalysis research and engineering communities. I recommend publication of the manuscript after minor revision.

1. Additional calculations on the STH efficiency of the system should be provided that fully consider all energy inputs for operation, incl. the energy consumption of the water pumps and of the

membrane gas separation system.

2. For the spark ignition test, what was the impact on the two 3L intermittent polycarbonate storage tanks?
3. For the aerial photograph, please provide a description of the spark gap in the caption.
4. There are several errors in the labeling of the Extended Data Figures, e.g. Fig 2 is supposed to highlight the catalyst microstructure, but the actual pdf for Fig.2 shows a block diagram.

Referee #3 (Remarks to the Author):

A. Summary of the key results:

The manuscript reports on the use of SrTiO₃:Al photocatalyst together with co-catalysts with limited PGM (Rh) content i.e. Na₃RhCl₆, Cr(NO₃)₃ and Co(NO₃)₂ to demonstrate direct solar hydrogen production on several hundred square meters scale.

48 reactor units each of 25 cm × 25 cm solar collection area with an injection moulded polycarbonate housing, were assembled into a module with an area of 3 m². An array of such reactor units formed the final field with 1600 m² area. A 100 m² device achieved a hydrogen production rate under natural sunlight of than 3 L/min of hydrogen for incident irradiance ≥ 800 W/m². The oxyhydrogen gas mixture that is generated is separated using a membrane with a higher permeability to H₂ than to O₂. Nevertheless, there is still a need to prevent the accumulation of O₂/H₂ gas mixtures within the explosion limits.

B. Originality and significance: if not novel, please include reference.

An actual demonstration of this scale for particulate-based photocatalytic system as presented in this manuscript is possibly a first in the available published literature.

C. Data & methodology: validity of approach, quality of data, quality of presentation

D. Appropriate use of statistics and treatment of uncertainties

The focus of the paper was to demonstrate a concept in which the use of statistical data is not very important.

E. Conclusions: robustness, validity, reliability

The article does not have a specific conclusions section and these comments are based on the conclusions drawn from the abstract

This assertion "The system components were undamaged even under intentional ignition causing explosion and detonation, confirming that the gaseous products could be handled safely when employing a suitable system design" should be re-written. This confirmation of safety would certainly not be the case if larger volumes of gas are produced from a more efficient photocatalyst using the presented set-up (they do mention issues with leakage beyond 5kPa internal pressure).

F. Suggested improvements: experiments, data for possible revision

No extra experiments required within the scope of this work. However, there are a few topics that require clarification:

- (i) A discussion of reactor, sealing and plumbing material choices is missing especially in the context of preventing explosion related hazards, which is more critical in this type of system than in "traditional" anode-membrane-cathode configurations.
- (ii) The explosion limits for H₂ in O₂ are also dependent on both temperature and pressure. Would operating pressure rise with improved hydrogen production rate per unit area? Would the

prefiltered gas mixture still be safe?

(iii) Could the authors explain why the prefiltered gas mixture lying within the 4% to 95% of H₂ in O₂ window did not explode on ignition? How much is the moisture content in this mixture?

(iv) Since there is a minimum critical loading of the particles above which the H₂ yield does not exceed 0.1 mmol/(h cm²), this seems to be a limitation of the SrTiO₃:Al photo-absorber. Are there known materials with a narrower bandgap than SrTiO₃:Al that could capture a larger portion of the incident photons?

(v) The videos show very vigorous bubble formation. How would bubble management be implemented to maximise the photons reaching the absorber

G. References: appropriate credit to previous work?

O.K

H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

OK. Include a conclusions section

Author Rebuttals to Initial Comments:

Response to Referees

Referee #1 (Remarks to the Author):

We appreciate Referee 1 for reading our manuscript in detail and giving us an opportunity to clarify the details of the experiment, and the novelty and importance of this work. The reviewer's comments are very instructive in improving our manuscript. They are also of significance for the future practical application of the technology reported here. We discussed the reviewer's questions and comments carefully and reply to them one by one as what follows.

The paper discusses the demonstration of a 100 m² solar water splitting system based on a photocatalyst sheet of SrTiO₃:Al that includes a commercial H₂/O₂-separation membrane system.

While this is one of the first scaled demonstration of a photocatalyst sheet-based water splitting, which is an important achievement, I have troubles identifying the (scientific) novelty of this contribution (especially in the light of a similar publication by Goto et al., Joule, 2018, where the same material and similar scaling approach was used). What is the novelty here? The addition of a (commercial) separation unit seems – in my opinion – not a justification for publication.

We regret that the novelty of this work was not clearly explained in the original manuscript. The concept of using panel reactors was already reported by the authors as the referee pointed out. However, this work is not a simple extension of our previous work but does present significant scientific and technological advancement in the research and development of renewable solar hydrogen. First, we demonstrate that, by confining the gaseous oxyhydrogen product in narrow spaces in our newly devised reactor and transporting the gases using tubes with relatively small inner diameters, spontaneous explosions causing damage or failure of the system were prevented for a period of one and a half years under naturally occurring weather conditions. Even if intentionally induced, the explosions and/or detonations were harmless and terminated in our solar hydrogen production system. Of course, as we mentioned in the text, such a safety issue should be strictly examined by the experts for future practical application. Second, the mechanism of hydrogen and oxygen evolution in a photocatalyst sheet was revealed and discussed. We believe such a mechanism has not discussed in other

works. Third, a system to regulate the feed rate of the moist oxyhydrogen product gas to a gas-separating membrane unit was devised, so that high purity hydrogen could be recovered simply by using a commercial filter element, even under natural sunlight that fluctuated in intensity. Neither of these has been reported in earlier studies. The commercial separation membrane was employed only because they were readily available for demonstrating this approach and would not be a major reason for discounting the novelty of this work. It would rather be encouraging that a membrane commercialized for other purposes exhibited decent performance. In our project, several different types of membranes including organic and inorganic ones are being developed for hydrogen separation from moist oxyhydrogen gas. But it is beyond the scope of this paper. Forth, our demonstration of photocatalytic solar hydrogen production larger than laboratory scale indicates the general viability of this process as well as the challenging problems toward practical application. These points are described in the manuscript as follows:

“The total system incorporating photocatalyst sheets was operated under field conditions for **more than a year**. ... These individual parts investigations suggest that oxyhydrogen gas can be safely handled by confining the gas in narrow **passage** in each compartment and using the appropriate tubes for gas transportation.” **(Line 173)**

“Although no signs of critical hazards were observed during our preliminary safety tests, such units should be inspected and approved by chemical engineering safety experts to ensure safety and with regard to legal liability issues” **(Line 217)**

“Bubbles of oxyhydrogen gas 0.1–0.6 mm in size were formed at specific spots on the photocatalyst sheet surface (Supplementary Movie 2), similar to the nucleation of bubbles on hydrophobic pits during water electrolysis.¹⁴ It is likely that hydrogen and oxygen migrated through the mesoporous channels between the hydrophilic silica nanoparticles in the liquid phase under supersaturated conditions to form bubbles on the surface of the photocatalyst sheet.” **(Line 107)**

“The gas-separating membrane unit was observed to function during the field test period without any apparent deterioration regardless of the varying **production** rate of humid oxyhydrogen gas at different weather conditions (Extended Data Fig. 8), exhibiting excellent durability in the presence of the humid gases.” **(Line 168)**

“The experiments of the scaled up process in a field environment reported herein provides helpful information related to potential technology transfer and the maturity of the basic technologies for solar hydrogen production via photocatalytic water splitting. We expect that this work will stimulate future research in various fields with the aim of establishing cost-effective large-scale renewable solar hydrogen production systems.”
(Line 221)

The two videos showing some explosion tests and that are used to argue the safety of this co-evolution approach, are confusing and not well explained (what do we see, what experiment was conducted, what pressures/temperatures/concentration were applied/measured, how many times was the experiment conducted, etc.).

We are sorry that the explanation of the experimental conditions and results was insufficient. We have updated the main text and the Supplementary Information guide. Briefly, oxyhydrogen gas at the hydrogen/oxygen ratio of two and saturated with water vapour was ignited to cause explosions and/or detonations intentionally to examine a damage to the respective components of the system. Essentially, the system components were undamaged, as is written in the main text. In the case of soft polyvinyl chloride tubes with an inner diameter of 10 mm, the propagation speed of the reaction was $2.8 \times 10^3 \text{ m s}^{-1}$. Therefore, the detonation occurred by the reaction of hydrogen and oxygen gas mixture. However, despite the detonations, the respective components of the system remained intact and functional as a system, because the gas confined in narrow gaps and tubes with relatively small inner diameters would not cause destructive explosions and/or detonations. We also tested up to 20 mm inner diameter soft polyvinyl chloride tubes and found that the tubes were undamaged. Accordingly, we have revised our manuscript as follows:

“We also examined the safety issues of each component associated with the present solar hydrogen production system by the intentional ignition of the oxyhydrogen gas at the hydrogen-to-oxygen ratio of two and saturated with water vapour.” **(Line 175)**

“In the case of soft polyvinyl chloride tubes with an inner diameter of 10 mm, the propagation speed of the reaction of oxyhydrogen gas was estimated to be $2.8 \times 10^3 \text{ m s}^{-1}$ from Supplementary Movie 6, indicative of the occurrence of detonation. However, the tube was undamaged and used repeatedly. Similarly, soft polyvinyl chloride tubes with an inner diameter of 20 mm were undamaged when the inner oxyhydrogen gas was

detonated.” (Line 501)

Supplementary Movie 4 | Intentional ignition of the oxyhydrogen product gas in polyurethane gas collection and carrying tubes with an inner diameter of 8 mm connected to the water splitting panel reactor with a 70-m² light receiving area during water splitting under natural sunlight at 10 am on August 20, 2020, played in slow motion (1/240 of the original speed). Reactor internal pressure = 101 kPa, temperature = 30°C. This experiment was conducted twice without damaging the setup.

Supplementary Movie 5 | Intentional ignition of a mixed gas of hydrogen and oxygen (H₂/O₂ = 2) saturated with water vapour, filled in the soft polyvinyl chloride tube with an inner diameter of 10 mm and a length of 100 m, played in the original speed. Internal pressure = 101 kPa, temperature = 20°C. This experiment was conducted five times without any damage.

Supplementary Movie 6 | The same experiment with Supplementary Movie 5 but recorded from a different angle and played in slow motion (1/132 of the original speed).

The abstract and the paper in general are missing scientific precision and quantitative description (for example, line 101: "...were more active and durable..."),

The abstract is intended to direct the interest of a wide range of readers to the article and is not written in detail in Nature. So, we do not think that the reviewer's criticism to the abstract is reasonable. On the other hand, we admit that the description in the main text were not very quantitative. This is because the scope of this work is not the comparison of the materials or system properties but the demonstration of operation and safety of a large-scale system integrating a solar hydrogen production photocatalyst and gas-separation equipment. Considering the reviewer's opinion as well as the nature of a scientific journal, the manuscript has been revised to be as accurate and quantitative as possible. The changes made during the revision are listed below.

“The STH efficiency decreased gradually with time and became lower than 0.40% in 280 h. Photocatalyst sheets fabricated on the frosted glass were more active and durable (Extended Data Fig. 4b). The STH efficiency reached 0.51% after the activation and

remained above 0.40% for 1600 h.” **(Line 99)**

abstract is missing average production rates [ideally in kg/day]).

In the outdoor measurement, the weather conditions such as sunlight intensity, temperature and humidity etc. vary depending on the season and time. Even in the same day, the weather conditions fluctuate from moment to moment. Because the performance of the photocatalyst panel reactors follows the fluctuation of the weather conditions quickly, it is not very meaningful to consider the average value in the abstract. To make this point clear, time courses of the oxyhydrogen gas production rate and the weather conditions are provided in a main text figure (Figure 3). The related texts have also been revised as follows.

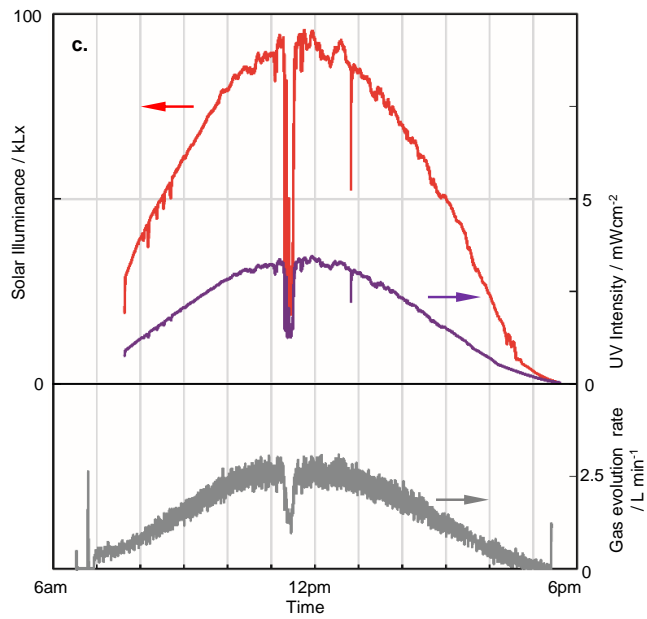
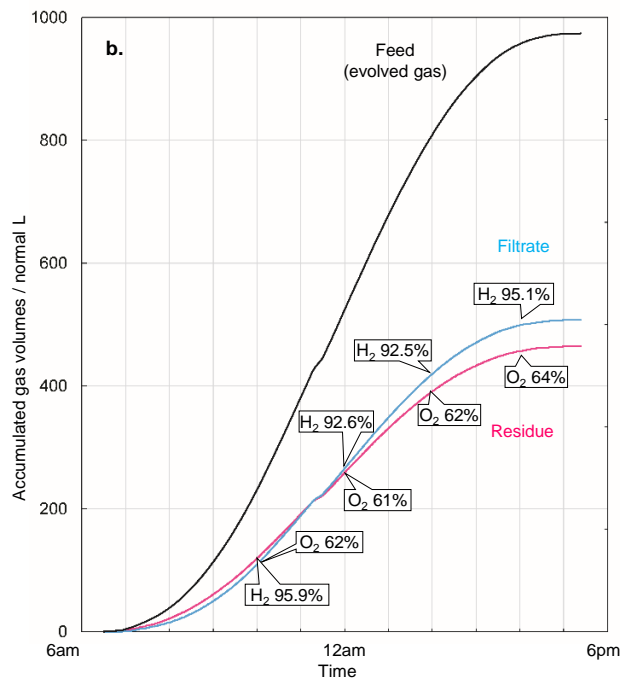
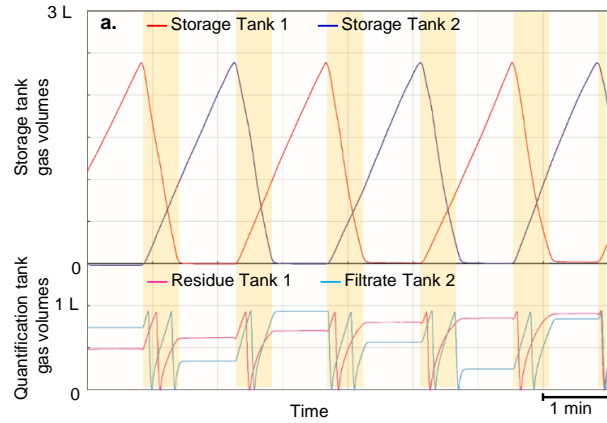


Fig. 3 | Performance of the gas-separation unit connected to the 100 m² water-splitting photocatalyst panel reactor on October 2, 2020 at the Kakioka Research Facility. (a) Time courses of the gas volumes contained in the storage and quantification tanks. The periods during which the filter cartridge was operational are shaded. (b) The accumulated amounts of moist oxyhydrogen feed, filtrate and residue gases. The ratios of hydrogen and oxygen in the filtrate and residue gases excluding water vapour are notated along the curves, respectively. (c) The variations of solar illumination intensity (red), ultraviolet intensity (purple), and the gas evolution rate in the water splitting panel reactor (grey).

“The gas production rate was correlated with the sunlight intensity, ...” (Line 117)

“The variations of solar illumination intensity, ultraviolet intensity, and the gas evolution rate in the water splitting panel reactor are also shown in Fig. 3c. The performance of the photocatalyst panel reactors follows the fluctuation of the weather conditions quickly. The total feed of humid oxyhydrogen gas on the day was 970 L under the average atmospheric pressure and ambient temperature of 106.9 kPa and 24.4°C on average of the daytime. The feed gas contained hydrogen and oxygen at the molar ratio of 2.0 as well as water at its saturation vapor pressure (approximately 3.0 kPa). Therefore, the total amount of hydrogen in the feed gas equalled 27.2 mol. The feed gas was separated into 505 L of hydrogen-enriched filtrate gas saturated with water vapour. The hydrogen-to-oxygen molar ratio in the filtrate gas exceeded 94% on average. Therefore, the hydrogen yield in the filtrate was 19.9 mol. Accordingly, the hydrogen recovery proportion reached 73% ...” (Line 155)

“The hydrogen recovery proportion was calculated according to the equation:

$$\begin{aligned} \text{Hydrogen recovery proportion} &= \frac{\text{Amount of recovered hydrogen}}{\text{Amount of generated hydrogen}} \\ &= \frac{\text{Amount of filtrate gas} \times \text{Concentration of hydrogen}}{\text{Amount of generated gas} \times \text{Concentration of hydrogen}} \end{aligned}$$

Both the filtrate gas and generated gas were at the atmospheric pressure and contained hydrogen, oxygen, and water at the saturated vapour pressure. Therefore, the sum of the partial pressures of hydrogen and oxygen was equal to the pressure obtained by subtracting the water vapor pressure from the atmospheric pressure. The ratio of hydrogen to oxygen in the gaseous product mixture was confirmed to be 2.0 and that in the filtrate gas was measured by mass spectroscopy.” (Line 469)

The engineering design is not motivated (what are the reasons for the dimensions of the panels, their thickness, what is the design process behind the design of the panels, etc.).

In our previous work (ref. 3), a panel reactor with a light-accepting area of 1 m² was produced. However, it is too large to be manually handled in a university laboratory. Therefore, the size of the unit panel reactor was reduced before building a large-size reaction facility. The size of 25 cm × 25 cm was chosen considering a balance between the ease of manual construction work in the laboratory and the availability of human resources and time to install a 100-m² scale reaction facility. Therefore, it was not necessarily motivated by scientific or technological aspects but was subjected to miscellaneous factors related to our specific research environment. In a future, all the components should be designed according to the cost effectiveness, safety issues and so on by the experts. We have revised our text as follows:

“The size of the reactor units was chosen considering a balance between the ease of manual construction work in the laboratory and the availability of human resources and time to install a 100-m² scale reaction facility. In future, all the components should be designed considering the cost effectiveness, safety issues, and other factors by the experts.” (Line 339)

Humidity of the O₂/H₂ combined and separated gas streams is not consistently indicated, the molar fraction of hydrogen and oxygen is indicated as 2.0, without proof or indication of potential variation. Generally, the experimental data is not indicating the experimental error/reproducibility (i.e. error bars). In my opinion, every experimental data point (efficiency, rates, stoichiometric ratios, separation efficiency, etc.) requires an error bar.

The product gas has hydrogen and oxygen at the ratio of two to one and is saturated with water vapor. This is already written in the manuscript. The photocatalyst used is shown to be stable for more than 1000 h in this work and our previous work (ref. 11). Therefore, it is very unlikely that the H₂/O₂ ratio is deviated from two, and no further confirmation is needed about the occurrence of photocatalytic water splitting into the stoichiometric H₂ and O₂. In this work, nitrogen was not detected by mass spectroscopy during the experiment, and so the contamination of air was also ruled out. This information is added in the revised version of the manuscript.

“The mass spectra indicated that nitrogen was not detected during the reaction and thus there were no air leaks in the reactor or filtration apparatus.” (Line 412)

Following the reviewer’s request and the policy of the journal, we provide the experimental data points in Supplementary Information as much as possible. Note that, at the initial stage of this work, all parameters were not able to be acquired at all times because automatic measurement systems were missing.

The weather conditions vary from moments to moments and cannot be reproduced repeatedly. Therefore, the concept of error bars is not applicable.

It seems that this demonstration has been operating over multiple months. However, only a small subset of data is actually shown in this manuscript. Which is a pity. Such data is extremely valuable, difficult to obtain and a tremendous achievement! It would be interesting to see the performance over multiple months to get an understanding of the dynamics and durability of the system, and to support economic arguments.

We appreciate the reviewer for finding the value in the data acquired over multiple months. Since the beginning of September 2020 till now, the gas production rate of the water splitting panel reactor has been recorded continuously, by the aid of our new Internet-aided data logging set up. Simultaneously, the solar power, UV index, and the ambient temperature have also been recorded. The product rate was measured by a soap-film flowmeter (Horiba, model SF-2U/VP-4U). The solar power, UV index, and ambient temperature were logged by an integrated meteorological instrument (Vantage Pro II Plus, Davis Instruments). These data were gathered at a sampling rate of 1 min⁻¹ and processed by a microcomputer and transmitted via Internet to our laboratory. The experimental data points are provided in Supplementary Information of the revised manuscript, and the related explanation is included in the Method section. The figure below, produced from the Supplementary Information, shows a long-term record of the solar power, the UV index, the product gas flow rate, and ambient temperature at Kakioka Research Facility from September 20 to December 27, 2020.

“The product rate was measured by a soap-film flowmeter with automatic correction by referring to the atmospheric pressure, water vapour pressure, and temperature (Horiba, model SF-2U/VP-4U). Insolation, UV index data defined by World Health Organization,

and temperature were acquired from a weather station including ultraviolet and solar radiation sensors (Vantage Pro II Plus, Davis Instruments). The weather conditions and the gas production rate were periodically recorded since Sep 20, 2020 by Internet-aided data logging setup. These data were gathered at a sampling rate of 1 min⁻¹ and processed by a microcomputer and transmitted via Internet to our laboratory and the acquired data are available in Supplementary Information. Note that the oxyhydrogen gas was not produced in late December 2020, because of the cold weather freezing the panel reactor units and other equipment. On October 2, 6, and 30, the gas was directed to the gas separation equipment, without delivery to the gas flowmeter.” (Line 448)

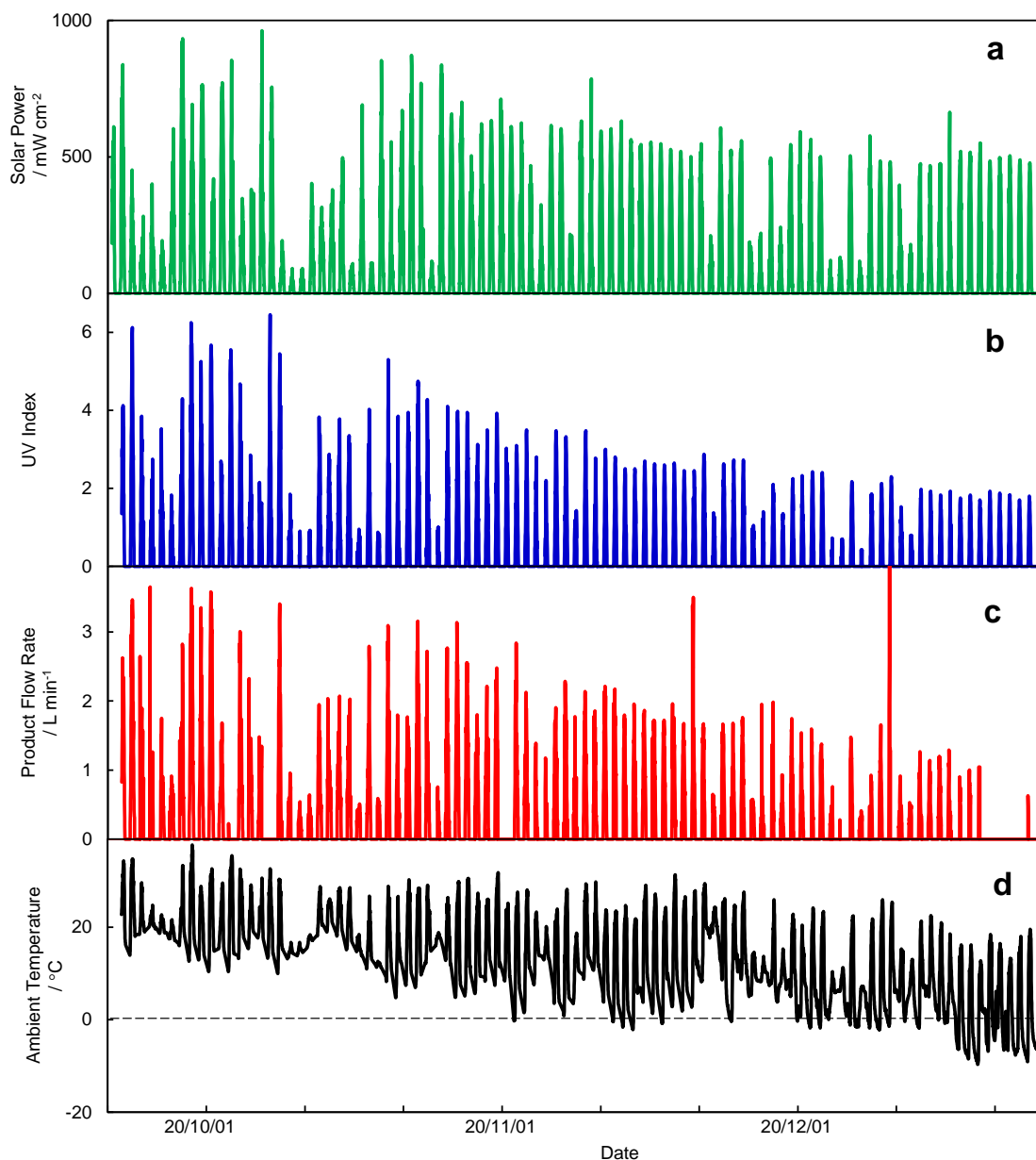


Fig. | Long-term records of solar power (a), UV index (b), product gas flow rate (c), and ambient temperature (d) of the photocatalyst panel reactor at Kakioka Research Facility from September 20 to December 27, 2020. The oxyhydrogen gas was not produced in late December 2020, because of the cold weather (see the ambient temperature) freezing the panel reactor units and other equipment. On October 2, 6, and 30, the gas was directed to the gas separation equipment, without delivery to the gas flowmeter.

Scaling description in the manuscript are purely based on area (is a “mega-scale solar plant” based on MW, i.e. power? “Mega-scale” as such seems not a very scientific

description of a system).

We agree that Mega-scale is not really a scientific term but is widely accepted in public. By convention, the term mega-scale is quoted.

“Solar energy is widely expected to be important as a sustainable energy resource in the future, and commercial “mega-scale” solar plants have been already extended at low latitudes, where intense, stable solar radiation is available.^{5”}. (Line 48)

Representing scaling only based on area seems an incomplete view. A same area system but 10x more efficient is more valuable. It seems output power or production rates might be a more reasonable “scaling” argument or comparison (or need to be considered equally). Correspondingly, clear indication of the produced mass of pure (after separation) hydrogen and oxygen should be given per day (not only peak rates) for the different seasons and should be clearly stated in the abstract.

We agree to the reviewer’s opinion. This is why the performance of the solar hydrogen production system is compared based on the solar hydrogen output with citation of ref. 15. The gas separation efficiency is considered to be constant because the input gas flow rate is governed constant. Therefore, the requested numbers can be obtained from the results provided in Supplementary Information. However, the weather conditions vary depending on the season and time, and the performance of the photocatalyst panel reactors follows the fluctuation of the weather conditions. These are explained in the main text but cannot be fully described in the abstract.

Additional comments:

- Techno-economic study of Pinaud et al. For their type 1 and type 2 system (photocatalytic system) cannot be used to justify this photocatalyst sheet based demonstration. Additionally, the cost number of Pinaud et al are outdated.

We agree to the reviewer’s criticism. In the techno-economic study cited (ref. 16), those systems were hypothetical and did not really consider safety and feasibility issues, but were presented to initiate the discussion. The corresponding reaction system does not exist in reality and the assumed cost is not realistic. Therefore, the contents of the study should be considered essentially different from the actual technical level and ultimate target. Nevertheless, it has served as an important trigger for a wide range of

researchers to start the discussion, and it seems worth citing the study in the introductory part of this work.

We do not claim that the panel reactor system and gas-separation process presented in our work is the most ideal, either, because we know that the performance of the photocatalyst is insufficient and the cost of the system and process is too much at present. Our system embodies the enlargement of the system that integrates the functions of both photocatalytic solar hydrogen generation and hydrogen recovery by membrane separation. From this, we expect to see the technological gaps toward the practical application of solar hydrogen production and recovery from water. This point will be clear from the manuscript.

“... because the current panel system was designed without considering the production costs. There is certainly a requirement to minimize the construction costs of the system and to reduce the power requirements associated with water and gas processing.¹⁶”
(Line 207)

“The experiments of the scaled up process in a field environment reported herein provides helpful information related to potential technology transfer and the maturity of the basic technologies for solar hydrogen production via photocatalytic water splitting. We expect that this work will stimulate future research in various fields with the aim of establishing cost-effective large-scale renewable solar hydrogen production systems.”
(Line 221)

- Generally, here we discuss a photocatalyst sheet approach, but arguments are mixed with photocatalytic slurry systems (for example the cost numbers from Pinaud et al. paper) and even separate PV-driven electrolysis (for example the PV-driven, two-electrolyzer in-series approach by Jia et al. with 30% efficiency). I believe it is confusing and unreasonable to directly compare these three approaches, i.e. they should be compared with care and clear identification and mentioning of their differences.

We thank the reviewer for her/his professional comment. We understand the difference of the PV-assisted electrolyzers, photoelectrochemical cells, and photocatalyst slurry/sheet in the working mechanisms. In addition, some devices are intended to record a high STH value without consideration of scale-up or cost, and other systems are designed for scaling up at the expense of the efficiency. Because of the

difference in purposes and factors, it is not appropriate to compare them. Therefore, we removed the description of the specific systems and just mention different approaches in a generalized manner. Then, we state that we aimed at demonstration of a solar hydrogen production and recovery system beyond the laboratory scale in a field environment. The text has been modified as follows:

“Any potential solar fuel production system must be scalable to dimensions of the order of square kilometres and be cost competitive with existing fuel production technologies.^{1,6} Photovoltaic-assisted electrochemical, photoelectrochemical, and photocatalytic systems are widely recognized as a means of producing renewable solar hydrogen from water.² Amongst them, particulate photocatalyst systems can be ...”
(Line 53)

- The photocatalyst sheet layers seem rather non-uniform (Extended data Fig. 2), especially for the manually sprayed type. Can you comment on the effect of this? The thickness in the text is indicated as 4-10 um, a significant variation, as well. What would be the optimal thickness?

The STH may be reduced due to optical loss by light transmission when the thickness of the particle layer is too thin. Multiple scattering by photocatalyst particles may mitigate the optical loss. However, it is difficult to theoretically predict the optimal thickness. It is also difficult to control the evenness of the thickness with a manual sprayer. Therefore, we optimized the loading amount of the photocatalyst powder used in the photocatalyst sheet. As shown in Extended Fig. 10, the water splitting rate levelled off when the appropriate amount of the photocatalyst was used. We expect that the data resolve the reviewer’s question adequately.

- UV transparent glass is used for the system. This seems economically a disadvantage. Can you comment on the availability/economics/technical details of such glass?

Admittedly the UV transparent glass is expensive. UV transparent glass was adopted to build a secure panel reactor and examine the panel reactor containing the UV-active SrTiO₃:Al photocatalyst for a long time in a field environment. We are aware of the necessary of minimizing the construction cost of the system. This is described in the manuscript.

“... because the current panel system was designed without considering the production costs. There is certainly a requirement to minimize the construction costs of the system and to reduce the power requirements associated with water and gas processing.¹⁶”

(Line 207)

- Is supplementary movie 1 in real time? The evolution rates seem high.

It sounds like the reviewer's impression, but the movie is played in the real-time speed. The rate of the oxyhydrogen gas evolution was 13 mL min⁻¹, as is written in the Supplementary Information guide.

- It is claimed that “the activation period for this system is evidently a result of the relocation of impregnated chromium...”. However, I cannot find evidence for this, for example elemental analysis or so.

We speculated from our previous work (Maeda, K. *et al.* Characterization of Rh-Cr Mixed-Oxide Nanoparticles Dispersed on (Ga_{1-x}Zn_x)(N_{1-x}O_x) as a Cocatalyst for Visible-Light-Driven Overall Water Splitting. *J. Phys. Chem. B*, 110, 13753-13758 (2006)) that the cocatalyst prepared by air-calcination contains hexavalent chromium species. The hexavalent chromium species is dissolved and photodeposited during the water splitting reaction. However, this is not directly observed in this work because the characterization of the cocatalyst is not the key point of this study. Accordingly, we have revised the text and cite the literature as follows:

“The activation period for this system was likely a result of the relocation of impregnated chromium components onto Rh sites as Cr(III) species on the surface of the SrTiO₃:Al.¹³” **(Line 105)**

- What is the scientific reason for the difference in frosted versus non-frosted glass? Optical? Mechanical?

We expected some improvement in the wettability to the sprayed solution and the mechanical strength of the sprayed particle layer by the use of frosted glass. However, the effect was not systematically examined before the construction of the 100-m² scale panel reactor. Therefore, we shortly added the reason for the use of the frosted glass sheet.

“..., sand-blasted frosted glass sheets (OA-11, 250 mm × 250 mm × 0.4 mm thick, Nippon Electric Glass) were employed in expectation of enhancing the wettability to the suspension and the mechanical strength of the photocatalyst particle layer, ...” (Line 311)

The scope of this work aiming at demonstrating a large-scale solar hydrogen production and recovery system. Therefore, this point can be examined in follow-up studies on the optimization of the photocatalyst sheet structure.

- STH efficiency under natural and simulated light are compared (it seems they vary between 0.48% and 0.76%) and it is argued by the spectral variation of the solar irradiation. It seems almost a doubling of the UV/violet is required to almost double the efficiency, which seems quite extreme. Is this indeed only a result of the spectrum? Also, what is the thermodynamic limit of this material, and what are the losses that results in an efficiency <1%? This should be discussed.

The absorption edge wavelength of SrTiO₃ is 385 nm and absorbs only UV light. The maximum STH, calculated based on the apparent quantum yield of unity till this absorption edge wavelength, is 1.2%. The observed STH is lower than this because the apparent quantum yield was approximately 50% at 365 nm as is written in the Method section. The decrease of the quantum yield is due to the recombination of electrons and holes, and this has been discussed frequently in earlier studies including our works on the SrTiO₃:Al photocatalyst (ref. 3 and 8). Therefore, we expect that citing these articles will be sufficient considering the scope of this work aiming at demonstrating a solar hydrogen production and recovery system.

The solar simulator generally simulates the energy output of AM1.5G spectrum at the respective wavelength windows ranging from 400 to 1100 nm. Therefore, a significant spectrum mismatch may occur in the near UV region where SrTiO₃ functions even if the output energy was adjusted properly near the absorption edge. Moreover, considering only natural sunlight, the proportion of UV light changes significantly depending on the season as already shown in Extended Fig. 6. We have UV index data as an evidence, and the UV part in the sunlight was approximately six times greater in summer than in winter. In the revised version of the manuscript, the UV index and the total solar energy over seasons are additionally provided in

Supplementary Information. Also, Fig. 3 includes variations in the solar illumination intensity and the ultraviolet intensity on the day.

- Generally: I assume not only production rates are measured in the system, but also temperatures and pressures, which are important information to report and should also be given (in addition or humidity, etc.). For example, what is the pressure in the panels/tubes/etc.?

The panel pressure is maintained at the atmospheric pressure. The relative humidity is 100% at the given ambient temperature. These are described in the manuscript, for example, as follows:

“Using a water-tolerant polyimide membrane,⁴ hydrogen with a concentration of 92–96% excluding water vapour was collected from the moist gaseous product mixture at near atmospheric pressure, at a recovery proportion of up to 73%. ”.
(Line 38)

“Both the filtrate gas and generated gas were at the atmospheric pressure and contained hydrogen, oxygen, and water at the saturated vapour pressure.” (Line 472)

The temperature and pressure were not always recorded in the beginning of this study because automatic measurement systems were absent. In the latter part of this work and till now, we have been monitoring experimental conditions and results and provide them in Supplementary Information.

- Minor: the figure number of the uploaded extended data do not match the provided figure legend (fig 2 corresponds to figure 10 legend, and figure 3 corresponds to figure 2 legend etc.).

We are sorry for troubling the reviewer by our mistake. We have corrected the figure numbers during the revision.

Referee #2 (Remarks to the Author):

This submission by Nishiyama et al. is the first description of a practical photocatalytic solar hydrogen fuel generation system based on overall water splitting. In addition to

the detailed device configuration, its input, output and energy conversion parameters, the authors also provide long term operation data and an experimental assessment of the reactor safety with regard to spontaneous combustion of the fuel. The latter point is important because previous concerns over the safe co-evolution of hydrogen and oxygen in the same reactor space have created obstacles to research and development of photocatalysis technology. This report shows for the first time that these problems can be overcome with engineering controls, incl. the use of thin PVC tubes for gas transport and by reducing the water film on the catalyst to sub millimeter dimensions. Other notable aspects of the work are the description of the impact of water freezing on device performance and the implementation of a gas separation system for the production of nearly pure hydrogen at standard pressure. The energy efficiency of the photocatalysis device is lower than that of complementary photovoltaic and photoelectrochemical systems, but as the authors point out, their device can be scaled up without expected losses in efficiency. Higher efficiency is possible by optimizing the gas separation unit and by using photocatalyst particles with improved visible light activity. Overall, the design provides a blueprint for future solar hydrogen production systems based on photocatalysis technology. The work is the crowning conclusion of over 40 years of overall water splitting research, a very significant part of which was conducted by the authors. The publication comes at a time when demand for scalable technologies for solar fuel generation has never been higher. The impact of the work is expected to go well beyond that of the photocatalysis research and engineering communities. I recommend publication of the manuscript after minor revision.

We appreciate Referee 2 for giving positive comments on our work and also recognizing the importance of this work. We answer Referee 2's questions one by one as what follows:

1. Additional calculations on the STH efficiency of the system should be provided that fully consider all energy inputs for operation, incl. the energy consumption of the water pumps and of the membrane gas separation system.

The reviewer's question is related to the energy balance and is very important in energy application. On the basis of the one-day operation on October 2 (Fig. 3), the power supplied to the vacuum pump, which is the major part of energy consumption within the whole system, is calculated. The pump operation period was approximately 38 s to empty 2.4 L of the tank active volume. The produced oxyhydrogen gas (970 L) was

then filtered in $970 / 2.4 = 404$ cycles of operation. The pump power was 400 W at maximum, which is obviously over specification. These numbers yield a one-day power consumption of 1.7 kWh = 6.1 MJ. On the other hand, the amount of hydrogen energy produced on the same day was 5.0 MJ. Admittedly, the present reaction system does not convert solar energy into hydrogen energy in the net if the energy input is covered by the product hydrogen. The problem arises from the primitive design of the gas-separation unit requiring the large additional energy input, and it certainly needs to be improved by engineering refinement as is described in the manuscript (**Line 208**). We consider that, although the system was not energetically optimized at all, the demonstration of a safe and large-scale solar hydrogen production and recovery system should give us a vision for future development and strongly encourage engineers to design suitable oxyhydrogen gas-separation units.

2. For the spark ignition test, what was the impact on the two 3L intermittent polycarbonate storage tanks?

Intentional ignition experiment was performed for a 3 L water-submerged tank made of polycarbonate in our preliminary study. The explosion caused apparent damage and in most of the cases made the tank unusable. Therefore, we devised a spiral partitioning plate inside the tank. The spiral partitioning plate significantly reduced the impact of explosion and maintained the tank reusable, without deteriorating the tank input/output speed. We have added the explanation in the revised manuscript.

“The intentional ignition caused explosion and gave apparent damage to the gas reservoir tank submerged in water and in most of the cases made the tank unusable. However, installation of a spiral partitioning plate inside the tank significantly reduced the impact of explosion and maintained the tank reusable without deteriorating the function.” (**Line 506**)

3. For the aerial photograph, please provide a description of the spark gap in the caption.

We have added the following information in the legend of Extended Fig. 9.

“The spark gap was an assembly of two needle electrodes facing each other within a tube. The distance between the electrodes was adjusted at approximately 0.5 mm. The

ignition voltage was 15 kV AC and pulsed for approximately 1 s.”

4. There are several errors in the labeling of the Extended Data Figures, e.g. Fig 2 is supposed to highlight the catalyst microstructure, but the actual pdf for Fig.2 shows a block diagram.

We are sorry for troubling the reviewer by our mistake. We have corrected the figure numbers during the revision.

Referee #3 (Remarks to the Author):

A. Summary of the key results:

The manuscript reports on the use of SrTiO₃:Al photocatalyst together with co-catalysts with limited PGM (Rh) content i.e. Na₃RhCl₆, Cr(NO₃)₃ and Co(NO₃)₂ to demonstrate direct solar hydrogen production on several hundred square meters scale.

48 reactor units each of 25 cm × 25 cm solar collection area with an injection moulded polycarbonate housing, were assembled into a module with an area of 3 m². An array of such reactor units formed the final field with 1600 m² area. A 100 m² device achieved a hydrogen production rate under natural sunlight of than 3 L/min of hydrogen for incident irradiance ≥ 800 W/m². The oxyhydrogen gas mixture that is generated is separated using a membrane with a higher permeability to H₂ than to O₂. Nevertheless, there is still a need to prevent the accumulation of O₂/H₂ gas mixtures within the explosion limits.

We appreciate Referee 3 for her/his time to understand the whole part of our work and to evaluate the novelty and significance fairly. We answer Referee 3's questions one by one as what follows, if indicated:

B. Originality and significance: if not novel, please include reference.

An actual demonstration of this scale for particulate-based photocatalytic system as presented in this manuscript is possibly a first in the available published literature.

C. Data & methodology: validity of approach, quality of data, quality of presentation

D. Appropriate use of statistics and treatment of uncertainties

The focus of the paper was to demonstrate a concept in which the use of statistical data

is not very important.

E. Conclusions: robustness, validity, reliability

The article does not have a specific conclusions section and these comments are based on the conclusions drawn from the abstract

This assertion "The system components were undamaged even under intentional ignition causing explosion and detonation, confirming that the gaseous products could be handled safely when employing a suitable system design" should be re-written. This confirmation of safety would certainly not be the case if larger volumes of gas are produced from a more efficient photocatalyst using the presented set-up (they do mention issues with leakage beyond 5kPa internal pressure).

The panel reactor does not cause any leakage unless the pressure increase exceeds 5 kPa. As shown in Supplementary Movie 1, the product gas is expelled smoothly when the rate of oxyhydrogen gas evolution is increased to 13 mL min⁻¹, which is to be observed at the STH value of 2.2%. The resident time of the gas in the panel reactor unit is shortened, but no leakage occurs, indicating that the pressure increase does not reach 5 kPa. We are unable to increase the gas evolution rate of the reactor unit because of the limited output of the UV diode array. However, we have observed that a similar panel reactor can maintain a gas evolution rate at the level equivalent to 10%-STH in our previous study (ref. 3). Therefore, it is unlikely that the panel reactor causes leakage in practical operation, and so we did not modify the text in the abstract. When the water splitting rate becomes much higher, gas collection and carrying tubes with larger inner diameters and/or larger numbers can be employed to maintain the internal pressure low enough. It was confirmed that larger tubes were undamaged at least up to an inner diameter of 20 mm. This information is added to the revised manuscript.

“Similarly, soft polyvinyl chloride tubes with an inner diameter of 20 mm were undamaged when the inner oxyhydrogen gas was detonated.” (Line 504)

The safety of the gas-separation membrane was also confirmed as shown in the manuscript (Line 184).

F. Suggested improvements: experiments, data for possible revision

No extra experiments required within the scope of this work. However, there are a few topics that require clarification:

(i) A discussion of reactor, sealing and plumbing material choices is missing especially in the context of preventing explosion related hazards, which is more critical in this type of system than in "traditional" anode-membrane-cathode configurations.

We use plastic elements with a pressure tolerance of 1 MPa for piping and fitting. The reaction system is operated in an ambient atmosphere and does not need any special materials. This information is described in the revised version of the manuscript.

“The reaction system is operated in an ambient atmosphere, and plastic elements with a pressure tolerance of 1 MPa were employed for piping and fitting. Nevertheless, high internal pressure values were found to result in gas and water leakage at the rubber seals, and the maximum allowable pressure difference with respect to the atmospheric pressure was determined to be 5 kPa.” (Line 354)

(ii) The explosion limits for H₂ in O₂ are also dependent on both temperature and pressure. Would operating pressure rise with improved hydrogen production rate per unit area? Would the prefiltered gas mixture still be safe?

Within the all of equipment, including the photocatalyst panel reactor unit, the gas-collection tubes, the membrane filter module, and the water-submerged gas tanks, the oxyhydrogen pressure was maintained at atmospheric pressure. The increase in the water splitting rate would raise the internal pressure of the water splitting panel reactor unit, but below 5 kPa because the leakage did not occur. Therefore, our scope of intentional ignition experiment was conducted at the atmospheric pressure.

(iii) Could the authors explain why the prefiltered gas mixture lying within the 4% to 95% of H₂ in O₂ window did not explode on ignition? How much is the moisture content in this mixture?

A hydrogen and oxygen mixed gas with a hydrogen content between 4% and 95% causes a chain reaction of explosion or detonation, as is described in ref. 17. Probably, by “explosion”, Referee 3 means a destructive combustion leading to shattering or burst of vessels. In that sense, explosion did not occur in our experiments. However, we use explosion to mean rapid combustion. Intentional ignition to oxyhydrogen containing a saturated water vapor always caused explosion in the system in our meaning. However, because the oxyhydrogen gas was confined in narrow spaces and

small-diameter tubes, the damage of the system was negligible. This is described in the manuscript.

“These individual parts investigations suggest that oxyhydrogen gas can be safely handled by confining the gas in narrow passage in each compartment and using the appropriate tubes for gas transportation.” (Line 187)

“When the evolved gases were confined in a layer 0.1 mm thick in the panel reactor unit and were transported using polyurethane tubes with an inner diameter of 8.6 mm, any resulting explosions and detonations were harmless.” (Line 498)

(iv) Since there is a minimum critical loading of the particles above which the H₂ yield does not exceed 0.1 mmol / (h cm²), this seems to be a limitation of the SrTiO₃:Al photo-absorber. Are there known materials with a narrower bandgap than SrTiO₃:Al that could capture a larger portion of the incident photons?

The referee's point is correct: as long as ultraviolet-active SrTiO₃:Al is used, the rate of hydrogen production under sunlight is low. We are developing photocatalysts such as Ta₃N₅ (ref. 9) and Y₂Ti₂O₅S₂ (ref. 10) that can split water into hydrogen and oxygen. Articles related to these materials were cited in the manuscript. If the quantum efficiency is improved to the same level as SrTiO₃:Al, higher STH values can be obtained. This was already described in our recent publication in *Nature* (ref. 8). Considering the scope of this work demonstrating the large-scale solar hydrogen production and recovery system, we would like to minimize the discussion about the material by citing these articles.

(v) The videos show very vigorous bubble formation. How would bubble management be implemented to maximise the photons reaching the absorber

As the reviewer points out, bubbles would induce scattering and reflection losses. However, in our panel reactors, bubbles coalesce and grow larger, and the liquid/gas interface becomes short as in Supplementary Movie 1. Moreover, the photocatalyst layer is kept wet and maintains the water splitting activity. Therefore, the bubble formation is not problematic in our present system. We have added a comment about the coalescence of bubbles and disappearance of small bubbles in relation to Supplementary Movie 1.

“Bubbles coalesced and the liquid/gas interface minimized, so that the scattering of incident light could be minimized.” (Line 80)

G. References: appropriate credit to previous work?

O.K

H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

OK. Include a conclusions section

===== End of comments =====

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

My most critical comment - novelty of the reported work - is not addressed in the revised version of the manuscript (I can only see the addition of few words and one reference).

The authors reply as one of the novelties of the manuscript being mechanistic insight into hydrogen and oxygen evolution: I cannot find any mechanistic studies. Can you clarify and highlight this novelty?

The authors comment on the seasonal dependence of the production rate, however they show a daily production rate without indicating if this is a summer/winter/... case. Is Fig 3c your best case of the multi-month experiments or is it a representative case? This should be clarified in the text.

In my opinion, after 1600 hours of operation, stoichiometry of 1:2 of product gases needs to be proven to confirm that there is no degradation or to quantify degradation. In fact, we know there is degradation, given the decrease in performance within the 280 and 1600 hours.

Fig 4a: I assume this is day-averaged solar irradiation? This should be clearly stated.

Referee #2 (Remarks to the Author):

The authors have addressed all of my comments and I recommend publication in the present format. Congratulations on this important work. Point 1 about the STH efficiency of the system was only addressed in the rebuttal, but without making changes in the manuscript. The decision on this revision is up to the authors. But I would like to mention that the issue of the net energy efficiency of the system is very important, and it would increase the scientific merit of the work, if it was explicitly stated in the manuscript.

Referee #3 (Remarks to the Author):

A. Summary of the key results: OK

B. Originality and significance: if not novel, please include reference: OK

C. Data & methodology: validity of approach, quality of data, quality of presentation: OK
significant improvement

D. Appropriate use of statistics and treatment of uncertainties: OK data collected over several months covers statistical variations to some extent

E. Conclusions: robustness, validity, reliability: OK; to help the reader, it would be useful to include subtitles for the different sections of the paper.

F. Suggested improvements: experiments, data for possible revision: OK

G. References: appropriate credit to previous work? OK

E: Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions: OK; to help the reader, it would be useful to include subtitles for the different sections of the paper.

Author Rebuttals to First Revision:

Response to Referees

Referee #1 (Remarks to the Author):

My most critical comment - novelty of the reported work - is not addressed in the revised version of the manuscript (I can only see the addition of few words and one reference).

Author reply:

We regret that the novelty of the work was still unclear for the referee. For clarity, the main novelty of implementing gas collection and separation in an arrayed photocatalyst panel reactor and inspecting the safety issue of the entire system is explicitly described in the introductory paragraph of the revised version.

“The present study is the first to implement gas collection and separation and examine safety of the gas handling. At the same time, we have witnessed the need to substantially improve the overall energy and economic efficiencies, by improving the STH efficiency and durability of the water-splitting photocatalyst, the energy efficiency in the gas separation process, and the fabrication cost of the reaction systems, to make renewable solar hydrogen production via photocatalytic water splitting a practically useful technology.” (Line 48)

The authors reply as one of the novelties of the manuscript being mechanistic insight into hydrogen and oxygen evolution: I cannot find any mechanistic studies. Can you clarify and highlight this novelty?

Author reply:

The particulate layer is not clogged with product oxyhydrogen gas bubbles and so the water splitting rate is maintained on the photocatalyst sheet during continuous operations with varying irradiances. This is probably because hydrogen and oxygen migrated through the mesoporous channels between the hydrophilic silica nanoparticles in the liquid phase under supersaturated conditions and form bubbles on the surface of the photocatalyst sheet, as is described in the photocatalyst sheet section. This is an important finding that can change the mindset in the research and development, because many researchers are sceptical of the use of fixed thin layers of photocatalysts and stick to the use of suspensions or circulating slurries of particulate photocatalysts to avoid mass transfer issues. However, we consider that the main novelty of the work is attributed to

the implementation of gas collection and separation function in an arrayed photocatalyst panel reactor and the inspection of the safety issue of the entire system as stated before, and we will not argue about the novelty regarding the insight into gas evolution process in the photocatalyst particle layer.

The authors comment on the seasonal dependence of the production rate, however they show a daily production rate without indicating if this is a summer/winter/... case. Is Fig 3c your best case of the multi-month experiments or is it a representative case? This should be clarified in the text.

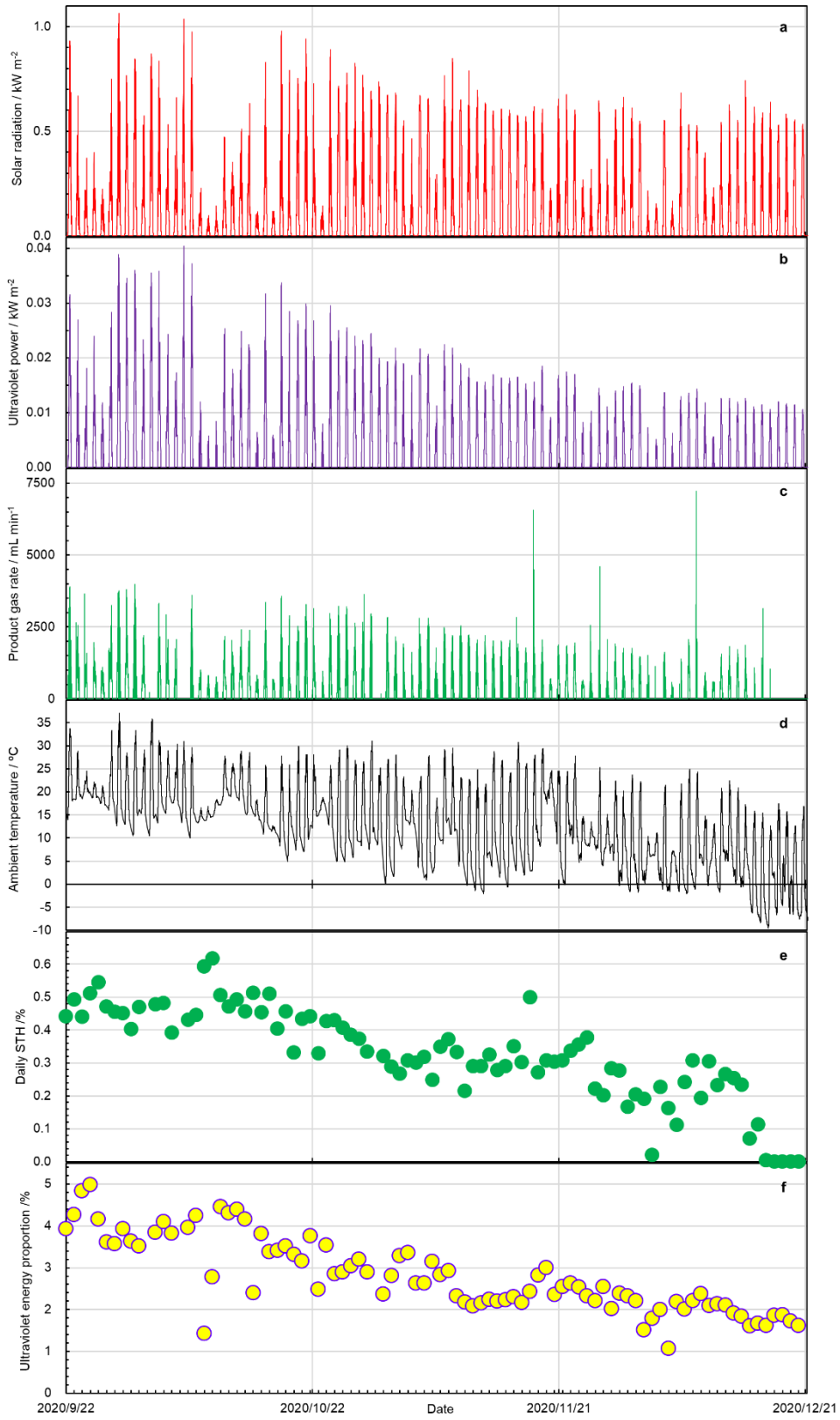
Author reply:

The date and place of the experiment are presented in the main text, Figure legends, and Methods. The weather conditions and the gas production rate have been constantly recorded since September 20, 2020, and the daily STH value were calculated over three months. The long-term performance of the arrayed photocatalyst panel is described in the revised manuscript.

“Extended Data Fig. 5 plots the continuous records of the sunlight intensity, the ultraviolet power, the amount of production of humid oxyhydrogen gas from the 100 m² photocatalyst panel reactor using photocatalyst sheets prepared on frosted glass, along with the ambient temperature, from September 22 to December 21, 2020, from autumn to winter. The daily STH efficiency and ultraviolet power proportion are also provided. The daily STH efficiency was 0.4–0.5% in the initial one month. On September 22, 2020, the peak production rate for the day was 3.6–3.7 L min⁻¹ at an outdoor temperature of 34 °C, observed from 11:00 to 11:30 a.m. The evolved gases being collected before the introduction into the hydrogen separation membrane are shown in Supplementary Movie 3. The STH value obtained under natural sunlight decreased gradually to approximately 0.3% by the middle of December 2020. This is attributable to variations in the weather condition considering the enough durability of the photocatalyst sheet (Extended Data Fig. 4b). The proportion of ultraviolet radiation in the total irradiance in natural sunlight at the Kakioka Research Facility decreased approximately from 5% to 2% (Extended Data Fig. 5f), whilst the SrTiO₃:Al photocatalyst employed was active only under ultraviolet light.

The 100 m² panel reactor based on photocatalyst sheets on flat, clear glass was found to continuously produce oxyhydrogen gas over a time span of eight months between November 2019 and July 2020 in a field test. The same panel reactor also worked after

the replacement of the internal photocatalyst sheets with those prepared on frosted glass from July 2020. However, in both cases, the daily STH efficiency dropped after December. This is attributed to degradation and detachment of the photocatalyst particle layer caused by repeated freezing and melting of the water in the system. From late December to February, the water in the panel reactors, tubes and gas reservoir was observed to repeatedly freeze overnight and then to melt in the daytime. Once the photocatalyst particle layer was peeled off the sheet, the photocatalyst settled at the lower part of the reactor unit and did not effectively receive sunlight.” (Line 145)



Extended Data Fig. 5 | Long-term records of the field test of the 100 m² photocatalyst panel reactor at Kakioka Research Facility from September 22 to December 21, 2020. (a) Solar radiation, (b) ultraviolet power, (c) oxyhydrogen gas production rate, (d) ambient temperature, (e) daily STH value, and (f) proportion of ultraviolet energy. The oxyhydrogen gas was not produced in late December 2020, because of the cold weather freezing the panel reactor units and other equipment. On October 2, 6, and 30, the gas was directed to the gas separation equipment, without delivery to the gas flowmeter. On October 9 and 10, the daily STH values were abnormally high. These values are not reliable because of bad weather and the low solar radiation. The data on November 18 and December 8 were not reliable, either, owing to malfunction of the soap-film flowmeter.

The rate of solar hydrogen evolution by the arrayed photocatalyst panel reactor follows the weather conditions (due to the variation in the UV intensity) and the operation history of the photocatalyst sheet (due to the degradation). The conditions were not identical amongst experiments. Therefore, all data should be regarded as representative cases in different experimental conditions.

In my opinion, after 1600 hours of operation, stoichiometry of 1:2 of product gases needs to be proven to confirm that there is no degradation or to quantify degradation. In fact, we know there is degradation, given the decrease in performance within the 280 and 1600 hours.

Author reply:

The ratio of hydrogen to oxygen in the gaseous product from the arrayed panel reactor was occasionally examined by mass spectroscopy as described in Methods. Activity degradation occurs even if hydrogen and oxygen are stoichiometrically produced from water and the turnover number far exceeds unity, because degradation of cocatalyst components can lower the reaction selectivity and the separation efficiency of photoexcited charge carriers. The possibility of activity deterioration during the long-term reaction owing to the cocatalyst degradation is mentioned in the revised version of the manuscript as what follows. However, there is no reason to link the activity degradation and the stoichiometry of the product. We also would like to note that no sacrificial electron donor was used throughout our work. These points are reflected in the revised manuscript.

“The deactivation likely resulted from the deterioration of the cocatalysts during the long-term operation,¹² because the microstructure of the photocatalyst layer were found to remain intact even after a field test of approximately six months, as shown in Extended Data Fig. 2d.” (Line 123)

“Note that the hydrogen-to-oxygen ratio of the product gas was two because no sacrificial reagent was used.” (Line 542)

Elucidation of the factors leading to activity deterioration is certainly interesting. However, considering the novelty and scope of this paper, the detailed factors of activity deterioration can be investigated in subsequent studies more focused on physical chemistry and catalytic science.

Fig 4a: I assume this is day-averaged solar irradiation? This should be clearly stated.

Author reply:

The measurement was conducted under continuous irradiation with simulated sunlight. This was stated in the main text and the figure caption. The reaction is under a steady condition and so there is no distinction between average and peak in this experiment. For clarity, we have added further explanations why the experiment was conducted under continuous irradiation in the revised manuscript.

“Prior to the construction of the arrayed panel reactor, the performance of the photocatalyst sheet was examined indoor using a small panel reactor under continuous exposure to simulated standard sunlight (AM 1.5G, 1 kW m⁻²) for acceleration test.³” (Line 110)

The daily STH value under natural sunlight is provided in Extended Data Fig. 5.

Referee #2 (Remarks to the Author):

Point 1 about the STH efficiency of the system was only addressed in the rebuttal, but without making changes in the manuscript. The decision on this revision is up to the authors. But I would like to mention that the issue of the net energy efficiency of the system is very important, and it would increase the scientific merit of the work, if it was explicitly stated in the manuscript.

Author reply:

We appreciate the referee's suggestion. Following the referee's advice, we include the assessment of the net energy efficiency of the present gas processing facility in the main text and Methods.

“Admittedly, the present reaction system did not convert solar energy into hydrogen energy in the net if the energy input was covered by the product hydrogen (see Methods).”
(Line 260)

“The balance of output and input energy is important in energy applications. Based on the one-day operation on October 2 (Fig. 3), the power supplied to the vacuum pump, which was the major part of energy consumption within the whole system, was estimated. The pump operation period was approximately 38 s to empty 2.4 L of the tank active volume. The produced oxyhydrogen gas (970 L) was then filtered in 404 (= 970/2.4) cycles of operation. The pump power was 400 W at maximum. These numbers yield a one-day power consumption of 1.7 kWh = 6.1 MJ. On the other hand, the amount of hydrogen energy produced on the same day was 5.0 MJ. Therefore, the present reaction system did not convert solar energy into hydrogen energy in the net, and improvement in the gas separation apparatuses and procedure is essential.” **(Line 544)**

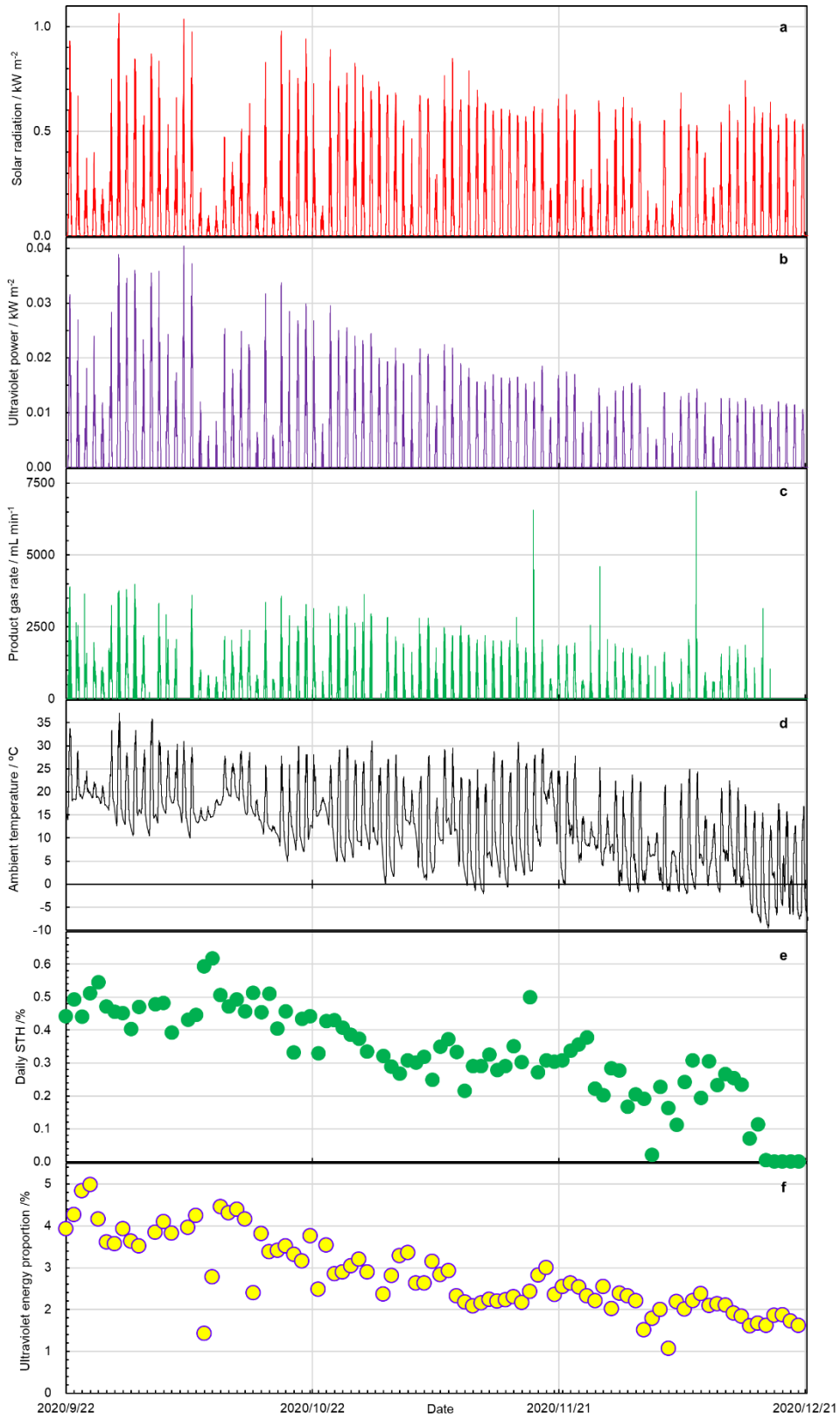
Referee #3 (Remarks to the Author):

- A. Summary of the key results: OK
- B. Originality and significance: if not novel, please include reference: OK
- C. Data & methodology: validity of approach, quality of data, quality of presentation: OK significant improvement
- D. Appropriate use of statistics and treatment of uncertainties: OK data collected over several months covers statistical variations to some extent
- E. Conclusions: robustness, validity, reliability: OK; to help the reader, it would be useful to include subtitles for the different sections of the paper.
- F. Suggested improvements: experiments, data for possible revision: OK
- G. References: appropriate credit to previous work? OK
- H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions: OK; to help the reader, it would be useful to include subtitles for the different sections of the paper.

Author reply:

We appreciate the referee for her/his time to evaluate our manuscript. Following the referee's advices, we have made following changes in the manuscript.

D: The data taken from September 22 to December 21, 2020 are presented in Extended Data Fig. 5 in the revised manuscript.



Extended Data Fig. 5 | Long-term records of the field test of the 100 m² photocatalyst panel reactor at Kakioka Research Facility from September 22 to December 21, 2020. (a) Solar radiation, (b) ultraviolet power, (c) oxyhydrogen gas production rate, (d) ambient temperature, (e) daily STH value, and (f) proportion of ultraviolet energy. The oxyhydrogen gas was not produced in late December 2020, because of the cold weather freezing the panel reactor units and other equipment. On October 2, 6, and 30, the gas was directed to the gas separation equipment, without delivery to the gas flowmeter. On October 9 and 10, the daily STH values were abnormally high. These values are not reliable because of bad weather and the low solar radiation. The data on November 18 and December 8 were not reliable, either, owing to malfunction of the soap-film flowmeter.

E and H: The following subtitles are added to the main text: Overview of arrayed panel reactor, Photocatalyst sheet, Arrayed panel reactor, Safety issue, and Challenge for practical use.