Peer Review File

Manuscript Title: Solar-to-hydrogen efficiency of >9% in photocatalytic water splitting

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #2 (Remarks to the Author):

This article focuses on the demonstration of practical solar water splitting with a complex device made of InGaN/GaN nanowires grown on Si by MBE. The authors enable the hydrogen and the oxygen evolution reaction (HER, OER) by photodepositing two sets of cocatalysts (Rh/Cr2O3 core/shell and Co3O4 nanoparticles). They claim to have achieved a world record in STH efficiency of 9.17% and demonstrate a 4x4 cm2 device under operation using tub water and concentrated natural solar light. Interestingly, they show the dependence of the STH on the operation temperature. It is suggested and demonstrated that IR light is not lost, because it can be used to heat water and reach an improved operation temperature.

The strong point of the paper is clearly the practical demonstration (tub water and natural solar light) and the operation temperature dependence of the STH including IR heating. These results are presented clearly and credibly. However, I have difficulties with the statement world record concerning the 9.17% device and the general STH performance assessment of overall water splitting devices (< 3%) in the introduction (references 6-10 and SI table 11). The authors compare to some publications on specific devices, but do not state clearly what the common feature is and why they are not comparing to other devices (with higher STH efficiencies).

An important review paper, which is summarizing STHs is missing (Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G)). This paper emphasizes that there is a relation between cost of the device and minimal STH efficiency in order to be economically viable. If the material and system cost is low, the threshold STH efficiency is low. Therefore, it is very important to look at this relation instead of STH efficiencies purely, if the focus is on practical application.
The authors use a complex (expensive) device with is made with elements like In and Ga, which are considered as critical elements in many countries (for example in Europe https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0474&from=EN) and need to achieve higher efficiencies to be economically viable than a particulate catalyst for example. Using a different point of comparison to the authors: in 1998 Khaselev and J.A. Turner made a photoelectrochemical device (Science, 1998. 280 425-427, DOI 10.1126/science.280.5362.425) using In and Ga with a STH efficiency of 12,4%. I cite this as an example, in which sense I miss a realistic assessment of this work in the context of solar water splitting.

Detailed comments:
Page 2/ 2. paragraph. Please explain what your contribution to the development of these devices is. If there was a previous article by the authors where they published the world record 9,17% it should be cited clearly. If the achievement of this result is part of this paper, it should also be stated clearly.
[7] The paper reviews cocatalysts and indicate H2 evolution rates but no STHs, although the paper is

cited in the STH context. An important review paper, which is indeed summarizing STHs however, is missing by Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G).
The authors write that based on thermodynamics 44% of the sun light can contribute to the water splitting reaction and cite [12]. In [12] thermodynamics is not mentioned. Is this number really based on a thermodynamic model? If it is the case, I would appreciate an explanation.
Hydrogen-oxygen recombination/ hydrogen-oxygen: It reads, as if hydrogen and oxygen molecules recombine or coevolve. This is not necessarily the case. Maybe the half reactions take place on different (cocatalyst) sites.

Referee #3 (Remarks to the Author):

This manuscript reports on a demonstration of a photoelectrochemical water splitting system which is based on InGaN. It shows results from indoor tests as well as test results when exposed to outdoor/real-sun conditions.

The manuscript reports an interesting lab-scale demonstration (indoor and outdoor) and also reports temperatures for such an experiment (which is not usually done but highly desired). It is argued that higher temperatures are suppressing hydrogen-oxygen recombination, and therefore the thermal part of the solar spectrum is essential in the demo. This is interesting and is a slightly different argument than what was previously argued (i.e. previously it has been argued that increasing temperature would mostly improve kinetics and therefore improve performance).

However, I cannot find sufficient proof for their hydrogen-oxygen recombination argument. The photo and thermal (infrared) input to the system is not truly controlled or optimized (i.e. this would require varying concentrations or varying thermal mass so that temperature is controlled and not simply a result of the external heating or insulation). Plus, it seems to me that irradiation concentration effect and a temperature effect are convoluted in the results (two different concentrations are used for indoor and outdoor experiments). I recommend for the authors to put more emphasis on this photo vs thermal scheme and to provide experimental data that allow for the de-convolution of photo and thermal effect and to provide theoretical analysis/quantification of the expected temperature effect to support their hypothesis of reduced oxygen-hydrogen recombination at high temperatures to be the dominating effect. Generally, I also regret the sparsity of provided data in the manuscript (two concentrations only, outdoor experiments for 140 min only for unknown intensities, …).

I find the taxonomy is somewhat misleading: photocatalytic water splitting is usually used in the context of suspension of semiconducting particles, while here we deal with immobilized nano-wires, which would belong to photoelectrochemical water splitting. Also, these nano-wire heterostructures are not properly characterized in the manuscript. Nowhere can I find the actual composition (or compositional range) of the In_xGa_yN, an exact characterization of the junction, and a band diagram which explains better the band structure and bending in this particular heterostructures. If the authors are using the exact same material as described in the ACS Nano 2013 paper, that should be more clearly stated.

The authors indicate that there is a maximum efficiency demonstration of 3% (line 37) without providing a reference. Also, this limit is only valid for suspended photocatalysts or catalyst sheets, but not for multi-junction heterostructures, where efficiencies as high as 15-20% have been achieved (see an overview of the demonstrated efficiencies for photoelectrochemical water splitting here: Ager et al., Energy Environ. Sci., 8, 2811–2824 (2015); Tembhurne et al., Nat Energy, 4, 399–407 (2019); Kim et al., Chem. Soc. Rev., 48, 1908-1971 (2019); or an overview over photocatalytic demonstrations here: Fabian et al., Energy Environ. Sci., 8, 2825-2850 (2015)). The introduction needs to be rewritten and descriptions of their demonstration as "world record"/"highest reported value"/… need to be exchanged in the light of these already demonstrated efficiencies and anyway should be replaced by more scientific language and quantitative comparisons.

The authors claim there is a "100% efficiency" (line 34) of the material, which is wrong and not precise (probably a quantum efficiency is meant here and should be properly defined, and efficiency and quantum yield should not be used interchangeably).

The number in the introduction, for example, "… nearly 44% of solar light lies in the visible spectrum (400-700 nm)…" is wrong (a quick calculation based on the blackbody fractional function indicates 38% is in the visible [and even lower for the Am1.5 spectrum]) and misleading, given that one photon can only produce one electron-hole pair. Furthermore, the indicated reference [12] is not suiting to support this number (ref [12] is discussing Si and luminescence, nothing that applies here). Probably better fitted are Shockley-Queisser's original paper or the paper by Fountaine et al., Nat. Com. (2016), both provide limit STH efficiencies for photocatalytic/photoelectrochemical applications.

The materials (In, Ga, Rh) used in the demonstration are very rare (see abundance plot by the geological survey of the US) and the process (molecular beam epitaxy) is not scalable. The authors should comment on scalability, economics, practical and implementation problems with this system.

Generally, the OER and HER-selective catalysts seem to be applied uniform along the nano-wire (see figure 1), this is in contrast to earlier publications of the same group where a spatial separation between HER and OER was partially achieved by applying HER catalyst on top of the nano-wire only and OER catalyst on bottom only. The authors need to comment on this difference and its implication.

The nano-wire reproducibility or uniformity seems very low. According to the authors, their band gaps range between 445 and 545 nm. What composition does this result in? Why is there such a large variation? Is this beneficial or not for the application? It is even argued that materials with band gaps of 632 nm are present. The authors should explain that if we have such a large variation of nano-wire types, is one of them current limiting? Also, given that it is argued that we have a dual junction (InGaN and GaN), what are the theoretical maximum efficiencies, and if they are in series, which junction is limiting?

The temperature effect is only associated to increased reaction temperature and enhanced mass transfer (line 101), however there is also a negative effect from recombination in the semiconductor. This should be included in the discussion, which might better explain the "optimal" performance at

70°C. I am not sure about the physical limit for OER with increasing temperature, what is the authors explanation (from a mechanistic point of view) that OER is limited by temperature (i.e. not further increasing beyond 70°C)?

It is argued that the system is stable by utilizing one SEM picture (extended data fig. 8), without any quantification or elemental analysis support. This is insufficient as an argument and a better and quantitative way needs to be introduced to argue stability.

The authors argue that there is a "temperature control" strategy. I cannot find a controller that is ensuring the temperature is maintained (for example for the outside experiment, how is the temperature "controlled"?). I believe the word "control" or "controlling" used in the manuscript is not properly used. The temperature is maybe monitored, but there is no active handling that maintains this temperature.

What are the partial pressures of hydrogen and oxygen in the headspace (is there inert/sweep gas)?

I am not fully following their dark recombination experiment. Hydrogen's viscosity and diffusivity is significantly higher than for oxygen. Can it be that the system is simply not tight enough? What is the pressure loss in 24h in the system? Is it the same for hydrogen and oxygen? Is there residual oxygen in the system? How was the system purged? All this should be detailed in the methods part. Also, when reporting hydrogen and oxygen in the recombination experiments (fig 2c and ex. data fig 11), these curves should show relative changes in hydrogen or oxygen (not absolute values).

In line with my previous comment, only when we see the relative recombination, we could maybe conclude that higher temperatures are reducing recombination and therefore the temperature effect is mostly inhibiting oxygen-hydrogen recombination (and it is not simply the higher production rates or improved mass transport). But in general, I believe the given empirical arguments are not sufficient to truly conclude that temperature is suppressing hydrogen-oxygen recombination. I believe an order of magnitude prediction (by theoretical calculations) of the temperature effect (positive or negative) due to kinetics, mass transport, semiconductor recombination, oxygen-hydrogen recombination etc. should be given to support the temperature argument.

What is "slightly lower" (line 146) or "relatively large scale" (line 147)? Please add quantitative statements. This is true throughout the manuscript.

Figure 3b: what is the intensities in this 140-minute experiment? What is the corresponding measure temperature? And especially, by how much is the temperature vary as a result of varying irradiation (the manuscript reports 75 +/- 3°C, but is this averaged over 140 minutes at constant intensities)?

The authors need to comment on the effect of irradiation concentration, and particularly the effect of different concentrations (3800 mW/cm2 indoors and 16070 mW/cm2 outdoors). The changing concentration will result in different current densities / production rates and therefore also different losses. All of this needs to be discussed and quantified. Also, the choice of these two concentrations seems arbitrary. How are they chosen and hat is the effect of varying concentrations? The arguments behind the design choice and the concentration choice needs to be detailed in the

manuscript.

The thermal mass of the system (volume of solution) is important for the thermal response of the system (temperature). This should be discussed in the manuscript. Also, the reported temperature, is this uniform throughout the solution or along the nano-wires? Or how much variation is there? Are we sure that all surfaces see the same temperature? Please provide quantitative arguments in the manuscript.

The proposed system is a batch type water splitting system. The authors need to comment on the practicability of batch type versus a continuous flow type system. The latter is more likely to be implemented in practice. Do they expect the same suppression of hydrogen-oxygen recombination in a continuous flow reactor type (given the mass, charge and heat transfer is different)?

Referee #4 (Remarks to the Author):

This paper by Zhou et al. demonstrates the successful application of overall water splitting into hydrogen and oxygen in a very simple reactor configuration. This study achieves literally the game changing results, introducing high impact of temperature dependence on the photocatalytic water splitting performance. High quality InGaN photocatalyst nanorods were developed by molecular beam epitaxy. This photocatalyst had 1.2 micron in length and 100 nm in width. This dimension is considered excellent for photon absorption in vertical direction, and charge separation in lateral direction. Using this type of semiconductor, photocatalytic overall water splitting has been demonstrated by Kibria et al., as cited in this paper. Excellent electrocatalyst modification is also achieved, which was already demonstrated by Domen and coworkers; namely Rh/CrOx core/shell hydrogen evolving catalyst and CoOx oxygen evolving catalyst. These electrocatalysts were deposited on InGaN by photodeposition, following the protocol of UV-responsive SrTiO3 photocatalyst in the recent Nature paper 2020.

The breakthrough finding by this study is established that this device shows much appreciable performance only at high temperatures (70 °C) and reaches >9 % solar to hydrogen (STH) energy efficiency. Efficiency is correctly calculated where the rate of production matches with the reported values. This temperature rise can be easily achieved in the proposed photoccatalyst system where concentrated solar light (up to 160 times AM 1.5 G sun equivalent) utilizing infrared part of photons. This temperature effects with high activation energy mean that the photocatalytic performance at low temperatures is limited by electrocatalytic performance, in contrast to semiconductor charge separation efficiency. This is very reasonable at high performances. Using sacrificial electron donor/acceptor, it is clear that OER by CoOx is limiting the overall performance, which is again reasonable from the previous works. The photocatalytic stability is excellent: this is somewhat surprising as the electrocatalytic conversion corresponding to this performance exceeds 200 mA cm−2, but under this electrolysis in conventional device, the CoOx may not be this stable. The difference may come from nanoscale electrolysis where pH gradient is minimal as well as solution resistance (enabling pure water can be used). The movie provided in the supplementary file is convincing enough to confirm the high performance of water splitting. Conclusions are well

supported by the experimental evidence.

Overall, the paper shows excellent achievement and the game-changing concept in this paper. The following are some aspects to improve further the clarity of this work.

• Would it be possible to provide the content of Rh, Cr and Co amount on the GaInN semiconductor? As a water splitting device, it is rather astonishing that CoOx OER electrocatalyst can sustain its performance over 200 mA/cm2 equivalent current density. This extreme stability reported in this study may originate from nanoscale electrochemistry that minimizes pH gradient and solution resistance, which are different from classical PV+E (photovoltaic + electrolyze) system.
• Tap water experiment is indeed interesting to report, but it lacks scientific reasoning of performance loss. Analysis of impurities (halogens, heavy metals, etc.) is probably helpful. Enhanced back reaction, loss in Faradaic efficiency, surface poisoning, etc. It would be interesting to know if the loss is recoverable or irreversible.

More minor comments
• The efficiency values of 9.17% (and those in other places) have too many digits in contrast to its measurement accuracy. This fundamental aspect is important as it reflects the quality of the work. At least the title should consist of more appropriate designation, such as >9% or over 9% STH efficiency.
• In Abstract, “a large-scale photocatalytic system” gives 6.21% STH, but it requires to report explicit dimension of the photoreactor used in this study.

Author Rebuttals to Initial Comments:

Referee #2 (Remarks to the Author):

Q1: This article focuses on the demonstration of practical solar water splitting with a complex device made of InGaN/GaN nanowires grown on Si by MBE. The authors enable the hydrogen and the oxygen evolution reaction (HER, OER) by photodepositing two sets of cocatalysts (Rh/Cr2O3 core/shell and Co3O4 nanoparticles). They claim to have achieved a world record in STH efficiency of 9.17% and demonstrate a 4x4 cm2 device under operation using tap water and concentrated natural solar light. Interestingly, they show the dependence of the STH on the operation temperature. It is suggested and demonstrated that IR light is not lost, because it can be used to heat water and reach an improved operation temperature.

R1: Thank you for your comment. In the revised **Extended Data Fig. 7c and 7d**, the heat insulating layer with a low thermal conductivity (50 mW m^{-1} K^{-1}) was used to help maintain the temperature of reaction system at ~70 ºC. Basically, the thermal loss was approximately the same as the thermal energy of IR input since a thermal balance was maintained during reaction. Hence, the role of the heat insulating layer is to produce a larger temperature difference between ambient and internal environment of reaction system, thus leading to an optimal temperature of ~70 ºC in the reaction system. The proof-of-concept demonstration can be further improved in future practical system design and implementation.

This discussion and corresponding model have been added into **Extended Data Fig. 7.**

Q2: The strong point of the paper is clearly the practical demonstration (tub water and natural solar light) and the operation temperature dependence of the STH including IR heating. These results are presented clearly and credibly. However, I have difficulties with the statement world record concerning the 9.17% device and the general STH performance assessment of overall water splitting devices (< 3%) in the introduction (references 6-10 and SI table 11). The authors compare to some publications on specific devices, but do not state clearly what the common feature is and why they are not comparing to other devices (with higher STH efficiencies). An important review paper, which is summarizing STHs is missing (Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G)). This paper emphasizes that there is a relation between cost of the device and minimal STH efficiency in order to be economically viable. If the material and system cost is low, the threshold STH efficiency is low. Therefore, it is very important to look at this relation instead of STH efficiencies purely, if the focus is on practical application.

R2: Thank you for your comment. Some reports with higher STH in the literature (Kim et al. Chem Soc Rev, DOI 10.1039/C8CS00699G) belong to photoelectrochemical (PEC) system instead of photocatalytic (PC) system. Compared to the conventional PEC water splitting, photocatalytic overall water splitting (OWS) does not require the use of conductive electrolyte, *e.g.,* strongly acidic or basic solutions. Instead, freshwater or seawater can be readily split into H_2 and O_2 via photocatalytic OWS without any external bias/circuitry, which can significantly reduce the system cost and mitigate photocatalyst corrosion, stability, and safety related issues. As an example, the commonly reported high efficiency PEC water splitting devices exhibit very poor stability, often limited to a few hours of stable operation under practical two-electrode configuration (Science, 1998, 280, 425-427 and Nature Energy, 2018, 3, 944–951). Hence, the PC system for water splitting owns a lower cost for hydrogen production due to its simpler structure, which is considered as one of most economic solar hydrogen methods (Domen et al. Nature Catalysis, 2019, 2, 387–399 and Lewis et al. Energy Environ. Sci., 2016,

9, 2354-2371).
This discussion has been added into the introduction, and the article suggested by Reviewer has also been cited. (Please see **Line 29-35**)

Q3: **(a)** The authors use a complex (expensive) device with is made with elements like In and Ga, which are considered as critical elements in many countries (for example in Europe https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52020DC0474&from=EN) and need to achieve higher efficiencies to be economically viable than a particulate catalyst for example. **(b)** Using a different point of comparison to the authors: in 1998 Khaselev and J.A. Turner made a photoelectrochemical device (Science, 1998. 280 425-427, DOI 10.1126/science.280.5362.425) using In and Ga with a STH efficiency of 12,4%. I cite this as an example, in which sense I miss a realistic assessment of this work in the context of solar water splitting.
R3: Thank you for your comment.
(a) Though In and Ga are relatively expensive in some countries, their reserves are still large in the word. Especially, the high efficiency, long lifetime and mature production technology of InGaN photocatalyst can significantly reduce the use of indium-containing materials and decrease the cost of solar hydrogen. As an example, indium has been widely used in LED lighting and the cost for LED light bulbs has decreased by nearly two orders of magnitude over the past two decades (https://www.osti.gov/servlets/purl/1163956), strongly suggesting that indium is not a limiting factor for the production of InGaN materials and devices.
(b) In the literature (Science, 1998. 280 425-427, DOI 10.1126/science.280.5362.425), the high-concentration electrolyte (3 M H_2SO_4) and numerous noble metal Pt materials are used in the PEC system, which undesirably increase the complexity and cost of system. It is noticed that the higher working light intensity can remarkably decrease the material cost per irradiated area unit. The PEC system mentioned by the reviewer, as a pioneering demonstration, only worked under 1190 mW cm^{-2} for ~20 mins. Subsequent studies have led to improved performance, but it has remained fundamentally challenging to simultaneously achieve high efficiency and long-term stability for PEC water splitting. Our PC system could work under 16070 mW cm^{-2} (concentrated natural solar light) with two to three orders of magnitude better stability. Moreover, our system is capable of splitting freshwater, or seawater with high efficiency. Related discussions have also been added in the revised manuscript.

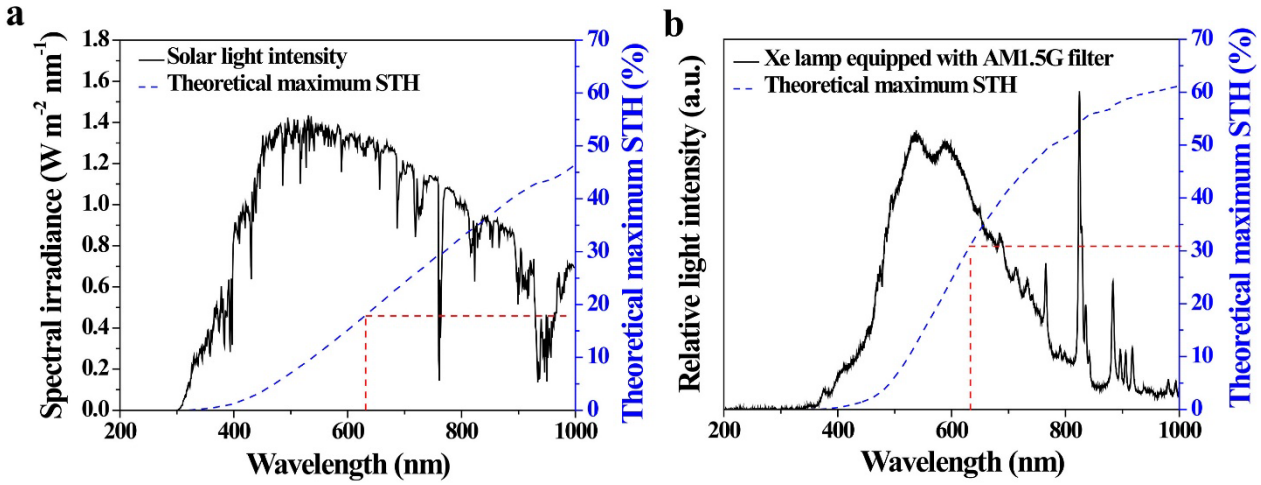
Detailed comments:

Q4: Page 2/ 2. paragraph. Please explain what your contribution to the development of these devices is. If there was a previous article by the authors where they published the world record 9,17% it should be cited clearly. If the achievement of this result is part of this paper, it should also be stated clearly.
R4: Thank you for your comment. We have developed various InGaN materials and used them in the photocatalytic water splitting in our previous works (Nature Communications, 2015, 6, 6797, Nature Communications, 2018, 9, 1707 and ACS Energy Lett. 2018, 3, 2230−2231). However, the STH of those materials is commonly limited below 3% in photocatalytic overall water splitting. In the present work, we first discovered the observable temperature-dependent hydrogen-oxygen recombination effect in PC water splitting. Guided by this finding, we proposed a high-efficiency reaction mechanism and successfully demonstrated a world-record STH of ~9.2% in photocatalytic OWS reaction with sunlight as the only energy source. Besides, we also further extended the visible-light-response range

of InGaN nanowires to 632 nm in the present work.
This discussion has been added into the revised manuscript. (Please see **Line 53-66**)

Q5: [7] The paper reviews cocatalysts and indicate H2 evolution rates but no STHs, although the paper is cited in the STH context. An important review paper, which is indeed summarizing STHs however, is missing by Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G).
R5: Thank you for your comment. Ref. [7] has been replaced. And the literature (Kim et al. Chem Soc Rev., DOI 10.1039/C8CS00699G) has been discussed and added into the introduction section. (Please see **Line 30**)

Q6: The authors write that based on thermodynamics 44% of the sun light can contribute to the water splitting reaction and cite [12]. In [12] thermodynamics is not mentioned. Is this number really based on a thermodynamic model? If it is the case, I would appreciate an explanation.
R6: Thank you for your comment. Based on the spectrum of solar light in **Extended Data Fig. 4a,** we recalculated the light intensity in 400-700 nm region and theoretical maximum STH. Nearly 40% of solar light lies in the visible spectrum (400-700 nm), which can contribute to a theoretical maximum STH of 24% in the photocatalytic OWS (Nature Communications, 2016, 7, 13706).
This has been discussed in the revised manuscript and the literature has also been updated. (Please see **Line 41-45 and Extended Data Fig. 4a**)



Extended Data Fig. 4. Theoretical maximum STH. Wavelength-dependent theoretical maximum STH in **(a)** natural solar light[4] and **(b)** simulated solar light produced by a Xe lamp equipped with a standard AM1.5G filter from Newport Corporation. The red dashed line corresponds to the photocatalyst with band gap of 1.96 eV (632 nm).

Q7: Hydrogen-oxygen recombination/hydrogen-oxygen: It reads, as if hydrogen and oxygen molecules recombine or coevolve. This is not necessarily the case. Maybe the half reactions take place on different (cocatalyst) sites.
R7: Thank you for your comment. Firstly, as shown in the revised **Fig. 2c**, the hydrogen and oxygen recombine at a stoichiometric ratio of 2:1, which indicates a synchronous hydrogen oxidation and oxygen reduction reaction. Secondly, the noble metal Rh has been considered the main hydrogen-oxygen recombination center and the Cr_2O_3 shell has been also used to inhibit this back reaction

(Domen et al. Angew. Chem. Int. Ed. 2006, 45, 7806–7809), which has been widely used in the previous photocatalytic water splitting (*Nat Mater, 2016,* **15**, 611-615 and *Nature, 2020,* **581**, 411-414). Thirdly, it is also possible that the partial hydrogen oxidation and oxygen reduction in back reaction occur on different cocatalysts. Thus, we used DFT calculations to study the hydrogen-oxygen recombination reaction on cocatalyst Co_3O_4, Rh and Cr_2O_3 (**Fig. 2d**). The results demonstrated that the desorption of product water was the rate-determining step in hydrogen-oxygen recombination on Co_3O_4, Rh and Cr_2O_3. Especially, the reaction energy (0.11 eV) of water desorption on Rh was remarkably less positive than that on Co_3O_4 (1.03 eV) and Cr_2O_3 (0.97 eV). Hence, Rh was the main hydrogen-oxygen recombination center. Besides, after water adsorption, hydrogen or oxygen was difficult to be adsorbed or activated on Co_3O_4 or Cr_2O_3 surface. Hence, the separated hydrogen oxidation or oxygen reduction on Co_3O_4 or Cr_2O_3 were difficult based on the thermodynamics.
The DFT calculations and corresponding discussion have been added into the revised manuscript. (Please see **Line 164-172**)

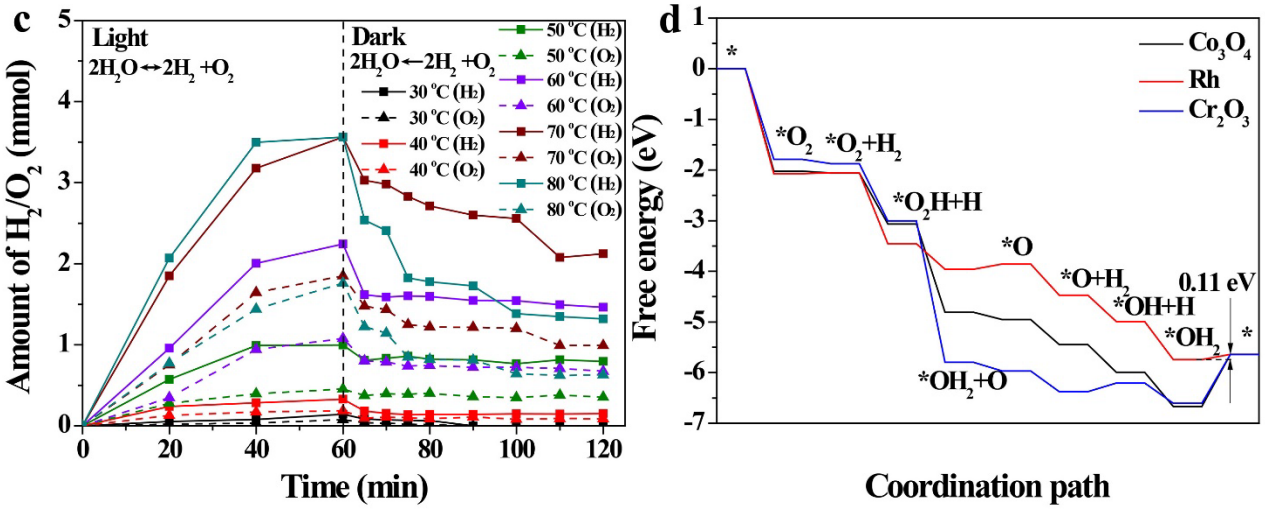


Fig. 2. (c) Temperature-dependent hydrogen-oxygen recombination reaction. **(d)** Free energy profile of hydrogen-oxygen recombination on the cocatalyst Co_3O_4, Rh and Cr_2O_3.

Referee #3 (Remarks to the Author):

This manuscript reports on a demonstration of a photoelectrochemical water splitting system which is based on InGaN. It shows results from indoor tests as well as test results when exposed to outdoor/real-sun conditions.

The manuscript reports an interesting lab-scale demonstration (indoor and outdoor) and also reports temperatures for such an experiment (which is not usually done but highly desired). It is argued that higher temperatures are suppressing hydrogen-oxygen recombination, and therefore the thermal part of the solar spectrum is essential in the demo. This is interesting and is a slightly different argument than what was previously argued (i.e. previously it has been argued that increasing temperature would mostly improve kinetics and therefore improve performance).

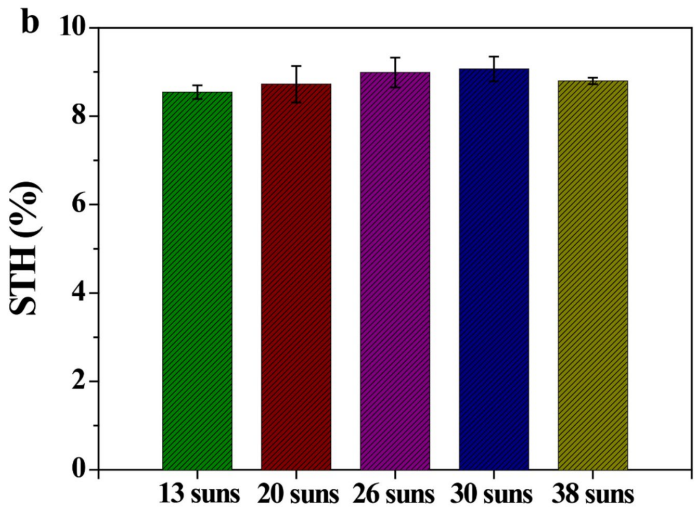
Response: We appreciate the reviewer comments. However, we would like to point out that this work is related to the demonstration of a ***photocatalytic*** water splitting system, instead of ***photoelectrochemical*** system. The taxonomy of photocatalytic and photoelectrochemical water splitting depends on the reaction condition. The photocatalytic water splitting is free from electrical wires, or bias. In contrast, the photoelectrochemical water splitting is conducted in an electrolytic tank. More detailed explanation is further described in **R2**. ***Significantly, photoelectrochemical water splitting systems generally require the use of highly conductive electrolyte, e.g., sulfuric acid, which severely limits their practical application, whereas photocatalytic water splitting utilizes pure water, sea water, or tap water, as demonstrated in this experiment, which is much more suited for practical application.***

Q1: (a) However, I cannot find sufficient proof for their hydrogen-oxygen recombination argument. **(b)** The photo and thermal (infrared) input to the system is not truly controlled or optimized (i.e. this would require varying concentrations or varying thermal mass so that temperature is controlled and not simply a result of the external heating or insulation). Plus, it seems to me that irradiation concentration effect and a temperature effect are convoluted in the results (two different concentrations are used for indoor and outdoor experiments). I recommend for the authors to put more emphasis on this photo vs thermal scheme and to provide experimental data that allow for the de-convolution of photo and thermal effect and to provide theoretical analysis/quantification of the expected temperature effect to support their hypothesis of reduced oxygen-hydrogen recombination at high temperatures to be the dominating effect. **(c)** Generally, I also regret the sparsity of provided data in the manuscript (two concentrations only, outdoor experiments for 140 min only for unknown intensities, …).

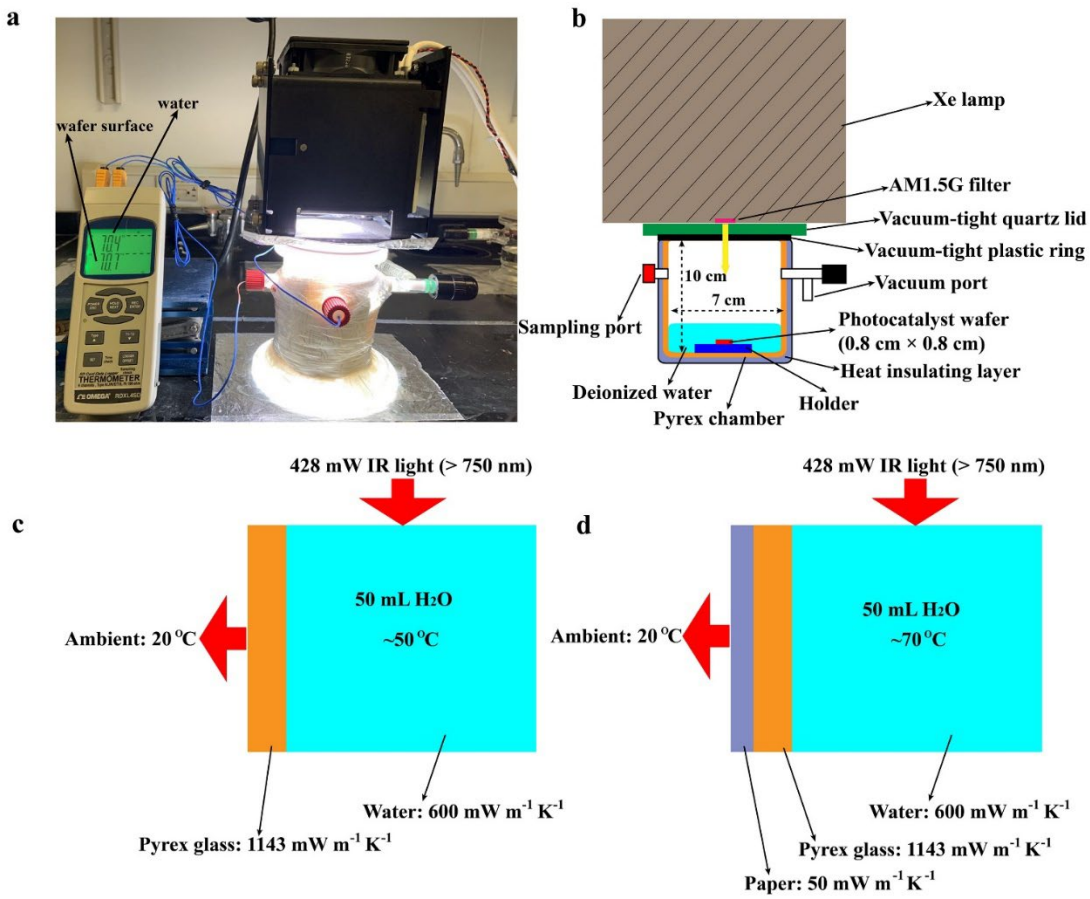
R1: Thank you for your comment. (a) To investigate the mechanism of hydrogen-oxygen recombination, we added the DFT calculations to simulate the hydrogen-oxygen recombination process on cocatalyst Co_3O_4, Rh and Cr_2O_3 at the atomic scale (**Fig. 2d**). The results demonstrated that the desorption of product water was the rate-determining step in hydrogen-oxygen recombination on Co_3O_4, Rh and Cr_2O_3. Especially, the reaction energy (0.11 eV) of water desorption on Rh was remarkably less positive than that those on Co_3O_4 (1.03 eV) and Cr_2O_3 (0.97 eV). Hence, Rh was the main hydrogen-oxygen recombination center. More importantly, most steps in the hydrogen-oxygen recombination on Rh were typically exothermal. Hence, increasing the temperature of reaction system in a certain range could desirably inhibit this hydrogen-oxygen recombination on Rh cocatalyst, which

was consistent with our experimental results. (Please see **Line 164-172**)

(b) In **Fig. 2a**, we firstly investigate the effect of temperature under the same light intensity (3800 mW cm^{-2}) and the temperature of sample was changed from 30 ºC to 80 ºC by a heated circulator which was connected with the double-layer chamber (**Extended Data Fig. 5**). The result in **Fig. 2a** showed that the highest STH was obtained at an optimal temperature of 70 ºC. Secondly, the temperature of sample was maintained at 70 ºC by the heated circulator and the light intensity on the photocatalyst wafer was varied from 1300 mW cm^{-2} to 3800 mW cm^{-2}. The obtained results showed that the STH was not observably changed with the light intensity (**Extended Data Fig. 6b**). Hence, the temperature is a determining factor on the STH of photocatalytic OWS on the present Rh/Cr_2O_3/Co_3O_4-loaded InGaN/GaN nanowires. Especially, the reaction temperature of 70 ºC was considered as the optimal condition. To avoid the dependence on the additional heated circulator and to only use the sunlight as the unique energy source, a heat insulating layer was used to equip the chamber and maintain a larger temperature difference (50 ºC) between ambient (20 ºC) and internal environment (70 ºC) of reaction system (**Extended Data Fig. 7**). As a result, the temperature of sample was maintained at ~70 ºC under the concentrated light intensity (3800 mW cm^{-2}). We would like to further mention that this proof-of-concept demonstration can be further improved in the design and implementation of practical systems. **Extended Data Fig. 6 and Extended Data Fig. 7** have been revised in the manuscript. The corresponding discussions are shown in **Line 99-103 and 106-111**.



Extended Data Fig. 6 (b) STH of Rh/Cr_2O_3/Co_3O_4-InGaN/GaN NWs under different light intensities at 70 ºC.



Extended Data Fig. 7. Self-heated photocatalytic OWS system. (a) Self-heated photocatalytic OWS system. **(b)** Schematic parameters of self-heated photocatalytic OWS system. Thermodynamic parameters of reaction system **(c)** without and **(d)** with heat insulating layer. The heat insulating layer (thickness of ~0.5 cm) consisted of ordinary A4 printing paper. The wall thickness of Prexy chamber was ~0.3 cm. A thermal transfer balance existed in our system during photocatalytic reaction, which was influenced by the thermal conductivity coefficients of materials used in the reaction system. The thermal conductivity coefficients of Prexy glass, heat insulating layer and water were 1143, 50 and 600 mW m^{-1} K^{-1}, respectively. In the absence of heat insulating layer, the temperature of water in chamber was maintained at ~50 ºC. However, with the addition of low thermal-conductivity heat insulating layer, the temperature of reaction system could be increased to ~70 ºC under the same IR input (428 mW). The role of the heat insulating layer is to produce a larger temperature difference between ambient and internal environment of reaction system, thus leading to an optimal temperature of ~70 ºC in the reaction system. Pure and tap water were used as the water source in the photocatalytic water splitting.

(c) For outdoor test, a higher resistance on light intensity can effectively decrease the materials cost per irradiated area in the large-scale hydrogen production. In the indoor test, we have demonstrated that the STH is independent of light intensity in a certain range at ~70 ºC. Our photocatalyst wafer can work under a maximum light intensity (~16070 mW cm^{-2}), which is limited by the mechanical strength of silicon wafer. Thus, the light intensity of ~16070 mW cm^{-2} was used in the outdoor test. Besides, the optimal reaction temperature of 70 ºC obtained from indoor test was also used in the outdoor test.

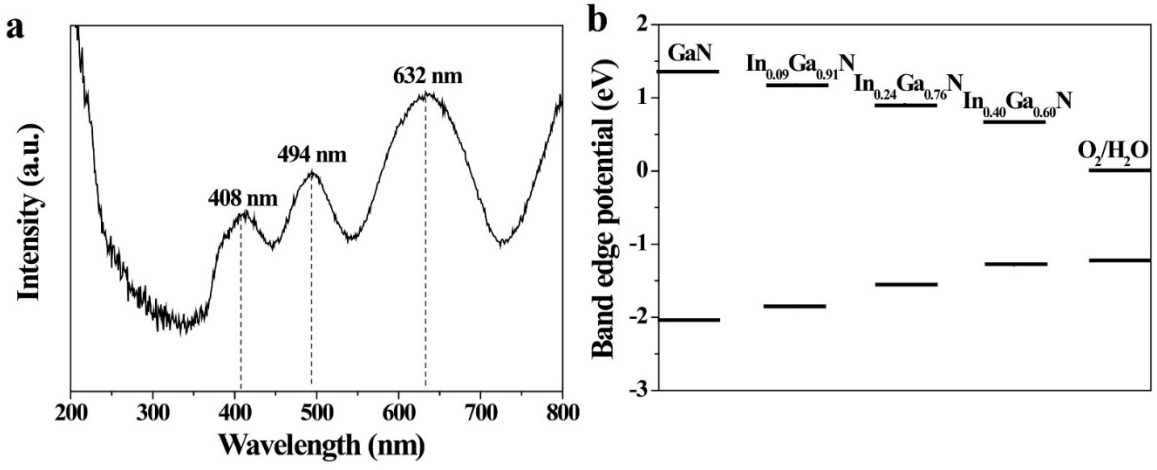
Q2: (a) I find the taxonomy is somewhat misleading: photocatalytic water splitting is usually used in the context of suspension of semiconducting particles, while here we deal with immobilized nano-wires, which would belong to photoelectrochemical water splitting. **(b)** Also, these nano-wire heterostructures are not properly characterized in the manuscript. Nowhere can I find the actual composition (or compositional range) of the InxGayN, an exact characterization of the junction, and a band diagram which explains better the band structure and bending in this particular heterostructures. If the authors are using the exact same material as described in the ACS Nano 2013 paper, that should be more clearly stated.

R2: Thank you for your comment. (a) While it is true that photocatalytic water splitting was first developed in the context of suspension of semiconductor particles, the taxonomy of photocatalytic and photoelectrochemical water splitting depends on the reaction conditions. The photocatalytic water splitting is free from any electrical wire, bias and conductive electrolyte. In contrast, the photoelectrochemical water splitting is conducted in an electrolytic tank. ***Besides, the materials used in photocatalytic water splitting are not limited to semiconducting particles. The semiconducting particles can also be coated onto the wafer to split water into hydrogen and oxygen, which is also noted as the photocatalytic water splitting (Nat. Mater. 2016, 15, 611-615 and Nat. Catal. 2019, 2, 387-399).*** Moreover, compared to the suspension of semiconducting particles, the photocatalyst wafer is easier to be instrumented, collected and separated from the water, which is beneficial to the practical operation.

The classification and comparison of photocatalytic and photoelectrochemical water splitting has been discussed in the revised manuscript (Please see **Line 29-35**).

(b) The actual composition of the $In_xGa_{1-x}N$ was calculated according to the experimental band gap and the reported formula (Appl. Phys. Lett. 2010, 96, 021908). The gradient In content along with *c*-axis direction of InGaN ranged from 0.09 to 0.40. The composition of InGaN nanowires in the present work was different from the previous work (ACS Nano 2013, **7**, 7886-7893) and a higher In content was achieved in the present InGaN/GaN nanowires. The band diagram of InGaN/GaN heterostructure was shown in **Extended Data Fig. 3b.** The results showed that the conduction band-edge potential was decreased with In content, while the valence band-edge potential was increased with In content. This is also consistent with the previous report (Appl. Phys. Lett. 2010, 96, 021908).

The analysis and discussion on the composition and band diagram of InGaN/GaN heterostructure has been discussed in the revised manuscript (Please see **Line 88-94 and Extended Data Fig. 3b**).



Extended Data Fig. 3. Light response characterization. (a) UV-vis diffuse reflectance spectroscopy

of InGaN/GaN suggests that the visible-light response range of InGaN/GaN nanostructures are extended to 632 nm (1.96 eV). **(b)** Band diagram of InGaN/GaN segments.

Q3: The authors indicate that there is a maximum efficiency demonstration of 3% (line 37) without providing a reference. Also, this limit is only valid for suspended photocatalysts or catalyst sheets, but not for multi-junction heterostructures, where efficiencies as high as 15-20% have been achieved (see an overview of the demonstrated efficiencies for photoelectrochemical water splitting here: Ager et al., Energy Environ. Sci., 8, 2811–2824 (2015); Tembhurne et al., Nat Energy, 4, 399–407 (2019); Kim et al., Chem. Soc. Rev., 48, 1908-1971 (2019); or an overview over photocatalytic demonstrations here: Fabian et al., Energy Environ. Sci., 8, 2825-2850 (2015)). The introduction needs to be rewritten and descriptions of their demonstration as "world record"/"highest reported value"/… need to be exchanged in the light of these already demonstrated efficiencies and anyway should be replaced by more scientific language and quantitative comparisons.

R3: Thank you for your comment. A maximum efficiency demonstration of ~3% in photocatalytic water splitting was shown in the literatures (ACS Energy Lett. 2018, 3, 2230 −2231 and Nat. Commun. 2018, 9, 1707). Really, a higher STH (10-15%) has been achieved in the PEC water splitting. However, PEC water splitting requires the use of highly conductive electrolyte, e.g., sulfuric acid, which severely limits the stability of these high efficiency devices to a few hrs in practical two-electrode configuration. The efficiency drops to negligible values when pure water, seawater, or tap water is utilized as the electrolyte. Moreover, there have been no demonstrations of high efficiency PEC water splitting under natural solar light. Compared to the PEC water splitting, the photocatalytic water splitting owns several critical advantages, e.g., the use of tap water, or seawater as demonstrated in this work. In our present work, we focused on the photocatalytic water splitting and highlighted the highest STH in the photocatalytic water splitting. In the statement of "world record", we specially noted that the STH was achieved with the photocatalytic method and for pH neutral water splitting in the revised manuscript.

Q4: The authors claim there is a "100% efficiency" (line 34) of the material, which is wrong and not precise (probably a quantum efficiency is meant here and should be properly defined, and efficiency and quantum yield should not be used interchangeably).

R4: Thank you for your comment. In the literature (Nature, 2020, 581, 411-414), an external quantum efficiency of up to 96 percent at wavelengths between 350 and 360 nanometer was reported, which is equivalent to an internal quantum efficiency of almost unity. This has been revised in the introduction. (Please see **Line 41-44**)

Q5: (a) The number in the introduction, for example, "… nearly 44% of solar light lies in the visible spectrum (400-700 nm)…" is wrong (a quick calculation based on the blackbody fractional function indicates 38% is in the visible [and even lower for the Am1.5 spectrum]) and misleading, given that one photon can only produce one electron-hole pair. **(b)** Furthermore, the indicated reference [12] is not suiting to support this number (ref [12] is discussing Si and luminescence, nothing that applies here). Probably better fitted are Shockley-Queisser's original paper or the paper by Fountaine et al., Nat. Com. (2016), both provide limit STH efficiencies for photocatalytic/photoelectrochemical applications.

R5: Thank you for your comment. (a) Based on the spectrum of solar light in **Extended Data Fig.**

4, we recalculated the light intensity in 400-700 nm region and theoretical maximum STH. Nearly 40% of solar light lies in the visible spectrum (400-700 nm), which can contribute to a theoretical maximum STH of 24% in the photocatalytic OWS.
(b) In the calculation of theoretical maximum STH, one photon can only produce one electron-hole pair. The relationship of band gap and theoretical maximum STH of photocatalyst under natural solar light and Xe lamp with AM1.5G filter was shown in **Extended Data Fig. 4.**
The related discussion and literature have been revised in the manuscript. (Please see **Line 44-45 and Extended Data Fig. 4**)

Q6: The materials (In, Ga, Rh) used in the demonstration are very rare (see abundance plot by the geological survey of the US) and the process (molecular beam epitaxy) is not scalable. The authors should comment on scalability, economics, practical and implementation problems with this system.
R6: Thank you for your comment. Though In and Ga are relatively expensive in some countries, their reserves are still large in the word. Especially, the high efficiency, long lifetime and mature production technology of InGaN photocatalyst can significantly reduce the use of indium-containing materials and further decrease the cost of solar hydrogen. As an example, indium has been widely used in LED lighting and the cost for LED light bulbs has decreased by nearly two orders of magnitude over the past two decades (https://www.osti.gov/servlets/purl/1163956), strongly suggesting that indium is not a limiting factor for the production of InGaN materials and devices.
Compared to photocatalyst InGaN, the content of cocatalyst Rh is very little (5.2 μg cm^{-2} or 0.54wt%). (Please see **Line 78-79**) The cost can be further reduced by utilizing atomic scale cocatalysts (Nature Communications, 2021, 12, 4412 and Nature Communications, 2017, 8, 1490) and/or by developing earth abundant co-catalysts (Chem. Soc. Rev., 2014, 43, 7787-7812 and Science, 2015, 347, 970-974). In this work, molecular beam epitaxy is used for the growth/synthesis of InGaN photocatalyst nanostructures since this is the tool available in our lab. It is noticed that similar nanostructures can also be readily synthesized utilizing chemical vapor deposition (CVD), sputter deposition, or even solution processing techniques, which can drastically reduce the cost for future commercial deployments. These discussions have been added in the revised manuscript. (Please see **Line 68-69**)

Q7: Generally, the OER and HER-selective catalysts seem to be applied uniform along the nano-wire (see figure 1), this is in contrast to earlier publications of the same group where a spatial separation between HER and OER was partially achieved by applying HER catalyst on top of the nano-wire only and OER catalyst on bottom only. The authors need to comment on this difference and its implication.
R7: Thank you for your comment. We think the reviewer may be referring to our earlier publication (*Nature communications 9 (1), 1-9, 2018*). In that study, the HER and OER catalysts were spatially separated: they are deposited on the two opposite *side walls* (lateral surfaces) of the nanowires. This spatial separation was defined by the unique photodiode geometry presented in the earlier work to help suppress charge carrier recombination.
Firstly, in the growth of our present materials, the bottom of InGaN/GaN nanowires directly contacts with the silicon substrate and the top is terminated with GaN segment. Secondly, according to the band diagram of GaN/InGaN in the revised **Extended Data Fig. 3b**, the heterojunction-type change transfer along with *c*-axis is not possible. Instead, the side surface of all InGaN segments below GaN were exposed to water. Hence, the top or bottom of InGaN segments did not directly contribute to the surface catalytic reaction. As the previously reported spatial separation between HER and OER on nanowires,

it easily suffers from a longer charge-transfer distance (the length of nanowires) before the hole-electron reach the surface (top or bottom), which undesirably increases the possibility of the electron-hole recombination. In contrast, the side surface of InGaN nanowires is the main reaction region. Thus, the charge transfer distance in our materials is decreased to the diameter scale of nanowires. Hence, the two approaches own their different advantages and disadvantages.

Q8: (a) The nano-wire reproducibility or uniformity seems very low. According to the authors, their band gaps range between 445 and 545 nm. What composition does this result in? Why is there such a large variation? Is this beneficial or not for the application? It is even argued that materials with band gaps of 632 nm are present. The authors should explain that if we have such a large variation of nano-wire types, is one of them current limiting? **(b)** Also, given that it is argued that we have a dual junction (InGaN and GaN), what are the theoretical maximum efficiencies, and if they are in series, which junction is limiting?

R8: Thank you for your comment. (a) The various band gaps in InGaN nanowires originated from the well-designed gradient In doping along with *c*-axis direction. According to the composition and band diagram of InGaN/GaN nanowires in **Extended Data Fig. 3b,** no Z-scheme or other heterojunction-type charge transfer exist in the multi-band InGaN structure. However, compared to a single-band photocatalyst, the multi-band photocatalyst can produce more active photogenerated electrons and holes since the redox ability of photogenerated electrons and holes are determined by the valence and conduction band-edge potentials of photocatalyst. Please kindly note the multi-band concept here is different from the multi-junction design in photoelectrochemical water splitting. In our multi-band design, each band (segment) functions independently for solar water splitting. For example, in **Extended Data Fig. 3b**, when InGaN nanowires only consist of $In_{0.4}Ga_{0.6}N$ segment with low band gap (1.96 eV), all available photons, including some high-energy photons, can only produce some low energy (hence less active) photogenerated electrons and holes. In contrast, when InGaN nanowires only consist of $In_{0.09}Ga_{0.91}N$ segment with high band gap (3.04 eV), only few high-energy photons can be absorbed. However, in the multi-band InGaN structure, the highly active charge carriers and the wide visible-light response range can be simultaneously achieved. (Please see **Line 88-93 and Extended Data Fig. 3b**)

(b) Based on the above band diagram (**Extended Data Fig. 3b**), the different InGaN segments could not form the most reported heterojunction or Z-scheme charge transfer. Instead, it was considered that the different InGaN segments independently worked in the charge separation/transfer. According to the obtained lowest band gap (1.96 eV) of InGaN segment in **Extended Data Fig. 3**, the theoretical maximum efficiency is calculated to be 17.7% under natural solar light and 31.1% under simulated solar light from Xe lamp with the incorporation of an AM1.5G filter illustrated in **Extended Data Fig. 4**.

Q9: (a) The temperature effect is only associated to increased reaction temperature and enhanced mass transfer (line 101), however there is also a negative effect from recombination in the semiconductor. This should be included in the discussion, which might better explain the "optimal" performance at 70°C. **(b)** I am not sure about the physical limit for OER with increasing temperature, what is the authors explanation (from a mechanistic point of view) that OER is limited by temperature (i.e. not further increasing beyond 70°C)?

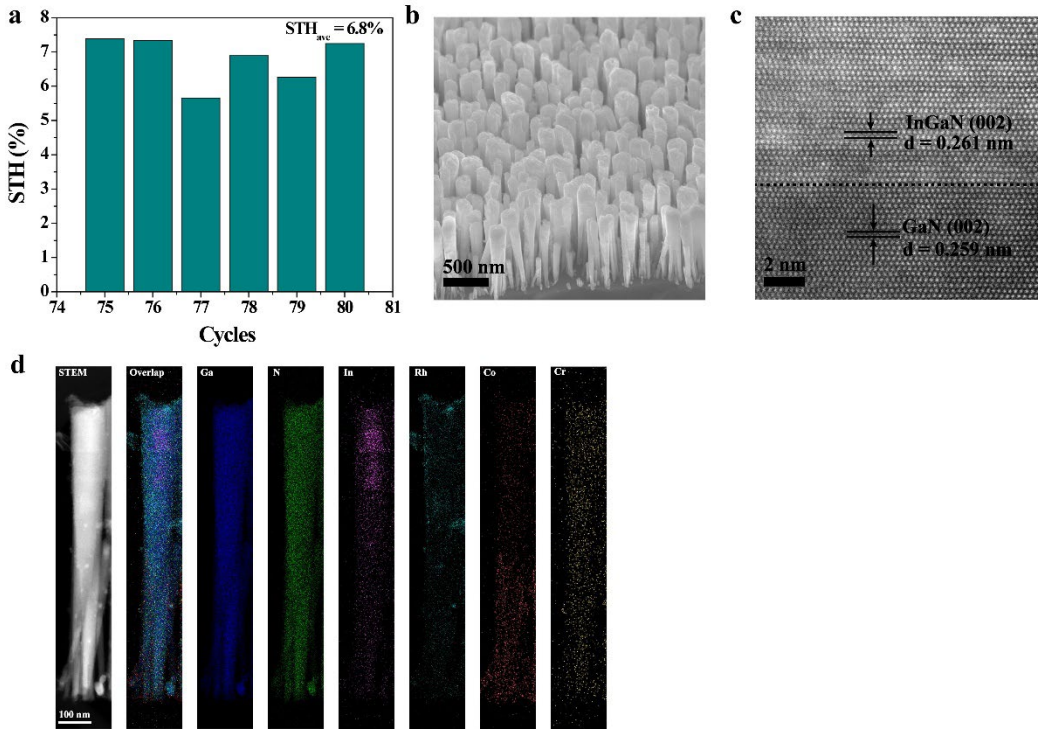
R9: Thank you for your comment. (a) As suggested by the reviewer, an excessively high temperature

can promote the non-radiative recombination of photogenerated electrons and holes in the semiconductor photocatalyst, which also contributes to an optimal temperature at 70 ºC. (Please see **Line 178-180**)

(b) Compared to HER, the OER owns a higher energy barrier in the surface catalytic process. Though improving temperature can accelerate the mass transfer between catalyst surface and water, it produces little effect on the formation of O-O bond with high energy barrier which is commonly considered as a rate-determining step in the overall water splitting (Catal. Lett., 2015, 145, 95-108 and J. Am. Chem. Soc. 2018, 140, 3264-3269). Hence, when the temperature is higher than a certain point (70 ºC), the mass transfer may no longer be the limiting factor. Instead, the formation of O-O bond in the surface catalytic OER, together with enhanced nonradiative recombination in the semiconductor, limits the further improvement of STH, as suggested by the reviewer. (Please see **Line 134-138**)

Q10: It is argued that the system is stable by utilizing one SEM picture (extended data fig. 8), without any quantification or elemental analysis support. This is insufficient as an argument and a better and quantitative way needs to be introduced to argue stability.

R10: Thank you for your comment. We have added the high-resolution STEM and elemental mapping of the sample after stability test in the revised supporting information. (Please see **Extended Data Fig. 9**) The results show that InGaN still maintained the high crystallinity and the cocatalysts $Rh/Cr_2O_3/Co_3O_4$ were still distributed on the nanowires. Especially, we found that the STH activity of photocatalyst after 74-hour was decreased by 26% in a further test. The decrease in the STH activity was attributed to the loss of cocatalyst according to the ICP test (**Extended Data Table 1**).



Extended Data Fig. 9. Stability evaluation. (a) Activity test after 74-hour photocatalytic OWS reaction. **(b)** FESEM, **(c)** HAADF-STEM and **(d)** elemental mapping of $Rh/Cr_2O_3/Co_3O_4$-InGaN/GaN NWs after 80-hour photocatalytic OWS reaction.

Q11: The authors argue that there is a "temperature control" strategy. I cannot find a controller that is ensuring the temperature is maintained (for example for the outside experiment, how is the temperature "controlled"?). I believe the word "control" or "controlling" used in the manuscript is not properly used. The temperature is maybe monitored, but there is no active handling that maintains this temperature.

R11: Thank you for your comment. In our work, we firstly used a heated circulator to connect with the double-layer chamber and investigated the temperature effect on STH (**Extended Data Fig. 5**). In this method, the reaction temperature was controlled and varied by the heated circulator. Based on the temperature-controlled OWS experiments, we found that 70 ºC was the optimal temperature for OWS. In order to maintain the reaction system at 70 ºC in the absence of heated circulator, we coated a suitable heat insulating layer (ordinary A4 printing paper) with the thickness 0.5 cm on chamber in this proof-of-concept demonstration, which could maintain the reaction system at 70 ºC (**Extended Data Fig. 7**). In this design, only sunlight was used as the energy source. Similarly, we also used a suitable heat insulating layer (ordinary A4 printing paper) with a thickness 0.3 cm on the chamber for outdoor test, which could also maintain the large-scale reaction system at ~70 ºC. In order to avoid the misunderstanding, we avoided the use of word "control" or "controlling" in the revised manuscript. In addition, we would like to mention that this proof-of-concept demonstration can be readily improved, optimized, and implemented in future solar hydrogen devices and systems to help transform a low efficiency operation to achieve high efficiency solar hydrogen fuel production.

Q12: What are the partial pressures of hydrogen and oxygen in the headspace (is there inert/sweep gas)?

R12: Thank you for your comment. The partial pressures of hydrogen and oxygen in the headspace increased with the reaction time. The average partial pressures of hydrogen and oxygen can reach 24.2 and 11.9 kPa after one-hour reaction in the stability test, respectively. The inert/sweep gas was not used in the test. The produced hydrogen and oxygen were manually sampled from the headspace of chamber by using a vacuum-tight syringe.

Q13: (a) I am not fully following their dark recombination experiment. Hydrogen's viscosity and diffusivity is significantly higher than for oxygen. **(b)** Can it be that the system is simply not tight enough? What is the pressure loss in 24h in the system? Is it the same for hydrogen and oxygen? Is there residual oxygen in the system? How was the system purged? All this should be detailed in the methods part. Also, when reporting hydrogen and oxygen in the recombination experiments (fig 2c and ex. data fig 11), these curves should show relative changes in hydrogen or oxygen (not absolute values).

R13: Thank you for your comment. (a) In the dark hydrogen-oxygen recombination experiments, the hydrogen and oxygen in gas phase were firstly diffused into the water and then recombine on the surface of catalyst. Really, the different viscosity and diffusivity of hydrogen and oxygen can influence the rate of stoichiometric hydrogen-oxygen recombination. Especially, the diffusion of gas in water is commonly lower than that in gas phase. Hence, the diffusivity of hydrogen and oxygen in water is one of the most important factors determining the hydrogen-oxygen recombination rate. Considering the stoichiometric ratio of 2:1 in hydrogen-oxygen recombination, a higher hydrogen diffusivity is considered to promote hydrogen-oxygen recombination. Especially, the diffusivity coefficient is two-fold higher than that of oxygen (Chemical Engineering Science, 1984, 39, 1535-1541), which can

effectively contribute to the stoichiometric hydrogen-oxygen recombination. Thus it is not strange that the dark hydrogen-oxygen recombination can greatly decrease the efficiency of photocatalytic water splitting. (Please see **Line 173-176**)

(b) Our reaction chamber was sealed via a vacuum-tight quartz lid and a vacuum-tight plastic ring. The vacuum-tight plastic ring together with the vacuum-tight quartz lid could maintain the pressure without change in more than one week. Besides, in the whole test process, the hydrogen and oxygen were gradually decreased with time at an approximate stoichiometric ratio of 2:1 after the light was removed (please see the revised **Fig. 2c**), implying significant chemical hydrogen-oxygen recombination. The gas leaking could also be excluded under vacuum condition. Besides, no additional nitrogen peak from air was found during test. All experimental details have been added into the methods part. (Please see **Line 246-250 and 252-256**)

Q14: In line with my previous comment, only when we see the relative recombination, we could maybe conclude that higher temperatures are reducing recombination and therefore the temperature effect is mostly inhibiting oxygen-hydrogen recombination (and it is not simply the higher production rates or improved mass transport). But in general, I believe the given empirical arguments are not sufficient to truly conclude that temperature is suppressing hydrogen-oxygen recombination. I believe an order of magnitude prediction (by theoretical calculations) of the temperature effect (positive or negative) due to kinetics, mass transport, semiconductor recombination, oxygen-hydrogen recombination etc. should be given to support the temperature argument.

R14: Thank you for your comment. The hydrogen-oxygen recombination has been an argued topic in the photocatalytic OWS. For the mechanism of temperature-dependent hydrogen-oxygen recombination, we specially added the DFT calculations on kinetics of hydrogen-oxygen recombination to explain it in the revised manuscript. As shown in **Fig. 2d**, we investigated the whole reaction pathway of hydrogen-oxygen recombination on cocatalyst Co_3O_4, Rh and Cr_2O_3. The results suggested that most steps in the hydrogen-oxygen recombination on cocatalyst were typically exothermal. Hence, increasing the temperature of reaction system can desirably inhibit this hydrogen-oxygen recombination on Rh cocatalyst. Besides, the desorption of product water was the rate-determining step in hydrogen-oxygen recombination. Especially, the reaction energy (0.11 eV) of water desorption on Rh was remarkably less positive than those on Co_3O_4 (1.03 eV) and Cr_2O_3 (0.97 eV). This also implied that water tended to be adsorbed on Co_3O_4 and Cr_2O_3, which inhibited the further hydrogen-oxygen recombination on them. Hence, Rh was the main hydrogen-oxygen recombination center, which also theoretically demonstrated previous report (Angew. Chem. Int. Ed., 2006, 45, 7806-7809). Hence, improving temperature can effectively reduce the hydrogen-oxygen recombination kinetics. The DFT discussion of temperature effect on hydrogen-oxygen recombination has been added into the revised manuscript. (Please see **Line 164-172**)

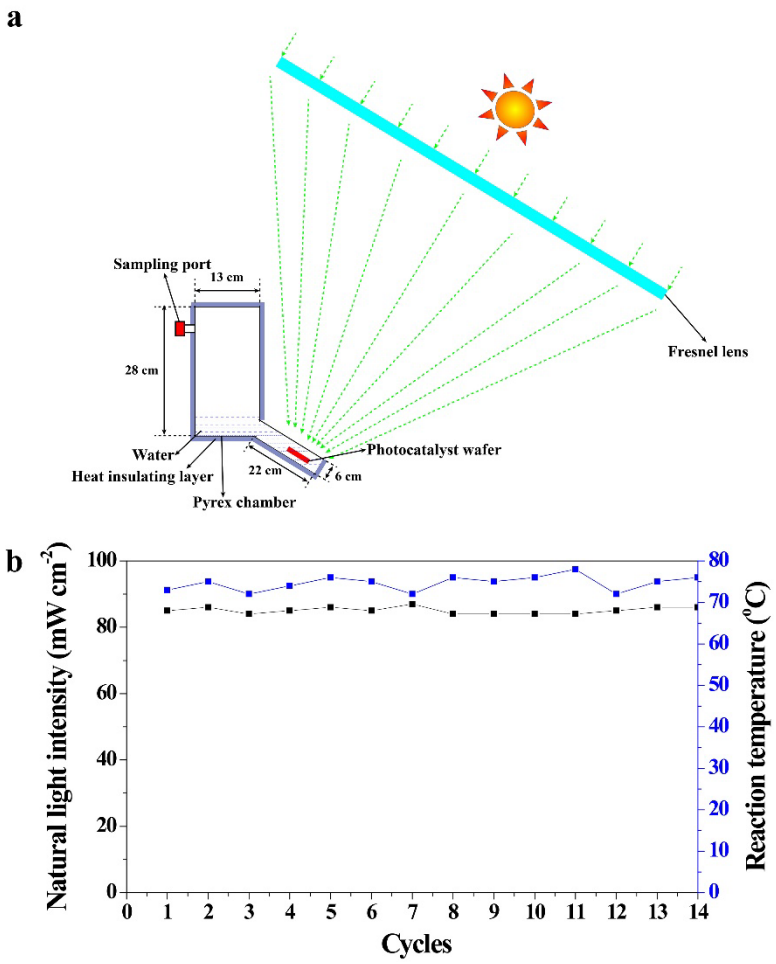
Besides, the mass transfer of hydrogen and oxygen is also one important factor determining the rate of the hydrogen-oxygen recombination. Improving temperature from 20 ºC to ~70 ºC can increase the diffusivity coefficient of hydrogen and oxygen in water by more than two times (Chemical Engineering Science, 1984, 39, 1535-1541), which greatly enhance the mass transfer in hydrogen-oxygen recombination. Thus, improving temperature can also improve the hydrogen-oxygen recombination by promoting mass transfer of hydrogen and oxygen. Hence, it is not strange that an optimized reaction temperature was obtained at 70 ºC. (Please see **Line 173-176**)

We also agree with the reviewer that, with increasing temperature, charge carrier recombination may

become more important, which also partly explain the reduced efficiency for temperatures above 70°C. Based on our previous studies on the quantum efficiency of GaN-based nanostructures, an increase of temperature from room temperature (~20 °C) to 70°C can lead to an increase of nonradiative recombination by ~20% (Nanotechnology, 2012, 23, 194012). (Please see **Line 178-181**) Thus, the above temperature effect synergistically contributes to an optimal temperature at 70 ºC. A detailed model considering all the chemical, physical, optical, electrical, catalytic, and thermal processes involved in the reaction is being studied and will be reported in the future. These discussions have been added in the revised manuscript.

Q15: What is "slightly lower" (line 146) or "relatively large scale" (line 147)? Please add quantitative statements. This is true throughout the manuscript.
R15: Thank you for your comment. We have revised those statements in the whole manuscript to make it clearer. (For example, please see **Line 194-195**)

Q16: Figure 3b: what is the intensities in this 140-minute experiment? What is the corresponding measure temperature? And especially, by how much is the temperature vary as a result of varying irradiation (the manuscript reports 75 +/- 3°C, but is this averaged over 140 minutes at constant intensities)?
R16: Thank you for your comment. In the outdoor test, we specially conducted the experiments between 11 pm and 3 pm from Nov. 5, 2020 to Nov. 7, 2020 at University of Michigan, Ann Arbor, Michigan, United States. The detailed temperature and light intensity in each cycle were summarized in **Extended Data Fig. 13b.** The results showed that the natural light intensity and temperature were maintained at ~85 mW cm^{-2} and ~75 ºC, respectively.



Extended Data Fig. 13. Photocatalytic OWS under natural concentrated solar light. (a) Schematic parameter illustration of outdoor photocatalytic OWS system. **(b)** Reaction temperature and natural light intensity in the outdoor test. The thickness of heat insulating layer (ordinary A4 printing paper) and wall of chamber were ~0.5 cm and ~0.3 cm, respectively. The outdoor photocatalytic OWS was conducted from Nov. 5, 2020 to Nov. 7, 2020. The average natural solar light intensity was determined to be ~85 mW cm^{-2} between 11 pm and 3 pm by a thermopile detector (919P, Newport) with a 5 cm^2 detector.

Q17: The authors need to comment on the effect of irradiation concentration, and particularly the effect of different concentrations (3800 mW/cm2 indoors and 16070 mW/cm2 outdoors). The changing concentration will result in different current densities / production rates and therefore also different losses. All of this needs to be discussed and quantified. Also, the choice of these two concentrations seems arbitrary. How are they chosen and hat is the effect of varying concentrations? The arguments behind the design choice and the concentration choice needs to be detailed in the manuscript.

R17: Thank you for your comment. We have investigated the effect of light intensity on STH in the revised manuscript. As shown in **Extended Data Fig. 6**, the temperature of reaction system was firstly maintained at 70 ºC by a heated circulator to exclude the temperature effect. The STH showed little change in the light intensity range of 13 suns and 38 suns. This indicated that the light intensity of concentrated solar light was not a determining factor on STH. Combining with above analysis, the system temperature produced an observable effect on STH. Besides, it should be noted that the light

intensity of 38 suns (3800 mW cm^{-2}) was the maximum we could achieve in our current indoor testing, which was also the reported highest light intensity in the indoor photocatalytic water splitting. To further decrease the materials cost per irradiated area in the large-scale reaction system, a higher light intensity (16070 mW/cm^2) produced by a Fresnel lens under natural solar light was adopted in the outdoor test because 16070 mW/cm^2 was the maximum allowable light intensity due to the limitation of our present reaction system. Those have been discussed in the revised manuscript. (Please see **Line 106-111 and 196-202**)

Q18: (a) The thermal mass of the system (volume of solution) is important for the thermal response of the system (temperature). This should be discussed in the manuscript. **(b)** Also, the reported temperature, is this uniform throughout the solution or along the nanowires? Or how much variation is there? Are we sure that all surfaces see the same temperature? Please provide quantitative arguments in the manuscript.

R18: Thank you for your comment. We specially maintained the system at a uniform temperature by using Pyrex glass, heat insulating layer and water. A thermal transfer balance existed in our system, which was influenced by the thermal conductivity coefficients of materials used in the reaction system. The thermal conductivity coefficients of Pyrex glass, heat insulating layer and water are 1143, 50 and 600 mW m^{-1} K^{-1}, respectively. In the absence of heat insulating layer, the temperature of water in chamber was only maintained at ~50 ºC (**Extended Data Fig. 7c**). However, with the addition of low thermal-conductivity heat insulating layer, a larger temperature difference (50 ºC) between ambient (20 ºC) and internal environment (70 ºC) of reaction system could be obtained (**Extended Data Fig. 7d**).

(b) In the reaction chamber, water could provide a stable environment for thermal transfer and balance. During reaction, the surface of wafer (70.7 ºC) and water (70.4 ºC) were examined to own nearly the same temperature (**Extended Data Fig. 7a)**. We have also performed detailed thermal analysis of GaN nanowires on Si substrate and have shown that the temperature distribution of GaN nanowires and the underlying Si substrate remain nearly identical in our past work (IEEE Journal of Quantum Electronics, 2014, 50, 483-490).

The above results and discussions have added into the revised **Extended Data Fig. 7.**

Q19: The proposed system is a batch type water splitting system. The authors need to comment on the practicability of batch type versus a continuous flow type system. The latter is more likely to be implemented in practice. Do they expect the same suppression of hydrogen-oxygen recombination in a continuous flow reactor type (given the mass, charge and heat transfer is different)?

R19: Thank you for your comment. Really, a continuous flow type system is a practical method. In the present work, we mainly investigated the physicochemical mechanism of photocatalytic OWS and further demonstrated the feasibility of using the revealed mechanism to improve the STH of a batch type system. We believe that the hydrogen-oxygen recombination still exists in the continuous flow type system since the produced hydrogen and oxygen will be full of chamber under atmospheric pressure before they are transferred or stored to other space. This will lead to a high-concentration hydrogen and oxygen in the chamber. The higher concentrations of oxygen and hydrogen will lead to the stronger recombination according to the time-course production and recombination of stoichiometric H_2 and O_2 (**Fig. 2c** and **Extended Data Fig. 12**). Besides, according to DFT calculation

(**Fig. 2d**), the adsorptions of O_2 and H_2 on Rh are the chemical process with the adsorption energy of >1.5 eV, which cannot be effectively solved by the physical method. Hence, the finding in the present batch type system can guide or provide an insight to improve the performance of some continuous flow type systems. This discussion has been added in the revised manuscript. (Please see **Line 140-151**)

Referee #4 (Remarks to the Author):

This paper by Zhou et al. demonstrates the successful application of overall water splitting into hydrogen and oxygen in a very simple reactor configuration. This study achieves literally the game changing results, introducing high impact of temperature dependence on the photocatalytic water splitting performance. High quality InGaN photocatalyst nanorods were developed by molecular beam epitaxy. This photocatalyst had 1.2 micron in length and 100 nm in width. This dimension is considered excellent for photon absorption in vertical direction, and charge separation in lateral direction. Using this type of semiconductor, photocatalytic overall water splitting has been demonstrated by Kibria et al., as cited in this paper. Excellent electrocatalyst modification is also achieved, which was already demonstrated by Domen and coworkers; namely Rh/CrOx core/shell hydrogen evolving catalyst and CoOx oxygen evolving catalyst. These electrocatalysts were deposited on InGaN by photodeposition, following the protocol of UV-responsive SrTiO3 photocatalyst in the recent Nature paper 2020.

The breakthrough finding by this study is established that this device shows much appreciable performance only at high temperatures (70 °C) and reaches >9 % solar to hydrogen (STH) energy efficiency. Efficiency is correctly calculated where the rate of production matches with the reported values. This temperature rise can be easily achieved in the proposed photoccatalyst system where concentrated solar light (up to 160 times AM 1.5 G sun equivalent) utilizing infrared part of photons. This temperature effects with high activation energy mean that the photocatalytic performance at low temperatures is limited by electrocatalytic performance, in contrast to semiconductor charge separation efficiency. This is very reasonable at high performances. Using sacrificial electron donor/acceptor, it is clear that OER by CoOx is limiting the overall performance, which is again reasonable from the previous works. The photocatalytic stability is excellent: this is somewhat surprising as the electrocatalytic conversion corresponding to this performance exceeds 200 mA cm−2, but under this electrolysis in conventional device, the CoOx may not be this stable. The difference may come from nanoscale electrolysis where pH gradient is minimal as well as solution resistance (enabling pure water can be used). The movie provided in the supplementary file is convincing enough to confirm the high performance of water splitting. Conclusions are well supported by the experimental evidence.
Overall, the paper shows excellent achievement and the game-changing concept in this paper.
R: Thank you for pointing out the significance of this study.

The following are some aspects to improve further the clarity of this work.

Q1: **(a)** Would it be possible to provide the content of Rh, Cr and Co amount on the GaInN semiconductor? **(b)** As a water splitting device, it is rather astonishing that CoOx OER electrocatalyst can sustain its performance over 200 mA/cm2 equivalent current density. This extreme stability reported in this study may originate from nanoscale electrochemistry that minimizes pH gradient and solution resistance, which are different from classical PV+E (photovoltaic + electrolyze) system.
R1: Thank you for your comment.
(a) The contents of Rh, Cr and Co have been added into the revised manuscript. (Please see **Extended Data Table 1**).
(b) Yes, we agree with the reviewer. In our present work, CoO_x cocatalyst was prepared in the nano

scale which owned the higher activity and stability than the conventional large-scale electrode used in electrolyzers. For example, we found that our materials with nano size structure could work in the simulated sea water, which showed a STH of 6.6% in a 10-hour test (See the following Figure). Besides, the addition of electrolyte easily accelerates the deactivation of cocatalyst or photocatalyst in conventional photoelectrochemical water splitting devices, due to the corrosion effect of ions from electrolyte. Hence, it is not unexpected that a 200 mA/cm^2 equivalent current density can be observed in pure water splitting. The discussion has been added into the revised manuscript. (Please see **Line 188-195**)

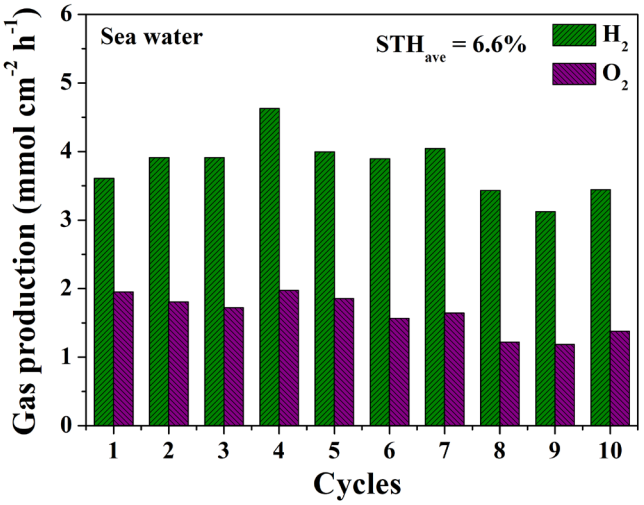


Fig. 3b. STH of Rh/Cr_2O_3/Co_3O_4-loaded InGaN/GaN nanowires in simulated sea water (3.5wt% NaCl aqueous solution). The intensity of simulated solar light from 300 W Xe lamp equipped with AM1.5G filter was 3800 mW cm^{-2}. Sample size: 0.64 cm^2. Each cycle: 1 hour.

Q2: Tap water experiment is indeed interesting to report, but it lacks scientific reasoning of performance loss. Analysis of impurities (halogens, heavy metals, etc.) is probably helpful. Enhanced back reaction, loss in Faradaic efficiency, surface poisoning, etc. It would be interesting to know if the loss is recoverable or irreversible.

R2: Thank you for your comment. Analysis of impurities are shown in the water quality report 2020 of Ann Arbor. Compared to the reaction in pure water, the water splitting in tap water shows a decreased lifetime and activity, which is considered from the poisoning effect of impurity ions, such as undesirable adsorption of ions on the catalytic active sites. That phenomenon has also been reported previously (Angew. Chem. Int. Ed. 2020, 59, 232–236 and J. Phys. Chem. C 2018, 122, 13797− 13802). Some of the impurities in tap water also leads to the loss of co-catalyst particles, or detachment of nanowires from Si substrate, which can be addressed by further stabilizing the co-catalyst nanoparticles and nanowires on the substrate. In addition, we have performed studies and showed that by re-depositing co-catalyst nanoparticles on the nanowire surface, the activity can be recovered (Journal of Materials Chemistry A, 2019, 7, 27612-27619). In the current stage, we mainly focus on investigating the effect of hydrogen-oxygen recombination on OWS and demonstrates that the proposed temperature-promotion strategy can also be used in tap water.

More minor comments

Q3: The efficiency values of 9.17% (and those in other places) have too many digits in contrast to its measurement accuracy. This fundamental aspect is important as it reflects the quality of the work. At least the title should consist of more appropriate designation, such as >9% or over 9% STH efficiency.
R3: Thank you for your comment. This has been revised in the whole manuscript.

Q4: In Abstract, "a large-scale photocatalytic system" gives 6.21% STH, but it requires to report explicit dimension of the photoreactor used in this study.
R4: Thank you for your comment. we have designed and developed a large-scale photocatalytic water splitting system with a natural solar light capacity of 257 W on a 4 cm × 4 cm photocatalyst wafer for photocatalytic OWS. In the outdoor experiments, a Fresnel lens was adopted to form the concentrated solar light (~16,070 mW cm^{-2}) on the 4 cm × 4 cm photocatalyst wafer, which could maintain the insulating layer-coated chamber at the optimized temperature (75±3 ^{o}C) in the outdoor photocatalytic OWS studies (**Extended Data Fig. 13 and Extended Data Video 1**). (Please see **Line 21-23**)

Reviewer Reports on the First Revision:

Referee #2 (Remarks to the Author):

In the revised version, the authors are clearer about the advantages of their system and the contribution of their work in many aspects. For example, they state now clearly that they compare performance within photocatalytic systems, excluding photoelectrochemical (PEC) and photovoltaics/fuel cell (PV) coupled systems, which are discussed in literature in the context of solar hydrogen generation and show higher performances than photocatalytic systems (Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G). There is no doubt that the authors made a significant contribution to advancing photocatalytic water splitting by demonstrating that higher temperatures are beneficial for reaching higher STH efficiencies.
However, I have still concerns about the claim that the authors´ results are a showcase for practical application of solar water splitting (abstract) and "guide the design and application of future large-scale solar hydrogen production systems". Although the authors addressed my concerns regarding the abundance and availability of In, I was not convinced by their answer that LEDs are a widely spread commodity. Small In containing chips are included in LEDs, a fact, which already stretches the limits of the In reserves to the extent that it is a critical element for the EU for example. This doesn´t make a case for using more InGaN for large scale energy production facilities as proposed by the authors. I was also not convinced by their argument that the system cost of this InGaN based photocatalytic (PC) system is low because it is a photocatalytic system. Lewis et al. Energy Environ. Sci., 2016, 9, 2354-2371 refers to the comparison of PEC and PV systems. PC systems are not discussed. Domen et al. Nature Catalysis, 2019, 2, 387–399 refer to oxide based catalysts which consist of mainly abundant elements and are produced by scalable cheap solid state chemical methods, which is very different from this work where MBE is used. The cost of waver production and InGaN MBE deposition is probably closer to the production cost of a PV device than of oxide particles produced by solid-state chemistry. Considering the argument given by Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G) that there is a relation between cost of the device and minimal STH efficiency in order to be economically viable, this system should have a efficiency close to PV devices to be economically viable, which is not the case. For these reasons I don´t think that the presented system is a good design guideline for future energy systems.
Detailed comments:
Abstract: I think that it is not correct to call other approaches to solar fuel production like photoelectrochemical water splitting "conventional". Photocatalytic systems, photoelectrochemical and the combination photovoltaics/fuel cells are under research, while the latter is the most advanced and already at demonstrator level.

Referee #4 (Remarks to the Author):

I have read the revised contribution with great interest and found that the authors addressed the concerns of this reviewer well. The paper is recommended for publication.
Only minor suggestions:
Line 15 pH neutral water => pure water (without electrolyte)

Line 31 basic => alkaline

Referee #5 (Remarks to the Author):

A. The authors report photocatalytic splitting of pure water (i.e. without external bias or electrolyte) on a InGaN/GaN nanowire photocatalyst modified with a Rh/Cr2O3 cocatalyst for hydrogen evolution, and a Co3O4 cocatalyst for oxygen evolution. Record-high solar-to-hydrogen efficiencies are claimed. This is particularly an effect of the higher temperature, and less an effect of the concentrated light. It must be noted that I have not reviewed the original version; instead, I received the revised article with the three reviewer reports of the original version.

B. As mentioned by the authors themselves, similar materials have been studied before. Indeed, the STH is very high, which is a novel observation worth reporting. In line with the comments or the previous Reviewer #2 (and somewhat also with Reviewer #1), I am hesitant to wholehearted recommend publication of the article, because some of the thermodynamic and kinetic fundamentals are not fully clear to me. I can recommend publication only if also the function of the material at the elevated temperature is properly explained.

C. The validity of the approach is all in all approved; however, some experiments appear to be missing. The data is presented very well, but some of the conclusions appear to be drawn on incomplete data sets or with ignorance of fundamental thermodynamics. Furthermore, important experimental detail is lacking.

D. not applicable.

E. The revised version is certainly significantly improved compared to the original version. However, some conclusions are still doubtful, such as the relative importance of light and heat. It may even be doubted that it is a light-driven reaction at all. Is there any hydrogen and oxygen evolution in the dark? Why was the light concentration not decreased to less than 13 suns? There must be a decrease in activity somewhere. Furthermore, the applicability of ground-state thermodynamics should carefully be checked: Other than classical catalysis, photocatalysis is not dependent on the position of the thermodynamic equilibrium, because the involvement of the excited state and the spatial separation of the reduction and oxidation reaction also enable reactions with positive deltaG (endergonic). Otherwise, water splitting (or CO2 reduction) would not be possible to a significant extent at room temperature (or slightly above) anyway. So arguing with the thermodynamic equilibrium is questionable, as will be outlined below.

F. The following issues should be considered:
(i) What was the pressure in the cell before the start of the experiment? If it was not vacuum, which gas was in the cell? If the cell was under vacuum, the nice bubbles in the video could just be evaporating water. If there was inert gas in the cell, has the temperature-related change in pressure been taken into account when calculating the yields of H2 and O2 (via the ideal gas law?).
(ii) How does the hydrogen (and oxygen) productivity behave at 70°C if the light intensity is more

and more decreased? It must decrease at some point. How does a dark experiment look like? Is pure thermal catalysis an option?
(iii) In regard to (ii), the authors should present an equilibrium curve of the water splitting equilibrium (in the dark) as a function of temperature. If the amount of hydrogen is in excess with respect to the equilibrium at the given conditions (T, p), there must be some photo-effect. Furthermore, does the concentration obtained in the dark approach the equilibrium? Only then can the authors argue with an effect of temperature on the extend of recombination (because far from equilibrium, kinetics would be dominant).

G. Appropriate.

H. Appropriate, subject to the corrections suggested above.

All in all, I think the article MAY reach a publishable state, but the experimental conditions and thermodynamic correlations must be clarified.

Referee #6 (Remarks to the Author):

I am aware that this manuscript has been reviewed previously by other referees. Hence, I'll split up my comments on the changes made by the authors in the latest version, those bits of the manuscript highlighted in yellow, and other bits of the manuscript, where I'll start with the former:

-) When comparing photocatalysis and photoelectrocatalysis on page 2 the authors write "Instead, fresh water, or seawater can be readily split into H2 and O2 via photocatalytic OWS without any external bias/circuitry, which can significantly reduce the system cost and mitigate photocatalyst corrosion, stability, and safety related issues". While I am sympathetic to the case of photocatalysis I wonder if this argument is as solid as the authors make it out to be, especially when it comes to system cost and safety. In photoelectrocatalysis, H2 and O2 production is spatially separated and in photocatalysis not. Would that not mean that the system cost in the case of photocatalysis would be potentially lower because there is no need for "leads" but higher because of the need for H2/O2 separation? Also, in terms of safety, are these H2/O2 mixture not potentially a safety issue, absent in the case of photoelectrocatalysis?

-) Following on from the point above, I agree with the authors that comparing photocatalysis with photoelectrocatalysis is nonsensible and that aiming to achieve a high %STH for photocatalysis is a laudable goal. I also think that the fact that the materials used are based on scarce elements is not relevant at this stage. Demonstration of high %STH with photocatalysts will drive work (from others), achieving the same but with materials based on more abundant elements.

-) I also agree with the authors in their reply to Q2 of referee 3, that the system studied here is clearly photocatalytic instead of photoelectrocatalytic. Yes, the photocatalyst is supported on a 2D substrate, like a photoelectrode, but both half reactions take place on the same photocatalyst, there are not leads, and no external applied bias.

-) Looking at the recent literature, see e.g., ACS Energy Lett. 2022, 7, 1043−106, the here reported %STH is considerably higher than previously reported for any photocatalytic system. Yes, higher %STH values have been reported for photoelectrocatalytic or photoelectrocatalytic + PV systems but as mentioned above comparing these values with that reported here feels like comparing cows and chickens.

-) Mechanistically overall water splitting is a combination of a large number of (photo)physical and chemical steps and hence it would be difficult to exactly understand the origin of any temperature dependence. I think the results in Extended Data Fig. 11 are convincing in terms of the temperature dependence of two half-reactions in isolation (in an ideal world I think data points at 90 degrees C would have made it even stronger) and I think the same holds for the overall data in Fig. 2A. The microscopic explanation of all three trends in terms of the dark back reaction sound sensible, which should be enough at this stage.

-) I cannot find any of the results of the DFT calculations other than the numbers quoted on page 5/6 of the main text and Figure 2D, which is so small that it's difficult to read of the results. I would have expected to see more (tabulated) data in the supporting information, as well as figures showing relevant structures. I would also have expected that the geometries of all relevant structures to be present in a machine-readable form as additional supporting information (e.g., as a zip file of POSCARs).

And my more general comments:

-) Is it possible to estimate what would happen to the %STH if one would also take into account the energetic cost of H2/O2 separation? I appreciate this might be difficult or not even tractable to calculate but more generally I wonder if there might be cases where a system would look better in %STH when excluding the energetic cost of separation but worse when including this? This is relevant when comparing photocatalysis and photoelectrocatalysis, which as discussed above probably would differ in the extent H2/O2 need to be separated.

-) I don't have access to reference 41 but do all the data in Extended Data Fig. 3B come from reference 41? The authors might want to add this to the caption of Extended Data Fig. 3B, as well as some information of how this data was obtained to put it in to context.

-) It might be me but defining TOF and TON values for heterogeneous catalysts is a bit odd as a lot of the catalyst material is far from the surface where the catalysis by definition takes place.

-) The equations on page 9 are oddly formatted, should probably use a division slash (/), and use a non-standard symbol for wavelength (L instead of lambda). The latter is especially confusing as L is normally used for the dimension length (which has the same units as wavelength) or the unit Litre.

-) In the Temperature-controllable photocatalytic OWS, Extended Data Fig. 5, does the water needs to be heated up for all temperatures in the temperature-dependent data (Extended Data Fig. 11 & Fig. 2A) or are their temperatures that require the reactor to be cooled down to achieve?

Overall, I think that if these (remaining) issues are addressed, this manuscript should be suitable for publication. I also think that the science in the manuscript is very interesting and the results relevant and novel.

Author Rebuttals to First Revision:

Referee #2:

Q1: In the revised version, the authors are clearer about the advantages of their system and the contribution of their work in many aspects. For example, they state now clearly that they compare performance within photocatalytic systems, excluding photoelectrochemical (PEC) and photovoltaics/fuel cell (PV) coupled systems, which are discussed in literature in the context of solar hydrogen generation and show higher performances than photocatalytic systems (Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G). There is no doubt that the authors made a significant contribution to advancing photocatalytic water splitting by demonstrating that higher temperatures are beneficial for reaching higher STH efficiencies. However, I have still concerns about the claim that the authors´ results are a showcase for practical application of solar water splitting (abstract) and "guide the design and application of future large-scale solar hydrogen production systems". Although the authors addressed my concerns regarding the abundance and availability of In, I was not convinced by their answer that LEDs are a widely spread commodity. Small In containing chips are included in LEDs, a fact, which already stretches the limits of the In reserves to the extent that it is a critical element for the EU for example. This doesn´t make a case for using more InGaN for large scale energy production facilities as proposed by the authors. I was also not convinced by their argument that the system cost of this InGaN based photocatalytic (PC) system is low because it is a photocatalytic system. Lewis et al. Energy Environ. Sci., 2016, 9, 2354-2371 refers to the comparison of PEC and PV systems. PC systems are not discussed. Domen et al. Nature Catalysis, 2019, 2, 387–399 refer to oxide based catalysts which consist of mainly abundant elements and are produced by scalable cheap solid state chemical methods, which is very different from this work where MBE is used. The cost of waver production and InGaN MBE deposition is probably closer to the production cost of a PV device than of oxide particles produced by solid-state chemistry. Considering the argument given by Kim et al. Chem Soc Rev. (DOI 10.1039/C8CS00699G) that there is a relation between cost of the device and minimal STH efficiency in order to be economically viable, this system should have an efficiency close to PV devices to be economically viable, which is not the case. For these reasons I don´t think that the presented system is a good design guideline for future energy systems.

R1: Thank you for your comment.

First, besides the high STH in our present work, another important advantage of our photocatalytic system is the use of concentrated sunlight (**160 suns**). Thus, the cost and amount of photocatalyst materials per irradiated area in our system can be reduced by **160 times** compared to those reaction systems using one sun (Domen et al. Nature Catalysis, 2019, 2, 387–399). (Please see **Line 233-235** in the revised manuscript.) Besides, the light intensity used in most PEC systems is one sun (Energy Environ. Sci. 2015, 8, 3, 166-3172) or lower than 12 suns (Science, 1998, 280, 425-427). Moreover, the thickness of photocatalyst layer consisting of uniform InGaN nanowires grown on silicon wafer in our work is only ~1 μm in height, which is significantly lower than the values (~10 μm) in some known PV devices consisting of oxide particles produced by solid-state chemistry (Nature, 2021, 598, 304-307 and Nature Materials, 2016, 15, 611-615), which can also decrease the amount of photocatalyst materials in the reaction. Furthermore, the low content and high light intensity can also contribute to the high TOF (24,063 h^{-1}) and TON (56,148) of InGaN under 160 suns, which can effectively reduce the cost of materials. (Please see **Line 237-239** in the revised manuscript.) Additionally, the use of high light intensity can decrease the size of reaction chamber, which can further reduce the complexity and cost of the whole system.

Second, besides MBE, the economical CVD technology has also been developed for the more scalable, lower cost synthesis of III-Nitride nanostructures, including InGaN nanowires (Journal of Crystal Growth, 2013, 370, 311–313 and Journal of Alloys and Compounds, 2009, 467, 472–476), which can also decrease the preparation cost of InGaN nanomaterials.

Third, the PC system, as presented in this work, does not involve the use of membrane, special electrolyte, or electrical wire components, thereby leading to significantly lower cost than PEC or PV-E systems.

In addition, **as Referee #6 stated, "I also think that the fact that the materials used are based on scarce elements is not relevant at this stage. Demonstration of high %STH with photocatalysts will drive work (from others), achieving the same but with materials based on more abundant elements."** Hence, we believe that the above features of our system can make a significant contribution to the future development of practical solar hydrogen-production systems. To avoid any confusion, we have changed "guide the design and application of future large-scale solar hydrogen production systems" to "offer a path for the design and application of future large-scale solar hydrogen production systems". (Please **Line 242**)

Q2: Abstract: I think that it is not correct to call other approaches to solar fuel production like photoelectrochemical water splitting "conventional". Photocatalytic systems, photoelectrochemical and the combination photovoltaics/fuel cells are under research, while the latter is the most advanced and already at demonstrator level.

R2: Thank you for your comment. We have revised it in the manuscript. (Please see **Line 12**)

Referee #4:

I have read the revised contribution with great interest and found that the authors addressed the concerns of this reviewer well. The paper is recommended for publication.

Q1: Only minor suggestions:

Line 15 pH neutral water => pure water (without electrolyte)

Line 31 basic => alkaline

R1: Thank you for your comment. We have revised it in the manuscript. (Please see **Line 18 and 34**)

Referee #5:

A. The authors report photocatalytic splitting of pure water (i.e. without external bias or electrolyte) on a InGaN/GaN nanowire photocatalyst modified with a Rh/Cr2O3 cocatalyst for hydrogen evolution, and a Co3O4 cocatalyst for oxygen evolution. Record-high solar-to-hydrogen efficiencies are claimed. This is particularly an effect of the higher temperature, and less an effect of the concentrated light. It

must be noted that I have not reviewed the original version; instead, I received the revised article with the three reviewer reports of the original version.

R: Thank you for your comment.

B. As mentioned by the authors themselves, similar materials have been studied before. Indeed, the STH is very high, which is a novel observation worth reporting. In line with the comments or the previous Reviewer #2 (and somewhat also with Reviewer #1), I am hesitant to wholehearted recommend publication of the article, because some of the thermodynamic and kinetic fundamentals are not fully clear to me. I can recommend publication only if also the function of the material at the elevated temperature is properly explained.

R: Thank you for your comment. The corresponding thermodynamic and kinetic information have been explained in **Response E and F** below. For a stable catalytic reaction, the thermodynamic and kinetic change before and after reaction only occurs in the reaction environment due to the production of new chemicals. In the present photocatalytic water splitting with continuous light irradiation and stable reaction temperature, the production of hydrogen and oxygen from the chemical water splitting directly increase the Gibbs free energy (+237000 J mol^{-1}) of the system. Besides, the production of gaseous hydrogen and oxygen increases the pressure of reaction environment (Please see **Extended Data Table 2**), which can also theoretically change the Gibbs free energy of system. However, this deltaG from those physical processes, only ~1% respective to the Gibbs energy change for chemical water splitting reaction (Nature Catalysis, 2019, 2, 387–399), is insignificant for the whole Gibbs free energy change of system compared to the chemical water splitting. Hence, the thermodynamic and kinetic changes mainly depend on the chemical water splitting process. It should be noted that the improved reaction temperature by infrared light cannot directly contribute to the energy storage into hydrogen due to the high energy uphill process in water splitting (**Extended Data Fig. 6f**). However, the improved reaction temperature can indirectly influence the production rate of hydrogen by inhibiting hydrogen-oxygen recombination.

C. The validity of the approach is all in all approved; however, some experiments appear to be missing. The data is presented very well, but some of the conclusions appear to be drawn on incomplete data sets or with ignorance of fundamental thermodynamics. Furthermore, important experimental detail is lacking.

R: Thank you for your comment. The corresponding information has been explained in the below **Response E and F**.

D. not applicable.

E. The revised version is certainly significantly improved compared to the original version. **(i)** However, some conclusions are still doubtful, such as the relative importance of light and heat. It may even be doubted that it is a light-driven reaction at all. Is there any hydrogen and oxygen evolution in the dark? **(ii)** Why was the light concentration not decreased to less than 13 suns? There must be a

decrease in activity somewhere. **(iii)** Furthermore, the applicability of ground-state thermodynamics should carefully be checked: Other than classical catalysis, photocatalysis is not dependent on the position of the thermodynamic equilibrium, because the involvement of the excited state and the spatial separation of the reduction and oxidation reaction also enable reactions with positive deltaG (endergonic). Otherwise, water splitting (or CO2 reduction) would not be possible to a significant extent at room temperature (or slightly above) anyway. So arguing with the thermodynamic equilibrium is questionable, as will be outlined below.

R: Thank you for your comment.

(i) Firstly, we have experimentally shown that hydrogen and oxygen evolution cannot be produced in the dark at 70 ^{o}C, which is reasonable since the Gibbs free energy of overall water splitting is up to 237000 J mol^{-1}. The thermochemical water splitting requires a reaction temperature of at least 500-1800 ^{o}C (Energy Conversion and Management, 2022, 205,112182). In our work, the UV-visible light is responsible for the photoexcitation of photocatalyst, while heat contributed by IR light can inhibit hydrogen-oxygen recombination. This data and discussion have been added into **Extended Data Fig. 6f and Line 180-182.**

(ii) Considering the advantage of high light intensity on reducing the cost of materials, we mainly focused on the concentrated sunlight (>13 suns). We have further tested the activity under a lower light intensity (10 suns) and observed a reduced STH at the same temperature (70 ^{o}C). This means that a light intensity in a certain low range can influence the STH. The underlying reasons include variations of surface recombination, charge carrier separation efficiency, and radiative recombination with light intensity, which has remained a subject of study in the photocatalytic field (Catal. Lett. 2015, 145, 95–108 and Nature materials, 2012, 11, 1044-1050). The activity under 10 suns has been added into **Extended Data Fig. 3d and Line 117-120.**

(iii) The ground-state thermodynamics in the photocatalytic water splitting can be divided into two parts: photocatalyst and reaction environment. In the present water splitting, the reaction temperature is maintained at a constant. Photocatalyst is used to produce the excited electrons and holes for the redox reaction of water. After reaction, photocatalyst is regenerated and returns to the ground state. Hence, the thermodynamics of photocatalyst remains unchanged before and after reaction. However, due to the production of gas products, the thermodynamics of reaction environment will be changed. The chemical production of hydrogen and oxygen directly contributes to a deltaG (237000 J mol^{-1}). Besides, the pressure of reaction environment will be improved due to the production of gaseous products (Please see **Extended Data Table 2**). However, Domen et al. (Nature Catalysis, 2019, 2, 387–399) have revealed that the energy change associated with the physical process of hydrogen and oxygen production corresponds to only ~1% with respect to deltaG for the overall water splitting reaction. Hence, this physical deltaG on pressure in the present stable water splitting cannot produce the significant effect on the whole photocatalytic water splitting. Instead, the chemical deltaG (237000 J mol^{-1}) is significant for photocatalytic overall water splitting. We added those pressure parameters before and after reaction at different temperatures in the revised manuscript (Please see **Extended Data Table 2**).

F. The following issues should be considered:

(i) What was the pressure in the cell before the start of the experiment? If it was not vacuum, which gas was in the cell? If the cell was under vacuum, the nice bubbles in the video could just be evaporating

water. If there was inert gas in the cell, has the temperature-related change in pressure been taken into account when calculating the yields of H2 and O2 (via the ideal gas law?).

(ii) How does the hydrogen (and oxygen) productivity behave at 70°C if the light intensity is more and more decreased? It must decrease at some point. How does a dark experiment look like? Is pure thermal catalysis an option?

(iii) In regard to (ii), the authors should present an equilibrium curve of the water splitting equilibrium (in the dark) as a function of temperature. If the amount of hydrogen is in excess with respect to the equilibrium at the given conditions (T, p), there must be some photo-effect. Furthermore, does the concentration obtained in the dark approach the equilibrium? Only then can the authors argue with an effect of temperature on the extend of recombination (because far from equilibrium, kinetics would be dominant).

R: Thank you for your comments.

At the start of the experiment, the chamber pressure was 31.2 kPa. Due to existence of water, water vapor contributes to the pressure in the chamber. The detailed pressures before and after the reaction have been described in **Extended Data Table 2**. No additional inert gas was added into chamber (please see **Line 387-388**). In the whole reaction process, the pressure was always lower than 1 atm (101 kPa), which could approximately satisfy the ideal gas law. Besides showing the dynamic production of gas, the given video in our work is also used to demonstrate the high stability of photocatalyst materials without desorption or degradation on silicon wafer under strong bubble production and high light intensity, which is often difficult to previously reported photocatalyst materials working under one sun (Nature, 2021, 598, 304-307 and Nature Materials, 2016, 15, 611-615). We have performed further studies to confirm that the major contribution to the most bubbles shown in the video is from hydrogen and oxygen, instead of water vapor, as described below.

- Control experiments under identical conditions except light illuminations showed that there was virtually no bubble formation (please see the **Extended Data Video for Referee #5**).
- Moreover, we also used a low-intensity 365 nm LED (beam size ~0.5 cm × 0.5 cm, and power density of 200 mW cm^{-2}) to check the production of hydrogen and oxygen on photocatalyst wafer. The low-intensity 365 nm LED (200 mW cm^{-2}) cannot produce heating effect on photocatalyst wafer, which can exclude the production of water vapor. In the photocatalytic water splitting at 70 ºC, this LED could also contribute to the observable production of bubbles consisting of hydrogen and oxygen, which only occur on the irradiated region (Please see the **Extended Data Video for Referee #5**). This result can demonstrate the high activity of our materials.

(ii) As shown in **Extended Data Fig. 3d,** the results showed that the STH was not observably changed in the range of 13-38 suns under the same temperature (70 ºC). However, when light intensity was lower 13 suns, a reduced STH was observed under 10 suns. Due to the limitation of reaction system and lab safety, the light intensity of 38 suns was the highest value we could achieve in our lab. In the dark test, we could not observe any hydrogen and oxygen since the uphill water splitting has a high deltaG (237000 J mol^{-1}). (Please see **Extended Data Fig. 6f**) Typically, the thermochemical water splitting requires a reaction temperature of 500-1800 ºC in most cases (Energy Conversion and Management, 2022, 205,112182).

(iii) According to the response of **Extended Data Fig. 6f**, no hydrogen or oxygen was produced in the dark.

G. Appropriate.

H. Appropriate, subject to the corrections suggested above.

All in all, I think the article MAY reach a publishable state, but the experimental conditions and thermodynamic correlations must be clarified.

Referee #6:

I am aware that this manuscript has been reviewed previously by other referees. Hence, I'll split up my comments on the changes made by the authors in the latest version, those bits of the manuscript highlighted in yellow, and other bits of the manuscript, where I'll start with the former:

Q1: When comparing photocatalysis and photoelectrocatalysis on page 2 the authors write "Instead, fresh water, or seawater can be readily split into H2 and O2 via photocatalytic OWS without any external bias/circuitry, which can significantly reduce the system cost and mitigate photocatalyst corrosion, stability, and safety related issues". While I am sympathetic to the case of photocatalysis I wonder if this argument is as solid as the authors make it out to be, especially when it comes to system cost and safety. In photoelectrocatalysis, H2 and O2 production is spatially separated and in photocatalysis not. Would that not mean that the system cost in the case of photocatalysis would be potentially lower because there is no need for "leads" but higher because of the need for H2/O2 separation? Also, in terms of safety, are these H2/O2 mixture not potentially a safety issue, absent in the case of photoelectrocatalysis?

R1: Thank you for your comment. For H_2/O_2 separation, Domen et al. has demonstrated that the economical hollow polyimide fiber membrane could separate hydrogen (purity exceeding 94% excluding water vapor) from mixed hydrogen and oxygen under a safe condition (Nature, 2021, 598, 304-307). Besides, Pinaud et al. also conducted a techno-economic analysis of the cost of hydrogen produced by various types of photocatalytic and photoelectrochemical systems, including hydrogen/oxygen separation, which suggested a lower system cost of photocatalytic water splitting system. Moreover, besides the high STH efficiency in our present work, our photocatalytic system can use the high-intensity sunlight (**160 suns**). Thus, the cost and amount of photocatalyst materials in our system can be reduced by **160 times** compared to those reaction systems using one sun (Domen et al. Nature Catalysis, 2019, 2, 387–399). (Please see **Line 233-235** in the revised manuscript) Additionally, the use of high light intensity can decrease the size of reaction chamber, which can further reduce the complexity and cost of whole system, compared to photoelectrocatalysis.

Q2: Following on from the point above, I agree with the authors that comparing photocatalysis with photoelectrocatalysis is nonsensible and that aiming to achieve a high %STH for photocatalysis is a laudable goal. I also think that the fact that the materials used are based on scarce elements is not

relevant at this stage. Demonstration of high %STH with photocatalysts will drive work (from others), achieving the same but with materials based on more abundant elements.

R2: Thank you for your comment. The high-intensity sunlight (**160 suns**) used in our system can greatly decrease the cost of materials per irradiated area.

Q3: I also agree with the authors in their reply to Q2 of referee 3, that the system studied here is clearly photocatalytic instead of photoelectrocatalytic. Yes, the photocatalyst is supported on a 2D substrate, like a photoelectrode, but both half reactions take place on the same photocatalyst, there are not leads, and no external applied bias.

R3: Thank you for your comment.

Q4: Looking at the recent literature, see e.g., ACS Energy Lett. 2022, 7, 1043−106, the here reported %STH is considerably higher than previously reported for any photocatalytic system. Yes, higher %STH values have been reported for photoelectrocatalytic or photoelectrocatalytic + PV systems but as mentioned above comparing these values with that reported here feels like comparing cows and chickens.

R4: Thank you for your comment.

Q5: Mechanistically overall water splitting is a combination of a large number of (photo)physical and chemical steps and hence it would be difficult to exactly understand the origin of any temperature dependence. I think the results in Extended Data Fig. 11 are convincing in terms of the temperature dependence of two half-reactions in isolation (in an ideal world I think data points at 90 degrees C would have made it even stronger) and I think the same holds for the overall data in Fig. 2A. The microscopic explanation of all three trends in terms of the dark back reaction sound sensible, which should be enough at this stage.

R5: Thank you for your comment.

Q6: I cannot find any of the results of the DFT calculations other than the numbers quoted on page 5/6 of the main text and Figure 2D, which is so small that it's difficult to read of the results. I would have expected to see more (tabulated) data in the supporting information, as well as figures showing relevant structures. I would also have expected that the geometries of all relevant structures to be present in a machine-readable form as additional supporting information (e.g., as a zip file of POSCARs).

R6: Thank you for your comment. The corresponding tabulated data and structures have been added into the revised manuscript. (Please see **Extended Data Fig. 7** and **Extended Data Table 4**)

And my more general comments:

Q7: Is it possible to estimate what would happen to the %STH if one would also take into account the energetic cost of H2/O2 separation? I appreciate this might be difficult or not even tractable to calculate but more generally I wonder if there might be cases where a system would look better in %STH when excluding the energetic cost of separation but worse when including this? This is relevant when comparing photocatalysis and photoelectrocatalysis, which as discussed above probably would differ in the extent H2/O2 need to be separated.

R7: Thank you for your comment. Domen et al. (Nature Catalysis, 2019, 2, 387–399) have revealed that the minimum energy loss associated with the separation of hydrogen and oxygen corresponds to 1.1% with respect to the Gibbs energy change for the overall water splitting reaction. Besides, Domen et al. has also demonstrated the feasibility of hydrogen/oxygen separation (Nature, 2021, 598, 304-307). Hence, the hydrogen/oxygen separation will not be a challenge in the practical application of solar hydrogen production. Instead, how to improve the stability of photocatalyst materials will be the important topic in the photocatalytic water splitting.

Q8: I don't have access to reference 41 but do all the data in Extended Data Fig. 3B come from reference 41? The authors might want to add this to the caption of Extended Data Fig. 3B, as well as some information of how this data was obtained to put it in to context.

R8: Thank you for your comment. Band diagram of InGaN/GaN segments in in Extended Data Fig. 3B were calculated according to reported formula (*Am. Mineral.* **85**, 543-556 (2000)):

$$E_{CB} = \chi + E_O - 0.5E_g$$

where E_{CB}, χ and E_g are the conduction band-edge potential, absolute electronegativity and band gap of $In_xGa_{1-x}N$, respectively. E_O is one constant (-4.5 eV) which stands for the Fermi level of normal hydrogen electrode at 25 °C with respect to the vacuum level. The valence band-edge potential (E_{VB}) can be directly calculated by the following formula:

$$E_{VB} = E_{CB} - E_g$$

The above calculation details have been added into the caption of **Extended Data Fig. 2**.

Q9: It might be me but defining TOF and TON values for heterogeneous catalysts is a bit odd as a lot of the catalyst material is far from the surface where the catalysis by definition takes place.

R9: Thank you for your comment. For some catalytic reaction, such as thermocatalysis and electrocatalysis, the reaction rate mainly depends on the number of active surface sites in catalyst. Thus, it is expected that the number of active surface sites is often used in the calculation of TOF and TON. However, for photocatalytic reaction, the reaction rate is not only determined by the number of active surface sites, but also the photogenerated electrons and holes produced by the internal crystal structure of photocatalyst. Hence, we used the amount of whole photocatalyst materials in the calculation of TOF and TON, which can better evaluate the performance and utilization efficiency of photocatalyst materials. The use of TOF and TON for heterogeneous catalysts has also been reported previously by others (Green Chem., 2018, 20,3450–3456 and Mater. Chem. Front., 2018, 2, 7 96-806).

Q10: The equations on page 9 are oddly formatted, should probably use a division slash (/), and use a non-standard symbol for wavelength (L instead of lambda). The latter is especially confusing as L is normally used for the dimension length (which has the same units as wavelength) or the unit Litre.

R10: Thank you for your comment. We have corrected those in the revised manuscript. (Please see **Line 404-409**)

Q11: In the Temperature-controllable photocatalytic OWS, Extended Data Fig. 5, does the water needs to be heated up for all temperatures in the temperature-dependent data (Extended Data Fig. 11 & Fig. 2A) or are their temperatures that require the reactor to be cooled down to achieve?

R11: Thank you for your comment. In previous Extended Data Fig. 5 (**Extended Data Fig. 3a** in the revised manuscript), the water needs to be heated up for all temperatures in the temperature-dependent data (**Extended Data Fig. 6c, 6d & Fig. 2A**). Normally, without heat insulating layer, the reaction temperature is about 50 ºC under 38 suns (**Extended Data Fig. 6a**). Thus, the reaction temperature of <50 ºC in the double-layer chamber equipped with water circulator is obtained by cooling the chamber. In contrast, the reaction temperature of >50 ºC is obtained by heating the chamber, if there is double-layer insulation.

Overall, I think that if these (remaining) issues are addressed, this manuscript should be suitable for publication. I also think that the science in the manuscript is very interesting and the results relevant and novel.

Reviewer Reports on the Second Revision:

Referee #5 (Remarks to the Author):

In their newly revised version, most of the issues raised with respect to the previous version are now clear. I am particulatly grateful for the additional video, which clarifies bubble formation with light only. One issue remains to be clarified.

The water vapor pressure in the Extended Data Table 2 was only calculated, not measured. This, again, is a thermodynamic quantity, which would only be valid if the equilibrium with the vapor phase is established. If the reactor is evacuated initially, it may well be that water still evaporates once the light is switched on (due to heating of the reactor). In other words, the authors have to prove that the violent bubble formation they show in the video (the video initially submitted, not the video especially for me) is predominantly caused by rapid formation of H2 and O2, and not by rapid evaporation of water. One way to achieve this is to record an additional video under the same conditions, but without photocatalyst, i.e. with a blank wafer under the same irradiation conditions. Any bubbles formed then should result from evaporating water only.

Referee #6 (Remarks to the Author):

I have no comments anymore other than that based on the reply of the authors to comment F of reviewer 5, they are doing their water splitting experiments at reduced pressure. This is a crucial experimental detail as reducing the pressure will reduce the back reaction and increase the observed hydrogen and oxygen production rates. There is some mention of this in the methodology section "In the stability test of photocatalyst, the chamber was repeatedly vacuumized each hour to exclude the hydrogen and oxygen produced in the last cycle before the next cycle." and the actual pressure is reported in Extended Data Table 2 but I think the authors should be much clearer about this in the methodology section, such that the results are more reproducible and comparable. Related to this I am not sure Extended Data Table 2 is referenced anywhere in the manuscript.

Author Rebuttals to Second Revision:

Referee #5:

In their newly revised version, most of the issues raised with respect to the previous version are now clear. I am particulatly grateful for the additional video, which clarifies bubble formation with light only. One issue remains to be clarified. The water vapor pressure in the Extended Data Table 2 was only calculated, not measured. This, again, is a thermodynamic quantity, which would only be valid if the equilibrium with the vapor phase is established. If the reactor is evacuated initially, it may well be that water still evaporates once the light is switched on (due to heating of the reactor). In other words, the authors have to prove that the violent bubble formation they show in the video (the video initially submitted, not the video especially for me) is predominantly caused by rapid formation of H2 and O2, and not by rapid evaporation of water. One way to achieve this is to record an additional video under the same conditions, but without photocatalyst, i.e. with a blank wafer under the same irradiation conditions. Any bubbles formed then should result from evaporating water only.

Reply: Thank you for your comment. Water vapor bubbles are unavoidably produced in water splitting process under high light intensity, which is important for thermal equilibrium of reaction system. Firstly, the water vapor is produced on sample surface and then transferred to the gas phase of chamber. Finally, water vapor is converted into liquid water after contacting the wall of chamber. Meanwhile, the thermal energy from the liquefaction of vapor is transferred to wall of chamber, such as the process in **Extended Data Fig. 4**. This process maintains the reaction system in a thermal equilibrium. It should be noted that the reaction system can reach a thermal equilibrium in 2 mins. All videos were shot after thermal equilibrium. We have added two new videos (**Extended Data Video 2** and **Extended Data Video 3**) into the revised manuscript. One green filter was installed in the camera to reduce the effect of high light intensity on the observation. **Extended Data Video 2** is the dynamic process of gas (hydrogen, oxygen and water vapor) production on silicon-wafer-supported InGaN photocatalyst, corresponding to the inset in **Fig. 3c.** The control experiment with the production of sole water vapor by using pristine silicon wafer as sample is shown in **Extended Data Video 3**. We can find that the high light intensity can also produce vapor bubbles on silicon wafer. However, the production rate of bubbles on InGaN photocatalyst is observably higher than that on pristine silicon due to the additional hydrogen and oxygen production in the former. (Please see **Line 184-186** and **Extended Data Video 2** and **Extended Data Video 3**)

Referee #6:

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vacuumized each hour to exclude the hydrogen and oxygen produced in the last cycle before the next cycle." and the actual pressure is reported in Extended Data Table 2 but I think the authors should be much clearer about this in the methodology section, such that the results are more reproducible and comparable. Related to this I am not sure Extended Data Table 2 is referenced anywhere in the manuscript.

Reply: Thank you for your comment. **Extended Data Table 2** referenced in **Line 102**, which is used to describe the reaction condition. In addition, **Extended Data Table 2** was referenced in the Methodology section (**Line 373-374**). As suggested by the reviewer, we have added additional description of the reduced pressure in the methodology section to make it more clear. (Please see **Lines 367-369**: "Before the photocatalytic reaction, the chamber was vacuumized to a reduced pressure, which helps reduce the back reaction and to enhance the extraction of H_2 and O_2 produced in the reaction.")