

Fluorine-expedited nitridation of layered perovskite Sr₂TiO₄ for visible-light-driven photocatalytic overall water splitting

Corresponding Author: Professor Gang Liu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript from Yu et al. entitled “F-expedited nitridation of layered perovskite Sr₂TiO₄ for efficient photocatalytic overall water splitting under visible light” reports that nitridation of Sr₂TiO₄, could be improved, that is, the amount of N dopant incorporated into the Sr₂TiO₄ could be increased, by treating first with F, to create SrTiO₃F, which could be more effectively incorporate N during the nitridation. The authors also concluded that resulting of this fluorination-nitridation treatment the resulting photocatalysts are more active towards the overall solar water splitting reaching an AQE of up to 0.39% (at 420 nm). The manuscript is interesting, but neither the characterization is completely convincing, nor the results appear to be novel, since examples of fluorination and nitridation of these materials or very similar have been reported. Indeed, the overall performance is below the state of the art and, more importantly, the core idea of fluorinating the Sr₂TiO₄ has been reported before, in the field of photocatalysis. For instance, DOI: 10.1016/j.jchem.2020.03.025 revealed that the incorporation of Cr and F in the structure could result in an AQE of 1.16 % (at 420 nm), claiming the impact of the F in the strengthening of the built-in electric field. Overall, although the idea of performing a fluorination prior to the nitridation seems interesting, the result lack of the novelty required for publication in nature communications. Below I will discuss in detail some other specific weaknesses to be addressed by the authors prior submitting in a different journal they consider appropriate.

(1) Within the materials preparation, the best performing photocatalysts result from a “double” high temperature annealing treatment, whereas the control, nitridated samples only to one. It could be argued that the first high temperature treatment, even without the F-precursor, could affect the crystal structure and hence, the subsequent nitridation could result in an improved performance.

(2) The authors used TEM-EDX to evaluate the presence of N and F in the structure. Given the importance of such data, the authors should present other technique to determine the composition to corroborate that data.

(3) Following on the topic of the composition, a critical subject in this work, in page 9 the authors talk about, and specified the amount of oxygen vacancies. It is not clear how do they establish that. It seems the authors just took the EDX data from O, F, N and the missing oxygen was labelled as vacancies. A more consistent data to characterize the amount of O, F, and N is necessary.

(4) The authors used the PL intensity to support the claim that the recombination is higher in the case of the NF sample. However, both sample (N and NF) display a pretty distinct UV-Vis spectra, so, differences in the overall intensity could derived from the different absorption of incident or emitted light.

(5) To better define the role of the Fluor it could have been interesting to prepare an additional sample where the fluorination followed the nitridation, that could have revealed the actual role of the F intercalation. Likely, the fluorination plays a key role in the system, and although a larger amount of N is intercalated, the addition of F might be key. Maybe even if the N intercalated is low, the presence of F could boost the performance in a similar way.

Reviewer #2

(Remarks to the Author)

In this manuscript, an F-involved nitridation approach has been developed to introduce visible light sensitivity to a layered wide-band gap semiconductor, Sr₂TiO₄. This approach seems to be quite effective in bringing several desirable properties, such as strong visible light absorption, high N content, few defects, and most importantly, the activity for photocatalytic overall water splitting (POWS). The POWS activity is by far very challenging for a single-component semiconductor,

particularly under visible light. I think this manuscript made a large step forward in this area. I would like to recommend the publication of this manuscript, after some proper revisions to be addressed:

1. The F appears critical for a high N content in the nitridation product. The final F content in the Sr₂TiO₄-NF is much lower than the precursor Sr₂TiO₃F₂. How to understand the role of F if it is so volatile?
2. The authors argued that the POWS activity arises from fewer defects such as Ti³⁺. Some reports revealed that the Ti³⁺ might be good for high photocatalytic activity (<https://pubs.acs.org/doi/10.1021/nl404688h>; <https://pubs.acs.org/doi/10.1021/acscatal.3c04743>; etc.), the authors should give some comments on this issue.
3. A Ti oxyhydroxide layer has been deposited onto Sr₂TiO₄-NF, but the function of this layer has not been fully explained. The authors should elucidate the role of this Ti oxyhydroxide layer.
4. The stability analysis of the Sr₂TiO₄-NF is insufficient; XRD alone cannot resolve the changes at the sample surface. I suggest the authors collect more information on the Sr₂TiO₄-NF particles after POWS experiments.
5. Whereas this F-involved nitridation tactic is very interesting, it is not always easy to find a suitable fluorinated precursor. Can authors give some suggestions on the application of their strategy, because there are numerous wide-bandgap metal oxides?

Reviewer #3

(Remarks to the Author)

Photocatalytic overall water splitting is very promising for solar hydrogen production but is generally very difficult, especially under visible light and for a single type photocatalyst. Here, Yu et al reported a new type of layered perovskite that is active for photocatalytic overall water splitting under visible light. They developed a proper precursor Sr₂TiO₃F₂ that allows N/F codoping into Sr₂TiO₄ by a simple nitridation treatment. This NF-codoped Sr₂TiO₄ has an intense visible light absorption and good separation efficiency for photo-generated charges, which in turn, contribute to the activity for photocatalytic overall water splitting both under visible light and simulated sunlight. Overall, the findings in this manuscript are important, considering the fact that there are limited numbers of photocatalysts capable of overall water splitting. The samples in this work are sufficiently analyzed and the manuscript is well-written. I think this work is suitable for publication in Nature Communications. Here are some revision suggestions:

1. The defects play a vital role for the separation of photo-generated charges. How to understand the decrement of defect concentration when N/F is co-doped into Sr₂TiO₄? The authors should give some detailed explanation in the manuscript.
2. The precursor used for nitridation is critical here. Why Sr₂TiO₃F₂ has a wider bandgap than Sr₂TiO₄, considering their similar crystal structure? If F-containing precursor is useful, is it necessary to synthesize an F-rich precursor for nitridation every time? The authors should provide some suggestions on sample preparation in a more general sense.
3. Is Sr₂TiO₄ per se active for photocatalytic overall water splitting under simulated sunlight?
4. The prototype perovskite SrTiO₃ is very active for UV light driven overall water splitting. Previous reports showed that the cocatalysts, i.e. RhCrOy and CoOOH, are important. In this work, only RhCrOy is employed, what if CoOOH is also introduced? Have the authors attempted to deposit CoOOH onto Sr₂TiO₄-NF as an O₂-evolution cocatalyst?
5. The post-mortem analysis is not enough. The authors should provide additional characterizations such as SEM and XPS to verify the robustness of their sample.
6. If Ti oxyhydroxide serves merely as a protection layer, there shouldn't be an increment of the H₂/O₂ evolution. I think Ti oxyhydroxide should have additional functions, for instance, charge separation. Have the authors tested Ti oxyhydroxide alone as a photocatalyst?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have addressed the major concerns posed by the referee. I would suggest the authors to include a short comment in the main text about how the performance compared to the state of the art and include Figure R1 (from the Response to the Referees file) in the Supporting information.

Reviewer #2

(Remarks to the Author)

The authors have addressed what I am concerned about. Agree to accept.

Reviewer #3

(Remarks to the Author)

The authors have addressed fully my concerns. The revision can be accepted for publication in nature communications.

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Reviewer(s)' Comments to Author:

Reviewer #1:

The manuscript from Yu et al. entitled “F-expedited nitridation of layered perovskite Sr_2TiO_4 for efficient photocatalytic overall water splitting under visible light” reports that nitridation of Sr_2TiO_4 , could be improved, that is, the amount of N dopant incorporated into the Sr_2TiO_4 could be increased, by treating first with F, to create SrTiO_3F , which could be more effectively incorporate N during the nitridation. The authors also concluded that resulting of this fluorination-nitridation treatment the resulting photocatalysts are more active towards the overall solar water splitting reaching an AQE of up to 0.39% (at 420 nm). The manuscript is interesting, but neither the characterization is completely convincing, nor the results appear to be novel, since examples of fluorination and nitridation of these materials or very similar have been reported. Indeed, the overall performance is below the state of the art and, more importantly, the core idea of fluorinating the Sr_2TiO_4 has been reported before, in the field of photocatalysis. For instance, DOI: 10.1016/j.jchem.2020.03.025 revealed that the incorporation of Cr and F in the structure could result in an AQE of 1.16 % (at 420 nm), claiming the impact of the F in the strengthening of the built-in electric field. Overall, although the idea of performing a fluorination prior to the nitridation seems interesting, the result lack of the novelty required for publication in nature communications. Below I will discuss in detail some other specific weaknesses to be addressed by the authors prior submitting in a different journal they consider appropriate.

Response: We are very grateful for the reviewer’s comments! These useful comments are indeed very helpful for improving the quality of our work. We fully understand the reviewer’s concerns on the findings in this work, including the novelty of F-expedited nitridation measure, the performance of our materials compared to the state of the art, and the convincingness of the characterization. We would like to make some clarifications here:

(1). It is the first time to report an F-expedited nitridation measure on Sr_2TiO_4 which succeeds in photocatalytic overall water splitting (POWS) under visible light, to the

best of our knowledge. It should be pointed out that this concept is distinct from fluorination and nitridation alone because the products are structurally and/or compositionally different. For instance, the paper mentioned by the reviewer (DOI: 10.1016/j.jechem.2020.03.025) studied F-intercalated compound $\text{Sr}_2\text{TiO}_3\text{F}_2$ and its Cr-doped counterpart $\text{Sr}_2\text{Ti}_{1-x}\text{Cr}_x\text{O}_3\text{F}_2$, which differs both in the structure and composition from Sr_2TiO_4 and F/N-doped Sr_2TiO_4 studied in this work (Space group of $\text{Sr}_2\text{TiO}_3\text{F}_2$: $P 4/nmm$; space group of Sr_2TiO_4 : $I 4/mmm$). Therefore, there is no similar system or material reported yet. Moreover, the novelty of this work falls beyond the comparisons among existing systems and numerical values of the photocatalytic performance, but can be reflected from the following three aspects: (a) the unique F-expedited nitridation phenomenon. F elongates the Ti-O bonds which in turn, facilitates O/N exchange. This effect has not been reported yet and is critical to break the doping limit of nitridation ($< 1 \text{ atm}\%$). (b) The minimization of detrimental defects by F. Defects such as oxygen vacancies and Ti^{3+} hinder photocarrier migration and are rather difficult to be removed. The presence of F is quite effective in minimizing these defects therefore extending the toolbox for defect regulation. (c) The achievement of POWS under visible light. There are only a few compounds capable of single-component POWS under visible light (see **Figure R1** below) albeit hundreds of photocatalytic materials have been reported. More importantly, the POWS activity is achieved by a simple F-expedited nitridation of a conventional photocatalyst which implicates more POWS-active photocatalysts to be developed following the same strategy.

(2). The performance of the material studied in this work outcompetes or at least is comparable to the state of the art in terms of POWS under visible light. It must be pointed out that AQE of POWS should not be compared with AQE of water-splitting half reactions, as the reaction conditions are different (i.e. pure water for the former while sacrificial agent for the latter). For instance, the paper mentioned by the reviewer (DOI: 10.1016/j.jechem.2020.03.025) reported the AQE of water-splitting half reactions where sodium sulfite solution was used as the sacrificial agent to

scavenge the photo-generated holes. This has no comparability with the one studied in this work where pure water was used as the reactant. Actually, the POWS is much more challenging intrinsically than water-splitting half reactions, given the fact that there are only a few compounds capable of POWS under visible light but hundreds of compounds can do water-splitting half reactions. **Figure R1** below summarize the visible-light-active compounds for POWS reported. Our material outcompetes or at least is comparable to these compounds both in AQE and solar-to-hydrogen (STH) efficiency.

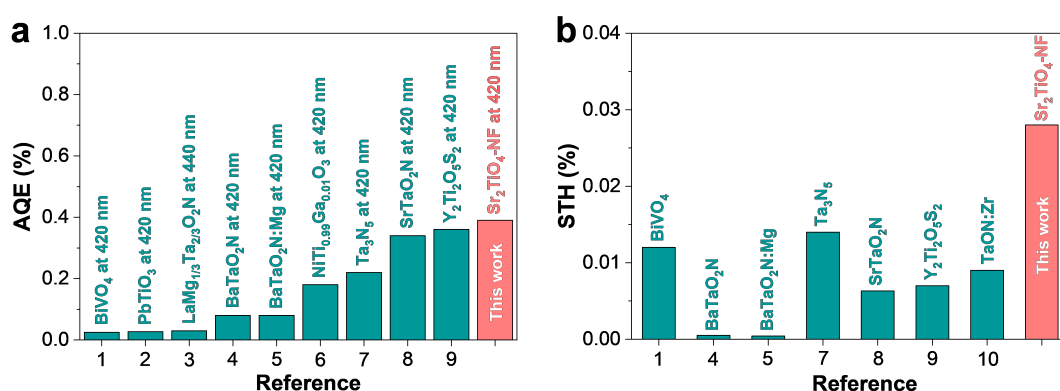


Figure R1. Comparisons of visible-light-active compounds reported for POWS: (a) AQE of POWS under visible light; (b) STH of POWS.

Reference:

1. Dai, D. et al. Strain adjustment realizes the photocatalytic overall water splitting on tetragonal zircon BiVO₄. *Adv. Sci.* **9**, 2105299 (2022).
2. Wan, G. et al. Photocatalytic overall water splitting over PbTiO₃ modulated by oxygen vacancy and ferroelectric polarization. *J. Am. Chem. Soc.* **144**, 20342-20350 (2022).
3. Pan, C. et al. A complex perovskite-type oxynitride: The first photocatalyst for water splitting operable at up to 600 nm. *Angew. Chem. Int. Ed.* **54** 2955-2959 (2015).
4. Nishimae, S. et al. Active BaTaO₂N photocatalysts prepared from an amorphous Ta₂O₅ precursor for overall water splitting under visible light. *J. Mater. Chem. A.* **11** 6299-6310 (2023).
5. Li, H. et al. One-step excitation overall water splitting over a modified Mg-Doped BaTaO₂N photocatalyst. *ACS. Catal.* **12** 10179-10185 (2022).

6. Wang, L. et al. A Ga doped NiTiO₃ photocatalyst for overall water splitting under visible light illumination. *Adv. Funct. Mater.* **32** 2208101 (2022).
7. Wang, Z. et al. Overall water splitting by Ta₃N₅ nanorod single crystals grown on the edges of KTaO₃ particles. *Nat. Catal.* **1** 756-763 (2018).
8. Chen, K. et al. Overall water splitting by a SrTaO₂N-based photocatalyst decorated with an Ir-promoted Ru-based cocatalyst. *J. Am. Chem. Soc.* **145** 3839-3843 (2023).
9. Wang, Q. et al. Oxysulfide photocatalyst for visible-light-driven overall water splitting. *Nat. Mater.* **18** 827-832 (2019).

(3). The characterization of the materials is performed by convincing techniques. The composition of the synthetic samples is determined by combining several reliable analytic techniques rather than the TEM-EDX mentioned by the reviewer. For instance, The Sr and Ti contents within the samples are determined by the inductively coupled plasma optical emission spectrometry (ICP-OES, PE 8300, USA). The O and N content are determined by an oxygen-nitrogen-hydrogen analyzer (ONH2000, USA). The F content is determined by dissolving the sample powders into *aqua regia* which was then analyzed using an ion chromatograph (ICS-1100, USA). These analyses quantitatively determine the composition of the samples with high convincingness.

In summary, it should be emphasized that the findings of this work are fundamentally different from the reported ones with regard to the role of fluorine and have not been recognized by the previous studies. The achievement of POWS under visible light is a real step forward, considering the simple F-expedited nitridation measure used here that has wide applicability to many other conventional semiconductors. We believe these findings, in conjunction with the high performance (both AQE and STH for POWS) compared to the state of the art and the high convincingness of the materials characterization, deserve a reconsideration. Below, please find our point-to-point replies to your comments.

1. Within the materials preparation, the best performing photocatalysts result from a “double” high temperature annealing treatment, whereas the control, nitrdated samples only to one. It could be argued that the first high temperature treatment, even without the F-precursor, could affect the crystal structure and hence, the subsequent nitridation could result in an improved performance.

Response: We are very grateful for the reviewer’s comments! We fully understand the reviewer’s concerns on the effect of annealing treatment. To address the reviewer’s concerns, a new control sample has been prepared by an additional annealing treatment before nitridation in order to meet the “double” annealing standard. The new control sample has been denoted as $\text{Sr}_2\text{TiO}_4\text{-N}_2$ in order to distinguish from the old one $\text{Sr}_2\text{TiO}_4\text{-N}$ that has been annealed only once. Our results show that the new control sample, *i.e.* $\text{Sr}_2\text{TiO}_4\text{-N}_2$ is very similar to the old one $\text{Sr}_2\text{TiO}_4\text{-N}$ in terms of crystal structure, light absorption, and photocatalytic activity (see **Figure R2** below). It remains inactive to photocatalytic overall water splitting (POWS) both under visible light and simulated sunlight. From these results, we are confident to conclude that the annealing history does not play an important role here. The POWS activity of F-expedited nitridized sample, *i.e.* $\text{Sr}_2\text{TiO}_4\text{-NF}$, is attributed to other factors.

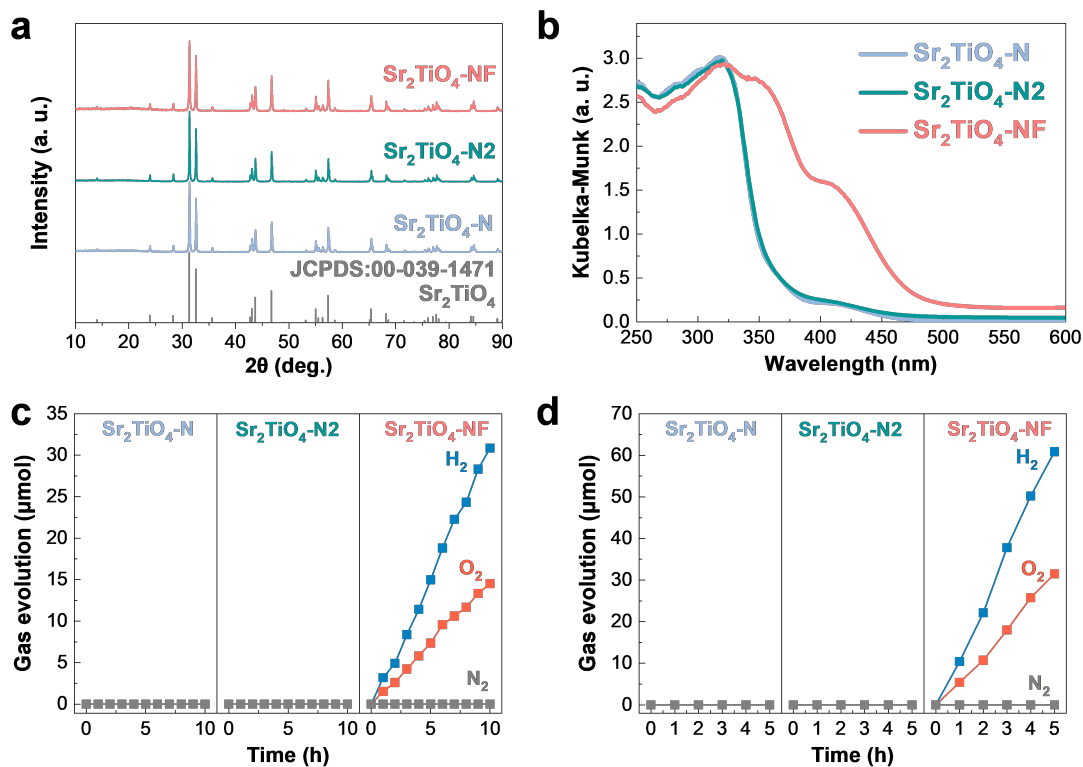


Figure R2. (a) XRD patterns of $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N}_2$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$, standard patterns of Sr_2TiO_4 are also included for comparisons; (b) UV-vis DRS spectra of $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N}_2$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$; (c) photocatalytic overall water splitting for $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N}_2$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$ under visible light ($\lambda \geq 420 \text{ nm}$); (d) photocatalytic overall water splitting for $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N}_2$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$ under simulated sunlight ($100 \text{ mW}\cdot\text{cm}^{-2}$).

Action: In the manuscript, we have added a new control sample $\text{Sr}_2\text{TiO}_4\text{-N}_2$ for comparisons in order to clarify the influence of annealing history for photocatalytic performance.

2. The authors used TEM-EDX to evaluate the presence of N and F in the structure. Given the importance of such data, the authors should present other technique to determine the composition to corroborate that data.

Response: We are very grateful for the reviewer's comments! We would like to clarify that the composition of our samples was not determined by TEM-EDX. The composition is determined by combining several reliable analytic techniques. For

instance, The Sr and Ti content within the samples are determined by the inductively coupled plasma optical emission spectrometry (ICP-OES, PE 8300, USA). The O and N content are determined by an oxygen-nitrogen-hydrogen analyzer (ONH2000, USA). The F content is determined by dissolving the sample powders into *aqua regia* and then analyzed using an ion chromatograph (ICS-1100, USA). These analyses quantitatively determine the composition of the samples with high convincingness.

3. Following on the topic of the composition, a critical subject in this work, in page 9 the authors talk about, and specified the amount of oxygen vacancies. It is not clear how do they establish that. It seems the authors just took the EDX data from O, F, N and the missing oxygen was labelled as vacancies. A more consistent data to characterize the amount of O, F, and N is necessary.

Response: We are very grateful for the reviewer's comments! As we stated in the previous reply, the compositions of our samples were determined by a combination of several reliable analytic techniques, including ICP, oxygen-nitrogen-hydrogen analyzer and ion chromatograph. The exact amounts of oxygen, nitrogen and fluorine can be accurately determined. The missing oxygen, i.e. oxygen vacancies, can be easily deduced by comparing experimental and theoretical values.

4. The authors used the PL intensity to support the claim that the recombination is higher in the case of the NF sample. However, both sample (N and NF) display a pretty distinct UV-Vis spectra, so, differences in the overall intensity could derived from the different absorption of incident or emitted light.

Response: We are very grateful for the reviewer's comments! It should be pointed out that our claim in the manuscript is quite opposite, i.e. the recombination is lower in case of the NF sample (i.e. $\text{Sr}_2\text{TiO}_4\text{-NF}$). We fully understand the reviewer's concerns on the linkage between the differences of light absorption and the differences of PL intensity. We would like to make some clarifications here. The PL experiments were conducted using a 420 nm laser excitation. The $\text{Sr}_2\text{TiO}_4\text{-NF}$ has a stronger absorption than $\text{Sr}_2\text{TiO}_4\text{-N}$ at 420 nm, according to the UV-vis DRS spectra

(Figure 1c-d). On the contrary, the $\text{Sr}_2\text{TiO}_4\text{-NF}$ shows much weaker PL intensity than $\text{Sr}_2\text{TiO}_4\text{-N}$ (Figure 4a). In other words, $\text{Sr}_2\text{TiO}_4\text{-NF}$ absorbs more light but emit less light, comparing to $\text{Sr}_2\text{TiO}_4\text{-N}$. This phenomenon unequivocally indicates that $\text{Sr}_2\text{TiO}_4\text{-NF}$ has less radiative recombination events than $\text{Sr}_2\text{TiO}_4\text{-N}$.

5. To better define the role of the Fluor it could have been interesting to prepare an additional sample where the fluorination followed the nitridation, that could have revealed the actual role of the F intercalation. Likely, the fluorination plays a key role in the system, and although a larger amount of N is intercalated, the addition of F might be key. Maybe even if the N intercalated is low, the presence of F could boost the performance in a similar way.

Response: We are very grateful for the reviewer's valuable comments and suggestions! We absolutely agree with the reviewer's opinion that the fluorination treatment following nitridation helps to elucidate the role of F. Therefore, we have prepared an additional sample by fluorinating the $\text{Sr}_2\text{TiO}_4\text{-N}$, i.e. fluorination after nitridation. The new sample was denoted as $\text{Sr}_2\text{TiO}_4\text{-N@F}$ in order to discriminate from the sample $\text{Sr}_2\text{TiO}_4\text{-NF}$ which was fluorinated before nitridation. The fluorination is successful according to the composition analysis that reveal F signal. This new sample has a large similarity to $\text{Sr}_2\text{TiO}_4\text{-N}$ in terms of structure and light absorption (see **Figure R3** below). However, $\text{Sr}_2\text{TiO}_4\text{-N@F}$ is inactive to photocatalytic overall water splitting (POWS) under visible light and shows very poor POWS activity with nonstoichiometric H_2/O_2 evolution under simulated sunlight (see **Figure R3** below). These results suggest that it is N rather than F that plays the critical role for POWS.

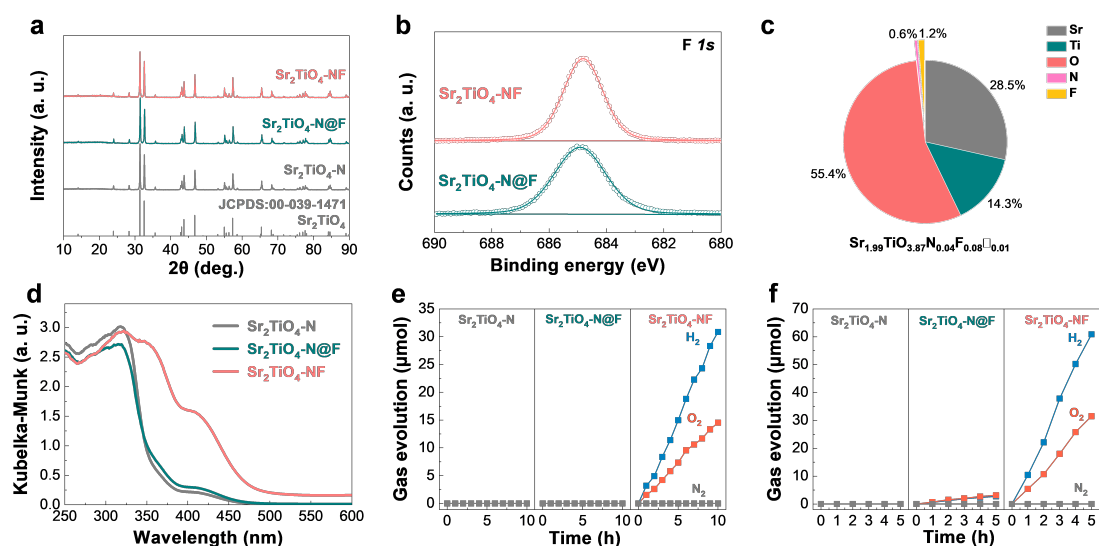


Figure R3. (a) XRD patterns of $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N@F}$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$, standard patterns of Sr_2TiO_4 are also included for comparisons; (b) XPS F 1s spectra of $\text{Sr}_2\text{TiO}_4\text{-N@F}$ and $\text{Sr}_2\text{TiO}_4\text{-NF}$; (c) element content of $\text{Sr}_2\text{TiO}_4\text{-N@F}$ by ICP, ONH and ion chromatograph analysis, deduced chemical formula are shown at the bottom (oxygen vacancies are represented by empty squares ' \square '); (d) UV-vis DRS spectra of $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N@F}$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$; (e) photocatalytic overall water splitting for $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N@F}$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$ under visible light ($\lambda \geq 420$ nm); (f) photocatalytic overall water splitting for $\text{Sr}_2\text{TiO}_4\text{-N}$, $\text{Sr}_2\text{TiO}_4\text{-N@F}$, and $\text{Sr}_2\text{TiO}_4\text{-NF}$ under simulated sunlight ($100 \text{ mW}\cdot\text{cm}^{-2}$).

Action: In the manuscript, we have added a new control sample $\text{Sr}_2\text{TiO}_4\text{-N@F}$ for comparisons in order to clarify the role of F to the photocatalytic activity.

Reviewer #2:

In this manuscript, an F-involved nitridation approach has been developed to introduce visible light sensitivity to a layered wide-band gap semiconductor, Sr₂TiO₄. This approach seems to be quite effective in bringing several desirable properties, such as strong visible light absorption, high N content, few defects, and most importantly, the activity for photocatalytic overall water splitting (POWS). The POWS activity is by far very challenging for a single-component semiconductor, particularly under visible light. I think this manuscript made a large step forward in this area. I would like to recommend the publication of this manuscript, after some proper revisions to be addressed:

Response: We are very grateful for the reviewer's positive feedback! Below, please find our point-to-point replies to your comments.

1. The F appears critical for a high N content in the nitridation product. The final F content in the Sr₂TiO₄-NF is much lower than the precursor Sr₂TiO₃F₂. How to understand the role of F if it is so volatile?

Response: We are very grateful for the reviewer's comments and question. We absolutely agree with the reviewer's opinion that F is volatile during nitridation. However, some F will remain in the sample as a co-dopant to N. The presence of F is critical to break the doping limit of N (< 1 atm%) as it not only facilitates O/N substitution by elongating the Ti-O bonds but also balances the charge during N doping, i.e. $2O_o^{\times} \rightarrow N'_o + F'_o$. The latter effect is important to minimize the concentration of unwanted defects such as oxygen vacancies and Ti³⁺.

2. The authors argued that the POWS activity arises from fewer defects such as Ti³⁺. Some reports revealed that the Ti³⁺ might be good for high photocatalytic activity (<https://pubs.acs.org/doi/10.1021/nl404688h>; <https://pubs.acs.org/doi/10.1021/acscatal.3c04743>; etc.), the authors should give some comments on this issue.

Response: We are very grateful for the reviewer's comments and suggestions! We

would like to make some clarifications on the role of Ti^{3+} . The role of Ti^{3+} for photocatalytic performance depends on two factors. The first one is the energy level of Ti^{3+} with respect to the band edge positions. If Ti^{3+} has a deep energy level, *i.e.* deep defects, it is detrimental to photocatalytic activity as photocarriers trapped by Ti^{3+} are unlikely to escape. Conversely, if Ti^{3+} has a shallow energy level, *i.e.* shallow defects, photocarriers can jump to conduction band therefore is beneficial for photocatalytic activity. The second one is the spatial position of Ti^{3+} . It is generally considered that surface Ti^{3+} is helpful for photocarrier separation because it can drag photocarriers towards the surface. However, the Ti^{3+} in the bulk normally undermines the photocatalytic performance as photocarriers are retained in the bulk and inaccessible to surface reactions. In the case of Ti^{3+} in this work, it is mostly distributed in the bulk and has relatively deep energy level with respect to the conduction band edge. Therefore, the Ti^{3+} is detrimental to the photocatalytic activity and should be eliminated.

Action: In the manuscript, we have added some comments on the role of Ti^{3+} : “It is generally considered that defects with shallow energy states (*i.e.* shallow defects) may play a positive role for photocarrier separation, particularly when they are located at the surface. However, defects with deep energy states (*i.e.* deep defects) generally undermine photocarrier separation as photocarriers can be tightly trapped and are unlikely to escape from these defects for surface reactions. This is particularly true for oxygen vacancies here as they form deep defects whose energy states lie close to or lower than the water reduction potential. Presumably, the trapped electrons by oxygen vacancies can hardly escape and would have inadequate driving force for water reduction reactions.”

3. A Ti oxyhydroxide layer has been deposited onto Sr_2TiO_4 -NF, but the function of this layer has not been fully explained. The authors should elucidate the role of this Ti oxyhydroxide layer.

Response: We are very grateful for the reviewer's comments and suggestions! The Ti oxyhydroxide layer has multi-functions here: (1) it serves as a permeation barrier for O₂, therefore suppressing the occurrence of water-splitting reverse reactions; (2) it enhances the injection of holes into the Ti oxyhydroxide layer, thereby avoiding excessive buildup of holes on the photocatalyst's surface which in turn reduces the likelihood of photocorrosion.

Action: In the manuscript, we have added some comments on the role of Ti oxyhydroxide layer: "The TiOXH is reported to have dual functions: (1) it serves as a permeation barrier for O₂, therefore suppressing the occurrence of water-splitting reverse reactions; (2) it facilitates hole injection from photocatalyst to the TiOXH layer, therefore avoiding excessive buildup of holes at the photocatalyst's surface and reducing the likelihood of photocorrosion."

4. The stability analysis of the Sr₂TiO₄-NF is insufficient; XRD alone cannot resolve the changes at the sample surface. I suggest the authors collect more information on the Sr₂TiO₄-NF particles after POWS experiments.

Response: We are very grateful for the reviewer's suggestions! We have additionally collected XPS (**Figure R4**) and SEM (**Figure R5**) information of the Sr₂TiO₄-NF samples before and after photocatalytic overall water splitting reactions. Sr₂TiO₄-NF is a stable photocatalyst under photocatalytic overall water splitting conditions, as supported by XPS and SEM analysis after the photocatalytic experiment.

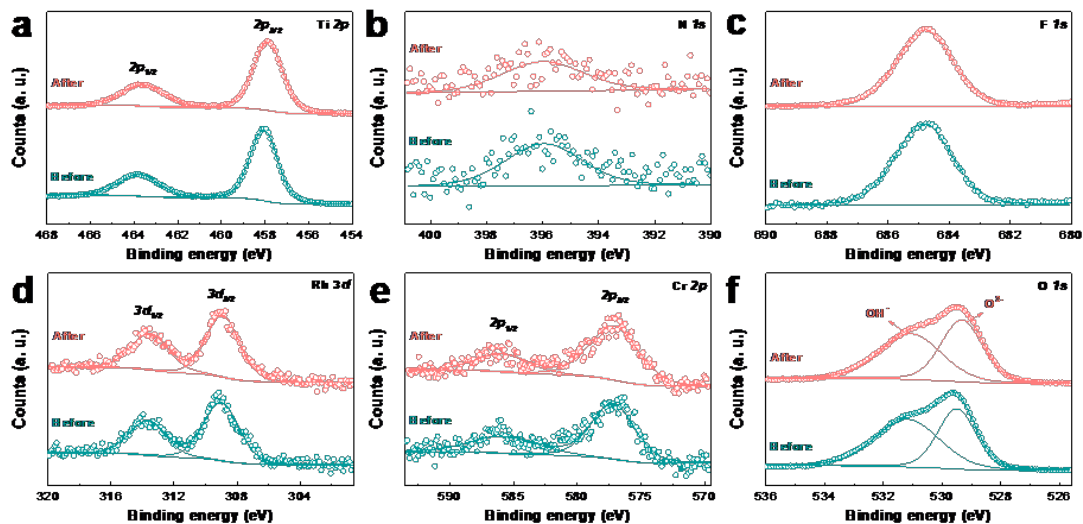


Figure R4. XPS of $\text{Sr}_2\text{TiO}_4\text{-NF}$ before and after photocatalytic overall water splitting reactions: (a) Ti 2p; (b) N 1s; (c) F 1s; (d) Rh 3d; (e) Cr 2p; (f) O 1s.

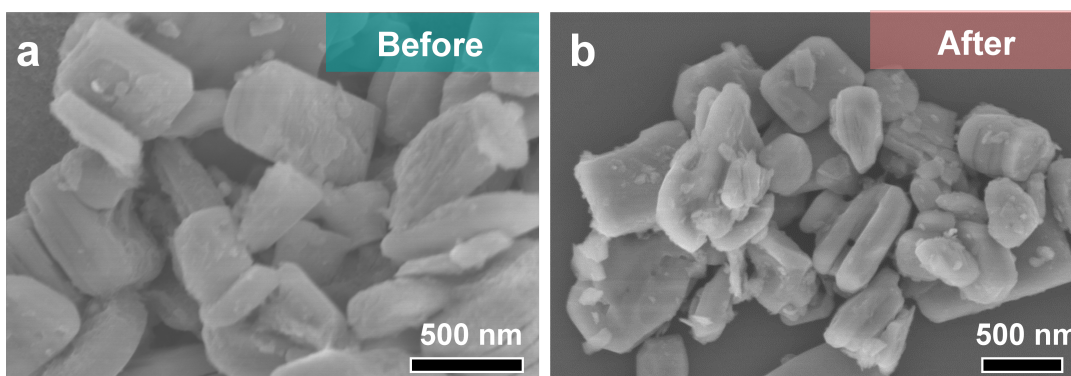


Figure R5. SEM image of $\text{Sr}_2\text{TiO}_4\text{-NF}$ before and after photocatalytic overall water splitting reactions: (a) before; (b) after.

5. Whereas this F-involved nitridation tactic is very interesting, it is not always easy to find a suitable fluorinated precursor. Can authors give some suggestions on the application of their strategy, because there are numerous wide-bandgap metal oxides?

Response: We are very grateful for the reviewer's comments and questions! As pointed out by the reviewers, there might not be always a fluorinated and crystallized precursor. However, it is still possible to prepare a fluorinated amorphous precursor for nitridation. For instance, by dissolving a fluorine compound (e.g. NH_4F) into the polymerized complex, it is easily to obtain an amorphous precursor containing fluorine. This amorphous precursor should work in a similar way during nitridation as

the fluorinated and crystallized precursor. We have added some suggestions into the manuscript.

Action: In the manuscript, we have added the statement: “For a more general application of the F-expedited nitridation strategy, an F-involving amorphous precursor can be easily prepared by the *Chimie douce* method, which shall work in a similar way as the crystallized precursor $\text{Sr}_2\text{TiO}_3\text{F}_2$ used in this work and will be our future study.”

Reviewer #3:

Photocatalytic overall water splitting is very promising for solar hydrogen production but is generally very difficult, especially under visible light and for a single type photocatalyst. Here, Yu et al reported a new type of layered perovskite that is active for photocatalytic overall water splitting under visible light. They developed a proper precursor $\text{Sr}_2\text{TiO}_3\text{F}_2$ that allows N/F codoping into Sr_2TiO_4 by a simple nitridation treatment. This NF-codoped Sr_2TiO_4 has an intense visible light absorption and good separation efficiency for photo-generated charges, which in turn, contribute to the activity for photocatalytic overall water splitting both under visible light and simulated sunlight. Overall, the findings in this manuscript are important, considering the fact that there are limited numbers of photocatalysts capable of overall water splitting. The samples in this work are sufficiently analyzed and the manuscript is well-written. I think this work is suitable for publication in Nature Communications. Here are some revision suggestions:

Response: We are very grateful for the reviewer's positive feedback! Below, please find our point-to-point replies to your comments.

1. The defects play a vital role for the separation of photo-generated charges. How to understand the decrement of defect concentration when N/F is co-doped into Sr_2TiO_4 ? The authors should give some detailed explanation in the manuscript.

Response: We are very grateful for the reviewer's comments and questions! The preparation of N doped Sr_2TiO_4 involves annealing a metal oxide precursor (Sr_2TiO_4) at high temperatures with ammonia gas, a nonequilibrium solid-gas reaction with slow kinetics due to the sluggish exchange of N species with O. The transformation is often incomplete, resulting in defects and anion nonstoichiometry. In this manuscript, we adopted $\text{Sr}_2\text{TiO}_3\text{F}_2$ as a precursor for doping N into Sr_2TiO_4 . Due to the higher electronegativity of F compared to O, the presence of F weakens the Ti-O bond through the inductive effect, facilitating O/N exchange. Furthermore, F, as a co-dopant with N, helps to balance the charge variations induced by N substitution for

oxygen, *i.e.* $2O_O^{\times} \rightarrow N'_O + F'_O$, thereby reducing the generation of anionic defects. The precursor $Sr_2TiO_3F_2$ contains fluoride anions both interlayer and intralayer, which facilitates the incorporation of N during high-temperature ammonolysis and reduces the concentration of defects.

Action: In the manuscript, we have added some explanations: “The decrement of defect concentration is fully consistent with earlier expectations: the presence of F not only facilitates O/N exchange by weakening Ti-O bonds but also balances the charge variations by serving as a co-dopant to N, both of which reduce the risks of defect formation.”

2. The precursor used for nitridation is critical here. Why $Sr_2TiO_3F_2$ has a wider bandgap than Sr_2TiO_4 , considering their similar crystal structure? If F-containing precursor is useful, is it necessary to synthesize an F-rich precursor for nitridation every time? The authors should provide some suggestions on sample preparation in a more general sense.

Response: We are grateful for the reviewer’s questions and suggestions! The wider bandgap of $Sr_2TiO_3F_2$ stems probably from two reasons. The first one is the high electronegativity of F that enlarges the energy differences between bonding and antibonding orbitals. The second one is the structure distortion in $Sr_2TiO_3F_2$ that narrows the band width. As pointed out by the reviewers, there might not be always a fluorinated and crystallized precursor. However, it is still possible to prepare a fluorinated amorphous precursor for nitridation. For instance, by dissolving a fluorine compound (*e.g.* NH_4F) into the polymerized complex, it is easy to obtain an amorphous precursor containing fluorine. This amorphous precursor should work in a similar way during nitridation as the fluorinated and crystallized precursor. We have added some suggestions into the manuscript.

Action: In the manuscript, we have added some discussions: “For a more general

application of the F-expedited nitridation strategy, an F-involving amorphous precursor can be easily prepared by the *Chimie douce* method, which shall work in a similar way as the crystallized precursor $\text{Sr}_2\text{TiO}_3\text{F}_2$ used in this work and will be our future study.”

3. Is Sr_2TiO_4 perse active for photocatalytic overall water splitting under simulated sunlight?

Response: We are grateful for the reviewer’s questions! Under AM1.5G simulated illumination, Sr_2TiO_4 is essentially inert for photocatalytic overall water splitting (Figure R6).

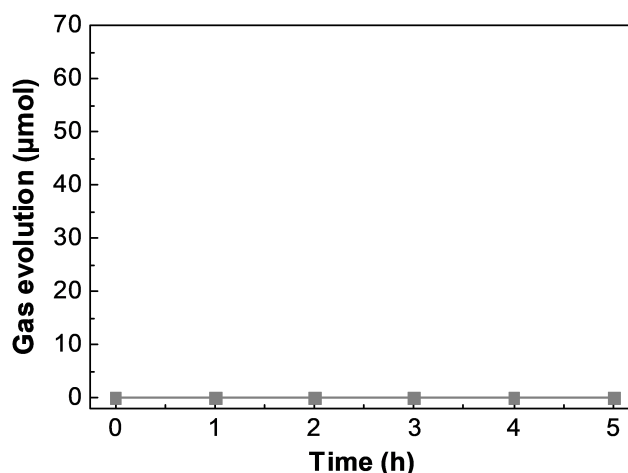


Figure R6. Photocatalytic overall water splitting reactions over Sr_2TiO_4 under AM1.5G ($100 \text{ mW}\cdot\text{cm}^{-2}$). Reaction conditions: 0.4 g catalysts, 100 mL deionized water.

4. The prototype perovskite SrTiO_3 is very active for UV light driven overall water splitting. Previous reports showed that the cocatalysts, i.e. RhCrO_y and CoOOH , are important. In this work, only RhCrO_y is employed, what if CoOOH is also introduced? Have the authors attempted to deposit CoOOH onto $\text{Sr}_2\text{TiO}_4\text{-NF}$ as an O_2 -evolution cocatalyst?

Response: We are grateful for the reviewer’s questions and suggestions! We have

tried to deposit CoOOH onto Sr₂TiO₄-NF as a cocatalyst for O₂ evolution, and the results are presented in **Figure R7**. The presence of CoOOH seems to have no positive effect on the photocatalytic activity. This is probably because CoOOH has a poor connection to the Ti oxyhydroxide layer coating on Sr₂TiO₄-NF.

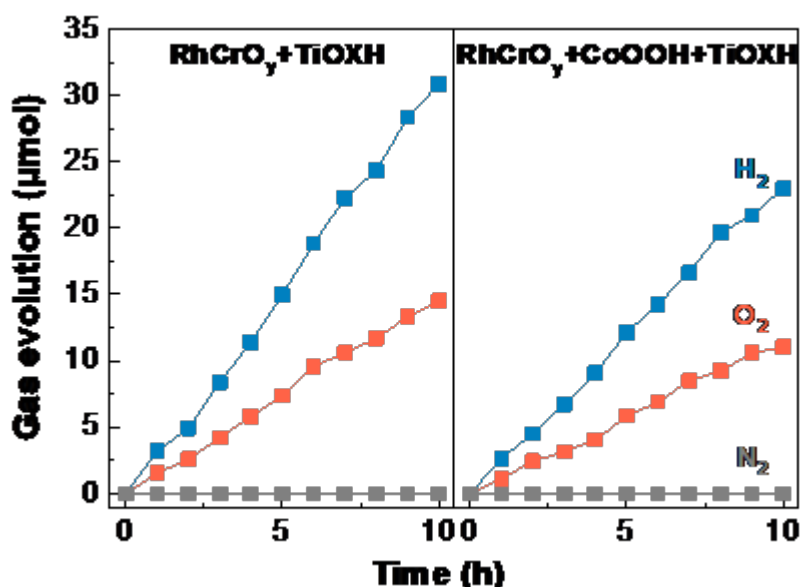


Figure R7. Photocatalytic overall water splitting reactions over Sr₂TiO₄-NF with or without CoOOH, the left image shows the result without CoOOH deposition and the right image shows the result with 0.5 wt% CoOOH deposition.

5. The post-mortem analysis is not enough. The authors should provide additional characterizations such as SEM and XPS to verify the robustness of their sample.

Response: We are very grateful for the reviewer's suggestions! We have additionally collected XPS (**Figure R8**) and SEM (**Figure R9**) information of the Sr₂TiO₄-NF samples before and after photocatalytic overall water splitting reactions. Sr₂TiO₄-NF is a stable photocatalyst under photocatalytic overall water splitting conditions, as supported by XPS and SEM analysis after the photocatalytic experiment.

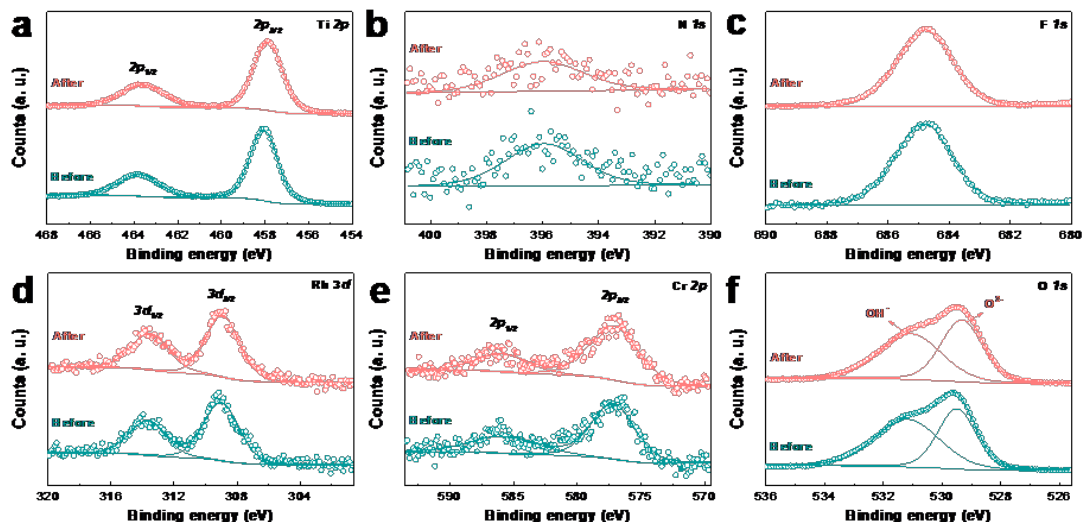


Figure R8. XPS of $\text{Sr}_2\text{TiO}_4\text{-NF}$ before and after photocatalytic overall water splitting reactions: (a) Ti 2p; (b) N 1s; (c) F 1s; (d) Rh 3d; (e) Cr 2p; (f) O 1s.

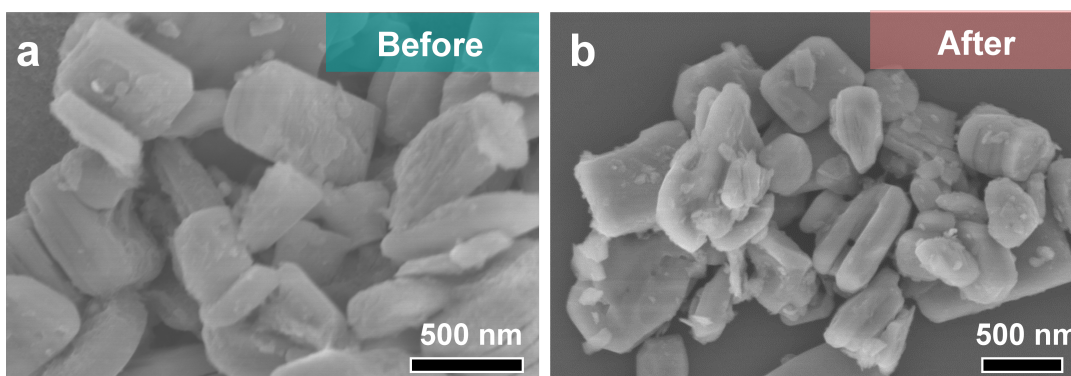


Figure R9. SEM image of $\text{Sr}_2\text{TiO}_4\text{-NF}$ before and after photocatalytic overall water splitting reactions: (a) before; (b) after.

6. If Ti oxyhydroxide serves merely as a protection layer, there shouldn't be an increment of the H_2/O_2 evolution. I think Ti oxyhydroxide should have additional functions, for instance, charge separation. Have the authors tested Ti oxyhydroxide alone as a photocatalyst?

Response: We are grateful for the reviewer's questions and suggestions! We absolutely agree with the reviewer's opinion that the Ti oxyhydroxide layer serves more than a protection layer. It has been reported that the Ti oxyhydroxide layer possesses two main functions: (1) it operates as a permeation barrier for O_2 ,

effectively suppressing the occurrence of water-splitting reverse reactions; (2) it enhances the injection of holes into the Ti oxyhydroxide layer, avoiding an excessive buildup of holes on the photocatalyst's surface which in turn, increases the resistance to photocorrosion (DOI: 10.1002/anie.201410961; DOI: 10.1039/c5cc01728a). Under our test conditions, we did not achieve photocatalytic overall water splitting reaction using Ti oxyhydroxide alone as a photocatalyst (see **Figure R10** below).

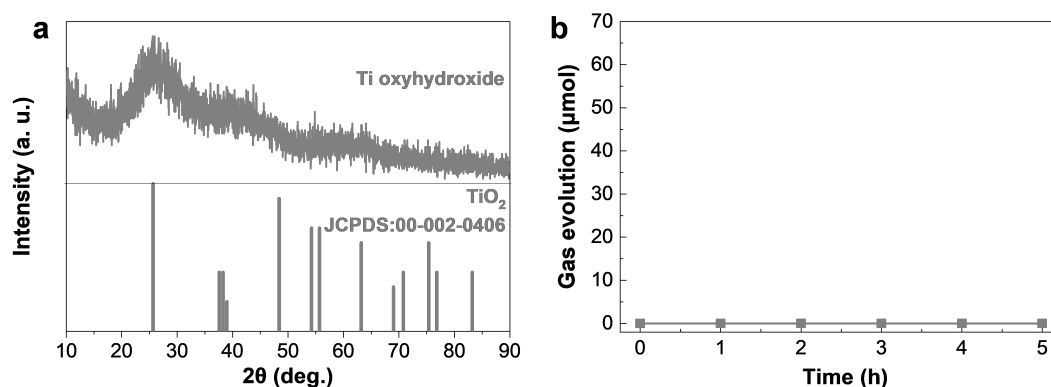


Figure R10. (a) X-ray powder diffraction (XRD) patterns of Ti oxyhydroxide. Standard patterns for TiO₂ (JCPDS: 00-002-0406) are shown for comparisons; (b) Photocatalytic overall water splitting reactions over Ti oxyhydroxide under AM1.5G (100 mW·cm⁻²). Reaction conditions: 0.4 g catalysts, 100 mL deionized water.

Action: In the manuscript, we have added some comments on the role of Ti oxyhydroxide layer: “The TiOXH is reported to have dual functions: (1) it serves as a permeation barrier for O₂, therefore suppressing the occurrence of water-splitting reverse reactions; (2) it facilitates hole injection from photocatalyst to the TiOXH layer, therefore avoiding excessive buildup of holes at the photocatalyst’s surface and reducing the likelihood of photocorrosion.”