Perspective
Challenges for photocatalytic overall water splitting

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SUMMARY

The hydrogen economy is a sunrise industry, which is considered the ultimate solution to power the future society. Photocatalytic overall water splitting is projected as a potential technology for H_2 production. However, its performance is still far from meeting the criteria for large-scale production. This paper argues that photocatalytic overall water splitting is theoretically and practically hard to achieve. The limiting factors, including unfavorable thermodynamics, slow kinetics, dissolved oxygen, and rapid backward reaction, are discussed. This paper is expected to give readers a better understanding of the photocatalytic overall water splitting and analyze the associated challenges in every subtle aspect.

INTRODUCTION

The shortage of fossil fuels and their negative impacts on the environment urges an energy revolution from fossil to renewable energy sources. Solar energy is renewable and nonpolluting. However, solar energy has low density, high temporal/seasonal variability, and poor portability. Therefore, photocatalysis is applied to convert sunlight into storable chemical energy, such as clean and efficient hydrogen energy. Apart from nuclear fuels, the combustion heat of hydrogen is the highest among all fossil fuels, chemical fuels, and biofuels. In addition, hydrogen burns to produce water without any pollution to the environment.[1] Therefore, hydrogen is called the ultimate energy source for humanity.[2]

In recent years, hydrogen technology based on photocatalysis has been developing rapidly. Moreover, efficient photocatalytic overall water splitting (OWS) has been pursued and regarded as the Holy Grail.[3] However, the H_2-production activities are unsatisfactory. Most research works do not achieve a solar-to-hydrogen (STH) efficiency of over 10%, a competitive benchmark efficiency in the hydrogen market.[4] Therefore, whether photocatalytic OWS is the best option for H_2 production remains questionable. Here, the challenges for photocatalytic OWS are evaluated in terms of thermodynamics, kinetics, dissolved oxygen, and backward reaction, and the future development of photocatalytic OWS is prospected.

PHOTOCATALYTIC HYDROGEN PRODUCTION

The intrinsic nature of photocatalyst determines that photogenerated carriers undergo several processes. Figure 1 shows the four main steps: (1) Photocatalyst absorbs photons from the light source to generate electron-hole pairs. (2) The photogenerated carriers transfer and separate in space. (3) Most carriers are annihilated within the bulk photocatalysts or on the surface through Coulomb force or captured by traps such as defects. (4) The surviving charge carriers are captured by cocatalysts for surface redox reactions. Only a minority of photogenerated carriers can

The bigger picture

Challenges and opportunities:

- Photocatalytic overall water splitting is an intriguing process to produce hydrogen. However, the photocatalytic efficiency is unsatisfactory. Thus, it is necessary to analyze the challenges for photocatalytic overall water splitting.

- The unfavorable thermodynamics, sluggish kinetics, dissolved oxygen, backward reaction, and side reaction make photocatalytic overall water splitting enormously difficult. These obstacles must be overcome to achieve efficiency in photocatalytic overall water splitting.

- Coupling hydrogen production with selective organic synthesis can be a more viable and attractive option than overall water splitting. The organic compounds can be converted into value-added oxidation products via single-electron processes, which are much easier than the four-electron oxygen evolution reaction.
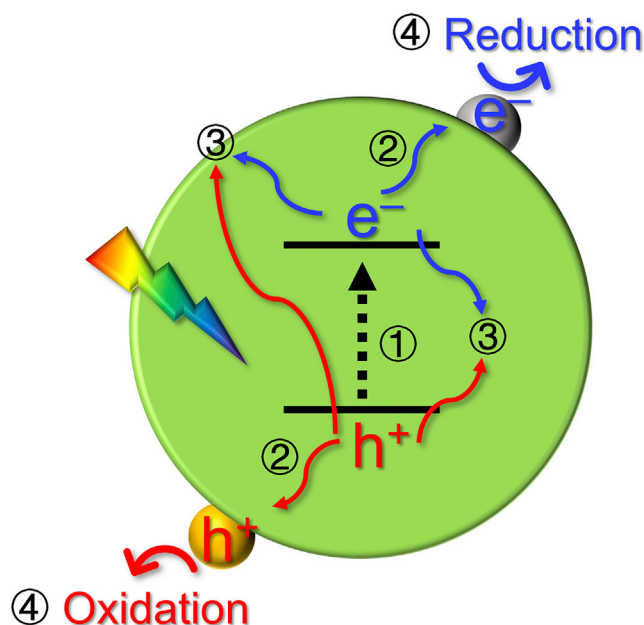
Figure 1. Microscopic view of photocatalysis
It mainly includes the (1) generation, (2) separation, (3) recombination of photogenerated carriers, and (4) surface redox reactions.

ultimately participate in the redox reactions, resulting in extremely poor photocatalytic activity and low quantum yield.

In addition to the inherent properties of photocatalysts, the ambient environment is also critical to H_2 production. Specifically, three prerequisites are essential for efficient H_2 production: oxygen removal, cocatalyst, and sacrificial agent (SA).

(1) Oxygen removal: oxygen dissolved in water can be reduced by photogenerated electrons to generate superoxide radicals ($O_2^{\cdot-}$) ($\varphi(O_2/O_2^{\cdot-})$ = −0.33 V versus normal hydrogen electrode [NHE]) and undergo a series of side reactions. This reaction competes with hydrogen evolution reaction (HER), which also requires the electrons to proceed. Oxygen removal can significantly suppress these side reactions to improve photocatalytic efficiency. It should be noted that it is hard to remove dissolved oxygen thoroughly by evacuation and bubbling an inert gas (e.g., N_2) through the water is more effective.

(2) Cocatalyst: photocatalysts without cocatalysts often exhibit very low or even no HER activity. The effects of cocatalysts are mainly classified into four aspects: (1) extracting photogenerated electrons or holes to reduce carrier recombination, (2) storing charge carriers to facilitate multielectron reactions, (3) providing active sites to bind and activate reactant molecules, and (4) reducing the overpotential of redox reactions.[5,6]

(3) SA: the employment of SA is one of the most effective ways to boost HER activity. In a typical photocatalytic H_2-production process, the photogenerated electrons reduce H^+ to H_2, although the holes are consumed in the oxidation half-reaction (e.g., oxygen evolution reaction [OER] in OWS). In particular, the role of SA is to provide a facile route to react with the holes, usually via a single-electron process, to replace the four-electron OER (Figure 2A).[7] The

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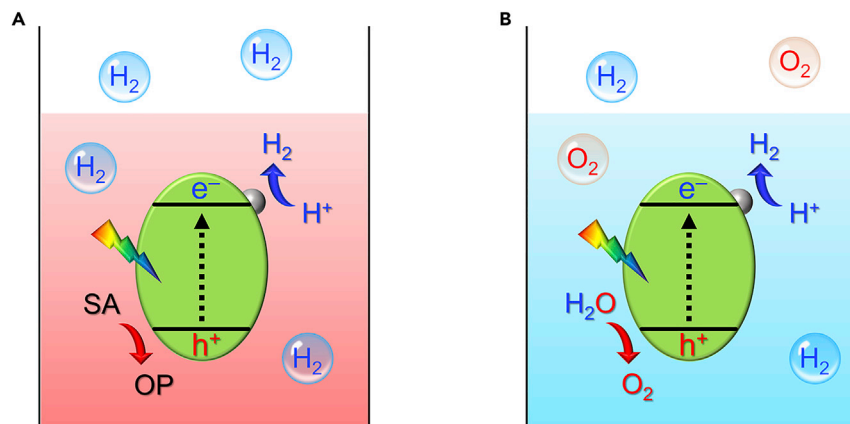
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Figure 2. Photocatalytic systems of SA-assisted HER and OWS
(A) Photocatalytic SA-assisted HER.
(B) Photocatalytic OWS.
Abbreviations: OWS, overall water splitting; SA, sacrificial agent; HER, hydrogen evolution reaction; OP, oxidation product.
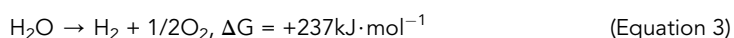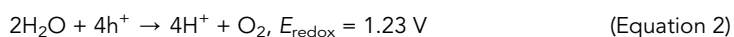
single-electron process usually presents a much lower overpotential and a faster reaction rate than OER. Furthermore, SA-assisted HER can avoid the generation of O_2 from OER, ensuring oxygen-free conditions throughout the whole photocatalytic process. Finally, by scavenging the free holes, the addition of SA can effectively suppress photocorrosion.

PHOTOCATALYTIC OVERALL WATER SPLITTING

Photocatalytic OWS proceeds in pure water, with O_2 and H_2 as the products (Figure 2B). Besides common problems for photocatalytic H_2 production, this process faces additional challenges compared with SA-assisted HER.

Thermodynamics

OWS is thermodynamically feasible when both the proton reduction and water oxidation potentials lie within the bandgap of a photocatalyst.[8] That is, the conduction band (CB) bottom and valence band (VB) top of the photocatalyst should be positioned above the proton reduction potential and below the water oxidation potential, respectively.[9] The potential for protons to hydrogen is 0 V versus NHE (Equation 1), whereas the potential for water to oxygen is 1.23 V versus NHE (Equation 2).[10] Photocatalytic OWS is inherently a challenging process due to the high stability of H_2O containing strong O–H bonds.[11] This reaction is energetically uphill (Figure 3A), taking 237 kJ to split 1 mol of water (Equation 3).[12] Contrarily, the direct reaction between H_2 and O_2 is highly exothermic (Figure 3B), which is thermodynamically much more favored than OWS.

$$2H^+ + 2e^- \rightarrow H_2, E_{redox} = 0 \text{ V} \qquad \text{(Equation 1)}$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2, E_{redox} = 1.23 \text{ V} \qquad \text{(Equation 2)}$$

$$H_2O \rightarrow H_2 + 1/2O_2, \Delta G = +237 \text{kJ} \cdot \text{mol}^{-1} \qquad \text{(Equation 3)}$$
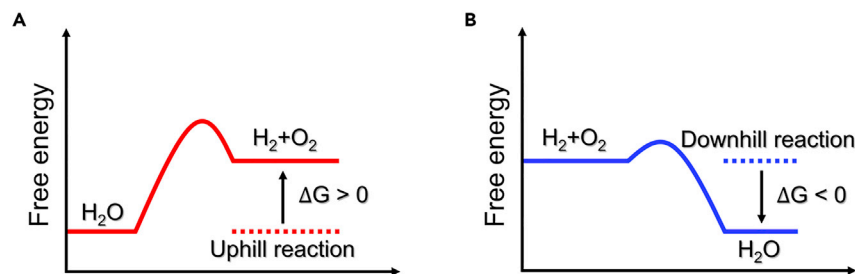
Figure 3. Thermodynamic feasibility
Gibbs free energy change for (A) OWS and (B) the reaction between H_2 and O_2.
Abbreviations: ΔG, Gibbs free energy change; OWS, overall water splitting.

Kinetics

Besides thermodynamic challenges, OWS is also hard to achieve in kinetics. In photocatalysis, the generation, separation, and transfer of photogenerated carriers belong to photophysical processes, usually taking a few femto- to nano-seconds.[13] The electrocatalytic process (i.e., surface redox reactions), on the other hand, takes much longer (micro- to seconds) to accomplish and is often the rate-limiting step. Particularly, the most stagnant steps in photocatalytic water splitting are surface reactions, including HER via proton reduction and OER via water oxidation. These surface reactions are multielectron processes. The HER produces H_2, whereas OER continually provides protons for HER and consumes photogenerated holes. Nevertheless, OER is often much slower than HER due to several factors.

(1) The effective mass of a hole is much larger than that of an electron, and hole transfer is much slower than electron transfer.[14]
(2) OER requires the participation of four holes, leading to much larger overpotential and more sluggish reaction kinetics than HER.[7,15,16] For example, transient absorption spectroscopy shows that HER over TiO_2 takes less than a microsecond to complete, whereas the OER takes as long as several seconds.[17]
(3) An oxygen atom is 16 times as massive as a hydrogen atom. Hence, the diffusion of O_2 is much slower than that of H_2, and O_2 is more difficult to escape from the photocatalyst surface than H_2.
(4) Most photocatalyst surfaces have high oxygen affinity but low hydrogen affinity. As a result, oxygen molecules are difficult to desorb from the photocatalyst surface. The sluggish OER is an important reason for the low photocatalytic OWS efficiency.

Dissolved oxygen

Since H_2 and O_2 are both soluble in water, photocatalytic OWS is actually carried out in an aerobic environment. Henry's law constants for H_2 and O_2 in water are 0.78 and 1.3 mmol L^{-1} atm^{-1} at 25°C, respectively,[18] indicating that the amount of dissolved H_2 and O_2 is significant compared with the state-of-the-art photocatalytic OWS activity. Meanwhile, H_2 is less soluble in water than O_2. Thus, in a photocatalytic OWS system with oxygen removed in advance, the ratio of H_2-evolution rate to O_2-evolution rate (the gas escaping from water) at an early stage should be greater than 2:1.

Moreover, the oxygen evolution process includes the dissolution of oxygen (Figure 4A), and the formation, growth, and escape of O_2 bubbles (Figure 4B). Firstly,
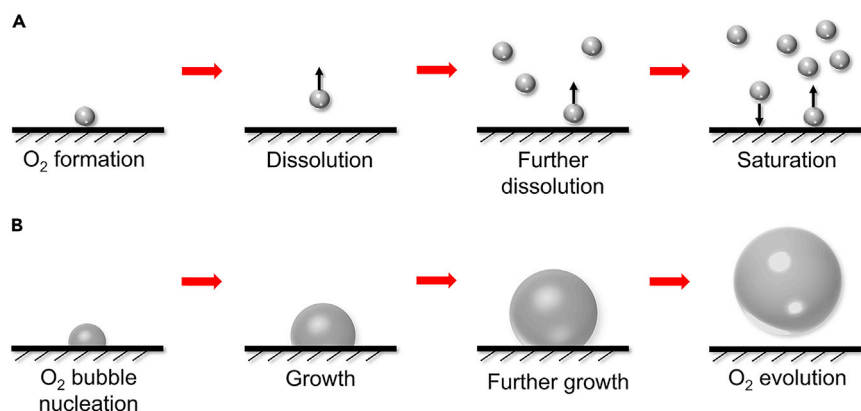
Figure 4. Oxygen evolution in OWS
(A) The dissolution of generated oxygen in water.
(B) The nucleation, growth, and evolution of O_2 bubbles.

molecular oxygen is produced on the photocatalyst surface via OER. Since the system is O_2 free at early state, the initially generated O_2 dissolves into the bulk water driven by the concentration gradient and hydrogen bonding between O_2 and H_2O. With the continuous dissolution of generated O_2, the concentration of dissolved oxygen in the water increases. Once the dissolved oxygen in the water reaches saturation, a dynamic dissolution equilibrium is established. The subsequently formed O_2 can adsorb to the photocatalyst surface. Due to the high surface energy of molecular O_2, the unstable molecular O_2 tends to aggregate and nucleate. The oxygen nuclei gradually grow into small bubbles while adhering tightly to the photocatalyst surface. Furthermore, under the effect of Ostwald ripening, large bubbles assimilate small bubbles. Spherical shapes are maintained during the growth of oxygen bubbles to minimize surface energy, and the contact area between the bubbles and the photocatalyst surface decreases, leading to a corresponding decrease in adhesion force. When the bubbles grow large enough, the buoyancy force gradually outweighs the adhesion force, and the bubbles desorb from the photocatalyst surface and escape from the water. In conclusion, only when the water is saturated with oxygen and the oxygen bubbles grow large enough can they finally evolve (hydrogen evolution undergoes a similar process).

Backward reaction and side reaction
Dissolved hydrogen and oxygen make the photocatalytic OWS proceed in an environment rich in H_2 and O_2. The coexisting H_2 and O_2 during OWS can produce water through backward reactions, leading to a tremendous loss in photocatalytic efficiency. The backward reaction is readily achieved by electrochemical processes.[19] Particularly, cocatalyst can promote the backward electrochemical processes. For instance, metallic Pt is regarded as one of the most effective cocatalysts in photocatalytic H_2 production. However, it is also widely used to catalyze the reaction between H_2 and O_2 (e.g., acting as an excellent electrocatalyst in fuel cells), which is the backward reaction of photocatalytic OWS. Therefore, cocatalyst is a double-edged sword in photocatalytic OWS.

More importantly, when H_2 and O_2 are continuously produced, the H_2 and O_2 concentrations in the water gradually increase, resulting in intensified backward reactions. The backward reaction can occur in four forms in an OWS system where H_2 and O_2 coexist (Figure 5).
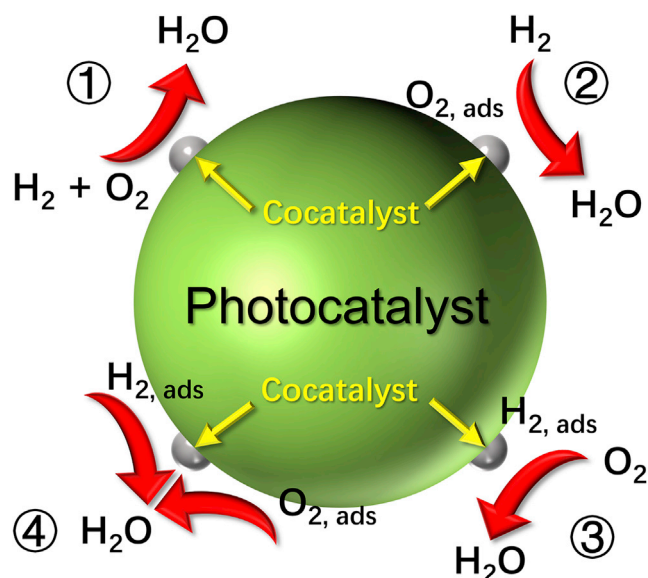
Figure 5. Backward reaction of hydrogen and oxygen on cocatalyst surface
(1) Backward reaction between dissolved H_2 and dissolved O_2.
(2) Backward reaction between dissolved H_2 and adsorbed O_2.
(3) Backward reaction between dissolved O_2 and adsorbed H_2.
(4) Backward reaction between adsorbed H_2 and adsorbed O_2.

(1) The dissolved H_2 and O_2 arrive at the cocatalyst (such as Pt) surface and react with each other.
(2) The dissolved H_2 reacts with the adsorbed O_2 on the cocatalyst surface.
(3) The dissolved O_2 reacts with the adsorbed H_2 on the cocatalyst surface.
(4) When the active sites for H_2 and O_2 production are close enough, the adsorbed H_2 and O_2 come into contact and produce water on the cocatalyst surface.

Moreover, the backward reaction further causes the decrease of dissolved H_2 and O_2, providing space for the dissolution of newly generated H_2 and O_2. Such a vicious cycle leads to extremely low photocatalytic OWS efficiency and a tremendous waste of the photogenerated charge carriers.

On the other hand, the presence of oxygen also interferes with the H_2 production process. Oxygen effortlessly combines with electrons to form superoxide radicals ($O_2^{\cdot-}$),[20] which is eventually converted to H_2O_2 or water (Figure 6). This undesirable competitive reaction plays a negative role in photocatalytic H_2 production.

CONCLUDING REMARKS AND FUTURE PERSPECTIVES

In conclusion, photocatalytic OWS is difficult to achieve. The unfavorable thermodynamics, sluggish kinetics (especially for the OER), dissolved oxygen, and severe backward reaction endow photocatalytic OWS with enormous difficulties. Therefore, H_2 production via photocatalytic OWS is challenging at present and even in the future. According to the above challenges, five comments are given below considering the difficulties in OWS.

(1) Given that the close contact between H_2 and O_2 easily leads to backward reactions, it is difficult to realize efficient OWS on nanoscale materials. For
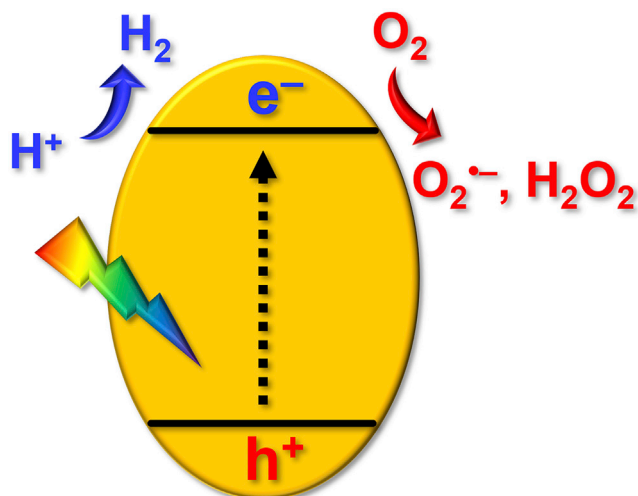
Figure 6. Oxygen reduction reaction as the competition reaction of HER

example, the reported photocatalysts for OWS are usually hundreds of nanometers or even several micrometers in size.[21–23] Therefore, morphological structures such as quantum dots, nanocrystals, and nanosheets should be avoided for OWS.

(2) Photocatalytic OWS is different from electrocatalytic OWS, where the cathode and anode reactions are spatially separated, significantly blocking the backward reaction. In photocatalytic OWS, however, the electrons and holes are generated on the same photocatalyst, leading to not only severe carrier recombination but also close contact of H_2 and O_2. Therefore, it is necessary to design photocatalytic systems that spatially separate H_2 and O_2.

(3) Due to Henry's law, dissolved H_2 and O_2 concentrations increase at a higher pressure due to gas generation and accumulation in a closed system. This leads to a faster backward reaction. As a result, a significant decrease in prolonged photocatalytic OWS activity is often observed in a system with a confined volume.[24] Besides, the accumulation of H_2 and O_2 in a closed system poses an explosion risk. Therefore, it is recommended to design sustainable systems with timely venting, separation, and collection of H_2 and O_2. Moreover, photocatalytic water splitting to H_2 and H_2O_2 is another effective route to prevent O_2 generation by producing H_2O_2 instead. The products are valuable and self-separated H_2O_2 and H_2.[25]

(4) The product of OWS is a mixture of H_2 and O_2 gases, whereas the products of SA-assisted HER are gaseous H_2 and dissolved organic products, which are automatically separated. Considering the low economic value of O_2 and the extra cost for H_2 purification, OWS is not as profitable as SA-assisted HER.

(5) The photocatalytic H_2 production rate can be observably improved with SA by replacing the four-electron OER with single-electron oxidation of SA. In this way, the SA boosts the HER activity and holds the promise to convert itself into a high value-added oxidation product. Coupling HER with selective organic synthesis can be a more accessible and attractive option in the future than OWS.

AUTHOR CONTRIBUTIONS

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

1. He, B., Bie, C., Fei, X., Cheng, B., Yu, J., Ho, W., Al-Ghamdi, A.A., and Wageh, S. (2021). Enhancement in the photocatalytic H_2 production activity of CdS NRs by Ag_2S and NiS dual cocatalysts. Appl. Catal. B 288, 119994.

2. Cheng, C., He, B., Fan, J., Cheng, B., Cao, S., and Yu, J. (2021). An inorganic/organic S-scheme heterojunction H_2-production pho-tocatalyst and its charge transfer mechanism. Adv. Mater. 33, e2100317.

3. Ryabchuk, V.K., Kuznetsov, V.N., Emeline, A.V., Artem'ev, Y.M., Kataeva, G.V., Horikoshi, S., and Serpone, N. (2016). Water will be the coal of the future-the untamed dream of jules verne for a solar fuel. Molecules 21, 1638.

4. Pinaud, B.A., Benck, J.D., Seitz, L.C., Forman, A.J., Chen, Z., Deutsch, T.G., James, B.D., Baum, K.N., Baum, G.N., Ardo, S., et al. (2013). Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. Energy Environ. Sci. 6, 1983–2002.

5. Meng, A., Zhang, L., Cheng, B., and Yu, J. (2019). Dual cocatalysts in TiO_2 photocatalysis. Adv. Mater. 31, e1807660.

6. Shinagawa, T., Cao, Z., Cavallo, L., and Takanabe, K. (2017). Photophysics and electrochemistry relevant to photocatalytic water splitting involved at solid–electrolyte interfaces. J. Energy Chem. 26, 259–269.

7. Antonietti, M., and Savateev, A. (2018). Splitting water by electrochemistry and artificial photosynthesis: excellent science but a nightmare of translation? Chem. Rec. 18, 969–972.

8. Bie, C., Cheng, B., Fan, J., Ho, W., and Yu, J. (2021). Enhanced solar-to-chemical energy conversion of graphitic carbon nitride by two-dimensional cocatalysts. EnergyChem 3, 100051.

9. Lin, L., Hisatomi, T., Chen, S., Takata, T., and Domen, K. (2020). Visible-light-driven photocatalytic water splitting: recent progress and challenges. J. Trends Chem. 2, 813–824.

10. Bie, C., Yu, H., Cheng, B., Ho, W., Fan, J., and Yu, J. (2021). Design, fabrication, and mechanism of nitrogen-doped graphene-based photocatalyst. Adv. Mater. 33, e2003521.

11. Takanabe, K. (2017). Photocatalytic water splitting: quantitative approaches toward photocatalyst by design. ACS Catal. 7, 8006–8022.

12. Zhang, G., and Wang, X. (2019). Oxysulfide semiconductors for photocatalytic overall water splitting with visible light. Angew. Chem. Int. Ed. Engl. 58, 15580–15582.

13. Kranz, C., and Wächtler, M. (2021). Characterizing photocatalysts for water splitting: from atoms to bulk and from slow to ultrafast processes. Chem. Soc. Rev. 50, 1407–1437.

14. Zhang, J., Zhou, P., Liu, J., and Yu, J. (2014). New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO_2. Phys. Chem. Chem. Phys. 16, 20382–20386.

15. Martinez Suarez, C.M., Hernández, S., and Russo, N. (2015). $BiVO_4$ as photocatalyst for solar fuels production through water splitting: a short review. Appl. Catal. A 504, 158–170.

16. Serpone, N., Emeline, A.V., Ryabchuk, V.K., Kuznetsov, V.N., Artem'ev, Y.M., and Horikoshi, S. (2016). Why do hydrogen and oxygen yields from semiconductor-based photocatalyzed water splitting remain disappointingly low? Intrinsic and extrinsic factors impacting surface redox reactions. ACS Energy Lett. 1, 931–948.

17. Tang, J., Durrant, J.R., and Klug, D.R. (2008). Mechanism of photocatalytic water splitting in TiO_2. Reaction of water with photoholes, importance of charge carrier dynamics, and evidence for four-hole chemistry. J. Am. Chem. Soc. 130, 13885–13891.

18. Sander, R. (2015). Compilation of Henry's law constants, (version 4.0) for water as solvent. Atmos. Chem. Phys. 15, 4399–4981.

19. Mei, B., Han, K., and Mul, G. (2018). Driving surface redox reactions in heterogeneous photocatalysis: the active state of illuminated semiconductor-supported nanoparticles during overall water-splitting. ACS Catal. 8, 9154–9164.

20. Vequizo, J.J.M., Matsunaga, H., Ishiku, T., Kamimura, S., Ohno, T., and Yamakata, A. (2017). Trapping-induced enhancement of photocatalytic activity on brookite TiO_2 pow-ders: comparison with anatase and rutile TiO_2 powders. ACS Catal. 7, 2644–2651.

21. Wang, Z., Inoue, Y., Hisatomi, T., Ishikawa, R., Wang, Q., Takata, T., Chen, S., Shibata, N., Ikuhara, Y., and Domen, K. (2018). Overall water splitting by Ta_3N_5 nanorod single crystals grown on the edges of $KTaO_3$ particles. Nat. Catal. 1, 756–763.

22. Goto, Y., Hisatomi, T., Wang, Q., Higashi, T., Ishikiriyama, K., Maeda, T., Sakata, Y., Okunaka, S., Tokudome, H., Katayama, M., et al. (2018). A particulate photocatalyst water-splitting panel for large-scale solar hydrogen generation. Joule 2, 509–520.

23. Wang, Q., Nakabayashi, M., Hisatomi, T., Sun, S., Akiyama, S., Wang, Z., Pan, Z., Xiao, X., Watanabe, T., Yamada, T., et al. (2019). Oxysulfide photocatalyst for visible-light-driven overall water splitting. Nat. Mater. 18, 827–832.

24. Wang, Q., and Domen, K. (2020). Particulate photocatalysts for light-driven water splitting: mechanisms, challenges, and design strategies. Chem. Rev. 120, 919–985.

25. Cao, S., Chan, T.-S., Lu, Y.-R., Shi, X., Fu, B., Wu, Z., Li, H., Liu, K., Alzuabi, S., Cheng, P., et al. (2020). Photocatalytic pure water splitting with high efficiency and value by Pt/porous brookite TiO_2 nanoflutes. Nano Energy 67, 104287.