

# Photocatalytic Transfer Hydrogenation Reactions Using Water as the Proton Source

En Zhao, Wenjun Zhang, Lin Dong, Radek Zbořil,\* and Zupeng Chen\*



Cite This: *ACS Catal.* 2023, 13, 7557–7567



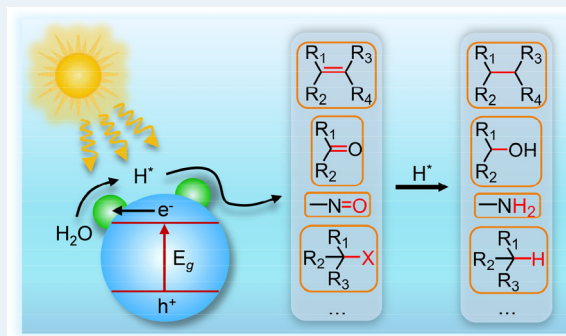
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** Transfer hydrogenation using liquid hydrogen carriers as the direct proton sources under mild conditions has received extensive attention in the research area of organic synthesis. The emerging photocatalytic water-donating transfer hydrogenation (PWDTH) is a promising alternative over the conventional hydrogenation technology due to the advantages of being eco-friendly. This paper focuses on the recent advances in the rising and rapidly developing field of PWDTH reactions, devoted to elucidating the mechanism of the hydrogen transfer process and rationalizing the design principles of efficient photocatalysts. Finally, the current challenges and future opportunities are described.



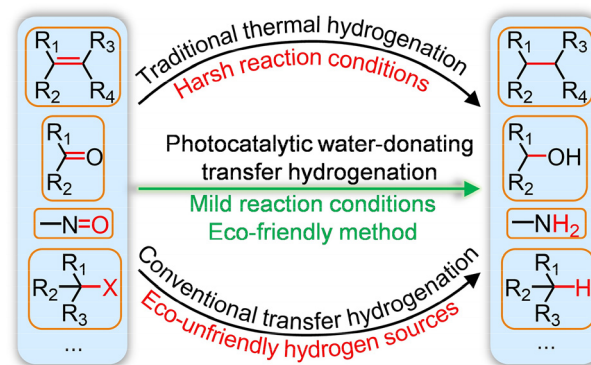
**KEYWORDS:** photocatalysis, transfer hydrogenation, water splitting, mild conditions, deuteration

## 1. INTRODUCTION

Hydrogenation, as one of the most important pillars of the chemical industry, has been widely used in the petrochemical, coal chemical, fine chemical, and pharmaceutical industries, and it has been assessed that 25% of chemical transformations involve at least one hydrogenation step.<sup>1,2</sup> Traditional thermal hydrogenation is an energy-intensive process that usually requires harsh conditions of high temperature and pressure with a flammable H<sub>2</sub> atmosphere (Scheme 1).<sup>3,4</sup> The transfer hydrogenation (TH) reaction, referring to the addition of hydrogen to an organic molecule from a non-H<sub>2</sub> source (e.g., formic acid, silane, and borane–ammonia), is a prospective method to access various hydrogenated organics.<sup>3</sup> For instance, Xu et al. reported the TH of alkene by taking ammonia borane as a hydrogen source.<sup>5</sup> Kappe et al. presented a catalyst-free process for the *in situ* generation of diimide, which was applied to the reduction of alkenes.<sup>6</sup> Zbořil et al. reported the selective hydrogenation of nitroaromatics using hydrazine as a proton source.<sup>7</sup> Moreover, alcohols and acids are also used as proton sources for the hydrogenation of diverse unsaturated bonds.<sup>8–13</sup> Nevertheless, these systems have the disadvantage of the use of non-environmentally friendly proton sources (Scheme 1).

In consideration of the ultimate goal of developing eco-friendly and sustainable processes in chemical industry production, water is regarded as the ultimate green source of a hydrogen donor for TH.<sup>14</sup> Unfortunately, the activation of water molecules is extremely challenging under mild conditions due to its intrinsic thermostability ( $\Delta G^\circ = +237$

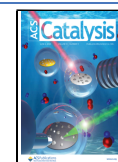
**Scheme 1. Traditional Thermal Hydrogenation Uses Flammable H<sub>2</sub> at High Temperature and Pressure and Conventional TH Uses Eco-Unfriendly Hydrogen Sources (e.g., Formic Acid, Hydrazine, and Borane–Ammonia), while Photocatalytic Transfer Hydrogenation Uses H<sub>2</sub>O as the Green Hydrogen Source at Normal Pressure and Temperature**



**Received:** January 21, 2023

**Revised:** April 1, 2023

**Published:** May 21, 2023



kJ mol<sup>-1</sup>).<sup>15,16</sup> Tremendous efforts had been devoted to exploring the feasibility of water as a hydrogen source. For example, Stokes et al. showed that the hazardous additive B<sub>2</sub>(OH)<sub>4</sub> could mediate the transfer of H or D atoms from H<sub>2</sub>O or deuterated D<sub>2</sub>O to alkenes and alkynes.<sup>17</sup> The explosive magnesium<sup>18</sup> and manganese<sup>19</sup> powders were also employed to activate H–O bonds in water for the hydrogenation of unsaturated bonds. These technologies have provided new opportunities in H–O bond activations, but they have important limitations due to the use of hazardous or toxic species. This encourages the employment of a safe and sustainable method to activate the water molecules.

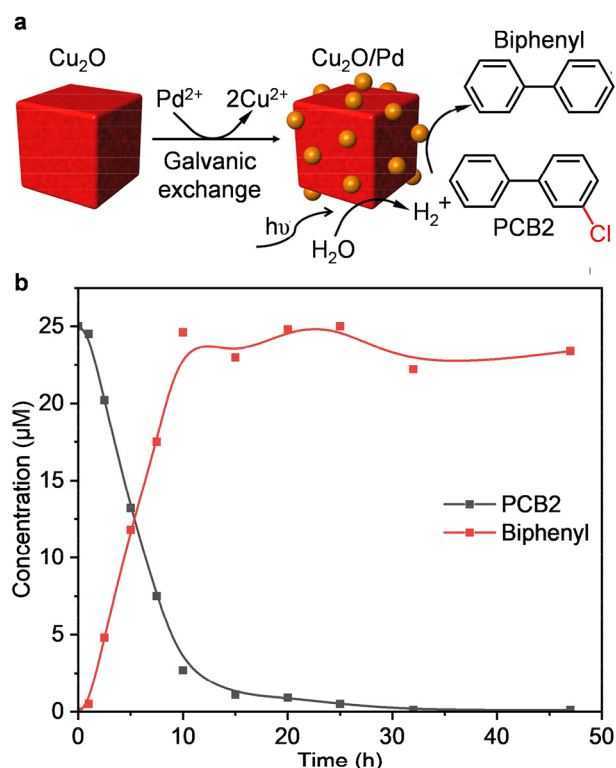
The development of photocatalytic water splitting has inspired sustainable concepts for the generation of “green hydrogen” within chemical energy storage schemes, enabling the pursuit of carbon neutrality and alleviating the energy crisis associated with the depletion of fossil fuels. It is well-known that H<sub>2</sub> is one of the most attractive fuels because it possesses a high energy density and does not produce pollutants during combustion.<sup>20</sup> However, the efficient storage and transport of flammable H<sub>2</sub> is challenging and increases the costs for the hydrogenation industry. In this context, the utilization of the active hydrogen intermediates (H\*) derived from water splitting for the hydrogenation of unsaturated bonds is intriguing (Scheme 1). Therefore, the photocatalytic water-donating transfer hydrogenation (PWDTH) efficiently integrates the processes of photocatalytic water splitting and hydrogenation, which could activate water under mild conditions, avert the storage and transport of H<sub>2</sub>, and generate high-value-added organic products in a more sustainable manner.<sup>14–16</sup>

Multiple excellent reviews have provided comprehensive coverage of transfer hydrogenation reactions in thermocatalytic, electrocatalytic, and photocatalytic processes, including the exploration of transition-metal catalyst diversity, the use of green hydrogen donors, and the investigation of TH mechanisms.<sup>2–4,21–23</sup> For instance, Choudhury's group reviewed the advantages of using biomass-derived alcohols as hydrogen sources to replace nonrenewable H<sub>2</sub> gas for the TH of CO<sub>2</sub>.<sup>21</sup> Xu's group outlined catalytic TH using formic acid or formate as an alternative to high-pressure hydrogen, despite the inevitable decomposition of FA or formate to the greenhouse gas CO<sub>2</sub> during the catalytic process.<sup>22</sup> Unfortunately, there is still no systematic summary concentrating on the photocatalytic transfer hydrogenation using water as the ultimate green proton source under mild conditions. Herein, we present a timely and concise perspective of the recent progress of the photocatalytic water-donating transfer hydrogenation reactions (Scheme 1). We first reveal the mechanism of PWDTH in this perspective. Then, the rational design of photocatalysts (i.e., single-atom catalysts and alloy catalysts) to achieve efficient conversion and high selectivity for PWDTH is emphasized. Furthermore, photocatalytic deuteration using D<sub>2</sub>O as a deuterium source is discussed. Finally, the challenges and opportunities are addressed to provide intriguing perspectives to further advance the PWDTH reactions.

## 2. FUNDAMENTALS OF PHOTOCATALYTIC WATER-DONATING TRANSFER HYDROGENATION

Photocatalytic water splitting into H<sub>2</sub> is widely regarded as a prominent approach for storing solar energy as chemical energy.<sup>24</sup> Meanwhile, photocatalysis has evolved over the last decades into a broadly used approach for organic synthesis

(e.g., transfer hydrogenation).<sup>25</sup> Inspired by these studies, a seminal work in the field of PWDTH was reported by Knecht's group in 2014.<sup>26</sup> They developed a palladium nanoparticle decorated Cu<sub>2</sub>O catalyst (Cu<sub>2</sub>O/Pd) via a galvanic exchange, which used the *in situ* generated H<sub>2</sub> from photocatalytic water splitting at the Cu<sub>2</sub>O surface for the subsequent hydrodehalogenation of polychlorinated biphenyls at the Pd nanoparticles (Figure 1a). Figure 1b shows that 3-chlorobi-

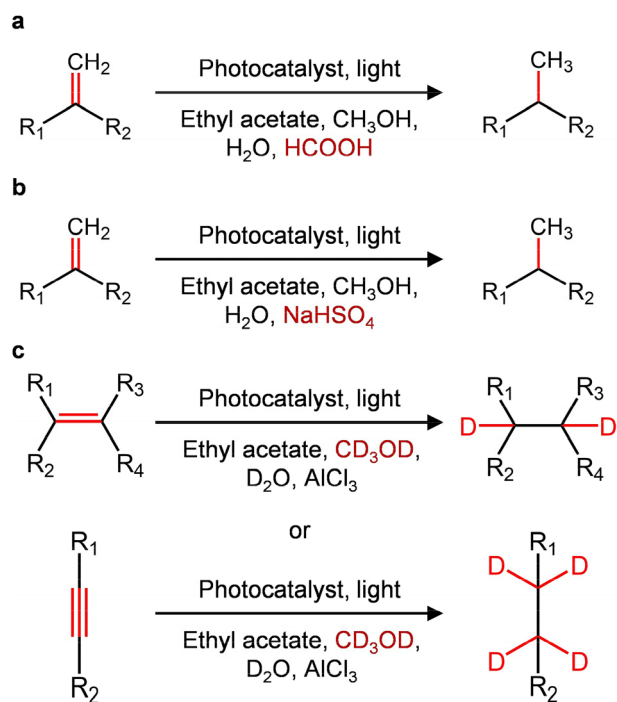


**Figure 1.** (a) Illustration of fabrication of Cu<sub>2</sub>O/Pd catalysts for photocatalytic water-donating dehalogenation. (b) Concentration changes of PCB2 and biphenyl product during the photocatalytic water-donating dehalogenation reaction over Cu<sub>2</sub>O/Pd. Reaction conditions: catalyst (100 mg), substrate (1.25 μmol), H<sub>2</sub>O (25 mL), CH<sub>3</sub>OH (25 mL), 450 W Hg lamp, pressure (1 bar), N<sub>2</sub> atmosphere. Reproduced with permission from ref 26. Copyright 2014 American Chemical Society.

phenyl (PCB2) could be fully dechlorinated to biphenyl within 15 h under visible-light irradiation. However, the work did not track the pathway of hydrogen addition during the PWDTH reaction, which is fundamental to the mechanistic study. Likewise, although the groups of Qiu<sup>27</sup> and Su<sup>28</sup> reported the PWDTH reaction using the *in situ* generated H\* species from water, the presence of additives (i.e., HCOOH and NaHSO<sub>4</sub>) increases the difficulty of mechanism investigation (Scheme 2a,b). Moreover, Su et al. presented the deuteration of alkenes and alkynes utilizing the *in situ* generated deuterium species (D\*) from D<sub>2</sub>O splitting.<sup>29</sup> Unfortunately, the presence of CD<sub>3</sub>OD in the reaction system complicated the identification of the source of active D species (Scheme 2c).

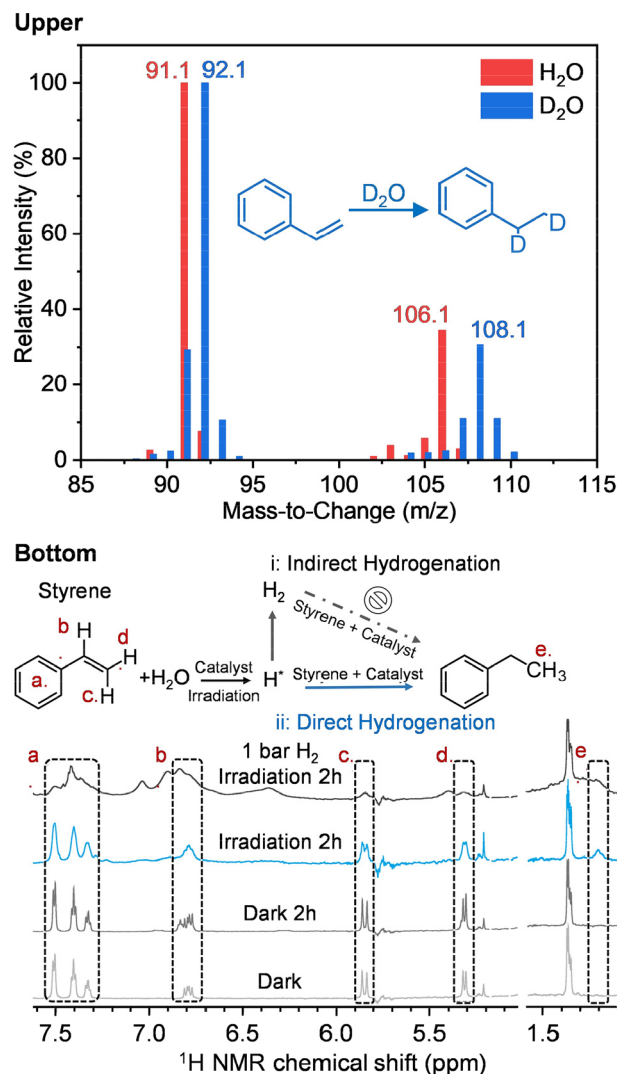
**2.1. Mechanism Investigation.** To disclose the origin of the hydrogen addition in the PWDTH reaction, Xu et al. employed isotope-labeling experiments,<sup>15</sup> in which styrene was tested as a model compound toward TH. As shown in the mass spectra (Figure 2, top), when H<sub>2</sub>O was used, the *m/z* values of 91.1 and 106.1 were assigned to the fragmentation ion [ph-

### Scheme 2. Illustration of the PWDTH Process in the Presence of Hydrogen-Rich Additives<sup>a</sup>



<sup>a</sup>Reaction conditions: (a) catalyst (10 mg), substrate (0.1 mmol), H<sub>2</sub>O (1.5 mL), ethyl acetate (2 mL), CH<sub>3</sub>OH (1.4 mL), additive (HCOOH, 0.1 mL), 20 W blue light ( $\lambda = 420$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere; (b) catalyst (10 mg), substrate (0.1 mmol), H<sub>2</sub>O (1.5 mL), ethyl acetate (2 mL), CH<sub>3</sub>OH (1.5 mL), additive (NaHSO<sub>4</sub>, 0.1 mmol), 20 W blue light ( $\lambda = 420$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere; (c) catalyst (10 mg), substrate (0.1 mmol), D<sub>2</sub>O (1.5 mL), ethyl acetate (2 mL), CD<sub>3</sub>OD (1.5 mL), additive (AlCl<sub>3</sub>, 0.1 mmol), 20 W blue light ( $\lambda = 420$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere.

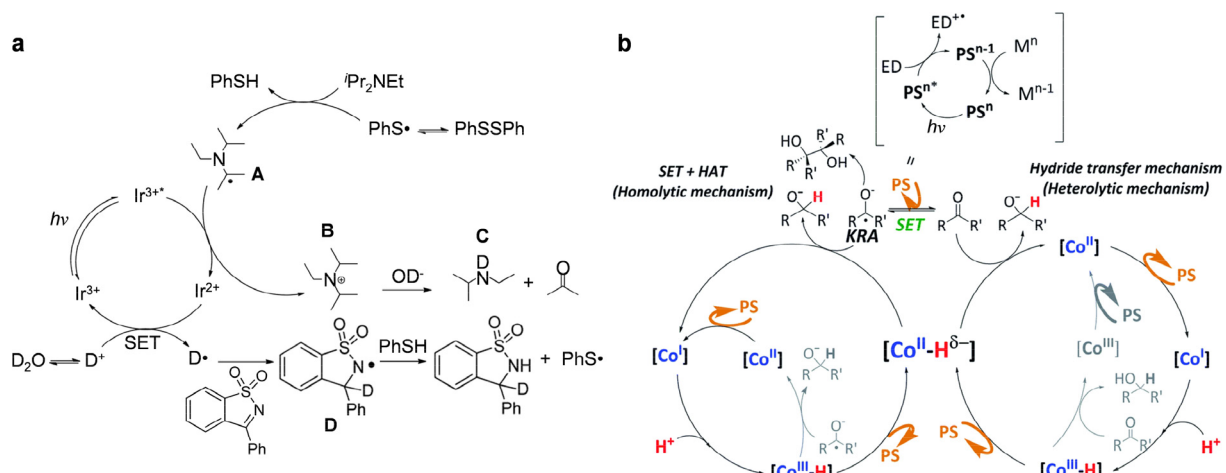
CH<sub>2</sub>]<sup>+</sup> and the molecular ion of ethylbenzene, respectively. These signals shifted to 92.1 and 108.1 when replacing H<sub>2</sub>O with D<sub>2</sub>O, suggesting that the proton source for TH originates from water. However, this method cannot identify the pathway of hydrogen addition in actual scenarios. To address the matter, our recent study employed *operando* nuclear magnetic resonance (NMR) measurements for the first time to track the reaction pathway during the PWDTH reaction.<sup>14</sup> As shown in the <sup>1</sup>H NMR spectra (Figure 2, bottom), proton signals from the benzene ring (region a) and ethenyl (regions b–d) of the styrene molecule were observed under dark conditions. Then, the signals of styrene remained untouched after 2 h in the dark, suggesting that the styrene is steady under dark conditions and the unsaturated structure reluctantly exchanges protons with D<sub>2</sub>O. After *in situ* illumination for 2 h, the ethenyl signal diminished, and the methyl structure (region e) on ethylbenzene began to appear, verifying the conversion of styrene toward ethylbenzene. Notably, a great deal of D<sub>2</sub>O was activated under the irradiation conditions and the D of D<sub>2</sub>O underwent a rapid proton exchange with the H of the benzene structure, broadening the <sup>1</sup>H NMR signals of the benzene ring in the region a. To exclude the possibility of indirect hydrogenation of styrene with the generated H<sub>2</sub> from water splitting, 1 bar of hydrogen gas was fed into the *operando* closed NMR tube. The results indicate that the proton addition occurs in both the benzene ring and ethenyl, whereas



**Figure 2.** (top) Mass spectra of the liquid product from the PWDTH reaction of styrene. Reproduced with permission from ref 15. Copyright 2020 American Chemical Society. (bottom) *Operando* <sup>1</sup>H NMR spectra of the liquid product from the PWDTH reaction of styrene. Reproduced with permission from ref 14. Copyright 2022 Wiley.

the proton addition only occurs in the ethenyl structure without H<sub>2</sub> introduction. Therefore, the *operando* NMR experiments unequivocally prove that the proton addition mechanism from styrene to ethylbenzene is a direct hydrogenation reaction utilizing the *in situ* generated protons from photocatalytic water splitting instead of *in situ* generated H<sub>2</sub> gas. Moreover, the strong proton exchange could efficiently activate water molecules for photocatalytic transfer hydrogenation.

Traditional thermal hydrogenation with flammable H<sub>2</sub> is carried out over transition-metal catalysts, which consists of multiple steps including bond cleavage, rearrangement, and recombination.<sup>22</sup> In terms of the PWDTH reaction, H<sub>2</sub> is replaced by H\* from photocatalytic water splitting, where the H\* could be used in the subsequent hydrogenation step and spill over from the metal sites to evolve into H<sub>2</sub>. Due to the competition between these two reactions, exploring the subtle relationship between hydrogenation and hydrogen evolution provides insight into the mechanism of the PWDTH reaction.

Scheme 3. Proposed Mechanism for the PWDTH Process of (a) *N*-Sulfonylimines and (b) Aromatic Ketones and Aldehydes<sup>42</sup>

<sup>42</sup>Reproduced with permission from refs 36 and 39. Copyright 2019 Royal Society of Chemistry.

For example, Xiong and co-workers used a  $\text{TiO}_2\text{-Pd}_{0.5}\text{Pt}_{0.5}$  hybrid catalyst for the PWDTH reaction and they detected the amount of hydrogen evolution in the presence and absence of the substrate, respectively.<sup>30</sup> Compared to a large amount of hydrogen evolution in the absence of a substrate, the catalyst exhibited little hydrogen evolution activity in the presence of a substrate, indicating that most of  $\text{H}^*$  (ca. 99%  $\text{H}^*$ ) was transferred to the hydrogenation reaction. This is due to the adsorption of  $\text{H}^*$  on the Pd surface as a hollow-site configuration with strong binding (discussed in detail in subsequent subsections). Similar phenomena have been found in other PWDTH systems, where either nanoparticle catalysts<sup>15,31</sup> or heterojunctions<sup>32</sup> were used. In our previous work,<sup>14</sup> we developed a palladium single-atom catalyst for the PWDTH reaction, and the performance of the transfer hydrogenation was much improved compared to the above works due to the intrinsic properties of the single-atom catalyst, resulting in superior hydrogen evolution activity and an abundance of catalytically active sites. However, the proportion of the  $\text{H}^*$  used in the PWDTH reaction has declined (ca. 85%  $\text{H}^*$ ) compared to the above works, suggesting that single-atom catalysts inevitably waste some of the  $\text{H}^*$  while improving the PWDTH performance. In summary, very few works have been done to investigate the competition between hydrogenation and  $\text{H}_2$  evolution. Available studies have found that most of the  $\text{H}^*$  is preferentially used in PWDTH reactions, and this is more evident in nanoparticle or heterojunction catalysts (i.e., catalysts with lower water-splitting activity). Although single-atom catalysts could enhance the performance of PWDTH reactions, they also promote hydrogen evolution. The effect of the structure of photocatalysts on the competition between hydrogenation and  $\text{H}_2$  evolution remains unknown. As more research is conducted, the relationship between them may be clearer.

Researchers have employed various techniques to probe the reaction mechanism of the subsequent hydrogenation process. To explore the detailed processes of the hydrogenation of nitrobenzene to aniline, Xu et al. employed *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).<sup>32</sup> First, nitrobenzene ( $\text{PhNO}_2$ ) adsorbed onto the catalytic site and formed a  $\text{PhN}(\text{OH})_2$  intermediate by two  $\text{H}^*$  transfers, followed by the removal of one molecule of water

to form a  $\text{PhNO}$  intermediate, then by two  $\text{H}^*$  transfers to form a  $\text{PhNHOH}$  intermediate, followed by the removal of one molecule of water to form a  $\text{PhN}$  intermediate, and finally by two  $\text{H}^*$  transfer to form aniline ( $\text{PhNH}_2$ ), which was desorbed from the catalyst. Zhao and co-workers examined a nickel single-atom catalyst preadsorbed by water under visible-light irradiation through extended X-ray absorption fine structure spectra (EXAFS) combined with density functional theory (DFT) calculations to propose an adsorption configuration of  $\text{H}^*$  (i.e.,  $\text{OH-Ni-N}_2\cdots\text{N-H}$ ).<sup>33</sup> The subsequent semi-hydrogenation of alkynes then began with the transfer of  $\text{H}^*$  from pyridinic N to the adsorbed substrate.

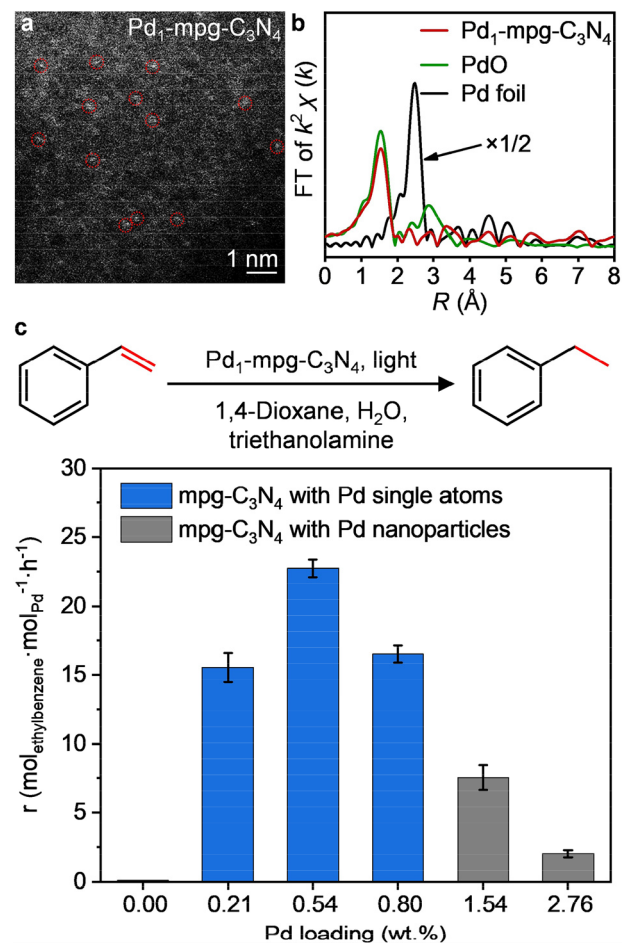
To investigate the mechanism of hydrogenation of aryl bromides, Ren et al. conducted some controlled experiments, in which the radical inhibitors 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were added to the reaction system.<sup>34</sup> The results showed that the presence of BHT or TEMPO resulted in a dramatic decrease in the content of the product aryl compounds. The electron-deficient aryl bromides possessed a higher reactivity under the reaction system. A single electron transfer (SET) mechanism could theoretically explain such an electron effect, as an increase in the electron density of the aromatic ring could hasten the SET from the catalyst to the substrate by enhancing the electron-accepting capacity of the substrate.<sup>35</sup> Fan and co-workers employed fluorescence emission spectroscopy to monitor the PWDTH process of *N*-sulfonylimines and similarly proposed a SET mechanism (Scheme 3a).<sup>36</sup> Under visible light irradiation, the photocatalyst *fac*- $\text{Ir}(\text{ppy})_3$  is excited to produce  $\text{Ir}^{3+*}$ , followed by a single electron transfer process with radical A. The resulting  $\text{Ir}^{2+}$  is highly reductive<sup>37</sup> and therefore capable of producing deuterium radicals.<sup>38</sup> The deuterium radicals are then added to the *N*-sulfonylimine, which produces the final products by further quenching of radical D. Lloret-Fillol et al. proposed that the hydrogenation of aromatic ketones could proceed via a single electron transfer–hydrogen atom transfer (SET-HAT) mechanism (Scheme 3b), which was confirmed by radical clock experiments.<sup>39</sup> It is well-known that  $[\text{Cu}(\text{bathocuproine})\text{-}(\text{Xantphos})](\text{PF}_6)$  ( $\text{PS}_{\text{Cu}}$ ), a photoredox catalyst, is excited under light irradiation and then reductively quenched by an electron donor (ED) to give  $\text{PS}_{\text{Cu}}^-$ ,<sup>40</sup> which reduces the reduction catalyst  $[\text{Co}(\text{OTf})(\text{Py}_2\text{T}^{\text{s}}\text{tacn})](\text{OTf})$  ( $[\text{Co}^{\text{II}}]$ ) to the

intermediate  $[\text{Co}^{\text{I}}]$ .<sup>41</sup>  $[\text{Co}^{\text{I}}]$  is protonated by water to form the putative  $[\text{Co}^{\text{III}}-\text{H}]$ , which is readily reduced to give the active  $[\text{Co}^{\text{II}}-\text{H}]$  species. Subsequently, for the hydrogenation of ketones and aldehydes, the substrate is converted to a carbonyl radical anion intermediate through a single electron transfer of  $\text{PS}_{\text{Cu}}^-$ . Ultimately, the intermediate is converted to the product via a hydrogen atom transfer from the  $[\text{Co}^{\text{II}}-\text{H}]$  species (homolytic pathway, Scheme 3b, left). Alternatively, a direct nucleophilic attack of a putative  $[\text{Co}^{\text{II}}-\text{H}]$  species may be also considered (heterolytic pathway, Scheme 3b, right). By similar methods, their group has proposed that the reduction of aromatic olefins in their reaction system takes place by a HAT mechanism, most likely via  $[\text{Co}-\text{H}]$  intermediates.<sup>42</sup>

**2.2. From Nanoparticle to Single-Atom Catalysts.** During the PWDTH reaction, the photogenerated  $\text{H}^*$  from water splitting could be adsorbed to the surface of metal species and subsequently added to various unsaturated organic substrates. Han et al. demonstrated that nitrobenzenes with different groups could be hydrogenated to the corresponding anilines by the  $\text{H}^*$  from photocatalytic water splitting over a  $\text{TiO}_2$ -supported Pd nanoparticle catalyst ( $\text{Pd}/\text{TiO}_2$ ).<sup>43</sup> Similarly, Xu et al. realized the proton addition of different unsaturated bonds ( $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ , and  $\text{N}=\text{O}$ ) over platinum nanoparticle loaded carbon nitride ( $\text{Pt}/\text{CN}$  or  $\text{PtPd}/\text{CN}$ ).<sup>15</sup> Unfortunately, these nanoparticle catalysts usually suffer from sluggish conversion efficiency and poor metal utilization because the metal atoms inside the bulk of nanoparticles are inaccessible to the reactants.

Single-atom catalysts (SACs) have recently received extensive research attention due to their maximum metal dispersion and atom-utilization efficiency, which have exhibited excellent catalytic performance in a broad range of applications including Suzuki coupling, selective oxidation, hydroformylation, etc.<sup>44,45</sup> In our recent work, we extended the employment of SACs to photocatalytic transfer hydrogenation for the first time. The reported carbon nitride supported palladium SAC ( $\text{Pd}_1\text{-mpg-C}_3\text{N}_4$ ) (Figure 3a,b) showed preeminent performance in the PWDTH reaction compared to its nanoparticle counterpart with a similar Pd loading ( $\text{Pd}_{\text{NP}}\text{-mpg-C}_3\text{N}_4$ ).<sup>14</sup> As shown in Figure 3c, a comparison on a metal basis manifested the highest ethylbenzene formation rate ( $22.73 \text{ mol}_{\text{ethylbenzene}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1}$ ) for the 0.54 wt % SAC sample. However, the rate of ethylbenzene formation decreased linearly to  $2.02 \text{ mol}_{\text{ethylbenzene}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1}$  when the Pd content was further increased to 2.76 wt %, which is 11-fold lower than that of the optimized  $\text{Pd}_1\text{-mpg-C}_3\text{N}_4$ . The inhibited reaction rate could be attributed to the formation of clusters or nanoparticles in samples with a Pd loading higher than 0.8 wt %, which emphasizes the advantages of the specific electronic properties (cationic form) of atomically dispersed sites over conventional zerovalent nanometals toward the PWDTH reaction.

The PWDTH reactions are a complex class of multistage catalytic reactions. In the process, the water molecule is first split to produce the  $\text{H}^*$ , which is then transferred to hydrogenated active sites where the substrate is adsorbed, and finally, the organic unsaturated bond is added. In the first step (i.e., photocatalytic water splitting), the rate of the  $\text{H}^*$  production determines the rate of the subsequent hydrogenation step. In other words, the O–H bond dissociation of water molecules may be involved in the rate-limiting step.<sup>33</sup> Over the past decades, researchers have been dedicated to boosting the activity of photocatalytic water splitting.<sup>46</sup> Loading of a cocatalyst has attracted a great deal of attention



**Figure 3.** (a) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image and (b) Fourier transform of Pd *K*-edge extended X-ray absorption fine structure (EXAFS) spectra of  $\text{Pd}_1\text{-mpg-C}_3\text{N}_4$ . Pd foil and PdO were applied for comparison purposes. (c) Metal-specific reaction rate toward ethylbenzene formation as a function of palladium content for the PWDTH reaction of styrene. Reaction conditions: catalyst (10 mg), substrate (0.1 mmol),  $\text{H}_2\text{O}$  (2 mL), 1,4-dioxane (3 mL), triethanolamine (0.5 mL), 40 W blue light ( $\lambda = 427 \text{ nm}$ ), temperature (308 K), pressure (1 bar),  $\text{N}_2$  atmosphere. Reproduced with permission from ref 14. Copyright 2022 Wiley.

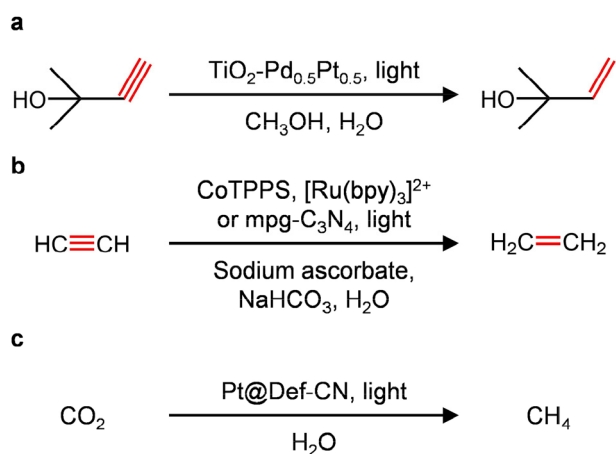
due to its significant advantages in terms of enhanced light absorption, photogenerated charge migration, and surface catalytic reactions (e.g., hydrogenation, oxidation, and coupling).<sup>47,48</sup> The photocatalytic water splitting activity of non-noble-metal-loaded catalysts, however, is currently far from being on par with noble-metal-loaded catalysts. As a result, the majority of studies on the PWDTH have relied on noble-metal-loaded catalysts (e.g.,  $\text{Pd}_{\text{NP}}\text{-CN}$ ,  $\text{Pt}_{\text{NP}}\text{-CN}$ ,  $\text{Pd}_{\text{NP}}/\text{TiO}_2$ , and  $\text{Cu}_2\text{O}/\text{Pd}_{\text{NP}}$ ).<sup>15,26,34,45,49</sup> SACs have the potential to greatly contribute to the rational design of targeted catalysts for preferred catalytic performance by acting as the perfect platforms to investigate catalytic mechanisms at the molecular or atomic level and to comprehend the relationship between structure and catalytic performance,<sup>50–52</sup> as confirmed in our previous work.<sup>14</sup> Meanwhile, non-noble-metal catalysts should be intelligently constructed to achieve efficient PWDTH in order to reduce excessive dependence on noble-metal catalysts. Zhao's group designed a  $\text{Ni}^{2+}\text{-N}_4$  site built on carbon nitride for photocatalyzed semihydrogenation of alkynes using water

as the hydrogen source without alkane production.<sup>33</sup> Moreover, Xu and co-workers developed a  $\text{TiO}_2/\text{Ce}_2\text{S}_3$  S-scheme heterojunction photocatalyst for aniline production by nitrobenzene hydrogenation with water as the proton source.<sup>32</sup> This is an innovative work, free from noble-metal catalysts, but the scope of heterojunction photocatalysts for various PWDTH reactions needs to be explored. In general, the design of the photocatalysts must meet the requirements for excellent water-splitting activity and the presence of hydrogenation active sites (normally metal species, e.g., VIII subgroup metals). In addition, several articles have confirmed that the specific electronic properties (cationic form) of atomically dispersed sites are perhaps more suitable for the PWDTH reactions.<sup>14,33</sup>

### 2.3. Photocatalytic Selective Transfer Hydrogenation.

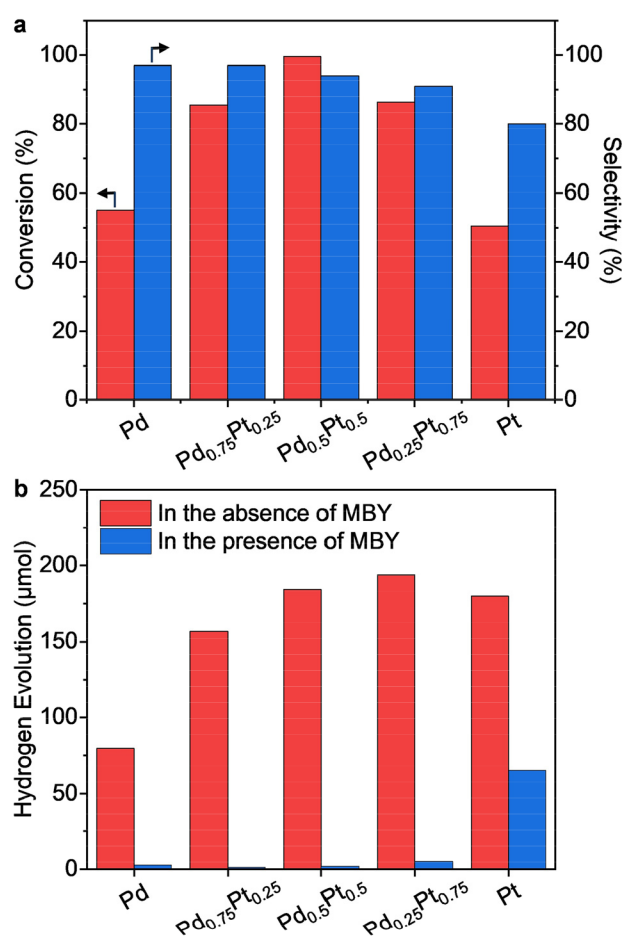
Selective hydrogenation is a class of highly important organic transformations for both petrochemical and fine chemical industries.<sup>2</sup> The critical aspect of selective hydrogenation relies on the fabrication of efficient and selective catalysts. Xiong et al. reported a  $\text{TiO}_2\text{-Pd}_x\text{Pt}_{1-x}$  hybrid catalyst toward photocatalytic selective 2-methyl-3-butyne-2-ol (MBY) semihydrogenation to 2-methyl-3-buten-2-ol (MBE) using water as a proton source (Scheme 4a).<sup>30</sup> As shown in Figure 4a, the

#### Scheme 4. Illustration of Photocatalytic Selective Transfer Hydrogenation Using $\text{H}_2\text{O}$ as an H Source<sup>a</sup>



<sup>a</sup>Reaction conditions: (a) catalyst (10 mg), substrate (0.5 mmol),  $\text{H}_2\text{O}$  (7.5 mL),  $\text{CH}_3\text{OH}$  (2.5 mL), 300 W Xe lamp ( $\lambda < 400$  nm), pressure (1 bar), Ar atmosphere; (b) catalyst (0.002  $\mu\text{mol}$ ), sensitizer (0.1  $\mu\text{mol}$   $[\text{Ru}(\text{bpy})_3]^{2+}$  or 2.5 mg mpg-CN), substrate (1 atm  $\text{C}_2\text{H}_2$ ,  $\geq 99.5$  vol %), aqueous bicarbonate buffer (2 mL, pH 8.4), sodium ascorbate (0.2 mmol), blue light ( $\lambda = 450$  nm), temperature (298 K); (c) catalyst (30 mg), substrate (1 atm  $\text{CO}_2$ ),  $\text{H}_2\text{O}$  (0.1 mL), 300 W Xe lamp.

$\text{Pd}_x\text{Pt}_{1-x}$  alloys vastly surmount the limitations in catalytic activity and semihydrogenation selectivity compared with pure Pd and Pt. To reveal the mechanism, the authors studied the hydrogen evolution performance, which is the competing reaction that consumes the active  $\text{H}^*$  species (Figure 4b). A significantly improved performance of photocatalytic hydrogen evolution was observed in the absence of MBY in all samples. When MBY was introduced, almost all samples were inactive for the  $\text{H}_2$  evolution process except for pure Pt, indicating that  $\text{H}^*$  was mostly used in the semihydrogenation of MBY. In terms of pure Pt,  $\text{H}^*$  species are weakly bound to Pt sites in either top-site or hollow-site configurations with barely any surface diffusion barrier. Therefore,  $\text{H}^*$  could readily spill over

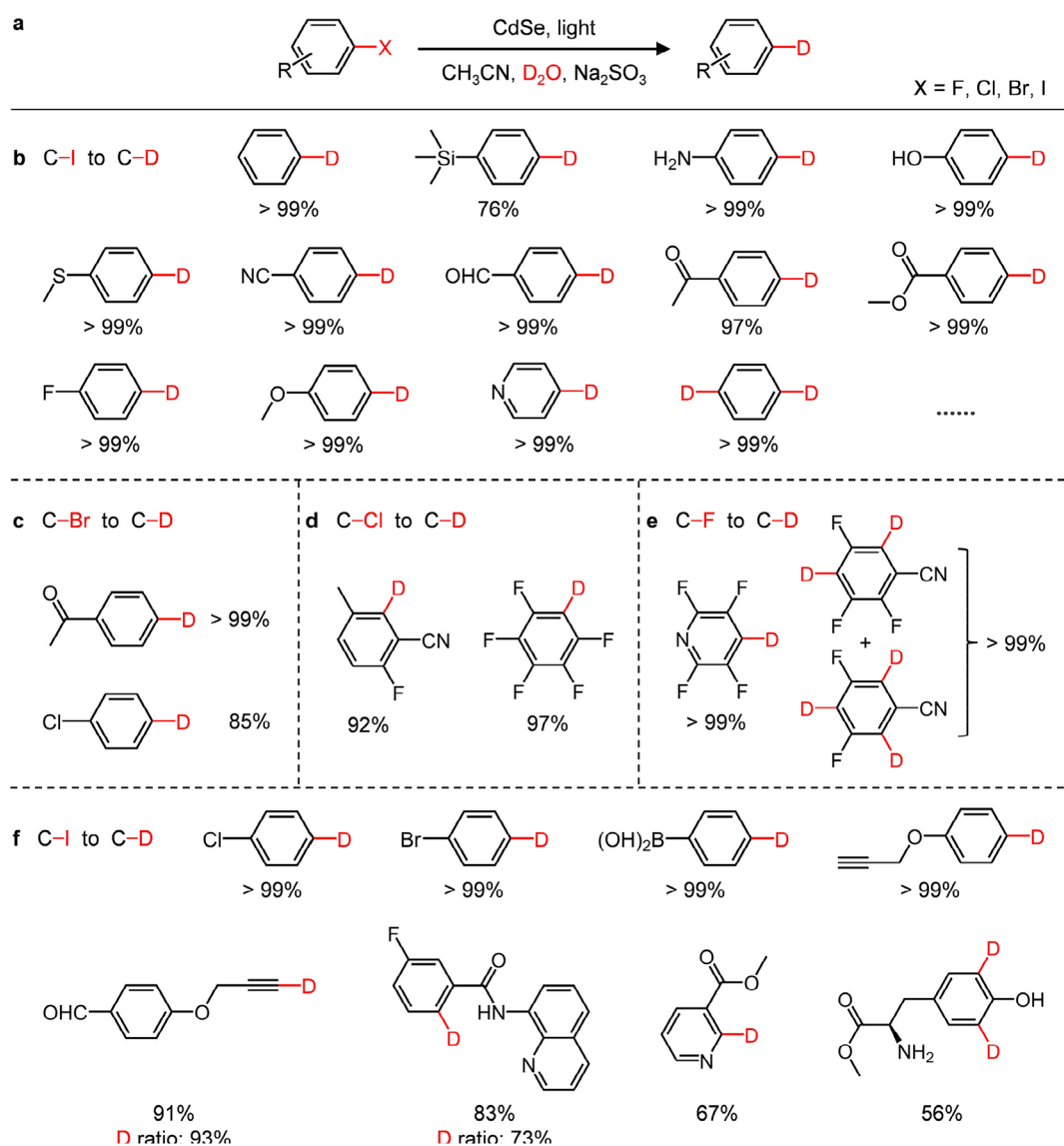


**Figure 4.** (a) The catalytic performance of selective 2-methyl-3-butyne-2-ol semihydrogenation to 2-methyl-3-buten-2-ol (MBY) using water as a proton source with various  $\text{TiO}_2\text{-Pd}_x\text{Pt}_{1-x}$  photocatalysts. Reaction conditions are as indicated in Scheme 4a. (b) The amount of hydrogen evolution in the presence of MBY or the absence of MBY. Reproduced with permission from ref 30. Copyright 2017 Wiley.

the surface and subsequently evolve into  $\text{H}_2$ , limiting the conversion of MBY. In contrast, the adsorbed  $\text{H}^*$  strongly binds to the Pd surface by a hollow-site configuration. Although pure Pd could retain a high semihydrogenation selectivity, the slow  $\text{H}^*$  diffusion and desorption would be a bottleneck in improving the conversion of MBY. Having this in mind, the authors envisaged that alloying Pd with Pt would offer Pd–Pt hollow sites for  $\text{H}^*$  adsorption, in which the M–H binding could be adjusted to a suitable range for appropriate diffusion and desorption of  $\text{H}^*$ . As expected, the selectivity of the  $\text{TiO}_2\text{-Pd}_{0.5}\text{Pt}_{0.5}$  sample remained high when the conversion approached 100% (Figure 4a). This work emphasized the importance of lattice engineering design on photocatalytic selective hydrogenation using water as a proton source.

Selective hydrogenation of acetylene to ethylene in the presence of an excess amount of ethylene is an important process for the petrochemical industry since a ppm level of acetylene poisons the ethylene polymerization.<sup>53</sup> Weiss et al. reported a PWDTH system that reduces acetylene to ethylene with  $\geq 99\%$  selectivity under both noncompetitive (no ethylene cofeeding) and competitive (ethylene cofeeding) conditions.<sup>54</sup> Importantly, nearly 100% conversion was achieved in the latter

**Scheme 5.** (a) Illustration of Photocatalytic Deuteration of Halogenated Compounds using D<sub>2</sub>O as a D Source, Scope of photocatalytic (b) C–I, (c) C–Br, (d) C–Cl, and (e) C–F to C–D Transformation, and (f) D-Labeled Toolbox from Photocatalytic C–I to C–D Transformation for Medical Intermediates<sup>a</sup>



<sup>a</sup>Reaction conditions: catalyst (5 mg), substrate (0.1 mmol), D<sub>2</sub>O (1.5 mL), CH<sub>3</sub>CN (2.5 mL), Na<sub>2</sub>SO<sub>3</sub> (1 mmol), 150 W Xe lamp, temperature (298 K), pressure (1 bar), Ar atmosphere. Reproduced with permission from ref 56. Copyright 2017 Nature Publishing Group.

case, which is more industrially relevant (Scheme 4b). This system used a molecular catalyst based on [*meso*-tetra(4-sulfonatophenyl)porphyrinato]cobalt(III) (CoTPPS) operating under ambient conditions and sensitized by either tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ([Ru(bpy)<sub>3</sub>]<sup>2+</sup>) or mesoporous graphitic carbon nitride (mpg-C<sub>3</sub>N<sub>4</sub>) under visible light. Moreover, Xiong et al. realized 99% selective CO<sub>2</sub> methanation in a pure water system by introducing Pt single atoms to defective carbon nitride (Pt@Def-CN) (Scheme 4c).<sup>55</sup> Despite the low catalytic activity (6.3 μmol<sub>CH<sub>4</sub></sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>), the photoreduction of CO<sub>2</sub> into a high-value-added product in pure water has been demonstrated.

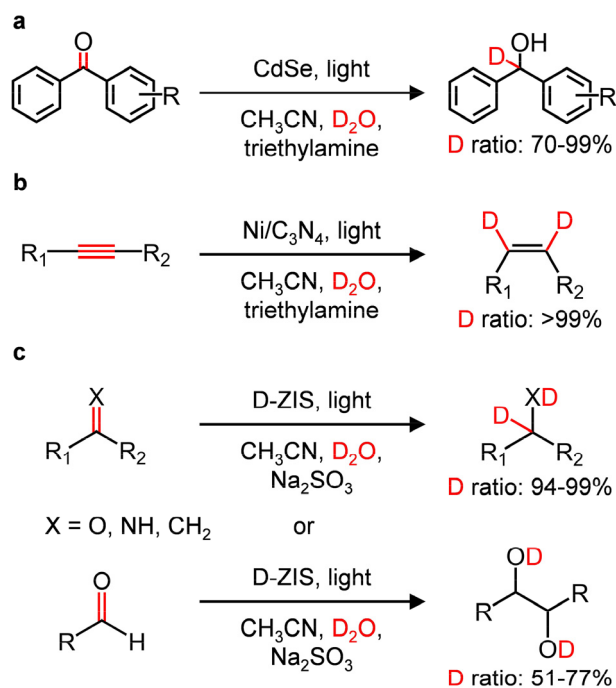
**2.4. D<sub>2</sub>O as a Deuterium Source.** Deuterium labeling is essential in organic synthesis and the pharmaceutical industry. Nevertheless, the state-of-the-art C–H/C–D exchange using noble-metal catalysts or strong bases/acids has the disadvantages of poor functional group tolerance and inferior

selectivity. Loh et al. proposed an innovative strategy for controllable deuteration of halogenated compounds by photocatalytic D<sub>2</sub>O splitting under mild conditions using porous CdSe nanosheets as the catalyst (Scheme 5a).<sup>56</sup> A variety of organic iodides including aryl, alkyl, and alkynyl iodides could be deuterated with satisfactory functional group tolerance (Scheme 5b). This approach is also competent to deuterate less reductively labile C–Br, C–Cl, and even C–F bonds in the presence of activating groups on the benzene ring (Scheme 5c–e). Moreover, the authors have developed a D-labeled toolbox containing deuterated aryl halogen, boric acid, alkyne, alkene, etc., which are valuable D-containing building blocks for drugs or advanced materials (Scheme 5f). This work provided an attractive and promising strategy for controllable deuteration.

Shortly thereafter, Wu et al. developed the deuteration of aromatic alcohols with D<sub>2</sub>O as a D source (70–99% D

incorporation) under visible-light irradiation using CdSe quantum dots as the photocatalyst (Scheme 6a).<sup>57</sup> Zhao et

### Scheme 6. Illustration of Photocatalytic Deuteration Using D<sub>2</sub>O as a D Source<sup>a</sup>

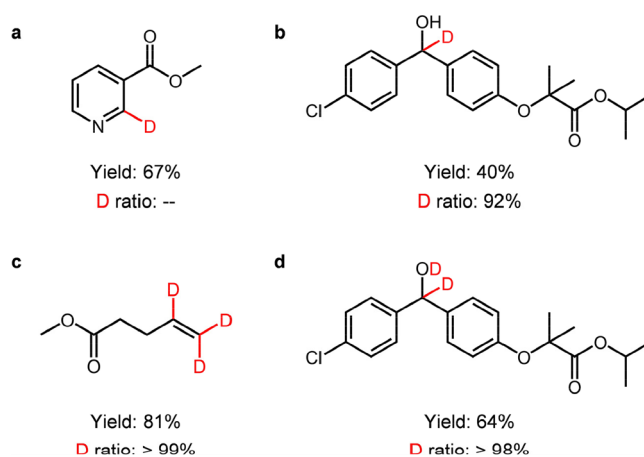


<sup>a</sup>Reaction conditions: (a) catalyst (20  $\mu$ M), substrate (0.2 mmol), D<sub>2</sub>O (5 mmol), CH<sub>3</sub>CN (2 mL), triethylamine (0.4 mmol), blue light ( $\lambda = 450$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere; (b) catalyst (3 mg), substrate (0.03 mmol), D<sub>2</sub>O (1.2 mL), CH<sub>3</sub>CN (4.8 mL), triethanolamine (0.6 mmol), blue light ( $\lambda = 420$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere; (c) catalyst (5 mg), substrate (0.1 mmol), D<sub>2</sub>O (1.8 mL), CH<sub>3</sub>CN (0.2 mL), Na<sub>2</sub>SO<sub>3</sub> (2 mmol), white LED light ( $\lambda > 420$  nm), temperature (298 K), pressure (1 bar), Ar atmosphere.

al. realized the synthesis of deuterium-labeled alkenes with distinguished levels of D incorporation (99%) over nickel nanoparticles supported on carbon nitride (Ni/C<sub>3</sub>N<sub>4</sub>) (Scheme 6b).<sup>58</sup> Also, Sun et al. reported a metal-free defective ultrathin ZnIn<sub>2</sub>S<sub>4</sub> nanosheet (D-ZIS) catalyst for photocatalytic deuteration of carbonyls utilizing the *in situ* generated D protons from D<sub>2</sub>O splitting with decent deuteration incorporation ratios (Scheme 6c).<sup>59</sup> These strategies provided promising insights into the sustainable and eco-friendly organic synthesis of value-added deuterated chemicals. In addition, all of the above deuteration studies have also attempted deuteration synthesis of pharmaceutical intermediates (Figure 5), pointing to the potential of the PWDTH technique for the pharmaceutical industry. Although they all only attempted the reaction of one pharmaceutical intermediate, the implications for the development of a green and safe pharmaceutical industry could be significant.

### 3. CONCLUSION AND OUTLOOK

Although photocatalytic transfer hydrogenation has found widespread use over the last decades, using water as the direct proton source remains underdeveloped. The innovative photocatalytic water-donating transfer hydrogenation enables the utilization of active H<sup>\*</sup> species from water splitting for



**Figure 5.** Deuterated synthesis of pharmaceutical intermediates through the PWDTH technique: (a) methyl nicotinate-2-*d*,<sup>56</sup> (b) isopropyl 2-(4-((4-chlorophenyl)(hydroxy-methyl-*d*)phenoxy)-2-methylpropanoate,<sup>57</sup> (c) methyl pent-4-enoate-4,5,5-*d*<sub>3</sub>,<sup>58</sup> and (d) isopropyl 2-(4-((4-chlorophenyl)(hydroxy-*d*)methyl-*d*)phenoxy)-2-methylpropanoate.<sup>59</sup>

hydrogenation under mild conditions. This strategy is attractive due to the safe, green, eco-friendly, and sustainable reaction conditions. This perspective highlights the reaction pathways and mechanisms, which provide insights into the construction of catalytic systems and the design of efficient photocatalysts, and discusses catalyst design, leading to guidance for tailoring the catalytic activity and selectivity of different heterogeneous catalysts. While some progress has been made in the field of PWDTH, it is in its infancy and many unsolved problems and challenges remain, as outlined below.

- (1) It is crucial to enhance the performance of the PWDTH while avoiding the evolution of H<sup>\*</sup> from water splitting. As far as current studies are concerned, most of the H<sup>\*</sup> is prioritized for the PWDTH reaction, which is more pronounced in nanoparticle or heterojunction catalysts. Whereas for SACs, they might boost the performance of the PWDTH reaction and hydrogen evolution simultaneously. Thus, the competitive relationship between hydrogenation and hydrogen evolution has to be explored. Meanwhile, the regulation of the supported metal species (i.e., nanoparticles, clusters, single atoms, or synergistic effect of different species) should be better studied, which might lead to unexpected results in the PWDTH reactions.
- (2) At present, noble-metal catalysts still dominate in PWDTH reactions. Due to the scarcity and expense of noble metals, it is vital to develop efficient non-noble-metal catalysts such as those of Ni and Co for PWDTH reactions.
- (3) Selective hydrogenation reactions have a wide range of applications in fine chemicals and pharmaceuticals as well as petrochemicals. However, photocatalytic selective hydrogenation using water as the hydrogen source remains to be developed: for example, selective hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds. The rational design of highly selective and versatile photocatalysts by precise modulation of the local coordination environment would be a promising direction.
- (4) The majority of existing studies of PWDTH reactions employ additional hole sacrificial agents (e.g., methanol,



triethanolamine, triethylamine, and  $\text{Na}_2\text{SO}_3$ ) to promote the generation of protons, which produce worthless substances at the oxidation side.<sup>30</sup> A promising strategy is to substitute the hole sacrificial agents with other valuable organics, which could produce value-added reductive and oxidative products at the same time.

- (5) In the PWDTH process, the water molecule is first split to produce the  $\text{H}^*$ , which is then transferred to catalytically active sites for the hydrogenation of organics or spills over to evolve into  $\text{H}_2$ . Nevertheless, the specific reaction pathways and mechanisms of PWDTH reactions remain complex and ambiguous. The understanding of reaction mechanisms requires more work, such as monitoring the reaction process at the molecular level by utilizing advanced *in situ/operando* characterization techniques and understanding the elementary reaction mechanism through theoretical calculations.
- (6) As the most common and nonpolluting solvent, water also has enormous potential for use in other types of reactions. It has been demonstrated that water can participate in reactions as an oxidizing or reducing agent, such as hydrogenolysis<sup>60</sup> and couplings.<sup>61,62</sup> This provides directions for the development of water involvement in reactions.

In conclusion, although the field is still in its nascent stage and has many challenges, discoveries will propel the field by solving these issues with an increasing understanding of their organocatalytic and photochemical reactivity, which will have a significant impact on the energy transition to a zero-carbon economy.

## AUTHOR INFORMATION

### Corresponding Authors

**Radek Zbořil** – Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute (CATRIN), Palacký University Olomouc, Olomouc 783 71, Czech Republic; Nanotechnology Centre, CEET, VŠB-Technical University of Ostrava, Ostrava-Poruba 708 00, Czech Republic; [orcid.org/0000-0002-3147-2196](https://orcid.org/0000-0002-3147-2196); Email: [radek.zboril@upol.cz](mailto:radek.zboril@upol.cz)

**Zupeng Chen** – Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing 210037, People's Republic of China; [orcid.org/0000-0002-7351-3240](https://orcid.org/0000-0002-7351-3240); Email: [czp@njfu.edu.cn](mailto:czp@njfu.edu.cn)

### Authors

**En Zhao** – Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing 210037, People's Republic of China; [orcid.org/0000-0003-3416-2414](https://orcid.org/0000-0003-3416-2414)

**Wenjun Zhang** – Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing 210037, People's Republic of China

**Lin Dong** – Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, Nanjing Forestry University, Nanjing 210037, People's Republic of China

Complete contact information is available at: <https://pubs.acs.org/10.1021/acscatal.3c00326>

### Author Contributions

E.Z. wrote the draft of the manuscript. W.Z., L.D., R.Z., and Z.C. revised the manuscript. R.Z. and Z.C. conceived and supervised the whole project.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (22202105, 22205113, 22002043), the Natural Science Foundation of Jiangsu Province (BK20210608, BK20210626), the Natural Science Foundation of Jiangsu Higher Education Institutions of China (21KJA150003, 21KJB150027), and the China Postdoctoral Science Foundation (2022M711645).

## REFERENCES

- (1) Zhang, L.; Zhou, M.; Wang, A.; Zhang, T. Selective Hydrogenation over Supported Metal Catalysts: From Nanoparticles to Single Atoms. *Chem. Rev.* **2020**, *120* (2), 683–733.
- (2) Guo, M.; Zhang, M.; Liu, R.; Zhang, X.; Li, G. State-of-the-Art Advancements in Photocatalytic Hydrogenation: Reaction Mechanism and Recent Progress in Metal-Organic Framework (MOF)-Based Catalysts. *Adv. Sci.* **2022**, *9* (1), 2103361.
- (3) Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. *Chem. Rev.* **2015**, *115* (13), 6621–6686.
- (4) Brieger, G.; Nestruck, T. J. Catalytic Transfer Hydrogenation. *Chem. Rev.* **1974**, *74* (5), 567–580.
- (5) Han, C.; Meng, P.; Waclawik, E. R.; Zhang, C.; Li, X. H.; Yang, H.; Antonietti, M.; Xu, J. Palladium/Graphitic Carbon Nitride ( $\text{g-C}_3\text{N}_4$ ) Stabilized Emulsion Microreactor as a Store for Hydrogen from Ammonia Borane for Use in Alkene Hydrogenation. *Angew. Chem., Int. Ed.* **2018**, *57* (45), 14857–14861.
- (6) Pieber, B.; Martinez, S. T.; Cantillo, D.; Kappe, C. O. *In-Situ* Generation of Diimide from Hydrazine and Oxygen: Continuous-Flow Transfer Hydrogenation of Olefins. *Angew. Chem., Int. Ed.* **2013**, *52* (39), 10241–10244.
- (7) Cheruvathoor Poulouse, A.; Zoppellaro, G.; Konidakis, I.; Serpetzoglou, E.; Stratakis, E.; Tomanec, O.; Beller, M.; Bakandritsos, A.; Zbořil, R. Fast and Selective Reduction of Nitroarenes under Visible Light with an Earth-Abundant Plasmonic Photocatalyst. *Nat. Nanotechnol.* **2022**, *17* (5), 485–492.
- (8) Huang, Z.; Wang, Y.; Leng, X.; Huang, Z. An Amine-Assisted Ionic Monohydride Mechanism Enables Selective Alkyne *cis*-Semi-hydrogenation with Ethanol: From Elementary Steps to Catalysis. *J. Am. Chem. Soc.* **2021**, *143* (12), 4824–4836.
- (9) Su, K.; Wang, Y.; Zhang, C.; Gao, Z.; Han, J.; Wang, F. Tuning the Pt Species on  $\text{Nb}_2\text{O}_5$  by Support-Induced Modification in the Photocatalytic Transfer Hydrogenation of Phenylacetylene. *Appl. Catal., B* **2021**, *298*, 120554.
- (10) Hao, C. H.; Guo, X. N.; Pan, Y. T.; Chen, S.; Jiao, Z. F.; Yang, H.; Guo, X. Y. Visible-Light-Driven Selective Photocatalytic Hydrogenation of Cinnamaldehyde over Au/SiC Catalysts. *J. Am. Chem. Soc.* **2016**, *138* (30), 9361–9364.
- (11) Hu, Y.; Huang, W.; Wang, H.; He, Q.; Zhou, Y.; Yang, P.; Li, Y.; Li, Y. Metal-Free Photocatalytic Hydrogenation Using Covalent Triazine Polymers. *Angew. Chem., Int. Ed.* **2020**, *59* (34), 14378–14382.
- (12) Fiorio, J. L.; Araújo, T. P.; Barbosa, E. C. M.; Quiroz, J.; Camargo, P. H. C.; Rudolph, M.; Hashmi, A. S. K.; Rossi, L. M. Gold-Amine Cooperative Catalysis for Reductions and Reductive Aminations Using Formic Acid as Hydrogen Source. *Appl. Catal., B* **2020**, *267*, 118728.

- (13) Kusy, R.; Grela, K. E- and Z-Selective Transfer Semi-hydrogenation of Alkynes Catalyzed by Standard Ruthenium Olefin Metathesis Catalysts. *Org. Lett.* **2016**, *18* (23), 6196–6199.
- (14) Zhao, E.; Li, M.; Xu, B.; Wang, X. L.; Jing, Y.; Ma, D.; Mitchell, S.; Pérez-Ramírez, J.; Chen, Z. Transfer Hydrogenation with a Carbon-Nitride-Supported Palladium Single-Atom Photocatalyst and Water as a Proton Source. *Angew. Chem., Int. Ed.* **2022**, *61* (40), No. e202207410.
- (15) Han, C.; Du, L.; Konarova, M.; Qi, D.-C.; Phillips, D. L.; Xu, J. Beyond Hydrogen Evolution: Solar-Driven, Water-Donating Transfer Hydrogenation over Platinum/Carbon Nitride. *ACS Catal.* **2020**, *10* (16), 9227–9235.
- (16) Zhang, D.; Ren, P.; Liu, W.; Li, Y.; Salli, S.; Han, F.; Qiao, W.; Liu, Y.; Fan, Y.; Cui, Y.; Shen, Y.; Richards, E.; Wen, X.; Rummeli, M. H.; Li, Y.; Besenbacher, F.; Niemantsverdriet, H.; Lim, T.; Su, R. Photocatalytic Abstraction of Hydrogen Atoms from Water Using Hydroxylated Graphitic Carbon Nitride for Hydrogenative Coupling Reactions. *Angew. Chem., Int. Ed.* **2022**, *61* (24), No. e202204256.
- (17) Cummings, S. P.; Le, T.-N.; Fernandez, G. E.; Quiambao, L. G.; Stokes, B. J. Tetrahydroxyboron-Mediated Palladium-Catalyzed Transfer Hydrogenation and Deuteration of Alkenes and Alkynes Using Water as the Stoichiometric H or D Atom Donor. *J. Am. Chem. Soc.* **2016**, *138* (19), 6107–6110.
- (18) Sharma, P.; Sasson, Y. Sustainable Visible Light Assisted *In-Situ* Hydrogenation via a Magnesium-Water System Catalyzed by a Pd-g-C<sub>3</sub>N<sub>4</sub> Photocatalyst. *Green Chem.* **2019**, *21* (2), 261–268.
- (19) Zhao, C.-Q.; Chen, Y.-G.; Qiu, H.; Wei, L.; Fang, P.; Mei, T.-S. Water as a Hydrogenating Agent: Stereodivergent Pd-Catalyzed Semihydrogenation of Alkynes. *Org. Lett.* **2019**, *21* (5), 1412–1416.
- (20) Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120* (2), 919–985.
- (21) Kumar, A.; Bhardwaj, R.; Mandal, S. K.; Choudhury, J. Transfer Hydrogenation of CO<sub>2</sub> and CO<sub>2</sub> Derivatives using Alcohols as Hydride Sources: Boosting an H<sub>2</sub>-Free Alternative Strategy. *ACS Catal.* **2022**, *12* (15), 8886–8903.
- (22) Nie, R.; Tao, Y.; Nie, Y.; Lu, T.; Wang, J.; Zhang, Y.; Lu, X.; Xu, C. C. Recent Advances in Catalytic Transfer Hydrogenation with Formic Acid over Heterogeneous Transition Metal Catalysts. *ACS Catal.* **2021**, *11* (3), 1071–1095.
- (23) Lau, S.; Gasperini, D.; Webster, R. L. Amine-Boranes as Transfer Hydrogenation and Hydrogenation Reagents: A Mechanistic Perspective. *Angew. Chem., Int. Ed.* **2021**, *60* (26), 14272–14294.
- (24) Wang, Y.; Suzuki, H.; Xie, J.; Tomita, O.; Martin, D. J.; Higashi, M.; Kong, D.; Abe, R.; Tang, J. Mimicking Natural Photosynthesis: Solar to Renewable H<sub>2</sub> Fuel Synthesis by Z-Scheme Water Splitting Systems. *Chem. Rev.* **2018**, *118* (10), 5201–5241.
- (25) Marzo, L.; Pagire, S. K.; Reiser, O.; Konig, B. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? *Angew. Chem., Int. Ed.* **2018**, *57* (32), 10034–10072.
- (26) Zahran, E. M.; Bedford, N. M.; Nguyen, M. A.; Chang, Y. J.; Guiton, B. S.; Naik, R. R.; Bachas, L. G.; Knecht, M. R. Light-Activated Tandem Catalysis Driven by Multicomponent Nanomaterials. *J. Am. Chem. Soc.* **2014**, *136* (1), 32–35.
- (27) Fan, X.; Yao, Y.; Xu, Y.; Yu, L.; Qiu, C. Visible-Light-Driven Photocatalytic Hydrogenation of Olefins Using Water as the H Source. *ChemCatChem.* **2019**, *11* (11), 2596–2599.
- (28) Xu, Y.; Qiu, C.; Fan, X.; Xiao, Y.; Zhang, G.; Yu, K.; Ju, H.; Ling, X.; Zhu, Y.; Su, C. K<sup>+</sup>-Induced Crystallization of Polymeric Carbon Nitride to Boost Its Photocatalytic Activity for H<sub>2</sub> Evolution and Hydrogenation of Alkenes. *Appl. Catal., B* **2020**, *268*, 118457.
- (29) Qiu, C.; Xu, Y.; Fan, X.; Xu, D.; Tandiana, R.; Ling, X.; Jiang, Y.; Liu, C.; Yu, L.; Chen, W.; Su, C. Highly Crystalline K-Intercalated Polymeric Carbon Nitride for Visible-Light Photocatalytic Alkenes and Alkynes Deuterations. *Adv. Sci.* **2019**, *6* (1), 1801403.
- (30) Li, M.; Zhang, N.; Long, R.; Ye, W.; Wang, C.; Xiong, Y. PdPt Alloy Nanocatalysts Supported on TiO<sub>2</sub>: Maneuvering Metal-Hydrogen Interactions for Light-Driven and Water-Donating Selective Alkyne Semihydrogenation. *Small* **2017**, *13* (23), 1604173.
- (31) Yao, F.; Dai, L.; Bi, J.; Xue, W.; Deng, J.; Fang, C.; Zhang, L.; Zhao, H.; Zhang, W.; Xiong, P.; Fu, Y.; Sun, J.; Zhu, J. Loofah-like Carbon Nitride Sponge towards the Highly-Efficient Photocatalytic Transfer Hydrogenation of Nitrophenols with Water as the Hydrogen Source. *Chem. Eng. J.* **2022**, *444*, 136430.
- (32) Xu, F.; Meng, K.; Cao, S.; Jiang, C.; Chen, T.; Xu, J.; Yu, J. Step-by-Step Mechanism Insights into the TiO<sub>2</sub>/Ce<sub>2</sub>S<sub>3</sub> S-Scheme Photocatalyst for Enhanced Aniline Production with Water as a Proton Source. *ACS Catal.* **2022**, *12* (1), 164–172.
- (33) Jia, T.; Meng, D.; Duan, R.; Ji, H.; Sheng, H.; Chen, C.; Li, J.; Song, W.; Zhao, J. Single-Atom Nickel on Carbon Nitride Photocatalyst Achieves Semihydrogenation of Alkynes with Water Protons via Monovalent Nickel. *Angew. Chem., Int. Ed.* **2023**, *62* (9), No. e202216511.
- (34) Guo, Y.; An, W.; Tian, X.; Xie, L.; Ren, Y.-L. Coupling Photocatalytic overall Water Splitting with Hydrogenation of Organic Molecules: a Strategy for Using Water as a Hydrogen Source and an Electron Donor to Enable Hydrogenation. *Green Chem.* **2022**, *24* (23), 9211–9219.
- (35) Chmiel, A. F.; Williams, O. P.; Chernowsky, C. P.; Yeung, C. S.; Wickens, Z. K. Non-Innocent Radical Ion Intermediates in Photoredox Catalysis: Parallel Reduction Modes Enable Coupling of Diverse Aryl Chlorides. *J. Am. Chem. Soc.* **2021**, *143* (29), 10882–10889.
- (36) Zhang, X.; Chen, J.; Gao, Y.; Li, K.; Zhou, Y.; Sun, W.; Fan, B. Photocatalytic Transfer Hydrogenation and Deuteration of Cyclic N-Sulfonylimines. *Org. Chem. Front.* **2019**, *6* (14), 2410–2414.
- (37) Dai, P.; Ma, J.; Huang, W.; Chen, W.; Wu, N.; Wu, S.; Li, Y.; Cheng, X.; Tan, R. Photoredox C-F Quaternary Annulation Catalyzed by a Strongly Reducing Iridium Species. *ACS Catal.* **2018**, *8* (2), 802–806.
- (38) Cuerva, J. M.; Campana, A. G.; Justicia, J.; Rosales, A.; Oller-Lopez, J. L.; Robles, R.; Cardenas, D. J.; Bunuel, E.; Oltra, J. E. Water: the Ideal Hydrogen-Atom Source in Free-Radical Chemistry Mediated by Ti(III) and Other Single-Electron-Transfer Metals? *Angew. Chem., Int. Ed.* **2006**, *45* (33), 5522–5526.
- (39) Call, A.; Casadevall, C.; Acuna-Pares, F.; Casitas, A.; Lloret-Fillol, J. Dual Cobalt-Copper Light-Driven Catalytic Reduction of Aldehydes and Aromatic Ketones in Aqueous Media. *Chem. Sci.* **2017**, *8* (7), 4739–4749.
- (40) Fischer, S.; Hollmann, D.; Tschierlei, S.; Karnahl, M.; Rockstroh, N.; Barsch, E.; Schwarzbach, P.; Luo, S.-P.; Junge, H.; Beller, M.; Lochbrunner, S.; Ludwig, R.; Brückner, A. Death and Rebirth: Photocatalytic Hydrogen Production by a Self-Organizing Copper-Iron System. *ACS Catal.* **2014**, *4* (6), 1845–1849.
- (41) Call, A.; Codola, Z.; Acuna-Pares, F.; Lloret-Fillol, J. Photo- and Electrocatalytic H<sub>2</sub> Production by New First-Row Transition-Metal Complexes Based on an Aminopyridine Pentadentate Ligand. *Chem. - Eur. J.* **2014**, *20* (20), 6171–6183.
- (42) Casadevall, C.; Pascual, D.; Aragon, J.; Call, A.; Casitas, A.; Casademont-Reig, I.; Lloret-Fillol, J. Light-Driven Reduction of Aromatic Olefins in Aqueous Media Catalysed by Aminopyridine Cobalt Complexes. *Chem. Sci.* **2022**, *13* (15), 4270–4282.
- (43) Zhou, B.; Song, J.; Zhou, H.; Wu, T.; Han, B. Using the Hydrogen and Oxygen in Water Directly for Hydrogenation Reactions and Glucose Oxidation by Photocatalysis. *Chem. Sci.* **2016**, *7* (1), 463–468.
- (44) Kaiser, S. K.; Chen, Z.; Faust Akl, D.; Mitchell, S.; Pérez-Ramírez, J. Single-Atom Catalysts across the Periodic Table. *Chem. Rev.* **2020**, *120* (21), 11703–11809.
- (45) Shi, Y.; Zhou, Y.; Lou, Y.; Chen, Z.; Xiong, H.; Zhu, Y. Homogeneity of Supported Single-Atom Active Sites Boosting the Selective Catalytic Transformations. *Adv. Sci.* **2022**, *9* (24), 2201520.
- (46) Wang, Q.; Domen, K. Particulate Photocatalysts for Light-Driven Water Splitting: Mechanisms, Challenges, and Design Strategies. *Chem. Rev.* **2020**, *120* (2), 919–985.
- (47) Li, X.; Bi, W.; Zhang, L.; Tao, S.; Chu, W.; Zhang, Q.; Luo, Y.; Wu, C.; Xie, Y. Single-Atom Pt as Co-Catalyst for Enhanced Photocatalytic H<sub>2</sub> Evolution. *Adv. Mater.* **2016**, *28* (12), 2427–2431.

- (48) Dong, P.; Wang, Y.; Zhang, A.; Cheng, T.; Xi, X.; Zhang, J. Platinum Single Atoms Anchored on a Covalent Organic Framework: Boosting Active Sites for Photocatalytic Hydrogen Evolution. *ACS Catal.* **2021**, *11* (21), 13266–13279.
- (49) Ling, X.; Xu, Y.; Wu, S.; Liu, M.; Yang, P.; Qiu, C.; Zhang, G.; Zhou, H.; Su, C. A Visible-Light-Photocatalytic Water-Splitting Strategy for Sustainable Hydrogenation/Deuteration of Aryl Chlorides. *Sci. China-Chem.* **2020**, *63* (3), 386–392.
- (50) Ji, S.; Chen, Y.; Wang, X.; Zhang, Z.; Wang, D.; Li, Y. Chemical Synthesis of Single Atomic Site Catalysts. *Chem. Rev.* **2020**, *120* (21), 11900–11955.
- (51) Mo, Q.; Zhang, L.; Li, S.; Song, H.; Fan, Y.; Su, C. Y. Engineering Single-Atom Sites into Pore-Confined Nanospaces of Porphyrinic Metal-Organic Frameworks for the Highly Efficient Photocatalytic Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2022**, *144* (49), 22747–22758.
- (52) Jin, X.; Wang, R.; Zhang, L.; Si, R.; Shen, M.; Wang, M.; Tian, J.; Shi, J. Electron Configuration Modulation of Nickel Single Atoms for Elevated Photocatalytic Hydrogen Evolution. *Angew. Chem., Int. Ed.* **2020**, *59* (17), 6827–6831.
- (53) Sholl, D. S.; Lively, R. P. Seven Chemical Separations to Change the World. *Nature* **2016**, *532* (7600), 435–437.
- (54) Arcudi, F.; Đorđević, L.; Schweitzer, N.; Stupp, S. I.; Weiss, E. A. Selective Visible-Light Photocatalysis of Acetylene to Ethylene Using a Cobalt Molecular Catalyst and Water as a Proton Source. *Nat. Chem.* **2022**, *14* (9), 1007–1012.
- (55) Shi, X.; Huang, Y.; Bo, Y.; Duan, D.; Wang, Z.; Cao, J.; Zhu, G.; Ho, W.; Wang, L.; Huang, T.; Xiong, Y. Highly Selective Photocatalytic CO<sub>2</sub> Methanation with Water Vapor on Single-Atom Platinum-Decorated Defective Carbon Nitride. *Angew. Chem., Int. Ed.* **2022**, *61* (27), No. e202203063.
- (56) Liu, C.; Chen, Z.; Su, C.; Zhao, X.; Gao, Q.; Ning, G. H.; Zhu, H.; Tang, W.; Leng, K.; Fu, W.; Tian, B.; Peng, X.; Li, J.; Xu, Q. H.; Zhou, W.; Loh, K. P. Controllable Deuteration of Halogenated Compounds by Photocatalytic D<sub>2</sub>O Splitting. *Nat. Commun.* **2018**, *9* (1), 80.
- (57) Nan, X. L.; Wang, Y.; Li, X. B.; Tung, C. H.; Wu, L. Z. Site-selective D<sub>2</sub>O-Mediated Deuteration of Diaryl Alcohols via Quantum Dots Photocatalysis. *Chem. Commun.* **2021**, *57* (55), 6768–6771.
- (58) Jia, T.; Meng, D.; Ji, H.; Sheng, H.; Chen, C.; Song, W.; Zhao, J. Visible-Light-Driven Semihydrogenation of Alkynes via Proton Reduction over Carbon Nitride Supported Nickel. *Appl. Catal., B* **2022**, *304*, 121004.
- (59) Han, C.; Han, G.; Yao, S.; Yuan, L.; Liu, X.; Cao, Z.; Mannodi-Kanakkithodi, A.; Sun, Y. Defective Ultrathin ZnIn<sub>2</sub>S<sub>4</sub> for Photo-reductive Deuteration of Carbonyls Using D<sub>2</sub>O as the Deuterium Source. *Adv. Sci.* **2022**, *9* (3), No. 2103408.
- (60) Yuan, J.; Li, S.; Yu, L.; Liu, Y.; Cao, Y. Efficient Catalytic Hydrogenolysis of Glycerol Using Formic Acid as Hydrogen Source. *Chin. J. Catal.* **2013**, *34* (11), 2066–2074.
- (61) Yan, D.-M.; Xu, S.-H.; Qian, H.; Gao, P.-P.; Bi, M.-H.; Xiao, W.-J.; Chen, J.-R. Photoredox-Catalyzed and Copper(II) Salt-Assisted Radical Addition/Hydroxylation Reaction of Alkenes, Sulfur Ylides, and Water. *ACS Catal.* **2022**, *12* (6), 3279–3285.
- (62) Tian, X.; Guo, Y.; An, W.; Ren, Y. L.; Qin, Y.; Niu, C.; Zheng, X. Coupling Photocatalytic Water Oxidation with Reductive Transformations of Organic Molecules. *Nat. Commun.* **2022**, *13* (1), 6186.