COFs-based Porous Materials for Photocatalytic Applications

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Abstract Covalent organic frameworks (COFs) are an emerging class of photoactive materials, solely composed of light elements. Their ordered structure, crystallinity, and high porosity led to enormous worldwide attention in many research fields. The extensive π-electron conjugation, light-harvesting and charge transport characteristics make them a fascinating polymer for photocatalytic systems. Versatile selection of building blocks and innumerable synthetic methodologies enable them to be a robust platform for solar energy production. In this mini-review, we summarized recent progress and challenges of the design, construction, and applications of COFs-based photocatalysts, and also presented some perspectives on challenges.

Keywords Covalent organic frameworks (COF); Covalent triazine frameworks (CTF); Photocatalysis

INTRODUCTION

The development of environmentally friendly and sustainable energy resources is highly challenging due to the increasing demand for energy. From the last decade, photocatalysis aiming to meet the world’s energy requirements by capturing and converting renewable solar energy into solar fuels (e.g., hydrogen, hydrocarbon fuels) has been intensively explored. In addition, the degradation of pollutants provides a blueprint for sustainable and carbon-neutral world thus overcoming the energy crisis and environmental problems.[1−4]

In general, the photocatalytic performance mainly depends on three basic steps: optical absorbance and excitation, charge separation, and surface reaction. Particularly, to achieve the maximum light absorption, up to date most of the conventional inorganic semiconductors with wide bandgap have been reported but these materials are deficient in efficiency as they only absorb UV light that accounts for 4% in the solar spectrum. Thus, the development of photocatalysts that possess suitable band structures and visible-light endurance is the key in photocatalysis research.[5] Herein, the porous organic polymers (POPs) are very promising candidates as photocatalysts owing to their broad absorption range, porosity, high surface area, and facile fabrication methodologies.

Porous materials include zeolites, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and porous polymers. They are important materials as membranes, adsorbents, catalysts, and other chemical applications. Because it is impossible to find a one-size-fits-all solution, choosing a suitable porous material for the given application is necessary.[6−9] For light-harvesting, extended conjugation is a typical property of COFs, but not for MOFs, which endows COFs with more effective adsorption of the solar spectrum, and convenience for "bandgap engineering".[6,9] Apart from light-harvesting, stability (e.g., thermal, mechanical, hydrolytic, chemical, or photolytic stability) also needs to be considered. COFs (e.g., imines, triazine-based COFs) are typically composed of strong covalent bonds and light elements, and show good stability, whereas MOFs are generally composed of metal-ligand bonds that are susceptible to water in some cases (although with the increasing number of water-stable MOFs).[8]

Compared with other porous polymers, the feature of COFs is its crystallinity.[10] It is easier to probe the structure of crystalline COFs by PXRD and TEM, and furthermore, to establish unambiguous models for functional design and the research of structure-activity relationship. However, it is particularly difficult for the amorphous porous materials.[9,11]

In summary, by virtue of COFs’ ordered structure, the extended conjugated network has endowed them with excellent visible-light responsive ability that offers promising potential as a visible light-responsive photocatalyst. COFs-based materials have caught scientist’s eyes for their fascinating merits: (1) Most of COFs reported have suitable energy level and moderate bandgap for visible light receptivity owing to the π-conjugated electronic structures; (2) Engineering the bandgap and energy level at molecular level is possible by carefully choosing monomers to change the conjugate degree or introducing different functional groups; (3) The nanometer-sized pore porosity is favorable for the mass transfer;
SYNTHETIC STRATEGIES

Up to date, various strategic designs and synthetic protocols have been developed by employing numerous building blocks and linking chemistry. Therefore, several types of COFs are reported with versatile covalent linkages, for instance, hydrazine, azine, imine, and triazine, and have presented a promising potential as photocatalyst. Typical synthetic strategies of these COFs are summarized and listed in Fig. 1.

Generally, the Boronate ester COFs are susceptible to moisture, so they are rarely reported used for photocatalytic applications. Hu et al. prepared phototherapeutic agent ICG@COF-1@PDA by loading indocyanine green (ICG) on COF1 that can be used in phototherapy.\[24\]

Wang’s group developed a series of ultrastable benzoazole-based COFs by the cascade imine formation/cyclization/oxidation reactions. These COFs showed excellent photocatalytic performance for hydrogen production on illuminating with visible light.\[28\]

Recently, Lu and coworkers suggested that Pd\(_0\)/TpPa-1 showed better photocatalytic H\(_2\) evolution rate than Pd/C.\[31\] Thomas et al. reported diacetylene functionalized \(\beta\)-ketenamine COFs, pointing out when sensitized by Eosin Y, the conjugate COFs could improve the photogenerated electron transfer. The keto-enol tautomerization under solvothermal conditions showed an efficient hydrogen evolution.\[32\] Chen’s group successfully synthesized two COFs by the “two-in-one” strategy based on Schiff reaction of bifunctional A\(_2\)B\(_2\) type monomer with two formyl and two amino-terminal groups. This strategy opens a new avenue for facile constructing novel functional COFs.\[33,34\]

Sp\(^2^\) carbon-conjugated COFs with C=C linkages prepared by Knoevenagel condensation under solvothermal condition were reported by Jiang et al.\[33\]. In this regard, 2D COFs with an extended \(n\)-delocalization have been synthesized by employing the condensation reaction at active arylmethyl car-

![Fig. 1](https://doi.org/10.1007/s10118-020-2394-x)
bon atoms of 3,5-dicyano-2,4,6-trimethylpyridine\textsuperscript{[36]} or 2,4,6-trimethyl-1,3,5-triazine\textsuperscript{[37]} with aldehydes. Their conjugated structures, tunable energy levels, and chemical stabilities endowed these COFs with appreciable high charge carrier mobility and aided in facile migration of excitons.

Covalent triazine frameworks (CTFs) are amongst the special types of COFs with ultra-stable triazine linkages, first reported by Thomas \textit{et al.} in 2008\textsuperscript{[38]}. The robust structures and rich nitrogen content make CTFs promising for practical applications. Various synthetic methodologies are employed, including ionothermal trimerization, phosphorus pentoxide ($\text{P}_2\text{O}_5$) catalyzed synthesis, superacid catalyzed method, amidine based polycondensation strategy, and Friedel-Crafts reaction.

In 2014, Song \textit{et al.} reported that amorphous CTF synthesized by an ionothermal trimerization strategy had been utilized for the photocatalytic degradation of methylene blue\textsuperscript{[39]}. Similarly, Lotsch \textit{et al.} found the phenyl-triazine oligomers prepared at lower temperature showed better photocatalytic properties than carbonization\textsuperscript{[40]}. A few examples of CTFs synthesized by superacid catalyzed method have shown effective photocatalytic water splitting\textsuperscript{[41,42]} and organic reaction transformation activity\textsuperscript{[43]}. Wu \textit{et al.} prepared different CTFs by trifluoromethanesulfonic acid-catalyzed method via different monomers, among which CTF-T1 showed H$_2$ evolution under visible light irradiation\textsuperscript{[41]}. Su \textit{et al.} found that sulfur-doped CTF-T1 showed better photocatalytic hydrogen evolution activity than non-doped CTF-T1\textsuperscript{[42]}.

Recently, Tan’s group reported the amidine polycondensation at low temperature to synthesize CTFs as demonstrated in Fig. 2\textsuperscript{[44]}. The two-step reaction between aldehyde and amidine dihydrochloride involved Schiff base formation and sequential Michael addition. This low-temperature polycondensation approach avoided the introduction of carbonaceous materials as in ionothermal trimerization strategy\textsuperscript{[40]} and also materials prepared at high temperature in conventional ionothermal condition,\textsuperscript{[40]} which overcame the use of corrosive acid via superacid catalyzed method\textsuperscript{[41]}. Indeed, the

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\textbf{Fig. 2} (a) Synthesis of CTF-HUST-X via a low-temperature polycondensation approach. (b–e) Simulated structures of CTF-HUST-X. (Reproduced with permission from Ref. [44]; Copyright (2017) John Wiley and Sons).
conjugated structure of CTFs constructed with this approach was stable and this strategic design has greatly expanded the choice of building blocks. Subsequently, this team has presented an impressive work in the development of CTFs via *in situ* oxidation of alcohols to aldehydes monomers. The generous control on the feeding rate of monomers had yielded a crystalline COFs with enhanced photocatalytic performance.

In summary, compared with COFs with imine, azine and hydrazine linkage, COFs with enamine, C=N and triazine linkage show better stability and extended conjugated networks, which endow them with promising prospects in photocatalysis area. Additionally, development of new type, stable and visible light response COFs will provide new chance for photocatalysis.

**PHOTOCATALYTIC APPLICATIONS OF COFS-BASED MATERIALS**

In this section, we will present the evolution of COFs-based materials applied in photocatalytic fields, like water splitting for \( \text{H}_2 \) and \( \text{O}_2 \) evolution, reduction of \( \text{CO}_2 \) into hydrocarbon fuels, and degradation of pollutants and some other photochemical application.

**Photocatalytic Water Splitting**

Water splitting technology has a profound impact on clean, economic and environment-friendly solar-hydrogen production as an ideal alternative fuel instead of conventional fossil energy. Presently, COFs-based materials are rising photocatalysts and high-throughput efforts are made to their efficient photocatalytic performance. When the N atoms were substituted on \(-\text{C}−\text{H}\) units, it gradually decreased the dihedral angle between the central aryl ring and the peripheral phenyl rings in the COF nodes and thus planarity increased. This phenomenon was exemplified by the COFs with triphenylaryl nodes that act as acceptor moieties.[20,40] Besides, the energy levels can also be adjusted by the rational design of donor moieties. For instance, Lotsch *et al.* used three azine-linked COFs as research model and found that the COF with lower nitrogen content in donor moieties had higher conduction band (CB) levels, which implies increasing thermodynamic driving force for \( \text{H}_2 \) reduction and higher hydrogen evolution rate.[52]

Constructing COFs-based heterostructures is a feasible and efficient strategy to accomplish the spatial separation of photogenerated electron-hole pairs. High surface area, porosity and crystalline structures make COFs excellent substrate for the loading and dispersion of inorganic semiconductor nanoparticles.[53−55] polymer,[56] and inorganic clusters[57] to construct heterojunction. For instance, CdS-COF exhibited the steep hydrogen production up to 3678 \( \mu\text{mol·h}^{-1}·\text{g}^{-1} \)than bulk materials.[55]

The surface reaction kinetic is a key constraining factor in polymer-based photocatalytic systems. In addition to this, the selection of co-catalyst is also important. Up till now, Pt is an

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**Table 1**

| Linkage | COF | Mass (mg) | Lamp | HER \( \text{a} \) (\( \mu\text{mol·h}^{-1}·\text{g}^{-1} \)) | AQY \( \text{b} \) | Ref. |
|---------|-----|-----------|------|---------------------------------|----------------|------|
| Hydrazine | TFPT-COF | 4 | 300 W Xe lamp (> 420 nm) | 1970 | 2.2% (400 nm) | [26] |
| Imine | CdS-COF | 30 | 400 W Xe lamp (> 420 nm) | 3678 | 4.2% (420 nm) | [53] |
| Imine | BpCo-COF-1@Pt | 10 | 300 W Xe lamp (> 420 nm) | 24.6 | – | [54] |
| Azine | N\(_2\)COF | 5 | 300 W Xe lamp (> 420 nm) | 1703 | 0.44% (450 nm) | [27] |
| Enamine | FS-COF+W5SF | 5 | 300 W Xe lamp (> 420 nm) | 1.63 \( \times \) 10\(^4\) | 2.2% (600 nm) | [28] |
| Enamine | NH\(_3\)-Uio-66/TpPa-1-COF (4/6) | 10 | 300 W Xe lamp (> 420 nm) | 2.341 \( \times \) 10\(^4\) | – | [55] |
| Enamine | Pt-PVP-COFs | 10 | 300 W Xe lamp (> 420 nm) | 8420 | 0.4% (475 nm) | [56] |
| C=C | spC-COF | 50 | 300 W Xe lamp (> 420 nm) | 1360 | 0.46% (420 nm) | [35] |
| C=C | g-C_3N_4-COF | 50 | 300 W Xe lamp (> 420 nm) | 50 | – | [36] |
| C=C | g-C_3N_4-COF | 50 | 300 W Xe lamp (> 420 nm) | 292 | 1.06% (420 nm) | [37] |

\( \text{a} \) The hydrogen evolution reaction; \( \text{b} \) The apparent quantum yield.

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According to thermodynamics, the photocatalyst should have a band gap larger than 1.23 eV to overcome the Gibbs free energy for the overall water splitting. In addition, a larger band gap (> 1.6 eV) is needed for additional overpotential associated with the electron transfer and gas evolution steps.[47,48]

Table 1 demonstrates the photocatalytic \( \text{H}_2 \) production performance by COFs. Lotsch’s group synthesized a series of hydrazine-based COFs with different nitrogen contents in monomer and the structure-property-activity relationships were explored systematically.[26,27,49−51] Their exploration showed that the electronic and steric features of monomers would transfer to the resultant frameworks and impart a significant impact on the structure, nanoscale morphology, and photocatalytic performance. When the N atoms were substituted on \(-\text{C}−\text{H}\) units, it gradually decreased the dihedral angle between the central aryl ring and the peripheral phenyl rings in the COF nodes and thus planarity increased. This phenomenon was exemplified by the COFs with triphenylaryl nodes that act as acceptor moieties.[20,40] Besides, the energy levels can also be adjusted by the rational design of donor moieties. For instance, Lotsch *et al.* used three azine-linked COFs as research model and found that the COF with lower nitrogen content in donor moieties had higher conduction band (CB) levels, which implies increasing thermodynamic driving force for \( \text{H}_2 \) reduction and higher hydrogen evolution rate.[52]

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efficient and commonly used co-catalyst to increase the hydrogen evolution reaction (HER) activity but its cost and rare abundance limit the applications. Regardless of the structural feature of COFs as a photocatalyst, exploration of toolbox that promises the long-term hydrogen production is a key factor in designing the photocatalyst. Therefore, Lotsch et al. have developed an efficient “COF molecular co-catalyst” based photocatalytic systems that used chloro-(pyridine) cobaltoxime as noble metal-free co-catalyst and N$_2$-COF as the photosensitizer.[49] Afterwards, this team has reported a versatile photocatalyst system composed of COF (TpDz)$_2$ and nickel-thiolate cluster as co-catalyst. The designed heterogenous photocatalyst had a significantly high H$_2$ evolution (941 μmol·h$^{-1}$·g$^{-1}$) in the presence of triethanolamine in water medium.[58] Recently, MoS$_2$[59] and Au[60] have been reported to act as efficient co-catalysts in COFs-based photocatalysts for photocatalytic H$_2$ production.

Theoretical simulation and experiment have confirmed that CTFs possess suitable bandgaps and energy levels for photocatalytic HER under visible light.[15,29,40,41,61–68] Therefore, as shown in Table 2, versatile synthetic strategies are employed to realize the practical applicability of CTFs as a photocatalyst. Thomas et al. combined ionothermal method with superacid catalysis method to shorten the ionothermal reaction time and avoid carbonization. The acquired CTF-1 materials showed high activities for photocatalytic hydrogen evolution from water.[65]

Tan’s group reported CTF-HUST-2 prepared by low-temperature polycondensation approach showing quite high photocatalytic hydrogen evolution rate (2647 μmol·h$^{-1}$·g$^{-1}$).[44] The ordered structure is considered to promote charge transfer. Recently, they developed an in situ oxidation approach to construct crystalline CTFs. The highly ordered CTFs (CTF-HUST-C1) showed higher HER performance (5100 μmol·h$^{-1}$·g$^{-1}$), which is 2.6 times of that of the corresponding amorphous CTFs.[63] More recently, the preparation of D-A1-A2 structure as illustrated in Fig. 3 has a considerable enhancement in photocatalytic HER performance under visible light illumination up to 19.3 mmol·h$^{-1}$·g$^{-1}$, and the apparent quantum yield (AQY) was 22.8%.[69] Except the structural design, engineering the morphology of CTFs is another crucial factor to enhancing photocatalytic HER performance. Tan’s group has prepared the CTFs hollow sphere using the hard template strategy (SiO$_2$ as template), which showed a better HER performance attributed to the reduced carriers transport length.[70]

Moreover, the heteroatom substitution changes the local electron density and affects the band structure and charge mobility. It is well documented that the heteroatom doping like sulfur-doping[61] or phosphorus doping[71] can dramatically enhance the HER activity. The heteroatom doping is easily accomplished by introducing monomers containing heteroatoms. Tan et al. demonstrated that engineering heteroatoms doping has significant impact on the HER activity. The doping with N atom (CTF-N) has effectively enhanced the electron donating ability and exhibited high HER activity (1.1 × 10$^4$ μmol·h$^{-1}$·g$^{-1}$).[72]

CTFs-based heterostructures also enhanced the spatial separation of the photogenerated electron-hole pairs. Zou et al. loaded CdS nanoparticles on the surface of CTF-1.[73–77] The optimized CdS NPs/3%CTF-1 showed the best performance (1.215 × 10$^4$ μmol·h$^{-1}$·g$^{-1}$), which is better than that of pristine CTF-1 or CdS.[73] Other semiconductors or clusters like C$_3$N$_4$, MoS$_2$ and MOF[76] have also been used for heterojunction construction.

Oxygen evolution reaction (OER) is another half reaction of water splitting, which is more difficult than HER. Wang et al. reported CTFs as photocatalyst with Co$^{2+}$ as the co-catalyst, where the photocatalytic activity could be adjusted by the length and electronic properties of monomers.[78] Tang and co-workers prepared ordered CTFs by microwave-assisted polymerization, and the CTF-1 showed high activity for oxygen evolution under visible light irradiation and the apparent quantum efficiency (AQE) nearly 4% at 420 nm.[79]

**Photocatalytic Carbon Dioxide Reduction**

The continuous increase of CO$_2$ concentration in the atmosphere has caused serious climate change and environmental issues. Conversion of CO$_2$ to value-added chemicals or fuels by electrochemical or photochemical processes has received significant attention. The direct photoreduction of the CO$_2$ molecule in the gas phase needs a high negative redox potential (~1.90 V versus NHE for CO$_2$/CO$_2^-$), which seems impossible for most of the semiconductors. Nevertheless, the potential of proton-assisted CO$_2$ photoreduction is relatively low (see reactions 4–8). The mechanism of these processes is quite complex, and still not very clear. The half-reaction of CO$_2$ fixation involves different multi-electron and proton processes with different types of intermedium species and so on.[47,48,80] The CO$_2$ adsorption ability is

| Method | COF | Mass (mg) | Lamp | HER (μmol·h$^{-1}$·g$^{-1}$) | AQY | Ref. |
|--------|-----|-----------|------|-----------------|-----|-----|
| TFMS catalyzed method by microwave | CTF-1-100W | 50 | 300 W Xe lamp (> 420 nm) | H$_2$: 5500 | 6.3% (400 nm) | [79] |
| TFMS catalyzed method at RT | CTF510 | 20 | 300 W Xe lamp (> 420 nm) | 5500 | – | [42] |
| TFMS catalyzed and ionothermal | CdS NPs/3%CTF-1 | 20 | 300 W Xe lamp (> 420 nm) | 1.215 × 10$^4$ | – | [73] |
| TFMS catalyzed method | CTF-BT/Th | 50 | 300 W Xe lamp (> 420 nm) | 6600 | 7.3% (420 nm) | [77] |
| Polycondensation method | CTF-N | 50 | 300 W Xe lamp (> 420 nm) | 1.076 × 10$^4$ | 4.1% (420 nm) | [72] |
| | CTF-HUST-2 | 50 | 300 W Xe lamp (> 420 nm) | 2647 | – | [44] |
| | CTF-HUST-C1 | 50 | 300 W Xe lamp (> 420 nm) | 5100 | – | [45] |
| | CTF-H5O.75-1 | 50 | 300 W Xe lamp (> 420 nm) | 6040 | 6.8% (420 nm) | [70] |
| | ter-CTF-0.7 | 50 | 300 W Xe lamp (> 420 nm) | 1.93 × 10$^4$ | 22.8% (420 nm) | [69] |

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particularly crucial to photocatalytic heterogeneous systems for CO2 conversion, so the porosity of COFs materials and high CO2 absorption capacity are favorable for photocatalytic CO2 conversion.\cite{81} Reports of photocatalytic carbon dioxide reduction are listed in Table 3.

\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{HCOOH} \\
\left(\varepsilon_{\text{red}}^\text{H} = -0.61 \text{ V versus NHE pH 7}\right) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{CO} + \text{H}_2\text{O} \\
\left(\varepsilon_{\text{red}}^\text{H} = -0.53 \text{ V versus NHE pH 7}\right)
\end{align*}

\begin{align*}
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- &\rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
\left(\varepsilon_{\text{red}}^\text{H} = -0.24 \text{ V versus NHE pH 7}\right)
\end{align*}

Huang et al. incorporated Re(bpy)(CO)\textsubscript{3}Cl into 2D triazine COF that contained bipyridyl linkers via post-synthetic modi-

\begin{table}[h]
\centering
\caption{The summary of photocatalytic CO\textsubscript{2} reduction performance for COFs.}
\begin{tabular}{lcccc}
\hline
Linkage & COF & Mass (mg) & Lamp & Product/Selectivity & AQY & Ref. \\
\hline
Imine & COF-367-Co NSs & 5 & 300 W Xe lamp (> 420 nm) & CO\textsubscript{2}: 10162 \mu mol h\textsuperscript{-1} g\textsuperscript{-1}; & \multicolumn{2}{c}{\text{H}_2: 2875 \mu mol h\textsuperscript{-1} g\textsuperscript{-1}} \\
Imine & Re-COF & 0.9 & 225 W Xe lamp (> 420 nm) & CO\textsubscript{2}: \sim 750 \mu mol h\textsuperscript{-1} g\textsuperscript{-1} & \multicolumn{2}{c}{\text{H}_2: 2055 \mu mol h\textsuperscript{-1} g\textsuperscript{-1}} \\
Enamine & DQTP COF-Zn & 20 & 300 W Xe lamp (> 420 nm) & CO\textsubscript{2}: 1020 \mu mol h\textsuperscript{-1} g\textsuperscript{-1} & \multicolumn{2}{c}{100% CO} \\
Enamine & DATP COF-Zn & 20 & 300 W Xe lamp (> 420 nm) & Formic acid: 152.5 \mu mol h\textsuperscript{-1} g\textsuperscript{-1} & \multicolumn{2}{c}{\text{H}_2: 170 \mu mol g\textsuperscript{-1} in 5 h} \\
Enamine & Ni-TpBpy & 10 & 300 W Xe lamp (> 420 nm) & CO\textsubscript{2}: 4057 \mu mol g\textsuperscript{-1} & & CO: 0.3% (420 nm) \\
Azine & N\textsubscript{2}-COF & 10 & 500 W Xe lamp (> 420 nm) & CH\textsubscript{3}OH: 13.7 \mu mol g\textsuperscript{-1} in 24 h & \multicolumn{2}{c}{\text{H}_2: 170 \mu mol g\textsuperscript{-1} in 5 h} \\
C=C & Re-Bpy-sp\textsuperscript{C}-COF & 1 & 300 W Xe lamp (> 420 nm) & 1040 \mu mol h\textsuperscript{-1} g\textsuperscript{-1} & \multicolumn{2}{c}{0.5% (420 nm)} \\
Triazine & Re-CTF-Py & 2 & 300 W Xe lamp (200–1100 nm) & 353.05 \mu mol h\textsuperscript{-1} g\textsuperscript{-1} & \multicolumn{2}{c}{\text{H}_2: 170 \mu mol g\textsuperscript{-1} in 5 h} \\
\hline
\end{tabular}
\end{table}

https://doi.org/10.1007/s10118-020-2394-x
fication as depicted in Fig. 4. The hybrid system showed high efficiency (15 mmol·g\(^{-1}\) in 20 h), selectivity (98%), and stability to reduce CO\(_2\) to CO in solution. Transient absorption spectroscopy (TA), X-ray transient absorption spectroscopy (XTA) and in situ diffuse reflectance UV-visible spectroscopy unraveled the charge separation and transfer dynamics between COF and Re moiety.\[82\]

Recently, Tan’s group reported a ternary artificial photosynthesis system fabricated by CTFs, α-Fe\(_2\)O\(_3\) nanoparticles, and Ru complex photosensitizer. The system showed a high CO evolution rate (8.0 μmol·h\(^{-1}\)) with 93% CO selectivity.\[83\]

Lan et al. reported a series of crystalline porphyrintetrathiafulvalene COFs to be used as photocatalysts for reducing CO\(_2\) with H\(_2\)O without additional photosensitizer, sacrificial agents, or noble metal co-catalysts.\[84\]

In short, the complexity of CO\(_2\) reduction reaction mechanism and multiple side products have led to a generous design of COFs that can realize an efficient, selective and stable photocatalytic CO\(_2\) conversion. Besides catalyzing the CO\(_2\) conversion to CO, other liquid products like CH\(_3\)OH, HCOOH or C\(_2\)H\(_5\)OH are more promising.

**Photocatalytic Organic Reaction Transformation**

Visible light-induced photo-redox catalysis is an emerging powerful method for the novel transformations in organic synthesis. The photocatalyst undergoes photoexcitation and generates highly reactive intermediates to activate organic molecules under mild conditions. As abundant organic reactions occur through “redox” processes, the electron transfer is involved between substrates and catalysts or radical initiators. Under light irradiation, a photocatalyst in the excited state can generate radical intermediates by reacting with the absorbed molecule or directly initiating the oxidative addition and/or reductive elimination reactions.\[91\]

Wu et al.\[92\] and Liu et al.\[93\] have reported the hydrazone-based COF (TFB-COF) and COF-JLU5 as photocatalysts in the

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**Fig. 4**  (a) Synthetic procedure of Re-COF; (b, c) Simulated structure of Re-COF; (d) Proposed catalytic mechanism for CO\(_2\) reduction. (Reproduced with permission from Ref. [82]; Copyright (2019) American Chemical Society).
oxidative cross-dehydrogenative coupling (CDC), respectively. Owing to the factors like permanent porosity, high crystallinity, and good light harvesting ability, the designed COFs showed high catalytic activity, broad substrate adaptability, and good recyclability. Except what have been mentioned above, several kinds of COFs and CTFs showed good photocatalytic activity in tandem dehydrogenation and hydrogenation reactions,[94] oxidation reaction,[95] photoreduction, dehalogenation reaction,[96] radical addition-cyclization,[97] and so on.[98–100] Wang’s group and Chen’s group have reported that benzoazole-based COFs (LZU-190) and (BBO-COF) exhibited extraordinary chemical stability and excellent activity for photocatalytic oxidation of arylobonic acids, respectively.[25,34] Besides, Chen’s group also reported one COF (A$_2$B$_2$- Por-COF) synthesized by the “two-in-one” strategy, which could be used as photocatalyst for the selective oxidation of sulfides and Knoevenagel condensation.[111] In addition, Thomas et al. have synthesized two donor-acceptor COFs for visible-light-induced free radical polymerization of methyl methacrylate (MMA) to poly(methyl methacrylate) (PMMA). These heterogeneous COF-based photoinitiators could be easily separated and showed good recyclability.[102] 

**Photocatalytic Environmental Remediation**

COFs and CTFs have also been used for photocatalytic environmental remediation. Under irradiation, the photogenerated electron and holes that have transferred to the surface will transform into some high activity radical species. For instance, electron reacts with adsorbed molecular O$_2$ to produce •O$_2$ and •O$_2$ reacts with H$^+$ to produce •OH. •OH can also be produced by the reactions of holes with OH$^-$ groups in aqueous systems. The strong oxidizing capability of •OH will eventually result in the mineralization of the pollutants.[103]

Tan’s group constructed porous carbon nitrides networks by the imine reaction between heptazine unit and different aldehydes. Ascribed to their high surface area and wide visible-light absorption, the products showed a high photocatalytic activity for RhB degradation.[104] Some other COFs and CTFs based materials were also used for the photodegradation of dyes, bacteria, and heavy metal ions.[105–109] Su et al. prepared Ag nanoparticles embedded COFs (Ag@TPHH-COF), which exhibited excellent photocatalytic activity for the reduction of nitroaromatic compounds and organic dyes.[110] Lang’s group reported three porphyrinic COFs that were suitable candidates for the design of antibacterial coating for high quantum yields of O$_2$ ($\Delta \Delta_{1}$) under illumination.[111]

CTFs were also applied to remove nitrogen oxide (NO$_2$) in air. Highly crystalline CTF-HUST-HC1 prepared by controlling the monomer feeding rate by Tan’s group showed superior performance for the removal of NO for its better separation of photogenerated carriers.[96] Construction of hybrid system composite of COFs and inorganic semiconductors is another facile approach to enhancing the photodegradation performance. Zhang et al. reported a NH$_2$-MIL-68@TPA-COF core-shell hybrid material that showed much higher performance for the degradation of rhodamine B than separate materials due to higher surface area and wider light absorb range.[112] Except for MOFs,[113] inorganic nanoparticles like BiOBr have also been used to construct hybrid materials to enhance the photocatalytic activity.[114]

**Other Photochemical Applications**

Photodynamic therapy (PDT) is a rapidly advancing treatment for multiple diseases. Under illumination, some photosensitizers (PS) can transfer light energy to heat or lead to the generation of reactive oxygen species (ROS) in the presence of oxygen; heat and ROS will cause cell death and tissue destruction.[115] COFs are excellent substrates for the loading of photosensitizer. Some COFs can even transfer light to heat or produce reactive oxygen species. Therefore, it is possible to use COFs-based materials for photodynamic therapy.

Singlet oxygen (¹O$_2$) presents promising applications in medicinal treatment, photo-oxidation catalysis, and photodynamic therapy, as a result of its high reactivity and oxidizing capability. Jiang’s group reported that squaraine-based COF (CuP-SQ-COF)[116] and imine-linked tetragonal porphyrin COFs can transfer O$_2$ to ¹O$_2$ under visible light.[117] Wang’s group reported two kinds of 3D COFs (3D-Por-COF and 3D-CuPor-COF), which could also be used for ¹O$_2$ production.[118] Moreover, Guo et al. reported that (Fe$_3$O$_4$@COF(TPBD)) could transfer photo energy to local heat.[119] As mentioned above, the production of ¹O$_2$ or local heat suggests that COFs-based materials might be used in photodynamic therapy and other medical applications.[120] For instance, Hu et al. prepared phototherapeutic agent ICG@COF-1@PDA by loading indocyanine green (ICG) on COF1; COF1 prevented the self-aggregation and avoided the self-quenching of ICG. In vivo studies showed the ICG@COF-1@PDA nanosheets effectively induced PTT/PDT dual-mode phototherapy and showed enhanced efficacy in antitumor photoinmunotherapy.[24]

**CONCLUSIONS AND PERSPECTIVES**

A lot of efforts have been made on design, synthesis and photocatalysis applications like photocatalysis water splitting, CO$_2$ reduction, photocatalytic organic reaction transformation, and environmental remediation in the last five years, proving COFs are ideal alternative materials for photocatalysis applications.

Despite great progress in photocatalysis, the research is still in its infancy in terms of inconvenient material preparation and low photocatalytic efficiency compared to inorganic catalysts. The research of COFs-based photocatalysis focused on how to obtain stabler COFs-based materials with suitable energy levels, stronger visible light responsibility, higher photocarriers separation and transfer, and fast surface reaction kinetics. Strategies like engineering consistent structure, adjusting crystallinity, constructing heterojunctions with other semiconductors, nanosizing, and applying suitable co-catalysts should be used.

Most of COFs are prepared by hydrothermal method at milligram scale in sealed tubes, which is difficult to scale up for practical applications. Convenient, controllable synthesis methods like solution phase or solid phase synthesis would be explored.

Another issue is only a few kinds of COFs showed good water and thermal stability till now. Moreover, CTFs prepared by irreversible reactions exhibited high chemical stability but
low crystallinity. So, obtaining COFs with high stability and crystallinity remains a considerable challenge.

Nanosizing (thinner layer, hollow spheres, nanotubes and so on) is a useful strategy to promote charge separation and transport. Other strategies like constructing D-A structure or heterojunctions are also convenient, but fundamental understanding of the mechanism behind the charge transport in D-A structure and heterojunctions system is required. Besides, introducing carbonaceous material benefits the charge transport and increases the conductivity of COFs.

Co-catalysts are indispensable for most of COFs materials. Low-cost alternatives (e.g. MoS\textsubscript{2}, Cu, and molecular catalysts that have been investigated in other photocatalysis systems) can be explored to replace the noble metals. Enhancing the atom utilization efficiency of noble metals like single-atom noble metal is also a useful strategy.

In summary, fantastic progress has been made in the research of COFs-based photocatalysts, but controllable syntheses and deep understanding of the photocatalytic mechanism are still challenges.

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**REFERENCES**

1. Barber, J. Photosynthetic energy conversion: natural and artificial. *Chem. Soc. Rev.* 2009, 38, 185–196.
2. Lewis, N. S. Toward cost-effective solar energy use. *Science* 2007, 315, 798–801.
3. Grätzel, M. Photovoltaic chemical cells. *Nature* 2001, 414, 338–344.
4. Wang, Z.; Li, C.; Domen, K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* 2019, 48, 2109–2125.
5. Fu, J.; Yu, J.; Jiang, C.; Cheng, Q. g-C\textsubscript{3}N\textsubscript{4}-based heterostructured photocatalysts. *Adv. Energy Mater.* 2018, 8, 1701503.
6. Slater, A. G.; Cooper, A. I. Porous materials. Function-led design of new porous materials. *Science* 2015, 348, aaa8075.
7. Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D. A belt-shaped, blue luminescent, and semiconducting covalent organic framework. *Angew. Chem. Int. Ed.* 2008, 47, 8826–8830.
8. Bertrand, G. H. V.; Michaelis, V. K.; Ong, T. C.; Griffin, R. G.; Dincă, M. Thiophene-based covalent organic frameworks. *Proc. Natl. Acad. Sci.* 2013, 110, 4923–4928.
9. Sprick, R. S.; Jiang, J. X.; Bonillo, B.; Ren, S.; Ratjivijotech, T.; Guiglion, P.; ZwiJenburg, M. A.; Adams, D. J.; Cooper, A. I. Tunable organic photocatalysts for visible-light-driven hydrogen evolution. *J. Am. Chem. Soc.* 2015, 137, 3265–3270.
10. Diercks, C. S.; Yaghici, O. M. The atom, the molecule, and the covalent organic framework. *Science* 2017, 355, eaal1585.
11. Dawson, R.; Cooper, A. I.; Adams, D. J. Nanoporous organic polymer networks. *Prog. Polym. Sci.* 2012, 37, 530–563.
12. Lohse, M. S.; Bein, T. Covalent organic frameworks: structures, synthesis, and applications. *Adv. Funct. Mater.* 2018, 28, 1705553.
13. Waller, P. J.; Gandara, F.; Yaghi, O. M. Chemistry of covalent organic frameworks. *Acc. Chem. Res.* 2015, 48, 3053–3063.
14. Yang, L. M.; Dornfeld, M.; Hui, P. M.; Frauenheim, T.; Ganz, E. Ten new predicted covalent organic frameworks with strong optical response in the visible and near infrared. *J. Chem. Phys.* 2015, 142, 244706.
15. Wang, P.; Jiang, X.; Zhao, J. Bottom-up design of 2D organic photocatalysts for visible-light-driven hydrogen production. *J. Phys. Condes. Matter* 2016, 28, 034004.
16. Chen, K.; Yang, L.; Wu, Z.; Chen, C.; Jiang, J.; Zhang, G. A computational study on the tunability of woven covalent organic frameworks for photocatalysis. *Phys. Chem. Chem. Phys.* 2019, 21, 546–553.
17. Pakhira, S.; Mendoza-Cortes, J. L. Intercalation of first row transition metals inside covalent-organic frameworks (COFs): a strategy to fine tune the electronic properties of porous crystalline materials. *Phys. Chem. Chem. Phys.* 2019, 21, 5785–5796.
18. Sakaushi, K.; Antonietti, M. Carbon- and nitrogen-based organic frameworks. *Acc. Chem. Res.* 2015, 48, 1591–1600.
19. Vyaz, V. S.; Lau, V. W. H.; Lotts, B. V. Soft photocatalysis: organic polymers for solar fuel productions. *Chem. Mater.* 2016, 28, 5191–5204.
20. Zhang, G.; Lan, Z. A.; Wang, X. Conjugated polymers: catalysts for photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.* 2016, 55, 15712–15727.
21. Zhang, Y.; Jin, S. Recent advancements in the synthesis of covalent triazine frameworks for energy and environmental applications. *Polymert* 2018, 11, 31.
22. Ball, B.; Chakravarty, C.; Mandal, B.; Sarkar, P. Computational investigation on the electronic structure and functionalities of a thiophene-based covalent triazine framework. *ACS Omega* 2019, 4, 3556–3564.
23. Song, Y.; Sun, Q.; Aguila, B.; Ma, S. Opportunities of covalent organic frameworks for advanced applications. *Adv. Sci.* 2019, 6, 1801410.
24. Gan, S.; Tong, X.; Zhang, Y.; Wu, J.; Hu, Y.; Yuan, A. Covalent organic framework-supported molecularly dispersed near-infrared dyes boost immunogenic phototherapy against tumors. *Adv. Funct. Mater.* 2019, 29, 1902757.
25. Wei, P. F.; Qi, M. Z.; Wang, Z. P.; Ding, S. Y.; Yu, W.; Liu, Q.; Wang, L. K.; Wang, H. Z.; An, W. K.; Wang, W. Benzoxazolene-linked ultrastable covalent organic frameworks for photocatalysis. *J. Am. Chem. Soc.* 2018, 140, 4623–4631.
26. Stegbauer, L.; Schwinghammer, K.; Lortsch, B. V. A hydrazone-based covalent organic framework for photocatalytic hydrogen production. *Chem. Sci.* 2014, 5, 2789–2793.
27. Vyaz, V. S.; Haase, F.; Stegbauer, L.; Savasici, G.; Podjaski, F.; Ochsenfeld, C.; Lortsch, B. V. A tunable azine covalent organic framework platform for visible light-induced hydrogen generation. *Nat. Commun.* 2015, 6, 8508.
28. Wang, X.; Chen, L.; Chong, S. Y.; Little, M. A.; Wu, Y.; Zhu, W. H.; Cloves, R.; Yan, Y.; ZwiJenburg, M. A.; Sprick, R. S.; Cooper, A. I. Sulfone-containing covalent organic frameworks for photocatalytic hydrogen evolution from water. *Nat. Chem.* 2018, 10, 1180–1189.
29. Chen, J.; Tao, X.; Tao, L.; Li, H.; Li, C.; Wang, X.; Li, C.; Yang, Q. Novel conjugated organic polymers as candidates for visible-light-driven photocatalytic hydrogen production. *Appl. Catal. B: Environ.* 2019, 241, 461–470.
30. Sheng, J. L.; Dong, H.; Meng, X. B.; Tang, H. L.; Yao, Y. H.; Liu, D. Q.; Bai, L. L.; Zhang, F. M.; Wei, J. Z.; Sun, X. J. Effect of different functional groups on photocatalytic hydrogen evolution in...
covalent-organic frameworks. ChemCatChem 2019, 11, 2313–2319.

31 Ding, S. Y.; Wang, P. L.; Yin, G. L.; Zhang, X.; Lu, G. Energy transfer in covalent organic frameworks for visible-light-induced hydrogen evolution. Int. J. Hydrogen Energy 2019, 44, 11872–11876.

32 Pachfule, P.; Achariya, A.; Roeser, J.; Langenhahn, T.; Schwarze, M.; Schomaecker, R.; Thomas, A.; Schmidt, J. Diacetylene functionalized covalent organic framework (COF) for photocatalytic hydrogen generation. J. Am. Chem. Soc. 2018, 140, 1423–1427.

33 Hao, W.; Chen, D.; Li, Y.; Yang, Z.; Xing, G.; Li, J.; Chen, L. Facile synthesis of porphyrin based covalent organic frameworks via an A,B monomer for highly efficient heterogeneous catalysis. Chem. Mater. 2019, 31, 8100–8105.

34 Yan, X.; Liu, H.; Li, Y.; Chen, W.; Zhang, T.; Zhao, Z.; Xing, G.; Chen, L. Ultrastable covalent organic frameworks via self-polycondensation of an A,B monomer for heterogeneous photocatalysis. Macromolecules 2019, 52, 7977–7983.

35 Jin, E.; Lan, Z.; Jiang, Q.; Geng, K.; Li, G.; Wang, X.; Jiang, D. 2D sp2 carbon-conjugated covalent organic frameworks for photocatalytic hydrogen production from water. Chem. 2019, 5, 1632–1647.

36 Bi, S.; Yang, C.; Zhang, W.; Xu, J.; Liu, L.; Wu, D.; Wang, X.; Han, Y.; Liang, Q.; Zhang, F. Two-dimensional semiconductor covalent organic frameworks via condensation at arylmethyl carbon atoms. Nat. Commun. 2019, 10, 2467.

37 Wei, S.; Zhang, F.; Zhang, W.; Qiang, P.; Yu, K.; Fu, X.; Wu, D.; Bi, S.; Zhang, F. Semiconducting 2D triazine-coated covalent organic frameworks with unsubstituted olefin linkages. J. Am. Chem. Soc. 2019, 141, 14272–14279.

38 Kuhn, P.; Antonietti, M.; Thomas, A. Porous, covalent triazine-based frameworks prepared by ionothermal synthesis. Angew. Chem. Int. Ed. 2008, 47, 3450–3453.

39 Niu, F.; Tao, L.; Deng, Y.; Gao, H.; Liu, J.; Song, W. A covalent triazine framework as an efficient catalyst for photodegradation of methylene blue under visible light illumination. New J. Chem. 2014, 38, 5695–5699.

40 Schwinghammer, K.; Hug, S.; Mesch, M. B.; Senker, J.; Lbotsch, B. V. Phenyl-triazine oligomers for light-driven hydrogen evolution. Energy Environ. Sci. 2015, 8, 3345–3353.

41 Bi, J.; Fang, W.; Li, L.; Wang, J.; Liang, S.; He, Y.; Liu, M.; Wu, L. Covalent triazine-based frameworks as visible light photocatalysts for the splitting of water. Macromol. Rapid Commun. 2015, 36, 1799–1805.

42 Li, L.; Fang, W.; Zhang, P.; Bi, J.; He, Y.; Wang, J.; Su, W. Sulfur-doped covalent triazine-based frameworks for enhanced photocatalytic hydrogen evolution from water under visible light. J. Mater. Chem. A 2016, 4, 12402–12406.

43 Huang, W.; Ma, B. C.; Lu, H.; Li, R.; Wang, L.; Landfester, K.; Zhang, K. A. I. Visible-light-promoted selective oxidation of alcohols using a covalent triazine framework. ACS Catal. 2017, 7, 5438–5442.

44 Wang, K.; Yang, L. M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Jin, S.; Tan, B.; Cooper, A. Covalent triazine frameworks via a low-temperature polycondensation approach. Angew. Chem. Int. Ed. 2017, 56, 14149–14153.

45 Liu, M.; Huang, Q.; Wang, S.; Li, Z.; Li, B.; Jin, S.; Tan, B. Crystalline covalent triazine frameworks by in situ oxidation of alcohols to aldehyde monomers. Angew. Chem. Int. Ed. 2018, 57, 11968–11972.

46 Liu, M.; Jiang, K.; Ding, X.; Wang, S.; Zhang, C.; Liu, J.; Zhan, Z.; Cheng, G.; Li, B.; Chen, H.; Jin, S.; Tan, B. Controlling monomer feeding rate to achieve highly crystalline covalent triazine frameworks. Adv. Mater. 2019, 31, 1807865.

47 Liras, M.; Barawi, M.; O’Shea, V. A. D. Hybrid materials based on conjugated polymers and inorganic semiconductors as photocatalysts: from environmental to energy applications. Chem. Soc. Rev. 2019, 48, 5454–5487.

48 Ong, W. J.; Tan, L. L.; Ng, Y. H.; Yong, S. T.; Chai, S. P. Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? Chem. Rev. 2016, 116, 7159–329.

49 Banerjee, T.; Haase, F.; Savasci, G.; Gottschling, K.; Ochsenfeld, C.; Lotosh, B. V. Single-site photocatalytic H2 evolution from covalent organic frameworks with molecular cobaltaloxide photocatalysts. J. Am. Chem. Soc. 2017, 139, 16228–16234.

50 Haase, F.; Banerjee, T.; Savasci, G.; Ochsenfeld, C.; Lotosh, B. V. Structure-property-activity relationships in a pyridine containing azine-linked covalent organic framework for photocatalytic hydrogen evolution. Faraday Discuss. 2017, 201, 247–264.

51 Banerjee, T.; Gottschling, K.; Savasci, G.; Ochsenfeld, C.; Lotosh, B. V. H2 evolution with covalent organic framework photocatalysts. ACS Energy Lett. 2018, 3, 400–409.

52 Stegbauer, L.; Zech, S.; Savasci, G.; Banerjee, T.; Podjaski, F.; Schwinghammer, K.; Ochsenfeld, C.; Lotosh, B. V. Tailor-made photoconductive pyrene-based covalent organic frameworks for visible-light-driven heterogeneous hydrogen generation. Adv. Energy Mater. 2018, 8, 1703278.

53 Thote, J.; Aiyappa, H. B.; Deshpande, A.; Diaz, D. D.; Kurungot, S.; Banerjee, R. A covalent organic framework-cadmium sulfide hybrid as a prototype photocatalyst for visible-light-driven hydrogen production. Chem. Eur. J. 2014, 20, 15961–15965.

54 Chen, J.; Tao, X.; Li, C.; Ma, Y.; Tao, L.; Zheng, D.; Zhu, J.; Li, H.; Li, R.; Yang, Q. Synthesis of bipyridine-based covalent organic frameworks for visible-light-driven photocatalytic water oxidation. Appl. Catal. B: Environ. 2020, 262, 118271.

55 Zhang, F. M.; Sheng, J. L.; Yang, Z. D.; Sun, X. J.; Tang, H. L.; Lu, M.; Dong, H.; Shen, F. C.; Liu, J.; Lan, Y. Q. Rational design of MOF/COF hybrid materials for photocatalytic H2 evolution in the presence of sacrificial electron donors. Angew. Chem. Int. Ed. 2018, 57, 12106–12110.

56 Ming, J.; Liu, A.; Zhao, J.; Zhang, P.; Huang, H.; Lin, H.; Xu, Z.; Zhang, X.; Wang, X.; Hofkens, J.; Roeffaers, M. B. J.; Long, J. Hot π-electron tunneling of metal-insulator-COF nanostructures for efficient hydrogen production. Angew. Chem. Int. Ed. 2019, 58, 1–6.

57 Cheng, Y. J.; Wang, R.; Wang, S.; Xi, X. J.; Ma, L. F.; Zang, S. Q. Encapsulating [Mo5S13]12+ clusters in cationic covalent organic frameworks: enhancing stability and recyclability by converting a homogeneous photocatalyst to a heterogeneous photocatalyst. Chem. Commun. 2018, 54, 13563–13566.

58 Biswal, B. P.; Vignolo-González, H. A.; Banerjee, T.; Grunenberg, L.; Savasci, G.; Gottschling, K.; Nuss, J.; Ochsenfeld, C.; Lotosh, B. V. Sustained solar H2 evolution from a thiazolo[S,4-d-thiazole-bridged covalent organic framework and nickel-thiolate cluster in water. J. Am. Chem. Soc. 2019, 141, 11082–11092.

59 Gao, M. Y.; Li, C. C.; Tang, H. L.; Sun, X. J.; Dong, H.; Zhang, F. M. Boosting visible-light-driven hydrogen evolution of covalent organic frameworks through compositing with MoS2: a promising candidate for noble-metal-free photocatalysts. J. Mater. Chem. A 2019, 7, 20913–20920.

60 Li, L.; Zhou, Z.; Li, L.; Zhuang, Z.; Bi, J.; Chen, J.; Yu, Y.; Yu, J. Thiioether-functionalized 2D covalent organic framework featuring specific affinity to Au for photocatalytic hydrogen production from seawater. ACS Sustain. Chem. Eng. 2019, 7, 18574–18581.

61 Liu, M.; Guo, L.; Jin, S.; Tan, B. Covalent triazine frameworks:
synthesis and applications. J. Mater. Chem. A 2019, 7, 5153–5172.
62  Xu, C.; Zhang, W.; Tang, J.; Pan, C.; Yu, G. Porous organic polymers: an emerged platform for photocatalytic water splitting. Front. Chem. 2018, 6, 592.
63  Meier, C. B.; Sprick, R. S.; Monti, A.; Guiglion, P.; Lee, J. S. M.; Zwinjnenburg, M. A.; Cooper, A. I. Structure-property relationships for covalent triazine-based frameworks: the effect of spacer length on photocatalytic hydrogen evolution from water. Polymer 2017, 126, 283–290.
64  Lin, L.; Wang, C.; Ren, W.; Ou, H.; Zhang, Y.; Wang, X. Photocatalytic overall water splitting by conjugated semiconductors with crystalline poly(triazine imide) frameworks. Chem. Sci. 2017, 8, 5506–5511.
65  Kuecken, S.; Acharjya, A.; Zhi, L.; Schwarze, M.; Schomaekere, R.; Thomas, A. Fast tuning of covalent triazine frameworks for photocatalytic hydrogen evolution. Chem. Commun. 2017, 53, 5854–5857.
66  Guiglion, P.; Butchosa, C.; Zwinjnenburg, M. A. Polymer photocatalysts for water splitting: insights from computational modeling. Macromol. Chem. Phys. 2016, 217, 344–353.
67  Jiang, X.; Wang, P.; Zhao, J. 2D covalent triazine framework: a new class of organic photocatalyst for water splitting. J. Mater. Chem. A 2015, 3, 7750–7758.
68  Lan, Z. A.; Fang, Y.; Chen, X.; Wang, X. Thermal annealing-induced structural reorganization in polymeric photocatalysts for enhanced hydrogen evolution. Chem. Commun. 2019, 55, 7756–7759.
69  Guo, L.; Niu, Y.; Razzaque, S.; Tan, B.; Jin, S. Design of D-A1-A2 covalent triazine frameworks via copolymerization for photocatalytic hydrogen evolution. ACS Catal. 2019, 9, 9438–9445.
70  Wang, N.; Cheng, G.; Guo, L.; Tan, B.; Jin, S. Hollow covalent triazine frameworks with variable shell thickness and morphology. Adv. Funct. Mater. 2019, 29, 1904781.
71  Cheng, Z.; Fang, W.; Zhao, T.; Fang, S.; Bi, J.; Liang, S.; Li, L.; Yu, Y.; Wu, L. Efficient visible-light-driven photocatalytic hydrogen evolution on phosphorus-doped covalent triazine-based frameworks. ACS Appl. Mater. Interfaces 2018, 10, 41415–41421.
72  Guo, L.; Niu, Y.; Xu, H.; Li, Q.; Razzaque, S.; Huang, Q.; Jin, S.; Tan, B. Engineering heteroatoms with atomic precision in donor-acceptor covalent triazine frameworks to boost photocatalytic hydrogen production. J. Mater. Chem. A 2018, 6, 19775–19781.
73  Wang, D.; Li, X.; Zheng, L. L.; Qin, L. M.; Li, S.; Ye, P.; Li, Y.; Zou, J. P. Size-controlled synthesis of CsD nanoparticles confined on covalent triazine-based frameworks for durable photocatalytic hydrogen evolution under visible light. Nanoscale 2018, 10, 19509–19516.
74  Zhou, G.; Zheng, L. L.; Wang, D.; Xing, Q. J.; Li, F.; Ye, P.; Xiao, X.; Li, Y.; Zou, J. P. A general strategy via chemically covalent combination for constructing heterostructured catalysts with enhanced photocatalytic hydrogen evolution. Chem. Commun. 2019, 55, 4150–4153.
75  Jiang, Q.; Sun, L.; Bi, J.; Liang, S.; Li, L.; Yu, Y.; Wu, L. MoS2 quantum dots-modified covalent triazine-based frameworks for enhanced photocatalytic hydrogen evolution. ChemSusChem 2018, 11, 1108–1113.
76  Li, F.; Wang, D.; Xing, Q. J.; Zhou, G.; Liu, S. S.; Li, Y.; Zheng, L. L.; Ye, P.; Zou, J. P. Design and synthesis of MOF/COF hybrid materials via postsynthetic covalent modification: an efficient strategy to boost the visible-light-driven photocatalytic performance. Appl. Catal. B: Environ. 2019, 243, 621–628.
77  Huang, W.; He, Q.; Hu, Y.; Li, Y. Molecular heterostructures of covalent triazine frameworks for highly enhanced photocatalytic hydrogen production. Angew. Chem. Int. Ed. 2019, 58, 8676–8680.
78  Lan, Z. A.; Fang, Y.; Zhang, Y.; Wang, X. Photocatalytic oxygen evolution from functional triazine-based polymers with tunable band structures. Angew. Chem. Int. Ed. 2018, 57, 470–474.
79  Xie, J.; Shevlin, S. A.; Ruan, Q.; Moniz, S. J. A.; Liu, Y.; Liu, X.; Li, Y.; Lau, C. C.; Guo, Z. X.; Tang, J. Efficient visible light-driven water oxidation and proton reduction by an ordered covalent triazine-based framework. Energy Environ. Sci. 2018, 11, 1617–1624.
80  Fresno, F.; Villar-García, I. J.; Collado, L.; Alfonso-González, E.; Rehones, P.; Barawi, M.; de la Peña O’Shea, V. A. Mechanistic view of the main current issues in photocatalytic CO2 reduction. J. Phys. Chem. Lett. 2018, 9, 7192–7204.
81  Wang, S.; Xu, M.; Peng, T.; Zhang, C.; Li, T.; Hussain, I.; Wang, J.; Tan, B. Porous hypercrosslinked polymer-TiO2-graphene composite photocatalysts for visible-light-driven CO2 conversion. Nat. Commun. 2019, 10, 676.
82  Yang, S.; Hu, W.; Zhang, X.; He, P.; Pattengale, B.; Liu, C.; Cendejas, M.; Hermans, I.; Zhang, X.; Zhang, J.; Huang, J. 2D covalent organic frameworks as intrinsic photocatalysts for visible light-driven CO2 reduction. J. Am. Chem. Soc. 2018, 140, 14614–14618.
83  Zhang, S.; Wang, S.; Guo, L.; Chen, H.; Tan, B.; Jin, S. An artificial photosynthesis system comprising a covalent triazine framework as an electron relay facilitator for photochemical carbon dioxide reduction. J. Mater. Chem. C 2020, 8, 192–200.
84  Lu, M.; Liu, J.; Li, Q.; Zhang, M.; Liu, M.; Wang, J. L.; Yuan, D. Q.; Lan, Y. Q. Rational design of crystalline covalent organic frameworks for efficient CO2 photoreduction with H2O. Angew. Chem. Int. Ed. 2019, 58, 12392–12397.
85  Liu, W.; Li, X.; Wang, C.; Pan, H.; Liu, W.; Wang, K.; Zeng, Q.; Wang, R.; Jiang, J. A scalable general synthetic approach toward ultrathin imine-linked two-dimensional covalent organic framework nanosheets for photocatalytic CO2 reduction. J. Am. Chem. Soc. 2019, 141, 17431–17440.
86  Lu, M.; Li, Q.; Liu, J.; Zhang, F. M.; Zhang, L.; Wang, J. L.; Kang, Z. H.; Lan, Y. Q. Installing earth-abundant metal active centers to covalent organic frameworks for efficient heterogeneous photocatalytic CO2 reduction. Appl. Catal. B: Environ. 2019, 254, 624–633.
87  Zhong, W.; Sa, R.; Li, L.; He, Y.; Li, B.; Ji, Z.; Zhuang, Z.; Yu, Y.; Zou, Z. A covalent organic framework bearing single Ni sites as a synergistic photocatalyst for selective photoreduction of CO2 to CO. J. Am. Chem. Soc. 2019, 141, 7615–7621.
88  Fu, Y.; Zhu, X.; Huang, L.; Zhang, X.; Zhang, F.; Zhu, W. Azine-based covalent organic frameworks as metal-free visible light photocatalysts for CO2 reduction with H2O. Appl. Catal., B 2018, 239, 46–51.
89  Fu, Z.; Wang, X.; Gardiner, A.; Wang, X.; Chong, S. Y.; Neri, G.; Cowan, A. J.; Liu, L.; Li, X.; Vogel, A.; Clowes, R.; Milton, M.; Chen, L.; Sprick, R. S.; Cooper, A. A stable covalent organic framework for photocatalytic carbon dioxide reduction. Chem. Sci. 2020, 11, 543–550.
90  Xu, R.; Wang, X. S.; Zhao, H.; Lin, H.; Huang, Y. B.; Cao, R. Rhodium-modified porous covalent triazine framework for highly efficient photocatalytic carbon dioxide reduction in a solid-gas system. Catal. Sci. Technol. 2018, 8, 2224–2230.
91  Romero, N. A.; Nicewicz, D. A. Organic photoredox catalysis. Chem. Rev. 2016, 116, 10075–10166.
92  Liu, W.; Su, Q.; Ju, P.; Guo, B.; Zhou, H.; Li, G.; Wu, Q. A hydrazono-based covalent organic framework as an efficient and reusable photocatalyst for the cross-dehydrogenative coupling reaction of N-aryl tetrahydroisouquinolines. ChemSusChem 2017, 10, 664–669.
93  Zhi, Y.; Li, Z.; Feng, X.; Xia, H.; Zhang, Y.; Shi, Z.; Mu, Y.; Liu, X.

https://doi.org/10.1007/s10118-020-2394-x
Covalent organic frameworks as metal-free heterogeneous photocatalysts for organic transformations. *J. Mater. Chem. A* 2017, 5, 22933–22938.

94 Sun, D.; Jang, S.; Yim, S. J.; Ye, L.; Kim, D. P. Metal doped core-shell metal-organic frameworks@covalent organic frameworks (MOFs@COFs) hybrids as a novel photocatalytic platform. *Adv. Funct. Mater.* 2018, 28, 1707110.

95 Chen, R.; Shi, J. L.; Lin, G.; Lang, X.; Wang, C.; Ma, Y. Designed synthesis of a 2D porphyrin-based sp² carbon-conjugated covalent organic framework for heterogeneous photocatalysis. *Angew. Chem. Int. Ed.* 2019, 58, 6430–6434.

96 Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent organic framework as an efficient, metal-free, heterogeneous photocatalyst for organic transformations under visible light. *Appl. Catal. B: Environ.* 2019, 245, 334–342.

97 Liu, S.; Pan, W.; Wu, S.; Bu, X.; Xin, S.; Yu, J.; Xu, H.; Yang, X. Visible-light-induced tandem radical addition-cyclization of 2-aryl phenyl isocyanides catalysed by recyclable covalent organic frameworks. *Green Chem.* 2019, 21, 2905–2910.

98 Bhadra, M.; Kandambeth, S.; Sahoo, M. K.; Addicoat, M.; Balaraman, E.; Banerjee, R. Triazine functionalized porous covalent organic framework for photo-organocatalytic E-Z isomerization of olefins. *J. Am. Chem. Soc.* 2019, 141, 6152–6156.

99 Zhao, Y.; Liu, H.; Wu, C.; Zhang, Z.; Pan, Q.; Hu, F.; Wang, R.; Li, P.; Huang, X.; Li, Z. Fully conjugated two-dimensional sp²-carbon covalent organic frameworks as artificial photosystem I with high efficiency. *Angew. Chem. Int. Ed.* 2019, 131, 5430–5435.

100 Huang, W.; Byun, J.; Roerich, J.; Ramanan, C.; Blom, P. W. M.; Lu, H.; Wang, D.; da Silva, L. C.; Li, R.; Wang, L.; Landfester, K.; Zhang, K. A. I. Asymmetric covalent triazine framework for enhanced visible-light photoredox catalysis via energy transfer cascade. *Angew. Chem. Int. Ed.* 2018, 57, 8316–8320.

101 Huang, W.; Wang, Z. J.; Ma, B. C.; Ghaismi, S.; Gehrig, D.; Laquai, F.; Landfester, K.; Zhang, K. A. I. Hollow nanoporous covalent triazine frameworks via acid vapor-assisted solid phase synthesis for enhanced visible light photoactivity. *J. Mater. Chem. A* 2016, 4, 7555–7559.

102 Pachfule, P.; Acharjya, A.; Roesser, J.; Sivasankaran, R. P.; Ye, M. Y.; Bruckner, A.; Schmidt, J.; Thomas, A. Donor-acceptor covalent organic frameworks for visible light induced free radical polymerization. *Chem. Soc. Rev.* 2019, 10, 8316–8322.

103 Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* 1995, 95, 69–96.

104 Pan, J.; Guo, L.; Zhang, S.; Wang, N.; Jin, S.; Tan, B. Embedding carbon nitride into a covalent organic framework with enhanced photocatalysis performance. *Chem. Asian J.* 2018, 13, 1674–1677.

105 He, S.; Rong, Q.; Niu, H.; Cai, Y. Construction of a superior visible-light-driven photocatalyst based on a C₃N₄ active center-photoelectron shift platform-electron withdrawing unit triadic structure covalent organic framework. *Chem. Commun.* 2017, 53, 9636–9639.

106 Liu, T.; Hu, X.; Wang, Y.; Meng, L.; Zhou, Y.; Zhang, J.; Chen, M.; Zhang, X. Triazine-based covalent organic frameworks for photocatalytic inactivation of bacteria as type-photosensitizers. *J. Photochem. Photobiol. B: Biol.* 2017, 175, 156–162.

107 He, S.; Yin, B.; Niu, H.; Cai, Y. Targeted synthesis of visible-light-driven covalent organic framework photocatalyst via molecular design and precise construction. *Appl. Catal. B: Environ.* 2018, 239, 147–153.

108 Chen, W.; Yang, Z.; Xie, Z.; Li, Y.; Yu, X.; Lu, F.; Chen, L. Benzothiadiazole functionalized D-A type covalent organic frameworks for effective photocatalytic reduction of aqueous chromium(VI). *J. Mater. Chem. A* 2019, 7, 998–1004.

109 Lv, H.; Zhao, X.; Niu, H.; He, S.; Tang, Z.; Wu, F.; Giesy, J. P. Ball milling synthesis of covalent organic framework as a highly active photocatalyst for degradation of organic contaminants. *J. Hazard. Mater.* 2019, 369, 494–502.

110 Wang, R. L.; Li, D. P.; Wang, L. J.; Zhang, X.; Zhou, Z. Y.; Mu, J. L.; Su, Z. M. The preparation of new covalent organic framework embedded with silver nanoparticles and its applications in degradation of organic pollutants from waste water. *Dalton Trans.* 2019, 48, 1051–1059.

111 Hynek, J.; Zelenka, J.; Rathousky, J.; Kubat, P.; Ruml, T.; Demel, J.; Lang, K. Designing porphyric covalent organic frameworks for the photodynamic inactivation of bacteria. *ACS Appl. Mater. Interfaces* 2018, 10, 8527–8535.

112 Peng, Y.; Zhao, M.; Chen, B.; Zhang, Z.; Huang, Y.; Dai, F.; Lai, Z.; Cui, X.; Tan, C.; Zhang, H. Hybridization of MOFs and COFs: a new strategy for construction of MOF@COF core-shell hybrid materials. *Adv. Mater.* 2018, 30, 1705454.

113 He, S.; Rong, Q.; Niu, H.; Cai, Y. Platform for molecular-material dual regulation: a direct Z-scheme MOF/COF heterojunction with enhanced visible-light photocatalytic activity. *Appl. Catal. B: Environ.* 2019, 247, 49–56.

114 Zhu, S. R.; Qi, Q.; Fang, Y.; Zhao, W. N.; Wu, M. K.; Han, L. Covalent triazine framework modified BiOBr nanoflake with enhanced photocatalytic activity for antibiotic removal. *Cryst. Growth Des.* 2018, 18, 883–891.

115 Castano, A. P.; Mroz, P.; Hamblin, M. R. Photodynamic therapy and anti-tumour immunity. *Nat. Rev. Cancer* 2006, 6, 535–545.

116 Nagai, A.; Chen, X.; Feng, X.; Ding, X.; Guo, Z.; Jiang, D. A squaraine-linked mesoporous covalent organic framework. *Angew. Chem. Int. Ed.* 2013, 52, 3770–3774.

117 Chen, X.; Addicoat, M.; Jin, E.; Zhai, L.; Xu, H.; Huang, N.; Guo, Z.; Liu, L.; Ifle, S.; Jiang, D. Locking covalent organic frameworks with hydrogen bonds: general and remarkable effects on crystalline structure, physical properties, and photocatalytic activity. *J. Am. Chem. Soc.* 2015, 137, 3241–3247.

118 Lin, G.; Ding, H.; Chen, R.; Peng, Z.; Wang, B.; Wang, C. 3D porphyrin-based covalent organic frameworks. *J. Am. Chem. Soc.* 2017, 139, 8705–8709.

119 Tan, J.; Namuangruk, S.; Kong, W.; Kungwan, N.; Guo, J.; Wang, C. Manipulation of amorphous-to-crystalline transformation: towards the construction of covalent organic framework hybrid microspheres with NIR photothermal conversion ability. *Angew. Chem. Int. Ed.* 2016, 128, 14185–14190.

120 Hu, C.; Cai, L.; Liu, S.; Pang, M. Integration of a highly monodisperse covalent organic framework photosensitizer with cation exchange synthesized Ag₂Se nanoparticles for enhanced phototherapy. *Chem. Commun.* 2019, 55, 9164–9167.