

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

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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] 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).^[6]

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.^[6,11]

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;

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(4) They consist of earth-abundant elements; (5) They are low-toxic. Thus, COFs are regarded as one kind of promising metal-free semiconductor photocatalysts for its stability, porosity, and crystallinity.^[12–23]

In this mini-review, we have briefly discussed the progress in the design and preparation of COFs, and mainly focused on their photocatalytic applications. In the second section, our emphasis is on the strategic design of COFs while the photocatalytic performance is summarized in the third section. In addition, some perspectives and challenges on the design of highly efficient COFs-based photocatalysts are also presented.

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 benzoxazole-based COFs by the cascade imine formation/cyclization/oxidation reactions. These COFs showed excellent pho-

toactivity and recyclability in the visible-light-driven oxidative hydroxylation of arylboronic acids to phenols.^[25]

Hydrazine and azine based COFs were developed by Lotsch and co-workers *via* the condensation reaction of hydrazide or hydrazine with aldehyde, respectively. The hydrazine-based COFs have shown superior photocatalytic performance for hydrogen production on illuminating with visible light.^[26,27]

Imine linked COFs were prepared by the condensation of aldehydes and amines using the solvothermal and hydrothermal methodologies.^[28–30] A sulfone functional COF reported by Cooper's group has shown long term stability and impressive photocatalytic hydrogen evolution.^[28]

Recently, Lu and coworkers suggested that Pd₀/TpPa-1 showed better photocatalytic H₂ evolution rate than Pd/C.^[31] Thomas *et al.* reported diacetylene functionalized β -keto-enamine 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 A₂B₂ type monomer with two formyl and two amino-terminal groups. This strategy opens a new avenue for facile constructing novel functional COFs.^[33,34]

Sp² carbon-conjugated COFs with C=C linkages prepared by Knoevenagel condensation under solvothermal condition were reported by Jiang *et al.*^[35] In this regard, 2D COFs with an extended π -delocalization have been synthesized by employing the condensation reaction at active arylmethyl car-

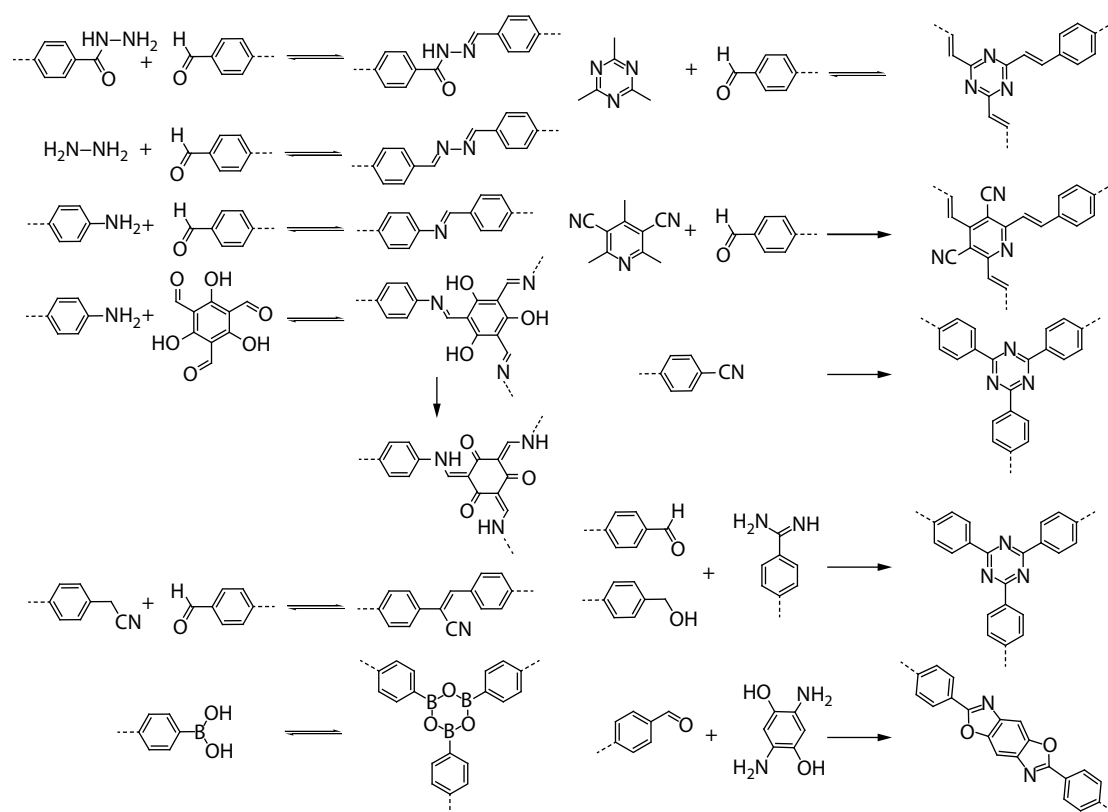


Fig. 1 Reactions for synthesizing COFs and CTFs related to photocatalytic applications.

bon atoms of 3,5-dicyano-2,4,6-trimethylpyridine^[36] or 2,4,6-trimethyl-1,3,5-triazine^[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 *et al.* in 2008.^[38] The robust structures and rich nitrogen content make CTFs promising for practical applications. Various synthetic methodologies are employed, including ionothermal trimerization, phosphorus pentoxide (P_2O_5) catalyzed synthesis, superacid catalyzed method, amidine based polycondensation strategy, and Friedel-Crafts reaction.

In 2014, Song *et al.* reported that amorphous CTF synthesized by an ionothermal trimerization strategy had been utilized for the photocatalytic degradation of methylene blue.^[39] Similarly, Lotsch *et al.* found the phenyl-triazine oligomers prepared at lower temperature showed better photocatalytic

properties than carbonization.^[40] A few examples of CTFs synthesized by superacid catalyzed method have shown effective photocatalytic water splitting^[41,42] and organic reaction transformation activity.^[43] Wu *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.^[41] Su *et al.* found that sulfur-doped CTF-T1 showed better photocatalytic hydrogen evolution activity than non-doped CTF-T1.^[42]

Recently, Tan's group reported the amidine polycondensation at low temperature to synthesize CTFs as demonstrated in Fig. 2.^[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^[40] and also materials prepared at high temperature in conventional ionothermal condition,^[40] which overcame the use of corrosive acid *via* superacid catalyzed method.^[41] Indeed, the

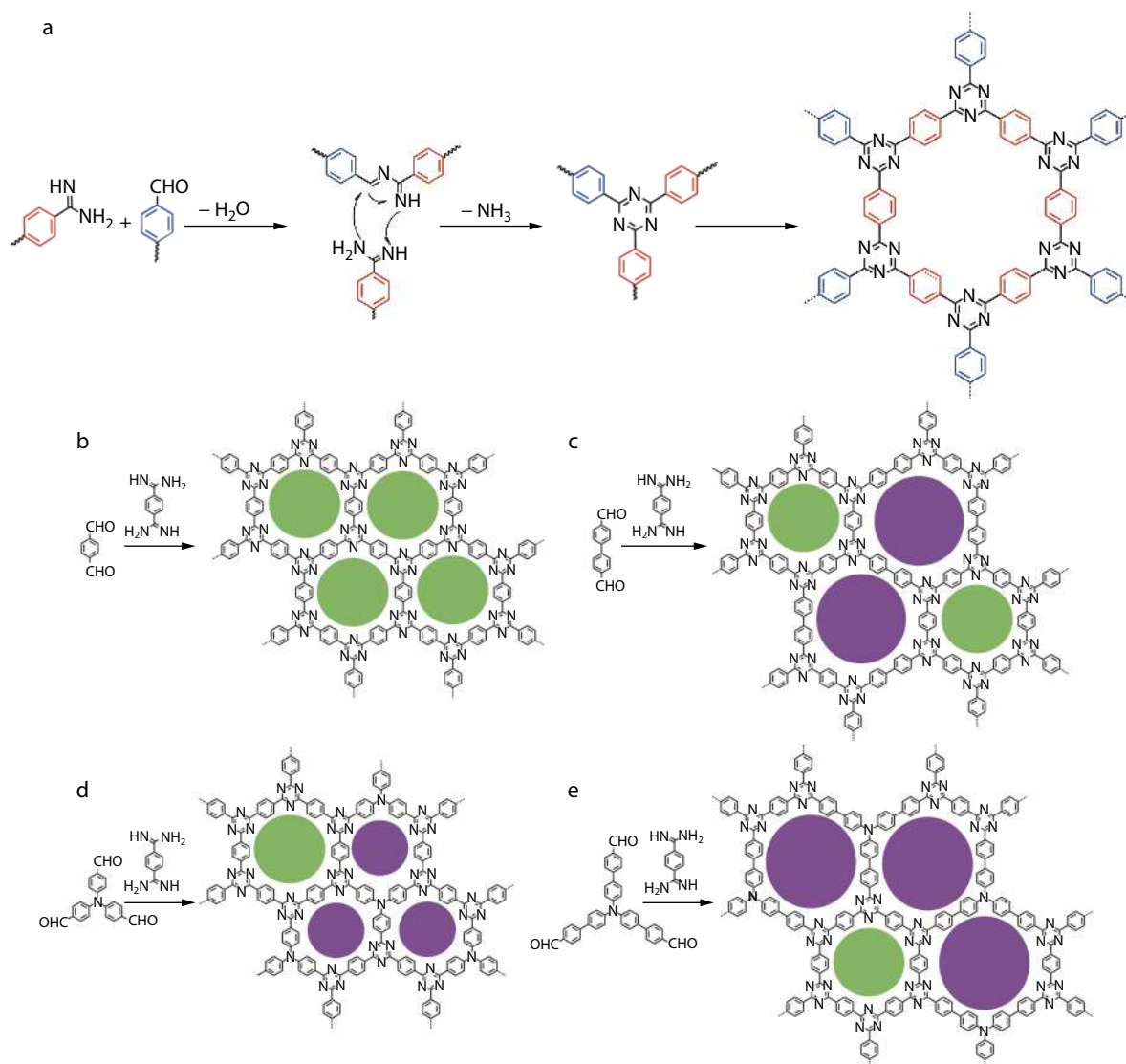


Fig. 2 (a) Synthesis of CTF-HUST-X *via* a low-temperature polycondensation approach. (b–e) Simulated structures of CTF-HUST-X. (Reproduced with permission from Ref. [44]; Copyright (2017) John Wiley and Sons).

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.^[45,46]

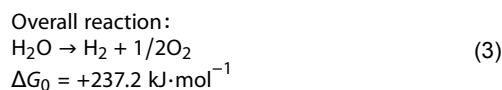
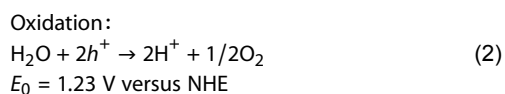
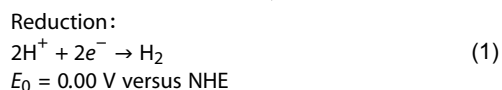
In summary, compared with COFs with imine, azine and hydrazone linkage, COFs with enamine, C=C and triazine linkage show better stability and extended conjugated networks, which endow them with promising prospects in photocatalysis area. Additionally, development of new type, stable and visible light 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 H₂ and O₂ evolution, reduction of CO₂ 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. Under light irradiation, photo-generated electron-hole pairs will transfer toward the surface of photocatalysts; the electrons or holes that migrate to reaction sites without recombination can reduce and oxidize adsorbed water molecules to evolve H₂ and O₂ by reactions (1)–(3) (NHE: normal hydrogen electrode), respectively.



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 H₂ production performance by COFs. Lotsch's group synthesized a series of hydrazone-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 –C–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 H⁺ 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 μmol·h⁻¹·g⁻¹.^[53] The hybrid materials NH₂-UiO-66/TpPa-1-COF constructed by covalently connecting COF and MOF showed much higher photocatalytic hydrogen evolution rate (23410 μmol·h⁻¹·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

Table 1 The summary of photocatalytic H₂ production performance for COFs.

Linkage	COF	Mass (mg)	Lamp	HER ^a (μmol·h ⁻¹ ·g ⁻¹)	AQY ^b	Ref.
Hydrazone	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 ₃ -COF	5	300 W Xe lamp (> 420 nm)	1703	0.44% (450 nm)	[27]
Enamine	FS-COF+WS5F	5	300 W Xe lamp (> 420 nm)	1.63 × 10 ⁴	2.2% (600 nm)	[28]
Enamine	NH ₂ -UiO-66/TpPa-1-COF (4/6)	10	300 W Xe lamp (> 420 nm)	2.341 × 10 ⁴	–	[55]
Enamine	Pt-PVP-COFs	10	300 W Xe lamp (> 420 nm)	8420	0.4% (475 nm)	[56]
C=C	sp ² C-COF	50	300 W Xe lamp (> 420 nm)	1360	0.46% (420 nm)	[35]
C=C	g-C ₄₀ N ₃ -COF	50	300 W Xe lamp (> 420 nm)	50	–	[36]
C=C	g-C ₁₈ N ₃ -COF	50	300 W Xe lamp (> 420 nm)	292	1.06% (420 nm)	[37]

^a The hydrogen evolution reaction; ^b The apparent quantum yield.

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) cobaloxime as noble metal-free co-catalyst and N₂-COF as the photosensitizer.^[49] Afterwards, this team has reported a versatile photocatalyst system composed of COF (TpDTz) and nickel-thiolate cluster as co-catalyst. The designed heterogeneous photocatalyst had a significantly high H₂ evolution (941 μmol·h⁻¹·g⁻¹) in the presence of triethanolamine in water medium.^[58] Recently, MoS₂^[59] and Au^[60] have been reported to act as efficient co-catalysts in COFs-based photocatalysts for photocatalytic H₂ 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.^[45] 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 (SiO₂ 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^[42] 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 × 10⁴ 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 × 10⁴ μmol·h⁻¹·g⁻¹), which is better than that of pristine CTF-1 or CdS.^[73] Other semiconductors or clusters like C₃N₄,^[74] MoS₂,^[75] 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 Co²⁺ 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]

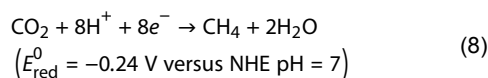
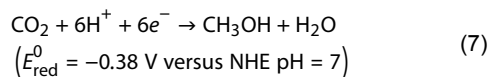
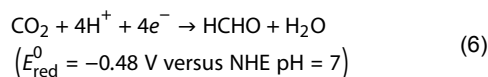
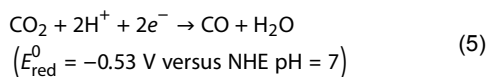
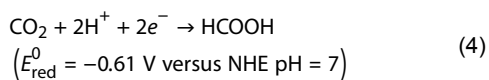
Photocatalytic Carbon Dioxide Reduction

The continuous increase of CO₂ concentration in the atmosphere has caused serious climate change and environmental issues. Conversion of CO₂ to value-added chemicals or fuels by electrochemical or photochemical processes has received significant attention. The direct photoreduction of the CO₂ molecule in the gas phase needs a high negative redox potential (−1.90 V versus NHE for CO₂/CO₂^{•-}), which seems impossible for most of the semiconductors. Nevertheless, the potential of proton-assisted CO₂ 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 CO₂ fixation involves different multi-electron and proton processes and leads to a great variety of photoproducts like CO, CH₄, formic acid, formaldehyde, and methanol. The selectivity of the desired product is significantly affected by the properties of both photocatalyst and cocatalyst, like energy levels, intermediate species and so on.^[47,48,80] The CO₂ adsorption ability is

Table 2 The summary of photocatalytic H₂ production performance for CTFs.

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 O ₂ : 140	6.3% (400 nm) 4.0% (400 nm)	[79]
TFMS catalyzed method at RT	CTFS10	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-HS0.75-1	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]

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.^[81] Reports of photocatalytic carbon dioxide reduction are listed in Table 3.



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

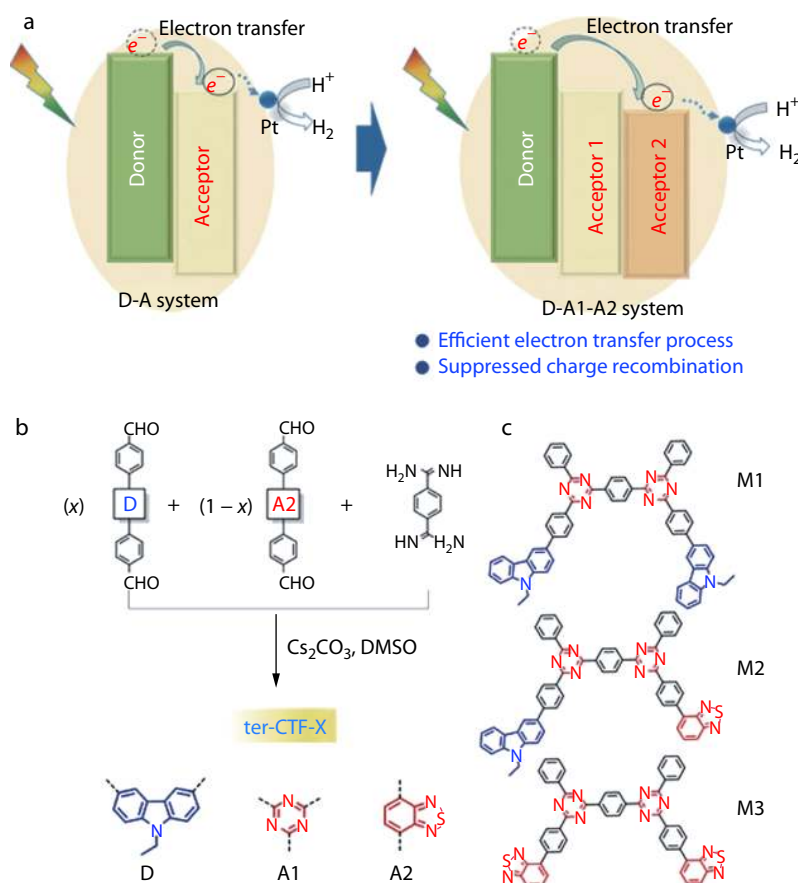


Fig. 3 (a) The comparison of D-A system with D-A1-A2 system; (b) The scheme of the synthetic procedure; (c) Three proposed model fragments in ter-CTF-X. (Reproduced with permission from Ref. [69]; Copyright (2019) American Chemical Society).

Table 3 The summary of photocatalytic CO₂ reduction performance for COFs.

Linkage	COF	Mass (mg)	Lamp	Product/Selectivity	AQY	Ref.
Imine	COF-367-Co NSs	5	300 W Xe lamp (> 420 nm)	CO: 10162 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; H ₂ : 2875 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	–	[85]
Imine	Re-COF	0.9	225 W Xe lamp (> 420 nm)	CO: ~750 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	–	[82]
Imine	TTCOF-Zn	100	300 W Xe lamp (> 420 nm)	CO: 2.055 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ 100% CO	–	[84]
Enamine	DQTP COF-Co	20	300 W Xe lamp (> 420 nm)	CO: 1020 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	–	[86]
Enamine	DATP COF-Zn	20	300 W Xe lamp (> 420 nm)	Formic acid: 152.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	–	[86]
Enamine	Ni-TpBpy	10	300 W Xe lamp (> 420 nm)	CO: 4057 $\mu\text{mol}\cdot\text{g}^{-1}$ H ₂ : 170 $\mu\text{mol}\cdot\text{g}^{-1}$ in 5 h	CO: 0.3% (420 nm)	[87]
Azine	N ₃ -COF	10	500 W Xe lamp (> 420 nm)	CH ₃ OH: 13.7 $\mu\text{mol}\cdot\text{g}^{-1}$ in 24 h	–	[88]
C=C	Re-Bpy-sp ² c-COF	1	300 W Xe lamp (> 420 nm)	1040 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	0.5% (420 nm)	[89]
Triazine	Re-CTF-Py	2	300 W Xe lamp (200–1100 nm)	353.05 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	–	[90]

fication as depicted in Fig. 4. The hybrid system showed high efficiency ($15 \text{ mmol}\cdot\text{g}^{-1}$ 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, $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, and Ru complex photosensitizer. The system showed a high CO evolution rate ($8.0 \mu\text{mol}\cdot\text{h}^{-1}$) with 93% CO selectivity.^[83] Lan *et al.* reported a series of crystalline porphyrin-tetrafulvalene COFs to be used as photocatalysts for reducing CO_2 with H_2O 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 pho-

tocatalytic CO_2 conversion. Besides catalyzing the CO_2 conversion to CO, other liquid products like CH_3OH , HCOOH or $\text{C}_2\text{H}_5\text{OH}$ 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

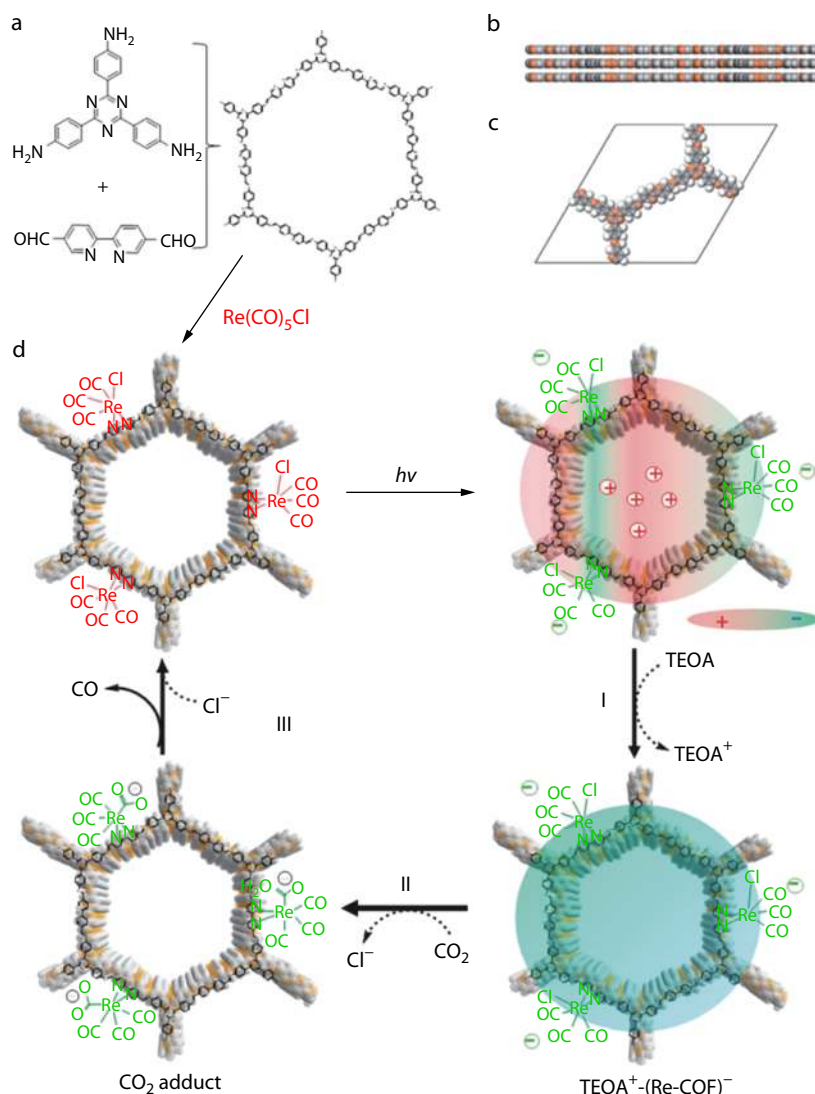


Fig. 4 (a) Synthetic procedure of Re-COF; (b, c) Simulated structure of Re-COF; (d) Proposed catalytic mechanism for CO_2 reduction. (Reproduced with permission from Ref. [82]; Copyright (2019) American Chemical Society).

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.^[98–101] Wang's group and Chen's group have reported that benzoxazole-based COFs (LZU-190) and (BBO-COF) exhibited extraordinary chemical stability and excellent activity for photocatalytic oxidation of arylboronic acids, respectively.^[25,34] Besides, Chen's group also reported one COF (A₂B₂-Por-COF) synthesized by the "two-in-one" strategy, which could be used as photocatalyst for the selective oxidation of sulfides and Knoevenagel condensation.^[33]

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 O₂ to produce •O₂ and •O₂ 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 O₂ (¹Δ_g) under illumination.^[111]

CTFs were also applied to remove nitrogen oxide (NO_x) 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.^[46]

Construction of hybrid system composite of COFs and inorganic semiconductors is another facile approach to enhancing the photodegradation performance. Zhang *et al.* reported a NH₂-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 (¹O₂) presents promising applications in sewage 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 O₂ to ¹O₂ 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 ¹O₂ production.^[118] Moreover, Guo *et al.* reported that (Fe₃O₄@COF(TPBD)) could transfer photo energy to local heat.^[119] As mentioned above, the production of ¹O₂ or local heat suggests that COFs-based materials might be used in photodynamic therapy and other medical application.^[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 photoimmunotherapy.^[24]

CONCLUSIONS AND PERSPECTIVES

A lot of efforts have been made on design, synthesis and photocatalysis applications like photocatalysis water splitting, CO₂ 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 photo-carriers 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. MoS₂, 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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