Topical Review

Self-assembled supramolecular materials for photocatalytic H₂ production and CO₂ reduction

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Abstract
Photosynthetic organisms harness solar radiation to produce energy-rich compounds from water and atmospheric CO₂ via exquisite supramolecular assemblies, which offers a design principle for highly efficient artificial photocatalytic systems. As an emerging research field, significant effort has been devoted to self-assembled supramolecular materials for photocatalytic H₂ production and CO₂ reduction. In this review, we introduce the basic concepts of supramolecular photocatalytic materials. After that, we will discuss recent advances in the preparation of supramolecular photocatalytic materials from zero-dimension to three-dimension which include molecular assemblies, micelles, hybrid nanoparticles, nanofibers, nanosheets, microcrystals, lipid bilayers, supramolecular organic frameworks, supramolecular metal-organic frameworks, gels, and host-guest metal-organic frameworks, etc. Furthermore, we show the recent progress in the photophysical properties of supramolecular photocatalytic materials, i.e. photocatalytic proton reduction, water splitting, CO₂ to HCOOH, CO₂ to CO, CO₂ to CH₄ conversions, etc. Finally, we provide our perspective for the future research, with a focus on the development of new structures and highly efficient photocatalysis.

Keywords: supramolecular materials, self-assembly, photocatalysis, hydrogen production, carbon dioxide reduction

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Future perspectives
In nature, self-assembly structures from all scales play vital roles in photosynthesis. Self-assembled supramolecular materials, which focus on the area of systems constructed through noncovalent interactions, can be a versatile and useful platform in the development of novel materials for production of solar fuels. In this review, we focus on the recent advances in self-assembled supramolecular materials from zero-dimensional to 3D which integral light-harvesting and catalytic functions in one body. We also highlight their photocatalytic properties for \( \text{H}_2 \) production and \( \text{CO}_2 \) reduction. The long-term goal of this research area is to learn how to design supramolecular materials containing photosensitizers and catalysts via self-assembly strategies to create artificial photosynthetic systems with high efficiency for conversion of solar energy into chemical fuels.

1. Introduction
Photosynthesis is considered as the most important chemical reaction in the biosphere [1]. Using sunlight as a primary source, nature continuously converts solar energy into chemical fuels over billions of years [2]. In the natural photosynthetic system, self-assembly of functional molecules plays a vital role in the implementation of functionalization [3, 4]. Photosynthetic organelles precisely locate and neatly arrange light-harvesting complexes and reaction centers within exquisite hierarchical self-assembled structures using lipids and proteins as scaffolds, i.e. the thylakoid in higher plants, chromatophore in cyanobacteria, and phycobilisome in red algae and glaucophytes, etc [5–8]. These elegant supramolecular assemblies exhibit highly efficient light harvesting, accurate electron transfer, and selective catalytic functions in one body. The most studied cellular photosynthetic systems, i.e. photosystem I and II, are all based on the supramolecular assembly structures [9, 10]. In a typical plant chloroplast, the chemical species are exquisitely organized into tailored assembled structures to execute complicated photocatalytic functions. All the functional protein components are perfectly organized and adjacent aligned by noncovalent interactions to work synergistically to form a highly efficient electron transport chain. The interplay and order of numerous subcomponents enable the photons to be funneled by the light-harvesting complexes to generate excited electrons which are further transported to the reaction centers for substrate transformations. The photosynthetic organelles within the lipid membrane of thylakoid take charge of light-harvesting, light-induced charge transfer, and connection of photosystem I, photosystem II, and the reaction centers for catalytic water splitting, \( \text{CO}_2 \) reduction, nicotinamide adenine dinucleotide phosphate, and adenosine triphosphate generation scheme (1).

The exploration of mimicking natural photosynthesis has evoked tremendous interest for scientists in the past century [11, 12]. To achieve this goal, tremendous endeavors have been made to develop the homogeneous and heterogeneous systems which includes molecular photocatalysts, inorganic photocatalytic materials, photoelectrochemical cells, etc [13–20]. Differing from above mentioned pathways, the past few decades have witnessed a fast development of supramolecular chemistry and self-assembly methodologies, which provided a novel approach towards more complex and highly efficient artificial photosynthetic systems [13–15, 21–31]. In natural photosynthesis, there are a couple of key points that the supramolecular chemists could learn from. First, the integration and precise spatial locations of proteins and lipids using noncovalent interactions play a key role in realizing multiple photocatalytic functions. Second, the self-assembly of chromophores leads to an efficient antenna effect and charge-separation which enable fast and directional energy funneling to the reaction centers. In addition, supramolecular preorganization of the photosensitizers, catalytic sites and the substrates not only leads to high local concentrations of the photocatalytic species, but also stabilize those species, and further enhance the whole catalytic efficiency. Taking advantage of self-assembly, it becomes promising to achieve efficient manipulation of photosensitizing, electron transport, catalysis, and relevant processes from structures to functions in supramolecular materials. Supramolecular assembly provides versatile solutions to realize and improve the above three key processes in the following aspects: (a) the self-assembly of light-harvesting chemical components into an ordered stacking pattern leads to broadening of absorption spectrum range and enhances the light absorption, (b) the antenna effect and electron transfer chain resulting from the assembly structures facilitate the transport of excitons and electrons within the supramolecular systems, (c) the precise assembly leads to spatial separation of redox active sites which prolongs the lifetime of charge separation and avoids their recombination, (d) the micro-environment of assembly structures increases the local concentration of reactive substrates and shortens the spatial distance between catalytic centers and reactive species and therefore enhances the catalytic performance. The realization of biomimetic integral systems of photosynthetic reaction centers and light-harvesting systems would further provide theoretical understandings of the design towards highly efficient self-assembled artificial photosynthetic systems. Supramolecular chemists have shown great interest in developing photosynthesis simulations over the years, many efficient light-harvesting artificial systems have been developed, but the coupling of these systems and catalytic reaction sites, especially for efficient solar fuel production, remains a great challenge [6, 32–37].

The production of carbon-neutral solar fuels offers a promising approach to confronting climate change and declining fossil fuel reserves for the sustainability of energy supply and fuel sources [6, 38, 39]. From an environmental, economic, and social point of view, the photocatalytic generation of \( \text{H}_2 \) from water and conversion of \( \text{CO}_2 \) to solar fuels based on artificial photosynthesis is among the most attractive routes in terms of using direct solar energy and water at room temperature and atmospheric pressure. [11, 40–44] This review highlights recent advances in supramolecular materials with self-assembled structures for solar fuel production. We classify the supramolecular materials into several subsections by structural dimensions and assembly complexities, and then discuss their properties of water splitting or proton reduction to produce \( \text{H}_2 \) and the \( \text{CO}_2 \) reduction to fuel molecules, respectively. The representative structures constructed through various
non-covalent interactions and their applications were summarized in scheme 2. We highlight the structure-activity relationship between self-assembled morphologies and photocatalytic properties and the role of self-assembly played in these materials for the promotion of artificial photosynthesis, i.e. spatial confinement, charge separation, electron transfer, antenna effect, etc. This review covers not only the primary fundamentals, such as light capturing and conversion, charge separation, electron/hole transfer, and catalysis in self-assembled structures, but also the combination of all of these for the construction of supramolecular architectures for solar fuel production. We also summarize the representative structures and their photocatalytic performance in tables 1 and 2. Finally, in the conclusion and outlook section, some remaining challenges in this rapidly growing field will be discussed. We hope that the principles behind the construction of self-assembled supramolecular materials compiled in this review will provide a guide to the future design of supramolecular photosynthetic materials that not only possess more controllable structures, but also enhanced photocatalytic performance.

Scheme 1. Scheme of natural photosynthetic chloroplast with incorporated functional supramolecular complexes within a plant chloroplast aligned for light-harvesting, light-induced charge transfer across the thylakoid membrane, and connection of photosystem II (PSII), photosystem I (PSI) and the reaction centers for catalytic water splitting, CO₂ reduction, nicotinamide adenine dinucleotide phosphate (NADPH), and adenosine triphosphate (ATP) generation.

Scheme 2. Schematic diagram of self-assembled supramolecular materials for photocatalytic H₂ production and CO₂ reduction and non-covalent interactions involved in these structures. HER: hydrogen evolution reaction, CO₂RR: CO₂ reduction reaction. SOFs: supramolecular organic frameworks, SMOFs: supramolecular metal-organic frameworks.
| Entry | Morphology | Photosensitizer | Catalyst | SA | Solvent | Light source | Rate (mmol g$^{-1}$ h$^{-1}$) | TON | TOF (h$^{-1}$) | QY (%) | Time (h) | References |
|-------|------------|----------------|----------|----|---------|--------------|----------------|----|-------------|-------|---------|-------------|
| 1     | 0D-host guest | Eosin Y | Cobaloxime | TEOA | H$_2$O/MeCN | LED, 100 W, λ > 450 nm | 51 | 43 | 1.5 | [51] |
| 2     | 0D-host guest | Fluorescein | Co-TFT | TEA | EtOH/H$_2$O | Xe, 500 W, λ = 470 nm | 11 000 | 750 | 24 | [52] |
| 3     | 0D-catenane | DA[2]C$_{4}^{+}$ | Pt NPs | EDTP | H$_2$O | LED, 370 mW × cm$^{-2}$, λ = 450 nm | 0.57$^a$ | 0.52 | 31.5 | [54] |
| 4     | 0D-PtNP Ir-Complex | Pt NPs | Co-TFT | EDTA | H$_2$O | Xe, 150 W | 8.5625 | — | — | 16 | [56] |
| 5     | 0D-micelle | [FeFe]$_{2}$-H$_2$ases | AA | H$_2$O | Hg, 500 W, λ > 400 nm | — | 0.13 | — | 1 | [30] |
| 6     | 0D-QDs CdTe QDs | [FeFe]-H$_2$ase | AA | H$_2$O | Hg, 120 ± 10 mW × cm$^{-2}$, λ > 400 nm | — | 505 | 50 | 8 | [59] |
| 7     | 0D-QDs CdTe QDs | [Fe$_{2}$S$_{2}$](CO)$_{2}$- (chitosan) | AA | H$_2$O/MeOH | LED, λ = 410 nm | — | 52 800 | 50 40 | — | 60 | [61] |
| 8     | 0D-QDs Ni$_{6}$-CdSe/CdS QDs | Ni$_{6}$-CdSe/CdS | IPA | IPA/H$_2$O | Hg, 120 ± 10 mW × cm$^{-2}$, λ = 410 nm | 153 | 18 000 | 18 00 | 11.2 | 10 | [60] |
| 9     | 0D-QDs CdTe QDs | PAA-γ-[Fe$_{2}$S$_{2}$] | AA | H$_2$O | LED, 165 mW × cm$^{-2}$, λ = 450 nm | 27 135 | 12 960 | 5.07 | 3 | [62] |
| 10    | 0D-QDs CdTe QDs | Fe$_{2}$S$_{2}$(CO)$_{2}$- complex | AA | H$_2$O | LED, 160 mW × cm$^{-2}$, λ = 410 nm | 8 781 | 596 | 82 | [63] |
| 11    | 0D-QDs CdSe QDs | PAA-γ-[Fe$_{2}$S$_{2}$] | AA | H$_2$O | LED, 300 W, λ = 450 nm | 83 600 | — | 28 | [64] |
| 12    | 0D-QDs CdSe QDs | Fe$_{2}$S$_{2}$-AD | IPA | H$_2$O | LED, 250 mW × cm$^{-2}$, λ = 410 nm | 112 000 | 54 36 | 48 | — | [66] |
| 13    | 0D-micelle | Ir-complex | (Na$_{6}$K$_{4}$-Ni$_{6}$P$_{2}$) | TEOA | DMF/toluene | Xe, 300 W, λ > 400 nm | 1 376 | 0.26 | 96 | [67] |
| 14    | 1D-ribbon PMI-CA | Ni$_{3}$P$_{2}$N$_{2}$-complex | AA | H$_2$O | Halogen, 250 mW × cm$^{-2}$, 400–700 nm | 3 40 ± 50 | 19 | 18 | [72] |
| 15    | 1D-ribbon PMI-CA | Ni$_{3}$P$_{2}$N$_{2}$ Complex | AA | H$_2$O | Halogen, 250 mW × cm$^{-2}$ | 3 67 | — | — | 18 | [77] |
| 16    | 1D-ribbon PMI-CA | (NH$_4$)$_3$[Mo$_3$S$_{13}$] | AA | H$_2$O | Halogen, 250 mW × cm$^{-2}$, 400–700 nm | 2 600 ± 880 | 144 | — | >100 | [78] |
| 17    | 1D-fiber PMI-CA | (NH$_4$)$_3$[Mo$_3$S$_{13}$] | AA | H$_2$O | Halogen, 150 W | 0.16 | 478 ± 63 | 26 | 0.023 | 18 | [79] |
| 18    | 1D-fiber BODIPY | Co-catalyst | TEOA | MeOH/H$_2$O | Xe, 500 W, λ > 420 nm | >244 | >7 000 | >1 400 | 4 | >5 | [73] |
| 19    | 1D-ribbon quinodimethane | (NH$_4$)$_3$[Mo$_3$S$_{13}$] | AA | H$_2$O | Halogen, 250 mW × cm$^{-2}$, 400–700 nm | 623 ± 119 | 35 | 18 | [80] |
| 20    | 2D-sheet PMI-CA | (NH$_4$)$_3$[Mo$_3$S$_{13}$] | AA | H$_2$O | Halogen, 250 mW × cm$^{-2}$, 400–700 nm | 2 000 | 111 | 18 | — | [86] |

(Continued.)
| Entry | Morphology | Photosensitizer | Catalyst | SA | Solvent | Light source | Rate (mmol g⁻¹ h⁻¹) | TON | TOF (h⁻¹) | QY (%) | Time (h) | References |
|-------|------------|----------------|----------|----|---------|-------------|---------------------|-----|----------|--------|----------|------------|
| 21    | 2D-sheet   | PMI-CA         | (NH₄)₂[Mo₃S₁₃] | AA | H₂O     | Halogen, 150 W, λ = 400–700 nm | 13500 | 123 | 0.13     | 110    | [87]       |
| 22    | 2D-sheet   | PMI polymer    | (NH₄)₂[Mo₃S₁₃] | AA | H₂O     | White LEDs | 22000 | 120 |         |        |            |
| 23    | 2D-crystal | PtTiCPP       | PtTiCPP (Pt NPs) | AA | H₂O     | Xe, 300 W, λ > 400 nm | 138.61 |    | 11.7     | 3      | [90]       |
| 24    | 2D-crystal | P-PMPDI-Zr     | P-PMPDI-Zr (Pt NPs) | AA | H₂O     | Xe, 300 W, 400 nm < λ < 780 nm | 50.46 |    |          |        |            |
| 25    | 2D-liposome| Ru(bpy)₂(bpy-R)⁺ Co-Complex | TEOA | H₂O/TEOA | LED, λ = 455 nm | 165 | 13 |        | [29]   |            |
| 26    | 3D-SOF     | K₄[Ru(BDC)₃] | Na₄[PW₁₂O₄₀]  | MeOH | H₂O     | Xe, 300 W, λ > 410 nm | 3319 | 19 |          | 100    | [101]      |
| 27    | 3D-SOF     | K₄[Ru(BDC)₃] | K₄[P₂W₁₆O₄₁₂] | MeOH | H₂O/MEOH | Xe, 300 W, λ > 410 nm | 7.079 | 781 |          | 20     | [102]      |
| 28    | 3D-SOF     | Ru(BDC)₃ | Ru-POM | MeOH | H₂O/MEOH | Xe, 300 W | 400 | 60 |          |        | [103]      |
| 29    | 3D-SOF     | Ru(BDC)₃ | Na₃[PW₁₂O₄₀]  | MeOH | H₂O/MEOH | Xe, 200 mW × cm⁻² | 1683 | 24 |          |        | [104]      |
| 30    | 3D-SOF     | Ru(bpy)[3]³⁺ | [K₃(PW₁₂O₄₀)] | TEA | DMF/MeOH | Xe, 300 W, λ > 500 nm | 141 | 120 |          |        | [106]      |
| 31    | 3D-SOF     | Ru(bpy)[3]³⁺ | [K₃(PW₁₂O₄₀)] | TEA | DMF/MeOH | Xe, 300 W, λ > 500 nm | 3.553 | 1820 |          | 50     | [105]      |
| 32    | 3D-SOF     | Ru(bpy)[3]³⁺, Trap Sites | TEOA | H₂O     | Xe, 100 mW × cm⁻² | 49.4⁺ | 47 | 0.12     | 24     | [107]      |
| 33    | 3D-gel     | TCPP/THPP     | Pt | AA | DMF     | Xe, 19.63 mw × cm⁻², λ = 440–780 nm | 1.3 | 25 |          |        | [108]      |
| 34    | 3D-gel     | Zn-TCPY-ANT   | Zn-TCPY-ANT | CPG | H₂O     | Xe, 300 W, λ > 400–750 nm | 0.546 | 22 |          |        | [109]      |

*µmol h⁻¹, SA = sacrificial agent, H2ases = Hydrogenases, AA = ascorbic acid, SDS = sodium dodecyl sulfate, dmgH2 = dimethylglyoxime, 4-ppy = 4-phenylpyridine, DA[2]C⁴⁺ = a donor-acceptor [2]catenane, EDTA = ethylenediamine tetraacetic acid, EDT/P = Poly(acrylic acid), AD = adamantyl group, IPA = isopropanol, PMI = perylene monomide, CA = chromophore amphiphilic, BODIPY = boron dipyrromethene, TPY-ANT = terpyridine-anthracene, CPG = coordination polymer gel, P-PMPDI = supramolecular N,N'-bis(phosphonomethyl)-3,4,9,10-perylenetetracarboxylic dianhydride, bpy-R = a bpyridine ligand with long alkyl chains, Co-TFT = a tetrahedral cage formed by Co₂⁺ and tridentate ligand TFT, TCPP = tetrakis(4-carboxyl-phenyl)porphyrin, THPP = tetrakis(4-(hydroxyl)-phenyl)porphyrin, bpy-R = a bpyridine ligand with long alkyl chains, Co-TFT = a tetrahedral cage formed by Co₂⁺ and tridentate ligand TFT, TCPP = tetrakis(4-carboxyl-phenyl)porphyrin, THPP = tetrakis(4-(hydroxyl)-phenyl)porphyrin, SMOF = supramolecular metal-organic framework, SOF = supramolecular organic framework, BDC = 2,2'-bipyridyl-5,5'-dicarboxylate, MCSOF = metal-covalent-supramolecular organic framework.
Table 2. Photocatalytic CO\(_2\) reduction performance of self-assembled supramolecular materials.

| Entry | Morphology | Photosensitizer | Catalyst | SA | Solvent | Light source | Rate (mmol g\(^{-1}\) h\(^{-1}\)) | TON (CO) | TOF (h\(^{-1}\)) | QY (%) | Time (h) | References |
|-------|------------|-----------------|----------|----|---------|--------------|-------------------------------|---------|----------------|-------|----------|------------|
| 1     | 0D-HB      | RuDAC Re-complex | BIH      | MeCN | LED, \(\lambda = 470\) nm | 100(CO) | 23.3 | 4 | [68] |
| 2     | 0D-π-π     | Ru Complex Re complex | TEOA | DMF/H\(_2\)O | Xe, 10 mW \(\times\) cm\(^{-2}\), \(\lambda > 390\) nm | 84 101(CO) | 876 | 5.20 | 96 | [70] |
| 3     | 0D-QDs     | CuInS\(_2\) QDs Co-porphyrin | NaAsc | H\(_2\)O | LED, 140 mW cm\(^{-2}\), \(\lambda = 450\) nm | 4645(CO) | >144 | [74] |
| 4     | 1D-fiber   | Ullazine-polymer Co-complex | TEOA | CH\(_3\)CN/H\(_2\)O | LED, 200 mW \(\times\) cm\(^{-2}\), \(\lambda = 450\) nm | 1518(CH\(_4\)) | 2 | [91] |
| 5     | 2D-bilayer | Ru complex Re(dtb)(CO)\(_3\)Cl | H\(_2\)Asc | Tris-HCl buffer | Xe, \(0.8\) mW \(\times\) cm\(^{-2}\), \(\lambda > 440\) nm | 3.5(CO)\(^a\) | 190(CO) | 93 | 2 | [91] |
| 6     | 2D-bilayer | Ru(bpy)\(_3\)Cl\(_2\) LG-Nico-Co | BIH | MeCN/H\(_2\)O | Xe, 300 W, \(\lambda = 420–800\) nm | 8.696(CO) | 310(CO) | 24 | [92] |
| 7     | 3 D-MOF    | [Ru(bpy)\(_3\)]Cl\(_2\) | Co\(_x\)-BW\(_2\)O\(_{40}\), POMPOs | TEOA | MeCN | Xe, 300 W, \(\lambda = 420–780\) nm | 10.852(CO) | 222.7(CO) | 0.86 | 5 | [116] |
| 8     | 3 D-MOF    | pyrene-based PS | FDH-enzyme, Rh-complex | TEOA | Tris buffer | Halogen, 150 W, 400–700 nm, | 20760(HCOOH) | 865 | 24 | [119] |
| 9     | 3 D-MOF    | Ru(bpy)\(_3\)Cl\(_2\) (PW\(_{12}\), Cp\(_{7}\)Rh) | TEOA | thin film on ITO | CH\(_3\)CN/TEOA | 280 W, \(\lambda > 415\) nm | 175(HCOOH) | 3 | [115] |
| 10    | 3 D-MOF    | Ru(bpy)\(_3\)Cl\(_2\) Zn/Co/Mo-MOF | TEOA | thin film on ITO | CH\(_3\)CN/TEOA | Xe, 300 W, \(\lambda > 420\) nm | 1.28(CO) | 0.77 | 6 | [117] |
| 11    | 3 D-MOF    | Ru complex | [ReBr(CO)\(_3\)(4,4\(^{'}\)-dcbpy)] | BIH | CH\(_3\)CN | LED, 5.1 W, \(\lambda = 450\) nm | 506(CO) | 48 | [118] |

\(^a\) \(\mu\)mol h\(^{-1}\). SA = sacrificial agent, HB = hydrogen bond, DAC = 4,4\(^{'}\)-bis(methyl acetamidomethyl)-2,2\(^{'}\)-bipyridine, BIH = 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzimidazole, bpy = 2,2\(^{'}\)-bipyridine, FDH-enzyme = formate dehydrogenase, POMPOs = polyoxometalate-based organo-metallophosphate frameworks, LG = L-glutamic acid derivatives, LG/Nico = LG with meta-pyridine as head group, dcbpy = dicarboxy-2,2\(^{'}\)-bipyridine.
2. Zero dimensional supramolecular materials

Molecular photocatalysts can be regarded as the simplest prototype of zero-dimensional (0D) photocatalytic systems which has a long research history started from 1970s pioneered by Kirch et al. [45–47] After that, one tradition supramolecular photocatalytic approach is the combination of the photosensitizer and catalyst via covalent bond led by Kimura et al. [48, 49] Recently, Wu group demonstrated that the molecular [FeFe]-H₂ase mimics displayed extraordinary photocatalytic hydrogen production properties. These representative works have been summarized in a couple of reviews [50].

In terms of the 0D supramolecular materials, we focus on the systems with characteristic self-assembly architectures beyond a single molecule. Specifically, the 0D self-assembled supramolecular materials could be classified as follows: (a) assemblies formed by host-guest interactions, (b) mechanically interlocked structures, (c) hydrogen bonding or π–π stacking assisted systems, (d) spherical micelles, (e) hybrid organic-inorganic nanoparticles (NPs), etc. In this section, we highlight some of the recent representative examples according to photocatalytic H₂ production and CO₂ reduction, respectively.

2.1. Molecular assemblies for H₂ production

Typically, a self-assembled 0D photocatalytic system must contains at least two key components: a photosensitizer and a catalyst. These two could be put together in close proximity via a host-guest interaction strategy. In 2020, Wang, Li, Sun and co-workers reported a self-assembled system for photocatalytic H₂ evolution reaction (HER) by encapsulation of Co(dmgH)₂(4-ppy)₂ (1) in the cavity of cucurbit[7]uril (CB[7]) (figure 1(A)) [51]. The Co complex 1, with two hydrophobic 4-phenylpyridine (4-ppy) groups as axial ligands, can be inserted into the cavity of CB[7] (figure 1(B)). The photosensitizer molecule Eosin Y (EY) with a negative electrostatic potential in the aromatic region interacted with the positive potential of the equatorial region of CB[7], and therefore provided the docking points for EY through ion–dipole interactions and intermolecular hydrogen bonding. The 1@CB[7]/EY assembly system displayed a HER turnover number (TON) of up to 51 and an initial turnover frequency (TOF) of 43 h⁻¹ under triethanolamine (TEOA) in H₂O/MeCN at pH = 7 during 150 min (table 1, entry 1). In contrast, the amount of TON and TOF sharply decreased for the 1/EY without CB[7]. The catalytic efficiency and lifetime were significantly improved in the presence of CB[7] which could be attributed to two reasons: (a) the supramolecular assembly efficiently reduced the distance between EY photosensitizer and 1, (b) the encapsulation by CB[7] has promoted the stability of 1 complex as a catalyst.

The similar host-guest encapsulation strategy could also be realized by the encapsulation of a photosensitizer into a metal-organic cage. In 2015, the Duang group reported a Co₃L₄ metal-organic tetrahedron cage which encapsulated a fluorescein (FI) as a photosensitizer for photocatalytic proton reduction [52]. The ligand 2 was prepared by the reaction of tris(4-formylphenyl)amine with thiosemicarbazide in a 1:3 mol ratio and then added Co(OAc)₂ × 4H₂O to yield Co-TFT (figure 2). The Co-TFT polyhedron in dimethylformamide (DMF) displayed the coupled Co⁹⁰/Co¹¹ and Co⁹⁰/Co¹¹ reduction potentials at −1.02 V (vs. Ag/AgCl), which was capable of directly reduction of protons. The addition of Co-TFT to the solution of FI in EtOH/H₂O solution significantly quenched the emission intensity of FI which might be attributable to the photoinduced electron transfer from the excited state FI⁺ to Co-TFT. The luminescent titration experiment of FI and Co-TFT suggested a 1:1 host – guest behavior with an association constant of 3.38 ±0.18) × 10⁴ M⁻¹. Light-driven HER of the FI/Co-TFT/Et₃N system resulted in an initial TOF of 750 h⁻¹ and a TON of 11 000 (table 1, entry 2). These values are comparable to the highest ones reported for cobalt/fluorescein systems, demonstrating the potential advantage of the supramolecular system in photocatalytic hydrogen production. Recently, Wang, Zhang, Jiang and coworkers reported a porous pyrene-based organic cage which displays

![Figure 1](image-url)
Figure 2. Synthesis and assembly of Fl/Co-TFT for photocatalytic proton reduction. Reprinted with permission from [52]. Copyright (2015) American Chemical Society.

Figure 3. An mechanically interlocked molecule DA[2]C4+ catenane for photocatalytic H2 production. (A) The chemical structure of DA[2]C4+ catenane. (B) The proposed mechanism for photocatalytic H2 production of DA[2]C4+ catenane. EDTP: N,N,N',N'-ethylenediamine tetrakis(methyleneephosphonic acid). Pt NPs: Pt nanoparticles. Reprinted with permission from [54]. Copyright (2021) American Chemical Society.

Mechanically interlocked systems have been demonstrated to enhance the charge transfer (CT) interactions between an electron-rich donor (D) and an electron-deficient acceptor (A), and therefore narrow down their molecular energy gaps. This offers a way to shift the absorbance of photocatalysts from ultraviolet (UV) to visible light region. In 2021, Stoddart, Stupp and co-workers synthesized a mechanically interlocked molecule (MIM) named DA[2]C4+ consisting of an electron-deficient cyclophane, cyclobis(paraquat-p-phenylene) (CBPQT4+) and an electron-rich ring, 1,5-dinaphtho[38]crown-10 (figure 3) [54]. The occupation of nanoconfined space within the kinetically trapped systems rendered a strong D-A interaction with an adsorption band at 525 nm of DA[2]C4+ which was suitable for potential photocatalytic activity under visible light. Using Pt NPs as a co-catalyst, the DA[2]C4+ catenane system displayed a photocatalytic HER activity. The reduced DA[2]C2++ served as an electron mediator and reduced the protons to produce H2 in conjunction with Pt NPs with a sacrificial donor. The amount of H2 evolution reached a total of 18.0 µmol measured over 31.5 h for this DA[2]C4+ catenane. (Table 1, entry 3).

2.2. Spherical micelles for H2 production

As a typical morphology with high surface curvature, spherical micelle self-assembled from amphiphiles in solution phase represents one kind of classic 0D supramolecular material. In 2010, Wu group reported that hydrophobic photosensitizers and H2ases mimics could be assembled into a sodium dodecyl sulfate micelle system for photocatalytic H2 production in aqueous solution [30]. In this system, the Re(I) (4,4′-dimethylbpy)(CO)3Br (7) or Re(I)(1,10-phenanthroline) (CO)3Br (8), were employed as photosensitizers and the [FeFe] H2ases mimics, [Fe2(CO)6(µ-adt)CH2C6H5] (9) or [Fe2(CO)6(µ-adt)C6H5] (10) [µ-adt = N(CH2)3] were used as catalysts with ascorbic acid (H2A) as a sacrificial electron donor and proton source (figure 4). The HER efficiency revealed that both the close proximity and the hydrophobic driving force are crucial for the electron transfer from the excited Re(I) complexes to [FeFe] H2ases catalysts, and thus enabled the H2 production under visible light irradiation. The steady-state and time-resolved investigations revealed that the electron transfer took place from the excited Re(I) complexes to [FeFe] H2ases catalyst, which led to the formation of a long lifetime Fe(I)Fe(0) charge-separated species that further reacted with a proton to generate Fe(I)Fe(II) × H intermediate for H2 production.

2.3. Hybrid NPs for H2 production

Hybrid inorganic-organic NPs could be treated as a special kind of 0D materials. As one of the important water-soluble hosts, cyclodextrins (CDs) display versatile molecule assembly patterns [55]. Hybrid 0D assembled supramolecular
photocatalytic materials could be constructed by encapsulation of photosensitizers or catalysts within surface-modified inorganic NPs with CD derivatives. In 2011, the Feiters group reported a three component system containing [Ru(bpy)$_2$(pytl-βCD)]$^2^+$ or [Ir(ppy)$_2$(pytl-βCD)]$^+$ as photosensitizers, a (substituted) viologen as electron relay linker, and platinum NPs as a functionalized platinum catalyst for photocatalytic H$_2$ production in water (figure 5) [56]. The photoinduced electron-transfer from photosensitizer to catalyst was improved by the three-component self-assembly strategy. The H$_2$ productivity was proportional to the emission quantum yield (QY) of the photosensitizer. Comparing to collision-controlled analogues in solution, the supramolecular self-assembly system displayed better efficiency of H$_2$ production. This host-guest assembly strategy could be extended to prepare other hybrid inorganic-organic NPs. The assembly of quantum dots (QDs) could also be used to construct nanoarchitectures. In 2014, Nie, Tang, Zhang, and coworkers developed a light-triggered strategy for the assembly of CdSe QDs into sub-50 nm vesicles with single or multiple layers which exhibited an improved photocatalytic H$_2$ production activity and stability compared with individual QDs [57]. In 2017, Zhang group further reported a self-assembled Au/CdSe nanocrystal cluster system prepared through an emulsion-based self-assembly strategy, which afforded a H$_2$ evolution rate of 73 mmol g$^{-1}$ h$^{-1}$ under visible-light illumination [58].

As a typical 0D inorganic semiconductor material with a diameter of 2–10 nm, QDs are attractive for potential use as photosensitizers for a variety of applications as they usually displayed unique photoelectrical properties with very narrow fluorescence spectra, high brightness and quantum yields, and resistance to photobleaching [59–65]. In 2021, Wu group successfully prepared a three-component supramolecular hybrid 0D material via host–guest interaction using CdSe QDs as photosensitizers [66]. The QDs were modified with per-6-thiol-cyclodextrin (CDSH) to encapsulate
adamantyl (AD) functionalized [FeFe]-H$_2$ase mimics (Fe$_2$S$_2$-AD) as catalysts driven by hydrophobicity. The β-CD was selected to be host based on its highest binding constant towards Fe$_2$S$_2$-AD. QDs and CDSH ligands are combined through Cd-S coordination with exceptional stability under acidic conditions obtained from multidentate ligands. The assembly exhibited excellent H$_2$ evolution performance under optimal conditions with isopropanol as sacrificial electron donor in the aqueous solution. The average diameter of CdSe QDs was screened for the quantum-confinement effects and selected to be 2.0 nm taking its better photocatalytic H$_2$ evolution activity and wider visible-light harvesting property into overall consideration. A total of 23.67 ml H$_2$ was produced in the presence of the assembly of Fe$_2$S$_2$-AD, QDs and CDSH under above conditions and the irradiation of 410 nm LEDs for 48 h with highest TON for the [FeFe]-H$_2$ase mimic in the photocatalytic H$_2$ evolution system of 1.12 × 10$^5$ (table 1, entry 12).

Polyoxometalates (POMs) with rich redox activity, adjustable structure, and extensive tunability have shown great potential in photocatalysis. However, bulk POMs usually display poor stability, low light absorption ability, low specific surface area, etc. In 2022, Yang group reported a dual-functional supramolecular photocatalytic system assembled from a positively-charged Ir-based chromophore and a negatively-charged nickel-substituted polyoxometalate catalyst via electrostatic driving force [67]. This dual-functional vesicle-like 0D assemblies performed HER efficiently as both light-absorber and catalyst under visible light. Under an optimized condition, a TON of over 4000 for HER was achieved over 96 h irradiation, which is 17 t higher than that of discrete components with identical conditions. Destruction of such ordered vesicle-like assemblies will lead to a remarkable decrease of photocatalytic hydrogen production activity. Mechanistic studies further revealed the presence of both oxidative and reductive quenching processes during photocatalysis and also confirmed that the formation of ordered supramolecule is beneficial for effective electron transfer between chromophore and catalyst.

### 2.4. Molecular assemblies for CO$_2$ reduction

The studies of molecular assemblies for CO$_2$ reduction applications are still very rare, we review here two representative examples constructed through hydrogen bonds and π-π interactions that were reported very recently. In 2019, the Kubiak group reported that a Re catalyst and Ru photosensitizer system could be assembled via hydrogen-bonding interaction for photocatalytic CO$_2$ reduction [68]. A ruthenium complex (3) and a rhenium complex (4) were employed as a photosensitizer and a catalyst, respectively (figure 6(A)). The 3/4 assembly system displayed a high rate of intramolecular electron transfer which may attribute to the interaction of hydrogen bonding. Photocatalytic study of 3/4 system in dry acetonitrile displayed a TON of ca. 100 for CO production with a 23.3% QY using a benzimidazole derivate as the sacrificial reagent under CO$_2$ atmosphere at 470 nm irradiation over 4 h (table 2, entry 1). The CO productivity of 3/4 system displayed a 3-fold increase comparing to the Ru(bpy)$_3$ control. The decrease of TON was observed when DMF was used as a solvent, which indicated that the hydrogen-bonding interaction within the dual-core metal-ligand photocatalytic system played a vital role.

Using similar Ru and Re complexes with large π-system and amide groups, in 2021, El-Roz group reported that a supramolecular assembly could be achieved via a combination...
of $\pi-\pi$ stacking and hydrogen bond and further used to photocatalytic conversion of CO$_2$ (figure 6(B)) [69]. The UV–Vis spectra showed an increasing absorption band in a 1:1 mixture of 5 and 6 in DMF, which indicated the additional interaction of the 5/6 complexes. The time resolved photoluminescence and absorption also revealed a faster electron transfer of the 5/6 system. Photocatalytic experiments were carried out in DMF with TEOA as a sacrificial reagent under saturated CO$_2$. The 5/6 (1:1) was found to produce CO with an initial reaction rate of 0.12 mmol h$^{-1}$ and TOF of 18 ± 2 h$^{-1}$ with a QY = 0.39%, which is ca. 3-fold higher than that of controls (table 2, entry 2). Notably, the systems with other ratios of 5/6, and the mashup catalytic system (e.g. Ru control/6 or 5/Re control) all reduced the photocatalytic performance indicating that the non-covalent interactions between 5 and 6 is critical for the photocatalytic activity.

3. One dimensional (1D) supramolecular materials

As a photosynthetic organelle, the phycobilisome in cyanobacteria, red algae and glaucophytes, elegantly integrates light harvesting, exciton/charge transport and catalysis in a hierarchically assembled cylindrical supramolecular complexes [71]. 1D self-assembled supramolecular materials have been demonstrated to display photosynthetic functions for solar fuel production [72–74]. In this section, two main types of 1D supramolecular materials and their photocatalytic applications will be discussed: (a) small molecule-based self-assembled structures, i.e. the 1D nanofibers and nanoribbons with high-aspect ratios, where the small molecular catalysts interacted with them through noncovalent interactions, (b) polymer-based nanofibers constructed via co-assembly of photosensitizer- and catalyst-modified block copolymers.

3.1. Nanoribbons for H$_2$ production

The nanoribbons with high aspect ratio represent one kind of typical 1D materials. Previous theoretical work has shown that on excitation of supramolecular assemblies, strong electronic coupling between chromophores can generate excitons.
that are decoupled from lattice phonon vibrations [75]. In 2014, Stupp and coworkers reported a nanoribbon-like 1D supramolecular catalytic system assembled from perylene monoamide (PMI) amphiphile 12 for photocatalytic hydrogen production (figure 8) [72]. As a charged chromophore amphiphile (CA), the compound 12 self-assembled into supramolecular polymers via hydrophobic collapse in water. In designing the artificial photosynthetic system, CA gel was used as the light absorption unit of the supramolecular catalytic system, and the NiP$_2$N$_2$ catalyst (figure 8(A)) developed by DuBois and co-workers was chosen as the catalyst [76]. The high positive charged catalyst displayed high water solubility and promoted electrostatic complexation with the anionic supramolecular ribbons. Nanoscale ribbon structures were observed by cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy. The small-angle x-ray scattering (SAXS) indicated that the ribbons consisted of interdigitated bilayers of 12. The formation of gels was also observed after adding salt to the aqueous solution containing 12 ribbons. The crystallization resulted in stronger excitonic coupling between adjacent PMI molecules, as well as larger π–π overlap, leading to an increase in overall electronic coupling. The self-assembly of CAs in water afforded the capture of a wider range of photons through spectral broadening. Due to this high coupling, excitons were not expected to reside on one molecule, but dispersed across multiple unit cells in the crystalline ribbons. The high potential energy state of excitons generated in these assemblies were used to drive electron transfer in photocatalytic processes. In the H$_2$ evolution experiments, the nanoribbons were aged overnight and suspended in a solution containing the nickel catalyst with ascorbic acid as the proton source and sacrificial electron donor. The system was illuminated with a white-light source (output 400–700 nm, ~250 mW × cm$^{-2}$). The gels formed with PDDA generated H$_2$ with the highest catalytic TON of 340 ± 50 at a TOF of 19 h$^{-1}$ (table 1, entry 14).

In 2015, the Stupp group further investigated the photocatalytic function of PMI CAs with different alkyl linker lengths separating their hydrophobic core and the hydrophilic carboxylate headgroup (figure 9) [77]. The CAs self-assembled nanostructures displayed in increasing aspect ratios as the linker length is increased. The different molecular packing arrangements led to differences of absorbance spectra, whereas the electronic properties of all PMI amphiphiles were maintained identical. The CAs formed electronically coupled H-aggregates, only CAs with intermediate linker lengths showed high intermolecular orbital overlap. Photocatalytic H$_2$ production using a nickel-based catalyst was observed in all assemblies, with the highest TONs observed for CA gels having intermediate linker lengths (figure 9). The improved photocatalytic performance of the 1D self-assembled supramolecular materials with intermediate linker lengths may cause by the improvement of exciton splitting efficiencies due to their higher orbital overlap.

In 2017, the same group reported a thermally driven crystalline order transition in the landscape of supramolecular...
nanostructures formed by charged chromophore amphiphiles in salt-containing aqueous solutions [78]. The supramolecular reconfiguration to the stable crystalline phase nanostructures was observed to enhance photosensitization of a proton reduction catalyst for HER performance. In 2018, the same group further investigated the PMI CA-based supramolecular materials with different substituents in 9-position of the PMI molecule [79]. The photocatalytic HER experiments indicated that only the moderate dipole compound had the appropriate molecular packing to access charge-transfer excitons leading to enhanced H2 production. In 2021, the same group further investigated the photocatalytic HER performance of CA assemblies of carboxylated naphtho-p-quinoxidimethane amphiphiles with different morphologies including ribbons, helically rolled ribbons, and twisted filaments [80].

3.2. Nanofibers for H2 production

Biological macromolecules display unique structures and conformations for assembling nanoscale scaffold-like materials with versatile functions. Supramolecular organization of molecular pigments, as is found in the natural light-harvesting antenna, has drawn attention for its potential applications to sensors, photocatalytic systems, and photonic devices [32, 35]. In 2010, Belcher and coworkers arranged molecular zinc phyrin pigments into a light-harvesting antenna using M13 viruses as a 1D filamentous scaffold [81]. This pioneer work demonstrated that the 1D nanofibers held great promise to integrate photocatalytic functions by co-assembly of pigments or other photosensitizing molecules.

Integrating and assembling all necessary photocatalytic components into controllable 1D systems is challenging. In 2020, Manners group reported a 1D nanofiber system constructed by co-assembly of block copolymers (BCPs) bearing either a catalyst or a photosensitizer for photocatalytic H2 production [73]. The block copolymers contain a poly-ferrocenylidimethylsilane (PFS) as a common core-forming block and a corona-forming block bearing either a catalyst (PFS-b-Cat) or a photosensitizer (PFS-b-Ps) (figure 10). The colloidal stable 1D nanofibers were readily obtained by a living crystallization-driven self-assembly (CDSA) approach, the length and spatial location of photocatalytic moieties were precisely controlled. Both PFS-b-Cat and PFS-b-Ps nanofibers with low-length-dispersion and controllable length could be achieved. The Cat/Ps blended nanofibers were also prepared by the CDSA process using PFS-b-Cat and PFS-b-Ps with a mass ratio of 1:10. The distribution of cobalt on the PFS-b-Cat nanofibers was characterized by scanning transmission electron microscopy (STEM) and energy-dispersive x-ray. Using TEOA as a sacrificial electron donor, the HER performance was tested in methanol/water under visible light irradiation (λ > 420 nm). Comparing to the segmented triblock Ps-Cat-Ps nanofibers and other controls, the TON was significantly promoted in the Cat/Ps blended nanofiber system which put together photosensitizer and catalyst in a close proximity. This also indicated that the microenvironment of assembly structures played key role in determining the HER efficiency. The highest TON = 7122 with a QY ca. 4% was achieved for Cat/Ps blend nanofibers using a 1:500 mass ratio of PFS-b-Cat and PFS-b-Ps over 5 h visible light irradiation. Remarkably, the integrated photocatalytic nanofibers displayed a good stability which functioned without obvious loss of efficacy for 300 h and were easy to recycle by centrifugation.

3.3. Nanofibers for CO2 reduction

In 2022, Stupp group developed a supramolecular nanofiber system using chromophore amphiphiles based on a diareno-fused ullazine core for light-driven CO2 reduction [74]. The absorption of visible light was enhance by the lateral π-extension of the ullazine core [82]. The absorption and emission spectra show narrow Stokes shifts and good fluorescence quantum yields for both 14a and 14b (figure 11(A)), which enabled to sensitize catalysts that require more negative potential than HER. Synchrotron solution SAXS showed that the self-assembly of monomers formed the supramolecular fibrous structures. Dinuclear Co-based catalysts 15a and 15b for CO2 reduction have been found to be highly active and have been recently used in aqueous solutions (figure 11(A)) [83, 84]. Using 15a as the catalyst and 14a as the sensitizer, the nanofiber system successfully reduced CO2 to CO and CH4 with TEOA as sacrificial donor under blue light (450 nm). The highest performance of TON_{CO} = 4645 ± 306, TON_{CH4} = 1518 ± 205, and TON_{H2} = 26 ± 3 were observed in the 14a/15b nanofiber system over 6 d.
Figure 10. Preparation and structures of self-assembled photocatalytic nanofiber. (A) Chemical structures of the catalytic (PFS-\textit{b}-Cat) and photosensitizer block copolymers (PFS-\textit{b}-Ps). (B) Schematic representation of the Cat/Ps blend nanofiber for photocatalytic H\textsubscript{2} production. Reproduced from [73], with permission from Springer Nature.

Figure 11. Supramolecular nanofibers for aqueous CO\textsubscript{2} reduction. (A) Chemical structures of the diareno-fused ullazine as photosensitizer and dicobalt cryptands catalysts. (B) Schematic illustration of self-assembly of the 1D nanofiber. Reprinted with permission from [74]. Copyright (2022) American Chemical Society.
4. Two-dimensional supramolecular materials

Two-dimensional (2D) materials, i.e. metal oxides nanosheet, metal chalcogenides nanosheet, graphene, and C3N4 nanosheets, have been demonstrated to show unique photocatalytic properties based on their thickness dependent optical and electro properties [85]. However, the tailored 2D supramolecular materials prepared by self-assembly strategy are still on the early stage of development. In this section, we will discuss some of recent progress on the emerging strategies for construction of 2D supramolecular materials and their photocatalytic functions.

4.1. Nanosheets for $\text{H}_2$ production

The amphiphilic PMI-based nanoribbon system was found to supported long-lived charge-transfer excitons in their crystalline core [72]. In 2018, Stupp group reported that a series of 2D crystalline supramolecular nanosheets could be achieved from assembly of amphiphilic PMI-based CAs for photocatalytic HER [86]. A series of amine-substituted CAs with propyl, isopropyl, n-pentyl, and 3-pentyl tails (16a–16d) were synthesized via a Buchwald-Hartwig coupling reaction (figure 12(A)). It was found that the morphology, ordering kinetics, and exciton behavior were highly based on substituents of CA monomers, thus the 2D nanosheets composed of those CAs displayed different photocatalytic HER performance. Comparing to bulkier tails, molecules with short tails rapidly crystallize in water. A PMI-based CA monomer with a 3-pentylamine tail showed strongly red-shifted in its absorbance indicating the formation of charge-transfer excitons. This particular supramolecular structure was found to have an enhanced ability to photosensitize a thiomolybdate catalyst ($\text{(NH}_4\text{)}_2\text{Mo}_2\text{S}_6\text{)}$ for $\text{H}_2$ production (figure 12(C)). This 2D nanosheets of 3-pentyl CAs displayed a highest TON of ca. 2000 for HER that outperformed all other CA controls studied (figure 12(C)). Exciton diffusion rarely occurred in non-crystalline 3-pentylamine assemblies and the assemblies of propyl, isopropyl, and n-pentyl crystalline CAs (figure 12(D)). This indicated that crystal packing affected the transition dipole moments/CT mixing states, which are important for photocatalysis.

In 2021, the same group further investigated the morphological changes in 2D PMI-based CA nanosheets during thermal annealing in high ionic strength aqueous environment and investigated their photocatalytic performance for HER [87].
The extra-large 2D nanosheets created loosely packed hydrogel scaffolds that greatly enhanced photocatalytic H\(_2\) production with TON as high as 13,500 over ~110 h (table 1, entry 21). Recently, they further reported a cocrystallization strategy of small molecules and chemically disordered polymers to create hybrid nanosheets and nanofibers containing a highly ordered lattice and studied their photocatalytic HER performance \[88\].

4.2. Microcrystals for H\(_2\) production

In 2022, the Bai, Zhu, and coworkers synthesized self-assembled 2D nanoleaves with crystalline porphyrins nanostructures for photocatalytic HER \[89\]. Selective aggregation of photoinduced electrons and holes at active sites of the 2D microcrystals were measured by Kelvin probe force microscopy and photodeposition of cocatalysts. It was found that the orderly packing of porphyrins induced a dipole along the \(\pi-\pi\) stacking direction, and therefore generated an inner electric field. The migration of photogenerated electrons and holes along different directions was driven by this build-in electric field. The photocatalytic HER experiments were performed under visible light (\(\lambda < 400 \text{ nm}\)) using ascorbic acid as a sacrificial agent. The nanoleaves reached a photocatalytic H\(_2\) production rate of 9.9 mmol g\(^{-1}\) h\(^{-1}\) over 5 h, which was 40 times higher than its molecular control. Remarkably, the H\(_2\) productivity of nanoleaves reached 138.61 mmol g\(^{-1}\) h\(^{-1}\) when Pt was used as the cocatalyst (table 1, entry 24). This suggested that the ordered self-assembly structures within the 2D microcrystals played a vital role for directional electron transfer and photocatalysis. Using a similar strategy, a perylene diimide (PDI)-based supramolecular microcrystal system doped by Zr cations for photocatalytic H\(_2\) evolution was also reported by Hua group in 2021, in which the phosphonate/Zr coordination bonds enhanced the catalytic efficiency \[90\].

4.3. Lipid bilayers for H\(_2\) production

The lipid bilayers with low curvatures could be regarded as a special kind of 2D supramolecular materials. One of the feasible ways for the construction of 2D supramolecular photocatalytic materials is co-embedding photosensitizer and catalytic subunits within a lipid bilayer membrane. Compared with molecular systems in which the photosensitizer and catalyst are connected by coordination or covalent bond, the lipid bilayer system may have following advantages: (a) the synthesis is much simpler for avoiding the use of bridging ligands, (b) the ratio of the photosensitizer to the catalyst is flexible and the composition can be varied, (c) the solubility of the amphiphilic photosensitizers and catalysts can be significantly improved in water.

In 2014, Burkhard König’s group reported a functionalized membrane system for photocatalytic HER \[29\]. In this system, the Ru complex as photosensitizer (17) and the Co complex as catalyst (18) were grafted with long alkyl chains and embedded into unilamellar vesicles by sonication in pure water (figure 13). As a result, the high local concentration of the two redox-active subunits at the membrane surface led to a close spatial proximity. The efficient dynamic reorganization of membrane fluidity also played a critical role as it accelerated the electron transfer and improved the catalytic activity. Under N\(_2\) atmosphere, the authors examined the influence of various factors on the HER performances. As the ratio of 18/17 varies from 8: 1 to 1: 32, the highest TON of photosensitizer was observed at 4: 1, while that of catalyst was at 1: 32. Besides, when the ratio was 1: 1, the largest amount of H\(_2\) was obtained with a value of 38.4 \(\mu\)mol over 13 h (table 1, entry 25). This indicated that the self-assembled supramolecular structures enhanced the high local concentration of co-embedded Co-catalyst, and therefore the productivity of H\(_2\). The influence of different phospholipids with different hydrophobic tails on catalytic activities were also investigated. The highest H\(_2\) productivity was observed by the dioleoylphosphatidylcholine (DOPC) lipid with a TON of 159 at 19 °C, because of the DOPC has a low \(T_m\) of \(-21\) °C. This indicated that a better liquidity of membrane promoted the diffusion of the embedded photocatalytic subunits. Therefore, the dynamic self-organization led to a high activity for an optimized distribution of the catalyst and photosensitizer.

Figure 13. Self-assembled lipid bilayers for photocatalytic H\(_2\) generation. (A) Chemical structure of ruthenium photosensitizer 17 and catalyst 18. (B) Schematic illustration of the lipid bilayer assembly for photocatalytic HER. \[29\] John Wiley & Sons. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
4.4. Lipid bilayers for CO\textsubscript{2} production

Using a similar lipid bilayer assembly strategy, a vesicles system for visible-light-driven CO\textsubscript{2} reduction in water was reported by Murata and coworkers in 2014 [91]. The dipalmitoylphosphatidylcholine (DPPC) lipid was used to construct the vesicles in water. In this vesicles system, Ru complexes 19 and Re complex 20 were embedded in the DPPC membrane as a photosensitizer and a CO\textsubscript{2} reduction catalyst, respectively. The mechanistic studies further demonstrated that the CO\textsubscript{2} reduction was initiated with the reductive quenching of the triplet metal-ligand charge transfer excited state of the Ru complex with the ascorbate (HAsc\textsuperscript{-}) as an electron donor, and then followed by an electron transfer process from the reduced Ru complex 19 to the Re complex 20 to generate reduced Re species with CO\textsubscript{2} reduction ability (figure 14). The highest productivity of CO was obtained \(\sim 3.5\ \mu\text{mol h}^{-1}\) and a TON of 190 with respect to the Re catalyst (table 2, entry 6).

In 2022, Jiang and co-workers also reported a supramolecular lipid bilayer system for photocatalytic CO\textsubscript{2} reduction to CO [92]. It was found that the alkyl chains of the lipid provided a hydrophobic microenvironment for efficient gas transfer, and the assembled bilayers induced a synergistic effect between two adjacent Co ions for photocatalytic CO\textsubscript{2} reduction reaction. This supramolecular system exhibited excellent photocatalytic CO\textsubscript{2} reduction performance, with 208.7 mmol g\textsuperscript{-1} CO production within 24 h and a CO/H\textsubscript{2} selectivity of 90% depending on the water content of the solvent (table 2, entry 7).

5. Three-dimensional supramolecular materials

Three-dimensional (3D) materials have received tremendous attention in photocatalysis because of their excellent light absorption ability, large specific surface area, high stability, and unique photophysical and photochemical properties, etc [93]. In the past decade, great progress has been achieved for the development of photocatalytic 3D metal-organic frameworks (MOFs), covalent organic frameworks (COFs), or porous organic polymers for solar fuel production owing to their tunable structures and tailorable functionalities [94–97]. However, only a handful of examples of 3D supramolecular photocatalytic materials via self-assembly strategy aiming for this purpose were reported. In this section, supramolecular organic frameworks (SOFs), supramolecular metal-organic frameworks (SMOFs), supramolecular gels, host-guest MOFs, and their applications for photocatalytic solar fuel production will be introduced.

5.1. SOFs for H\textsubscript{2} production

The fabrication of 3D SOFs have been successfully achieved by Li and co-workers since 2014, which represented a typical kind of homogeneous periodic porous materials in aqueous solution [98]. The 3D SOFs formed by co-assembly of CB[8] and rationally designed multitopic building blocks, have been demonstrated to efficiently adsorb various guest molecules in water [98–100]. Putting photosensitizers and catalysts in a confined cavity of 3D SOFs is expected to promote their performance of photocatalysis by the enhancement of photoexcited electron transfer.

In 2018, Li, Liu and coworkers reported the self-assembly of a highly stable 3D SOF assembled from a rigid bipyridine-derived tetrahedral monomer (21) and CB[8] in water and its simultaneous inclusion of both [Ru(bpy)]\textsubscript{3}\textsuperscript{2+}-based photosensitizers (25 and 26) and two types of POMs as HER catalysts for photocatalytic H\textsubscript{2} production in water (figure 15)
The enrichment of both photosensitizer and catalyst in pores (aperture diameter ~2.3 nm) of 3D SOFs significantly increased their local concentration for photocatalytic HER (figure 16). Comparing to the molecular combination of 26 and a Wells–Dawson-type polyoxometalate (WD-POM), this homogeneous 3D SOF system displayed a 110-fold increase of the TON for the H\textsubscript{2} evolution. This indicated that the nano-confinement of the sensitizers and catalysts within the self-assembled framework leads to the construction of a new family of homogeneous, recyclable, visible-light-driven photocatalytic systems that exhibit remarkably enhanced efficiency for HERs. The highest TON of 3319 of HER was observed for the SOF system ([21] = 50 µM) with 20 mM of compound 26 as photosensitizer and 2 mM K-POM\textsubscript{a} as catalyst (table 1, entry 26).

Using a similar self-assembly strategy in water, a diamondoid SOF with bigger pores (3.6 nm-aperture size) was achieved by the same group in 2019 [102]. This 3.6 nm-aperture SOF was assembled from a 1,4-bis(pyridin-4-yl)benzene-appended tetrahedral monomer (22) and CB[8]. This expanded SOF displayed highly stability and able to simultaneously adsorb photosensitizers (25 and 26) and WD-POM catalysts at very low concentrations, leading to enhanced efficiency of HER compared to the above mentioned prototypical SOF of 2.1 nm-aperture size [101]. Furtherly, utilizing a periodic SOF assembled from 23 and CB[8] as a template to direct the [2 + 2] photodimerization of the styrylpyridinium units (figure 15), the same group reported a first water-soluble 3D COF, termed as sCOF-101, in 2020 [103]. This water-soluble COF displayed high stability in
harsh acidic and basic media without any interpenetration. The sCOF-101 included the Ru complexes of 25 and 26 as photo-sensitizers and redox-active WD-POM as catalyst, which led to a significant increase of photocatalytic HER activity comparing to an irregular polymer counterpart. Additionally, the D-A interaction can also be introduced to the SOFs to generate more 3D assembly patterns. In 2022, the Li group reported a more stable 3D supramolecular polymer system through a \([2 + 2]\) binding motif from assembly of 24 and CB[8], in which two CB[8] rings encapsulate a dimer of CT complex (figure 15) [104]. As a water soluble porous supramolecular polymer, it also exhibited a confinement effect for enhancement of the proton reduction to produce \(H_2\) coupling with a \(L\)-methionine thioether oxidation reaction in water driven by visible light.

5.2. SMOFs for \(H_2\) production

MOFs-based hybrids are a promising class of photocatalysts for solar induced hydrogen evolution. However, the solid nature and rigid pore aperture limits the mass transportation within MOFs-based materials, and therefore lower the hydrogen evolution rates for this kind of materials. As a conceptual extension of water soluble 3D SOFs, Li group reported a 3D SMOF with both metal subunits and homogeneous periodicity, which combines the structural features of SOFs and MOFs, for photocatalytic HER application in water in 2016 [105]. The SMOF was co-assembled from a highly soluble hexaarmed \([Ru(bpy)_3]^{2+}\) complex (27) as an octahedral core with CB[8] (molar ratio 1:3) driven by the host encapsulation of intermolecular dimers of the peripheral 4-phenylpyridinium units in water (figure 17). The solution-phase periodicity of this 3D SMOF with a pore aperture of ca. 1.5 nm was confirmed by SAXS and x-ray diffraction (XRD) experiments. The cavity of SMOF displayed a one-cage-one-guest manner for adsorption of anionic WD-POMs as catalyst to give the resulting WD-POM@SMOF hybrid assemblies for photocatalytic HER under visible light (500 nm) irradiation. The WD-POM@SMOF assembly displayed a fast multi-electron injection from the Ru complex to redox-active WD-POM, leading to \(H_2\) production in both aqueous and organic media. Using TEOA as a sacrificial reagent, the TON of \(H_2\) production reached 1820 over 14 h irradiation, which is 5 times higher than that of the heterogeneous WD-POM@\([Ru(bpy)_3]^{2+}\)MOF hybrid (table 1, entry 30). This indicated that 3D SMOF not only promoted the diffusion and contact of \(H_3O^+\) with the POM catalyst, but also enhanced the transfer of excited \([Ru(bpy)_3]^{2+}\) electrons to WD-POM.

In 2018, the same group further reported a cubic metal-covalent-supramolecular organic framework hybrid (MCSOF) assembled from 28 and CB[8], in which the peripheral hydrophobic aromatic units of 28 were connected to the \([Ru(bpy)_3]^{2+}\) complex core through the hydrazone bond (figure 17) [106]. The MCSOF combines the structural features of MOF, COF, and SOF in one body and remarkably facilitated visible light-induced electron transfer from the Ru complex to the POM catalyst, which displayed enhanced photocatalytic HER in aqueous solution with a homogeneous manner and in organic media with a heterogeneous manner, respectively. Using the same hexaarmed \([Ru(bppy)_3]^{2+}\)-based precursor (27), Zhang, Li and co-workers further reported a binary hybrid 3D QD@SMOF material in 2021, which was constructed via co-assembly of negatively charged CdS-QDs with positively charged SMOF, for photocatalytic HER [107]. The photocatalytic HER of the QD@SMOF assemblies was performed at pH = 11 in water with TEOA. The highest photocatalytic activity of 49.4 mol h\(^{-1}\) with a TOF of 47.0 h\(^{-1}\), and a solar-to-hydrogen efficiency of around 1.04% was observed of the QD@SMOF, which was 80 times as high as that of pure CdS QDs, and almost 110 folds of the
parent SMOF itself (table 1, entry 32). At the mechanistic level, the QD@SMOF displayed a type I heterojunction property, in which the supramolecular assembly improved the separation efficiency and inhibited the recombination of photogenerated charges.

5.3. Supramolecular gels for H₂ production

The gels with self-assembled structures represent a typical kind of 3D supramolecular materials. In 2020, Jiang’s group developed a supramolecular gel containing an L-glutamic acid derivative and two types of free base porphyrins, 29 and 30, for photocatalytic HER (figure 18) [108]. Protonation is caused by the ionization of the carboxyl groups of 29 due to the close packing of molecules in the gel. As identified by the XRD patterns, the 31/29/30 assemblies were formed in DMF with a d spacing of 3.86 nm. Compared with 29 or 30 alone in DMF solution, a red shift of the fluorescence of the 29/30 mixture in DMF solution was observed, indicating the formation of the 29/30 exciplex in DMF solution. The porphyrin complexes displayed a smaller energy bandgap, which was beneficial for photo-induced electron generation and charge separation. Using ascorbic acid as a sacrificial reagent, the 3D gel was used for photocatalytic HER, and the total amount of H₂ generated under visible light irradiation over 5 h was 6.5 mmol × g⁻¹ porphyrin (table 1, entry 33).

In 2021, Tapas Kumar Maji group reported a 3D coordination hydrogel by self-assembly of Zn²⁺ and a low molecular weight polymer-based gelator in a 1: 1 ratio with a binding constant of 8.85 × 10³ [109]. The
H$_2$ evolution of the 3D coordination hydrogel produced $18.03 \pm 1.64$ mmol g$^{-1}$ H$_2$ over 22 h with an average production rate of 0.75 mmol g$^{-1}$ h$^{-1}$ under irradiation range from 400 nm to 750 nm using triethylamine (TEA) as sacrificial electron donor. The highest QY was calculated to be 2.41% at 400 ± 5 nm. The promotion of HER activity by the supramolecular gels indicated that hydrated environment of the assembly, e.g. the spatial arrangement and covalent linking of the photosensitizers and catalytic centers, played vital role for photocatalytic HER activity.

### 5.4. Host-guest MOFs for CO$_2$ reduction

The MOFs are regarded as a promising platform for photocatalytic purposes, which have already been summarized in a couple of reviews [110–114]. In this section, we only focus on a host-guest strategy to improve molecular catalyst stability, efficiency, and selectivity via guest immobilization using MOFs as host matrices. This could be regarded an analogous of host-guest concept in classic supramolecular chemistry.

In 2020, Mellot-Draznieks and co-workers reported a functionalized host-guest MOF for photocatalytic CO$_2$ reduction to produce HCOOH, in which a Keggin type POM as guest was encapsulated in the cavities of a UiO-67 MOF and the Rh complex as catalytic center was introduced via a postsynthetic linker-exchange procedure [115]. The MOF acted as a host and co-immobilized the POM and Rh complex, therefore significantly enhanced the photocatalytic activities of CO$_2$ reduction. Other POM@MOFs also displayed a photocatalytic CO$_2$ reduction property [116, 117]. In 2021, Warnan, Fischer, and co-workers reported a MOF system which hosted a photosensor and a catalyst for photocatalytic CO$_2$ reduction which further emphasized the host-guest interaction in MOFs [118]. The guest encapsulation of a Re complex as catalyst (32) and a Ru complex as photosensitizer (33) in the hosts of MOFs UiO-66–68 with a wide range of pore diameters of 8.0, 13.1, and 17.2 Å were examined, respectively (figure 19). Carboxy groups were chosen to anchor 32 and 33 at the MOFs via interaction of amine-modified linkers, in which the UiO-68 displayed a stable anchoring where photoinduced electron transfers from light-absorbing units to neighboring catalysts (figure 19). The specific host pore size of the host MOFs determined the catalyst and photosensitizer spatial location—either inside or outside of MOF particle surface. Therefore, the affecting catalyst stability, electronic communication between catalyst and photosensitizer, and consequently the apparent
catalytic rates were affected by the host-guest strategy, which allows for a rational understanding of an optimized supramolecular layout of catalyst, photosensitizer, and host matrix for MOFs. The similar host-guest strategy was also used to integral enzymes and photosensitizers in a hierarchical mesoporous MOF for light-driven CO₂ reduction to HCOOH by Farha group in 2020 [119].

6. Conclusions and outlook

As an emerging research field in materials science, supramolecular photocatalytic materials have the potential to confront energy and climate change by converting solar energy to fuels. The essence of this area is to understand natural photosynthesis beyond the molecular level and to guide the design of future artificial photosynthetic systems. This review summarizes the recent advances of self-assembled supramolecular materials in this area. Construction methodologies of these materials from 0D to 3D have been developed and photocatalytic applications have been achieved, including H₂ production from water splitting or proton reduction, and CO₂ reduction to molecular fuels, e.g., CO, HCOOH, CH₄, etc. The gaseous products, such as H₂, CO, CH₄, could be analyzed and quantified by the gas chromatography. The liquid products, such as HCOOH, could be analyzed and quantified by ion exchange chromatography. The performance of solar fuel conversion depends on their morphology and dimensions. It is clearly shown that the assembly structures and non-covalent interactions, e.g., hydrogen bond, π-π stacking, hydrophobic effect, host-guest interaction, crystallization, and electrostatic/ionic interaction, etc., play a crucial role in these systems. For example, the assemblies of chromophore amphiphiles have been demonstrated to exhibit promoted photoactivity through electronic coupling and delocalization of π-systems compared to their monomeric or macromolecular counterparts. The structures and related functions are already diverse but are expected to be extended and deepened in the future.

There are many challenges to be concerned with and also exciting possibilities to be introduced for the future studies. Currently, most of the self-assembled supramolecular systems only display the capability to produce H₂ under light irradiation. This is a good starting point to explore the transformation of solar energy to chemical fuels with the participation of assembly structures. However, the productivity and efficiency are still very low in comparison to the present industrial pathways, e.g., reformation of natural gas, oil, coal, or water electrolysis, which need to be further optimized toward a practical or industrial application standard. Additionally, more efforts need to be made for the development of supramolecular materials for CO₂ reduction. It should be pointed out that the examples of supramolecular systems for photocatalytic CO₂ conversion are very limited and the products of CO₂ conversion are mainly C₁ products. The reduction of CO₂ to methane is particularly challenging for organic photosensitizers and catalysts since multiple electron injection and proton transport are required than that of proton reduction. Moreover, the generation of C₂+ reduction products is currently still very challenging but with a great importance for future exploration. This is not only because multi-carbon products are of higher value, but also because it will facilitate the development of technologies for rational self-assembly design principles with tailored photocatalytic functions. In this context, many other gas or liquid products should be of interest for solar-fuel production within supramolecular materials. Another challenging endeavor concerns the improvement of stability of the catalytic systems and eliminating the presence of sacrificial agents. Mimicking natural photosynthesis to create a so-called ‘Z-scheme’ system also provides a fascinating strategy to simulate the whole process of photosynthesis which integrates the oxidation and reduction reactions in one body. For example, the Wang group recently reported a liposome-MOF assembly system which achieves overall photocatalytic water splitting with an apparent QY of 1.5% in the lipid bilayers [31]. Furthermore, the realization of photocatalytic functions for H₂ production and CO₂ reduction in supramolecular materials relies on the selection of different catalysts. The rational design of catalytic sites which integrate water or proton, and CO₂ absorption sites may be a useful strategy to consider in future research.

As inspired by plants and other photosynthetic creatures, nature exhibits a tailored assembly line for selective synthesis of complex chemicals through supramolecular assembly networks. However, the current reported hierarchical architectures with cooperative functions towards cascade or tandem photocatalytic reactions are extremely rare. To address this, other than the molecular level binding mode used to create subunits, the assembly strategies of mesoscopic supramolecular interactions in nano- to micrometer scale mimicking the macroscopic molecular recognition in cells should be developed. The combination of supramolecular materials with electrocatalysis, photoelectrochemical cells, and photovoltaics will also open tremendous opportunities for this purpose. Finally, it is also important to understand in depth the cooperative mechanism of the photocatalytic processes within self-assembled structures and identify the key factors and assembly modules determining the activity and selectivity in supramolecular materials. The in-situ characteristic technologies, for example, transient absorption and fluorescent spectroscopy, fluorescent life-time microscopy, and cryo-TEM techniques, to investigate the assembly behavior, and exciton and electron formation and transfer mechanisms of supramolecular photocatalytic materials should be developed.

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