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REVIEW

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Artificial photosynthesis bringing new vigor into plastic wastes

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Abstract

The accumulation of plastic wastes in landfills and the environment threatens our environment and public health, while leading to the loss of potential carbon resources. The urgent necessary lies in developing an energy-saving and environmentally benign approach to upgrade plastic into value-added chemicals. Artificial photosynthesis holds the ability to realize plastic upcycling by using endless solar energy under mild conditions, but remains in the initial stage for plastic upgrading. In this review, we aim to look critically at the photocatalytic conversion of plastic wastes from the perspective of resource reutilization. To begin with, we present the emerging conversion routes for plastic wastes and highlight the advantages of artificial photosynthesis for processing plastic wastes. By parsing photocatalytic plastic conversion process, we demonstrate the currently available routes for processing plastic, including plastic photodegradation, tandem decomposition of plastic and CO_2 reduction, selective plastic oxidation, as well as photoreforming of plastic. This review concludes with a personal perspective for potential advances and emerging challenges in photocatalytic plastic conversion.

KEYWORDS

degradation, hydrogen, photocatalysis, upgrading, value-added chemicals

1 | INTRODUCTION

Synthetic polymers, namely plastics, were well-known as a state-of-the-art innovation in the 20th century due to their merits of durability, adaptability, and portability, thus being widely utilized in all walks of life ranging from good section to clothing and electronics.[1–3] Accordingly, the global consumption of plastic has soared to 400 million tons (MTs) in 2021 from 335 MTs in 2016,[4,5] in the particular case of the breakout of the coronavirus pandemic that stimulates our demand for packaging materials and personal protective equipment.[6,7] In stark contrast to the gradually increased demand for plastics, the management of the postconsumer plastics seems to be something of a disappointment, as their reutilization is less than 10%.[8] Specifically, a large majority of plastic wastes have been discarded into the environment, and these plastics cannot be assimilated by microorganisms owing to the persistence of plastics, thus resulting in negative impacts on human health and ecosystem.[9] Another widely adopted route for processing plastic wastes is incineration that contributes to climate change owing to the mass of CO_2 emission, which runs counter to the global goal of carbon neutrality.[10,11] It was estimated that the released CO_2 in the lifespan of plastic production was up to 850 MTs, which accounted for 2.5% of the total carbon emission in 2019.[12] Actually, there has been a unanimous view on phase-out of lightweight plastic packages, including polyethylene terephthalate (PET) and low-density polyethylene (LDPE) plastics.[13] Unfortunately, these plastics that feature low cost, lightness, and corrosion resistance cannot be directly replaced by other durable materials like glass or metal.[14] In light of this, developing one reliable approach for processing plastic waste is extremely imperative, with the aim of enjoying the convenience brought by plastic and meanwhile realizing a carbon circular economy.

Photosynthesis was first found in most crop plants, which built the bridge from solar energy to chemicals with the aid of chlorophyllase.[15,16] Regrettably, natural photosynthesis only enables low solar-to-carbohydrate efficiency (e.g., ~2% or less for crops),[17] which renders it far from meeting our energy demand. Artificial photosynthesis, including CO_2 reduction reaction (CO_2RR), N_2 fixation, water treatment, and air purification,[18–25] seeks to overcome the obstacle of biological photosynthesis by elevating the solar-to-chemical conversion efficiency with the presence of semiconductor photocatalysts. Taking water splitting as an example, it is consisted of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), of which OER is associated with the sluggish four-hole transfer process for the formation of the O–O bond.[26–28] In comparison to OER, organics oxidation is kinetically favorable, as evidenced by the successful integration of HER and organics oxidation with less energy consumption. Considering the fact that plastics are comprised of organic molecule monomers, artificial photosynthesis has been recognized as a powerful tool to disposal plastic wastes, with the goal of achieving the transition to a circular carbon economy.

Although solar-driven plastic conversion is still a nascent technology, as evidenced by only a few effective photocatalysts reported recently, such as TiO_2, $g\text{-}C_3N_4$, and CdS,[29–31] it has sparked a widespread concern owing to the ambient operation conditions, less energy consumption, and the use of low-cost catalysts. As compared with the strategies, including thermocatalysis, incineration, mechanical reutilization, and landfill, photodriven plastic disposal possesses several unique advantages, including high product selectivity, less energy consumption, positive environmental impact, and considerable economic benefit (Figure 1). Accordingly, several reviews concerning photocatalytic conversion of plastic wastes have been proposed, with a fundamental understanding of plastic degradation or conversion into valuable chemicals and solar fuels.[32–34] Several reviews concerning the photocatalytic conversion of plastic wastes have been proposed, with a fundamental understanding of plastic degradation or conversion into valuable chemicals and solar fuels. Xie's group systematically reviewed the advanced techniques required under violent and mild conditions for plastic reforming, including pyrolysis, hydropyrolysis, solvolysis, photocatalysis, electrocatalysis, and biocatalysis.[35] Chen et al.[36] reviewed the latest achievements in plastic degradation, plastic conversion into fuel, and photothermal plastic upgrading, with a focus on the tandem catalytic strategy for plastic disposal. Wang and colleagues summarized the state-of-the-art photocatalysts for plastic processing, with an emphasis of introduction of plastic conversion routes.[32]

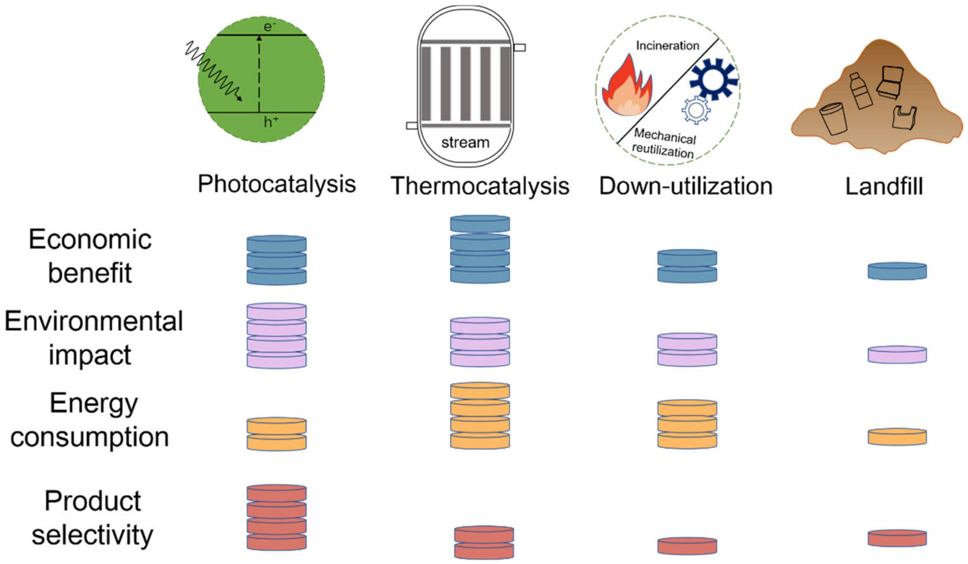

FIGURE 1 Comparison between different strategies toward plastic disposal.

Unfortunately, the design principle of photocatalysts for processing one specific plastic and plastic pretreatment strategies are overlooked in the previous reviews. This review offers an in-depth analysis of the photocatalytic conversion routes and design principles of photocatalyst for plastic conversion, and emphasizes the necessity of the pretreatment of raw plastics. Particularly, the strategies for photocatalysts engineering to upgrade plastic wastes into commodity chemicals with high productivity and selectivity have been discussed. Notably, the relationships between the structures of photocatalysts and their performance will be significantly discussed. Additionally, some in situ technologies or computer-assisted methods are also presented for understanding the underlying mechanism of plastic conversion. Finally, we concentrate on the innovative strategies (e.g., artificial intelligence technology and semi-artificial photosynthesis) needed in the future for the photocatalytic conversion of plastic wastes to valuable chemicals and the new views for catalyst design from both theoretical and experimental perspectives.

2 | FUNDAMENTALS OF PHOTOCATALYTIC PLASTIC CONVERSION

2.1 | Emerging routes

Referring to a well-defined photocatalytic process, the following three steps are involved: (1) semiconductor photocatalyst initially utilizing the photon energy to overcome the energy barrier for the generation of charge carriers; (2) immigration of charge carriers from the bulk to the surface of photocatalyst; (3) surface redox reaction induced by photogenerated charge carriers.[37,38] The redox photocatalysis represented by the overall water-splitting reaction includes HER driven by electrons, and OER triggered by holes. To undergo the water-splitting reaction, high energy is required owing to the high theoretical potential (1.23 V vs. reversible hydrogen electrode [RHE]) and sluggish kinetics of OER. Organic oxidation reactions with less energetical demand,[39,40] especially plastic oxidation, have been proven to be one of the promising approaches to replace OER, which enables the enhanced utilization of solar energy and meanwhile contributes to eliminating the negative impacts of plastic wastes on the environment. Depending on different purposes of plastic processing, the solar-driven plastic conversion can be divided into two typical routes: degradation and upcycling. The former pathway aims to convert the plastic wastes into inorganic small molecules (i.e., CO_2 and H_2O) via the C–C bonds breaking. Compared with photodegradation, photocatalytic upcycling enables plastic wastes as available feedstocks to generate value-added chemicals. Relying on the valorization routes, three different photocatalytic upcycling systems are proposed (Figure 2): (1) deep photooxidation of raw plastic into CO_2 followed by their photoreduction reaction; (2) selective oxidation of raw plastic into desired oxygenated chemicals; (3) photoreforming of pretreated plastics. In the first system, decomposition of plastic wastes into CO_2 proceeds via the direct transfer of photoinduced holes into plastic substrates followed by the photoreduction of CO_2 into commodity chemicals, which maximizes the utilization

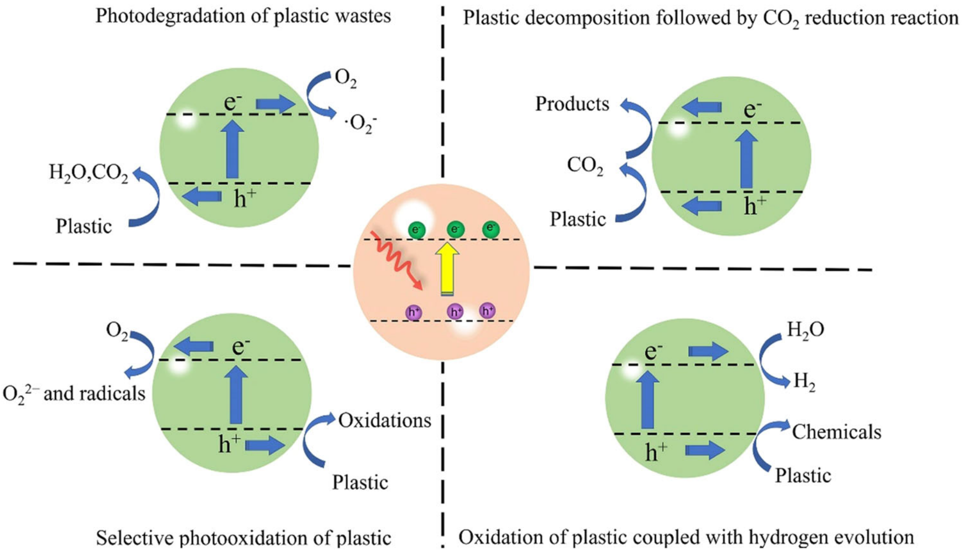

FIGURE 2 Emerging pathways towards solar-driven plastic conversion.

efficiency of electron-hole pairs and thus reduces the carbon footnote from the direct photodegradation of plastic wastes. In the second system, selective oxidation of plastics, especially polystyrene (PS), is set to realize the conversion into aromatic oxygenates (e.g., benzoic acid) under the O_2 atmosphere. Photoreforming of plastics involves two parallel processes: upgrading plastic into commodity chemicals via oxidation half-reaction paired with splitting water into hydrogen via reduction half-reaction. Taking polylactic acid (PLA) photoreforming as an example, PLA are oxidized into formate and acetate by photogenerated holes, while electrons are utilized for HER.

2.2 | Advantages of solar-driven plastic conversion

Significant efforts, such as landfill, incineration, and mechanical reutilization, have been implemented to reduce the accumulation of plastic wastes in the environment.[41–43] As a typical strategy, landfill is a time-honored and widespread solution for waste management. Nevertheless, the discarded plastics in the soil may evolve into poisonous materials, thus leading to a reduction in soil fertility. Another widely adopted way is incineration that partially utilizes the carbon resource of plastic wastes in the short term but fails to create extra economic value in the long term, while releasing a considerable amount of CO_2 and other pollutant gases that contribute to the climate change.[44] In comparison to these above two strategies, mechanical reutilization seems to be an eco-friendly route for plastic recycling, in which postconsumer plastics can be reused after being melted or remolded, but the plastics recycled mechanically suffer from the substantial loss of mechanical properties in contrast to virgin polymers. Overall, the forementioned traditional methods for plastic disposal remain a tricky challenge, which stimulates the development of some economically competitive and environmentally friendly tactics for recycling plastic wastes. Recent years have witnessed the evolution of innovative strategies, including advanced oxidation process, biological catalysis, thermocatalysis, and photocatalysis.[45–48] Among these, advanced oxidation process as remediation technology is implemented with the goal of plastics elimination via generating reactive oxygen species, such as $\cdot OH$, $O_2^{\cdot-}$, and $^1O_2$.[49–52] For instance, Tian et al.[53] developed a low-temperature frozen strategy to remove PS. In this case, the freezing condition was favorable for the dissolution of dioxygen, which benefited the formation of radical species (i.e., $^1O_2$ and $\cdot OH$), thus dramatically promoting the removal efficiency of PS. This method realized the PS degradation via an environmentally friendly route; however, the efficiency has intensely relied on the time consumption (several weeks), indicating the low processing capacity. Biological catalysis represented by enzyme engineering is carried out under moderate conditions and features high selectivity to desired chemicals. However, the enzymes reported recently only depolymerize pretreated plastics with a low degree of crystallinity but are unable to directly cope with most of the plastic wastes with high crystallinity.[54] Thermocatalysis, a well-known approach for plastic disposal, has been industrially implemented, in the particular case of polyolefin conversion.[36,55,56] Nevertheless, thermocatalysis suffers from several shortcomings, such as huge energy consumption, the use of expensive catalysts, along with wide product distribution, which are recognized as major hindrances to economic and environmental operation, especially in the background of global exhaustion of fossil energy. Compared with these newly-developed strategies, artificial photosynthesis is capable of converting plastic wastes into commodity chemicals under ambient conditions by directly harnessing solar energy, and their strengths for plastics processing have been summarized as the following three points (Figure 3). To begin with, one notable advantage of photocatalysis for plastic disposal is the direct use of solar energy, which is therefore regarded as an energy-saving process. Besides, photocatalytic process is designed to obtain the desired products via altering the catalytic pathways, which is distinguished from thermocatalysis that is prone to the generation of a complex mixture. Moreover, varied plastic streams ranging from polyolefin to polyurethane (PUR) as feedstocks can be utilized for realizing the transformation from trash into treasure.

2.3 | Design principles of photocatalyst for plastic conversion

The critical issue to realize highly efficient plastic conversion lies in the construction of photocatalysts, whereas the design principles of photocatalysts are usually ignored by previous reviews, which is vital for screening catalysts utilized in specific reactions. Plastics are consisted of their corresponding constituent monomers with different linkages, including C–C, C–O, and C–N bonds (Figure 4), which render plastics resistant to chemical decomposition. It is therefore imperative that we need to develop a portfolio of effective catalysts to break these linkages. Here, we separately discussed the design principles of photocatalysts for upgrading one specific plastic with C–C, C–O, or C–N linkages.

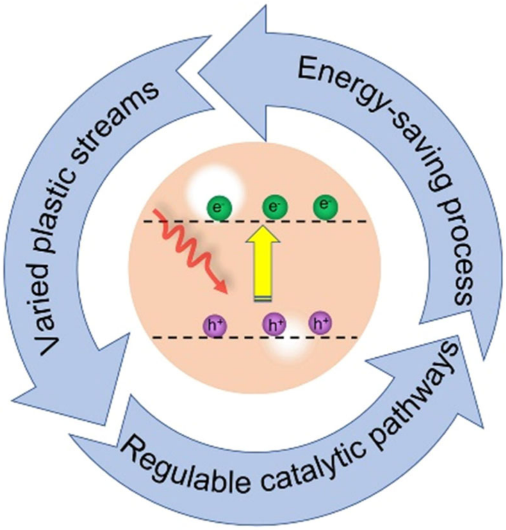

FIGURE 3 Advantages of artificial photosynthesis for plastics processing.

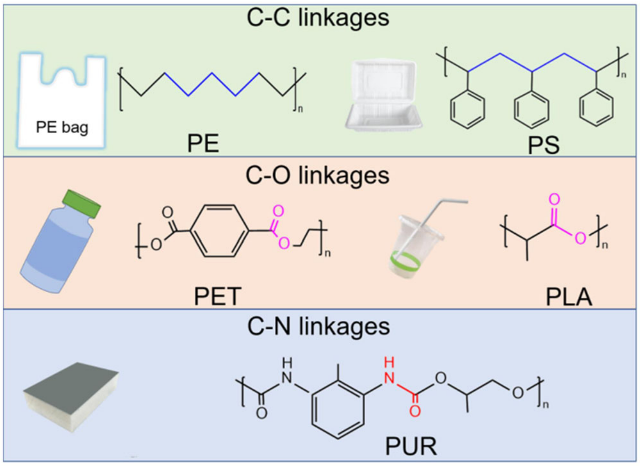

FIGURE 4 Illustration of chemical structure of plastics with diverse linkages.

The C–C linkages widely exist in polyolefins, such as PE and PS, and owing to the high dissociation energy of the C–C bond (~372 KJ/mol),[57] the available strategy to break them is to fabricate the photocatalysts with high oxidation potential (e.g., TiO_2, ZnO, Nb_2O_5, and Ga_2O_3). In this way, the photoinduced holes together with hydroxyl radicals can induce the cleavage of the C–C bond in polyolefin via direct oxidation processes. Of note, the oxidation species, especially hydroxyl radicals, can randomly attack the C–C linkages in plastic, thus resulting in overoxidation and even generating a carbon footprint. As for the photocatalysts with low oxidation potential (e.g., g-C_3N_4), pretreatment may be a well-adopted option before photocatalysis. After pretreatment, the C–C bond energy is decreased to ~300 KJ/mol,[58] which renders C–C bond cleavage thermodynamically favorable on the photocatalysts with low oxidation potential. In the case of PS upgrading,[59] preoxidation was required for the formation of intermediate products with oxygen-containing groups, which were utilized as feedstocks by the following oxidation process. Subsequently, the photocatalytic PS conversion was implemented over g-C_3N_4 catalysts, generating several aromatic components (e.g., benzoic acid, acetophenone, and benzaldehyde) as well as CO_2. This incomplete oxidation might be ascribed to the weak oxidation capacity of holes on C_3N_4 and the formation of mild reactive species (i.e., $O_2^{\cdot-}$). Overall, the photocatalysts with high oxidation potential are devoted to plastic degradation, while the photocatalysts with relatively poor oxidation ability enable plastic valorization into commodity chemicals.

As for the polyester/polyamide plastics (e.g., PET, PLA, and PUR) that feature C–O and C–N linkages, they are easy to be decomposed into their constituent monomers, and a detail discussion on plastic depolymerization will be provided in the following section. Here, we mainly discuss the design of photocatalysts for converting the monomeric units derived from polyamide depolymerization into value-added products. Taking lactic acid (the constituent monomer of PLA) conversion as an example,[60] lactic acid could be oxidized into pyruvic acid selectively on CdS/MoO_2/MoS_2, which also worked in conjunction with HER. This high selectivity to pyruvic acid was attributed to the mild oxidation potential of CdS and the MoO_2 cocatalyst that served as oxidation sites and showed favorable desorption of pyruvic acid. In parallel, the photoexcited electrons transfered to MoS_2 for hydrogen generation. In addition, propylene glycol derived from PUR underwent photoreforming over CdS/CdO_x catalyst, producing various commodify chemicals, including formate, lactate, pyruvate, and acetate.[61] This implied that the oxidation capacity of the CdS catalyst was incapable of converting organics into CO_2 effectively. In short, crucial to transforming aliphatic components in plastic into valuable chemicals is the designing photocatalyst with mild oxidation capacity and appropriate cocatalysts loading.

3 | PLASTIC PRETREATMENT

Generally speaking, plastics feature insolubility and chemical inertness induced by their polymeric nature, which may be a major obstacle for photocatalytic reactions. For plastic upgrading, the pretreatment procedure before artificial photosynthesis is essential, including physical, chemical, as well as biological processes (Figure 5).[62,63] The physical methods, such as

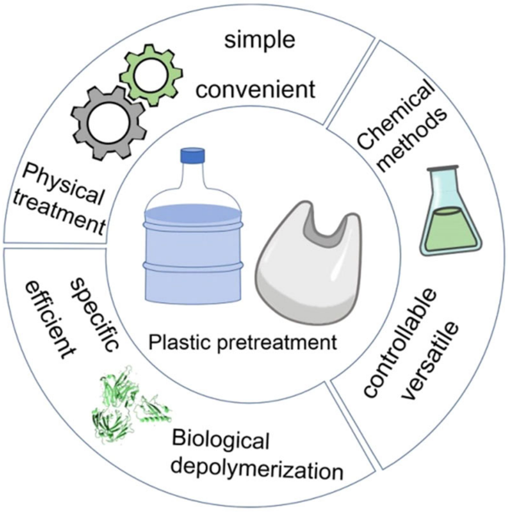

FIGURE 5 Emerging methods towards plastic pretreatment and their corresponding strengths.

ball-milling and remodeling using thermo-mechanical techniques,[64,65] are always targeted to decrease the crystallinity of plastic, which favor improving the specific surface area or increasing the solubility. Thanks to the fact that the constituent units or oligomers stemmed from plastic depolymerization can be photochemically valorized, numerous efforts have been devoted to pretreating plastic via chemical or biological processes.[66,67] Chemical methods, including hydrolysis, alcoholysis, and ammonolysis,[68,69] have been identified as convenient routes for plastic depolymerization. In general, the hydrolysis process is implemented with the pursuit of breaking the chemical linkages among monomers, which is the prerequisite step for the following photoreforming process. Owing to the diverse linkages in polymers (e.g., C–C linkages in polyolefin or C–O linkages in polyester), the strategy devoted to plastic depolymerization varies dramatically. For instance, alkaline hydrolysis is often selected to break the ester bonds in polyester plastics.[70,71] Moreover, alcoholysis is also widely employed to obtain the oligomers or the constituent monomers.[72] Taking PET alcoholysis as an example, bis(hydroxyethyl) terephthalate (BHET) or dimethyl terephthalate could be regenerated with the presence of catalysts and alcohol. Afterward, the obtained constituent units could be directly utilized in the reproduction of PET packages.[73] In one case, ultrathin ZnO nanosheets with heteroatom incorporation as catalyst was fabricated to realize PET glycolysis.[74] The results showed that Mo atoms doped ZnO catalyst achieved the conversion of PET into BHET with a yield of 94.5%, while 55.2% conversion and 51.7% yield to BHET were gained over ZnO nanosheet, demonstrating that the incorporation of Mo atoms significantly accelerated the glycolysis procedure. Specifically, the introduction of Mo atoms into ZnO induced the formation of the oxygen vacancies, which favored the adsorption of ethylene glycol, thus promoting the EG activation process. In addition, plastics ammonolysis is one of the well-accepted methods for depolymerization using animation reagents (e.g., methylamine and ammonia), with the aim of obtaining reutilized commodity chemicals under mild conditions. Taking PLA ammonolysis process as an example,[75] lactamide was first formed in the presence of ammonia, which was subsequently transformed into alanine with the help of catalyst under elevated temperature. Besides, Otsuka et al.[76] successfully realized the conversion of polymers into fertilizer via ammonolysis. Specifically, poly(isosorbide carbonate) could be completely converted into urea and isosorbide, which provided an emerging route towards plastic disposal as well as fertilizer production. Apart from the forementioned strategies, biological method is reckoned as the environmentally benign approach toward plastic depolymerization owing to their natural and eco-friendly capacity. Recently, several proteases (e.g., Ideonella sakaiensis PETase, leaf-branch compost cutinase) have been studied to decompose PET under ambient conditions. In detail, the depolymerization efficiency reached almost 100% with the presence of the buffer without any other auxiliaries.[77] Using PETase as an example, the pristine PETase was found to convert PET into its constituent monomer with poor activity, which suggested the necessity of the exploration of modified strategies towards improving the depolymerization efficiency of PETase.[78] In light of this, protein engineering via modifying amino acid residues on PETase has been proposed to be an efficient strategy for PET depolymerization.[79] After modification, the FAST-PETase stood out as the most active one under mild temperatures (50°C), in which 94.9% terephthalic acid (TPA) was recovered with a purity of 97%. Furthermore, the recovered TPA was utilized for PET regeneration, presenting closed-loop plastic use in this research. In another case, leaf-branch compost cutinizes, one of the well-known PET hydrolases, was devoted to PET bottles depolymerization and realized 90% recycling efficiency.[80] Accordingly, biological catalysis with high catalytic efficiency integrated with selectivity to constituent monomer products intrigued us, providing a new developing process for converting discarded plastics to components. Afterwards, the constituent units or low-crystalline plastic as the platform molecule can be upgraded for generating high-value chemicals via photocatalysis, which will be discussed in the following section.

4 | PHOTOCATALYTIC PLASTIC CONVERSION

As mentioned in Section 2.1, the emerging photocatalytic routes for plastic conversion mainly include gradation and upcycling (Table 1), of which the latter aims to utilize plastic wastes as feedstocks to produce value-added chemicals. To date, three ways for valorization of plastic wastes have been presented: (1) selective oxidation of plastics; (2) decomposition of plastics into CO_2 using holes followed by electron-induced CO_2RR; (3) photoreforming of plastics (i.e., oxidation of plastics paired with HER). In this section, the forementioned routes and their corresponding strengths and limitations will be discussed in detail.

4.1 | Photodegradation of plastic wastes

In general, plastics represented by microplastic or nanoplastic are reckoned to be the persistent pollutants that are harmful to the water environment and plant growth.[101,102] Especially, microplastic falls into the scope of global emerging contaminants based on the document of the United Nations Environment Programme.[103] Microplastic originated from polymer degradation can be found in soil, ocean, subsoil water, and stools, which may bring about uncertain biological effects. For instance, plastic debris in the ocean has been reckoned as one of the threats to marine organisms owing to the nondigestible and biotoxicity properties of microplastics. Especially, microplastics accumulated in biont may result in biomolecular changes, such as histological, cytological, and behavioral changes, which can significantly influence the health or breed of nature being and even result in species extinction.[104] To eliminate the negative effects that are originated from irresponsible management of postconsumer plastics, an attractive approach towards plastic degradation is presented via semiconductor photocatalysis. As mentioned above, photodegradation of plastic wastes into CO_2 and H_2O has been implemented via using TiO_2-based, ZnO-based, and BiOX-based photocatalysts with high oxidation potential that contributes to deep oxidation.[105–108]

The refractory plastic wastes as feedstocks utilized in photocatalysis can be categorized into two regimes: raw plastics and plastic-derived monomers. Of note, the constituent monomers originated from plastics depolymerization features high content of hydroxyl groups, which endows a good water-solubility and thus favors the photocatalytic plastic transformation. To date, many researchers have paid their attention to decomposing recalcitrant pollutants (e.g., bisphenol A [BPA], phthalic acid esters [PAEs], and polycyclic aromatic hydrocarbons [PAHs]), owing to their possible side-effects on the human body once released into the environment.[109–112] For example, BPA monomers extracted from food containers possibly led to abnormal physiological indexes after ingestion or absorption by humans (e.g., liver enzymes, fasting insulin, and serum total testosterone).[113] In light of this, resorcinol-formaldehyde resin (RF) was fabricated as a catalyst to eliminate BPA contaminants. Thanks to the high oxidation potential of RF (2.15 V vs. RHE), the photogenerated holes were capable of opening aromatic rings directly, leading to high performance for plastics mineralization.[81] In addition, the photoexcited holes could also drive the OER and the resulting oxygen was utilized for generation of H_2O_2 via a two-electron oxygen reduction pathway (Figure 6A). With the aid of additive ferrous ions, the Fenton reaction took place between ferrous ions and H_2O_2, resulting in the formation of $\cdot OH$ radicals, which could effectively induce the deep oxidation of organics. By integrating photoexcited holes with the Fenton reaction, nearly 100% of BPA was removed within 2 h, while two-thirds of BPA was converted into CO_2, manifesting the efficient photooxidation performance over RF (Figure 6B). Considering the possible formation of iron sludge in Fenton reaction and the unsatisfied mineralization performance, a heterojunction photocatalyst of $BiOCl_{0.75}I_{0.25}/g\text{-}C_3N_4$ nanosheet fixed on polyolefin polyester fiber has been designed to remove BPA molecule.[82] The constructed heterostructure between $BiOCl_{0.75}I_{0.25}$ and $g\text{-}C_3N_4$ favored the separation of photoinduced charge pairs, therefore elevating the photocatalytic degradation performance. One notable advantage of $BiOCl_{0.75}I_{0.25}/g\text{-}C_3N_4$ was its moderate reduction potential to form $O_2^{\cdot-}$ radicals that were deemed as the major species towards BPA degradation. Besides, the polyolefin polyester fiber as support was one contributor to the enhanced BPA degradation efficiency to some extent through offering a large specific surface area, while preventing the aggregation of catalysts (Figure 6C). The results manifested that BPA was completely degraded, with the realization of 75.2% total organic carbon (TOC) within an hour. Moreover, the BPA removal efficiency decreased slightly from 100% to 94.9% after eight cycles, demonstrating the excellent stability of the photocatalyst during the photodriven BPA degradation process.

Apart from plastic derivates, the raw plastics (e.g., PE, polypropylene [PP] and polyvinyl chloride [PVC]) have been investigated as feedstocks in photocatalysis as well.[114–117] Taking PE degradation as an example, the ZnO photocatalyst with high redox potential, low toxicity, and easy synthesis was chosen to decompose

TABLE 1 Summary of plastic conversion routes over photocatalysts.

Photocatalyst	Type of plastic	Conversion routes	Products	Refs.
Resorcinol-formaldehyde	BPA	Degradation	CO_2	[81]
BiOX/g-C_3N_4	BPA	Degradation	CO_2	[82]
O-doped g-C_3N_4	BPA	Degradation	CO_2	[83]
Bi/BiOBr	BPA	Degradation	CO_2	[84]
ZnO	LDPE	Degradation	CO_2	[85]
Humic acid-doped ZnO	PLA	Degradation	CO_2	[86]
TiO_2	PS	Degradation	CO_2	[87]
NiO/Fe_2O_3	PET	Degradation	CO_2	[88]
Co-Ga_2O_3	PE	Decomposition followed by CO_2RR	CO and H_2	[89]
Nb_2O_5	PE	Decomposition followed by CO_2RR	Acetic acid	[90]
Carbon dot/g-C_3N_4 with Methanosarcina barkeri	PLA	Decomposition followed by CO2RR	CH_4	[31]
p-Toluenesulfonic acid	PS	Selective oxidation	Benzoic acid and formic acid	[91]
Fluorenone	PS	Selective oxidation	Benzoic acid	[92]
g-C_3N_4	PS	Selective oxidation	Benzoic acid, benzaldehyde, and acetophenone	[59]
$FeCl_3$	PS	Selective oxidation	Benzoic acid	[93]
CdS/CdO_x	Pretreated PET	Plastic oxidation coupled with HER	H_2, formate, and glycolate	[61]
MoS_2/$Cd_xZn_{1\text{-}x}S$	Pretreated PET	Plastic oxidation coupled with HER	H_2, formate, glycolate, and methylglyoxal	[94]
Carbonized polymer dots/g-C_3N_4	Pretreated PET	Plastic oxidation coupled with HER	H_2, glycolic acid, glycolaldehyde, and ethanol	[95]
g-C_3N_4-CNTs-NiMo hybrids	Pretreated PET	Plastic oxidation coupled with HER	H_2, glyoxal, and glycolate	[96]
CdS/MoS_2	Pretreated PLA	Plastic oxidation coupled with HER	H_2 and pyruvate	[97]
$Ni_xCo_{1-x}P$/reduced graphene oxide/g-C_3N_4	Pretreated PLA	Plastic oxidation coupled with HER	H_2, acetate and formate	[98]
CN_x|Pt	Pretreated PE	Plastic oxidation coupled with HER	H_2, ethane, and ethylene	[99]
CdS/MoS_2	Pretreated PE	Plastic oxidation coupled with HER	H_2, methane, ethane, propane, and n-pentane	[100]

Abbreviations: BPA, bisphenol A; CO_2RR, CO_2 reduction reaction; HEX, hydrogen evolution reaction; LDPE, low-density polyethylene; PAE, phthalic acid ester; PAH, polycyclic aromatic hydrocarbon; PET, polyethylene terephthalate.

LDPE films into inorganic molecules.[85] In this case, a distinct variation of the surface morphology of LDPE films could be observed after photocatalysis as compared to pristine LDPE (Figure 6D,E). Furthermore, the carbonyl index and vinyl index were further measured to investigate the profound influence of photocatalysis on LDPE. The level of the oxygen-containing groups was enhanced obviously, which could be ascribed to the photoinduced surface oxidation reaction. During the photocatalytic process, photogenerated holes could react with water or oxygen to generate radical species that would attack polymer chains to result in long-chain breaking and morphology vicissitude. As a result, LDPE films were oxidized into short-chain compounds and

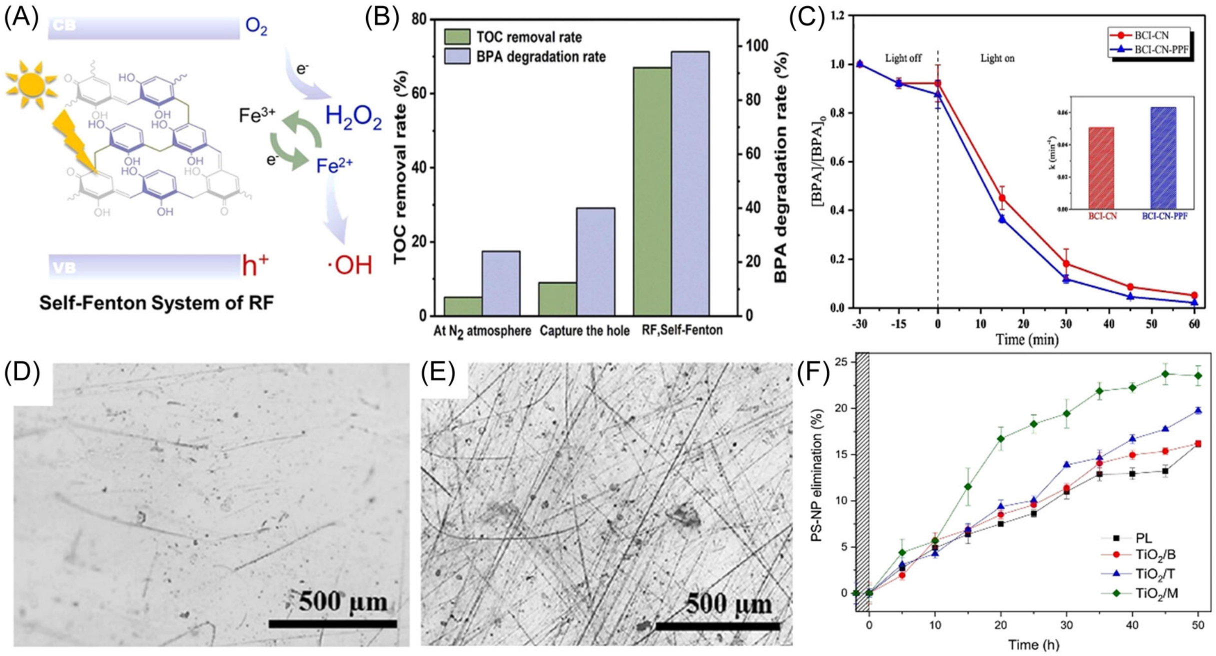

FIGURE 6 (A) The process of oxidation species generation in the self-Fenton system. (B) The comparison of total organic carbon (TOC) removal rate and bisphenol A (BPA) degradation between diverse conditions. Reproduced with permission: Copyright 2022, Elsevier.[81] (C) The photocatalytic performance of $BiOCl_{0.75}I_{0.25}/g\text{-}C_3N_4$ towards BPA removal efficiency. Reproduced with permission: Copyright 2022, Elsevier.[82] The morphology features of low-density polyethylene (LDPE) film before (D) and after photocatalysis (E). Reproduced with permission: Copyright 2019, Springer.[85] (F) The PS nanoparticles degradation efficiency during photocatalysis. Reproduced with permission: Copyright 2021, Elsevier.[87]

inorganic molecules. Likewise, much attention has been paid to studying PS degradation via photocatalysis. As an example, Jaimes and colleagues developed various TiO_2-based photocatalysts to investigate their effects on PS removal.[87] In this case, TiO_2 with diverse morphologies (e.g., barrier, nanotubular, and mixed structures) were successfully synthesized by controlling the electrolyte, among which TiO_2 with mixed barrier and nanotubular shapes exhibited a superior PS degradation performance under ultraviolet irradiation (Figure 6F). TiO_2 with abundant unsaturated-bond coordination favored the absorption of organic substance, and the holes in the value band of TiO_2 with high oxidation potential could oxidize organics into CO_2. Attenuated total reflection flourier transformed infrared spectroscopy (ATR-FTIR) was performed to analyze the PS degradation process. The new vibration bands, including $C\equiv C$ and $C=O$ bond stretching, were formed, indicating the dissociation of the carbon chain and oxidation of the polymer, which was confirmed by the carbonyl index measurement where the enhanced carbonyl index manifested the generation of several intermediates from PS degradation (e.g., ketone, aldehyde, and carboxylic acid). Apart from polyolefin degradation, raw PET could be degraded into CO_2 over NiO/Fe_2O_3 photocatalyst.[88] In this case, the internal electric field between NiO and Fe_2O_3 contributed to electron transfer from NiO to Fe_2O_3, as verified by the shift of Ni 2p in NiO/Fe_2O_3 to a higher binding energy as compared to pure NiO. Besides, the *Z*-scheme heterojunction between NiO and Fe_2O_3 was confirmed by ultraviolet-visible diffuse reflectance spectra and synchrotron radiation photoelectron spectroscopy, which accelerated the separation of photogenerated pairs and thus promoted catalytic activity. Subsequently, PET transformation over NiO/Fe_2O_3 composite was achieved with 100% selectivity to CO_2 at air atmosphere. A controlled experiment was conducted to evaluate whether the atmosphere would influence the PET degradation, and the results suggested that O_2 played a vital role in PET conversion. After that, in-situ characterizations (i.e., in-situ FTIR and electron spin resonance [ESR]) were used to reveal the main active species in PET transformation into CO_2, with the result that $O_2^{-\cdot}$ radicals were manufactured via the oxygen reduction process and some other intermediates (e.g., COOH*, CH_3O*, and CHO*) were produced in the PET photoconversion process. Based on the above, it could be concluded that PET was degraded into CO_2 via the gradual oxidation of CH_3O*, CHO*, and COOH* intermediates. This straightforward and affordable method provided a guidance for the practical decomposition of plastic into CO_2. In addition, the reutilization of the

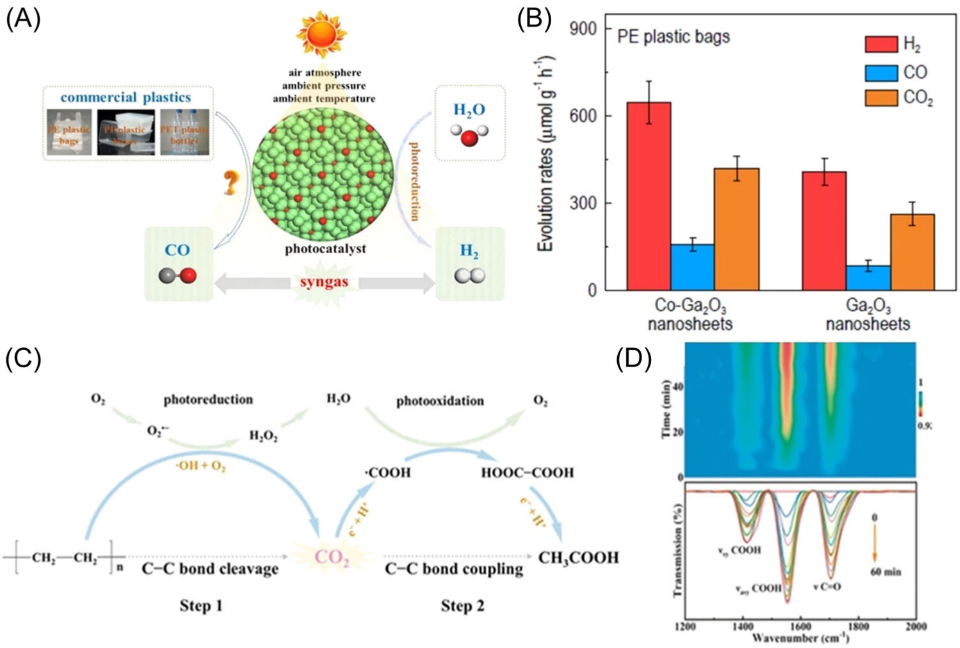

FIGURE 7 (A) The process of photodriven PE conversion into syngas. (B) The amounts of gaseous products after real-world PE photoreforming over Co-Ga_2O_3 photocatalyst. Reproduced with permission: Copyright 2022, Oxford University Press.[89] (C) Pathways toward the synthesis of acetic acid from plastic wastes. (D) In situ IR spectra during C2 fuel evolution. Reproduced with permission: Copyright 2020, Wily-VCH.[90]

photocatalyst was evaluated via recycling tests. The results showed that the hybrid wasn't passive during consecutive PET degradation, manifesting the favorable photostability of metal oxide hybrids.

Overall, artificial photosynthesis for plastic degradation presents a promising approach for alleviating the environment deterioration caused by inappropriate plastic disposal, and the degradation performances can be manipulated to some extent through the modulation of the structure and morphology of photocatalysts.[118,119] Countless efforts have been paid to studying plastic degradation; however, the progress is still painstakingly slow owing to the water-insoluble nature of raw plastics. In this context, the strategy for plastic mineralization should be devoted to the development of functional photocatalysts. For instance, photocatalysts with magnetic properties can promote the substances adsorption and thus accelerate the plastic degradation process.

4.2 | Plastic decomposition followed by CO_2 photoreduction reaction

As mentioned in Section 4.1, photocatalytic plastic degradation will reduce the negative effects of plastic wastes on environment but inevitably produces carbon footprint that contributes to the climate change. In light of this, a viable approach to reduce CO_2 that originates from plastic degradation is extremely desired. That is, deep photooxidation of plastic into CO_2 followed by photoreduction of CO_2 seems to be feasible, in which CO_2 can be transformed into value-added commodity chemicals, such as CO, CH_4, formic acid, and acetic acid. Although the conversion of CO_2 into reusable chemicals has been extensively studied over the past few decades,[120–122] less attention has been paid to the study of tandem photocatalytic decomposition of plastics and CO_2RR, which is deemed as a promising option for circular carbon economy.

As for the mineralization of the raw plastic followed by reduction of the evolved CO_2, crucial to enable this vision is the design and fabrication of suitable photocatalysts that allow great stability and appropriate potential for upgrading plastic wastes. In view of this, Xu et al.[89] synthesized a Ga_2O_3 nanosheet with high oxide potential for the mineralization of plastic wastes and the moderate reduced potential for CO_2RR. To boost the photocatalytic activity, the heteroatom substitution strategy was employed to introduce a foreign level, which tailored the band structure of Ga_2O_3 and thus improved the absorption capability and encouraged charge carrier separation. To make plastic upgrading close to pratical application, commercial plastic items (e.g., PE bags, PP boxes, and PET bottles) were introduced into the photocatalytic system after being grinded into powders (Figure 7A). Taking valorization of PE plastic bags over Co-Ga_2O_3 nanosheets as an example, the evolved gaseous products were H_2, CO, and CO_2 with the rate of 647.8, 158.3, and 419.3 μmol/(g h), respectively (Figure 7B). Of note, the products, including H_2 and CO (i.e., syngas), held the potential for further convertion into hydrocarbon chemicals.[123,124] Subsequently, long-term stability of Co-Ga_2O_3 nanosheets was demonstrated by observing the steady gas evolution more than 50 h. To deeply comprehend the PE reforming process, in situ ESR measurement was implemented and showed the formation of ·OH radicals and $O_2^{-\cdot}$ radicals. In addition, oxygen-isotope-involved CO_2 was found in the system when isotope-labeled $H_2{}^{18}O$ or $^{18}O_2$ was utilized as feedstocks, proving that both H_2O and oxygen contributed to PE plastic upgrading. Combining the aforementioned findings, the following three processes could be performed when the conversion of plastic wastes into syngas was realized. First, charge carriers migrated to Co-Ga_2O_3 surface and then underwent water splitting into hydrogen and oxygen. Subsequently, the degradation of the polymer into CO_2 was triggered by both oxygen and ·OH radicals from water photooxidation. Lastly, the formed CO_2 underwent a photoreduction process for the formation of CO. This strategy sheds light on solar-driven plastic upgrading; however, the obtained CO inevitably contains CO_2 component and therefore hinders the direct utilization of syngas. In this regard, transforming plastic into liquid chemicals is beneficial for subsequent separation of products. One notable tactic was proposed by Jiao et al.[90] who designed a Nb_2O_5 nanosheet photocatalyst to break C–C bonds in PE for the construction of acetic acid (Figure 7C). To cover the origin of acetic acid, a controlled experiment was carried out by using CO_2 as the only feedstock during photocatalysis, which proved that the acetic acid was stemmed from CO_2 reduction reaction. A variety of in situ characterization techniques, including in situ ESR and in situ FTIR, have been employed to probe into the active species and the intermediates throughout the entire reaction. The presence of four distinct characteristic peaks with the ratios 1:2:2:1 and 1:1:1:1 in in situ ESR spectra proved that the radicals of ·OH and $O_2^{-\cdot}$ were involved in the PE mineralization process. The appearance of the distinct stretching vibration of C=O groups at a frequency of 1650 cm^{-1} successfully supported the creation of ·COOH intermediates during the PE conversion (Figure 7D). In this scenario, the process of the acetic acid from reduction of CO_2 was described as the following. First of all, the generated CO_2 took advantage of photoinduced electrons to form ·COOH intermediates. Following this, the C–C coupling reaction between intermediates was realized, with the generation of oxalic acid. Finally, acetic acid was synthesized by photoreduction of the acquired oxalic acid.

As shown in the forementioned case, photoinduced redox reaction held great potential in the field of converting plastic wastes into desired products. Albeit the continuous progress concerning on the conversion of plastic into C1 or C2 products has been achieved, the long-chain compounds with rich chemical energy and high value from plastic valorization have been rarely realized, which stimulates us to develop an efficient approach to achieve the plastic upvaluing into biomolecules. One notable strategy by developing a tandem catalysis has been carried out for realizing the conversion from CO_2 to biomolecule (e.g., glucose and fatty acids).[125] In this regard, the sought to convert discarded plastics into long-chain compounds will broaden the utilization prospect of plastic upgrading. To date, there is no report concerning on the valorization from plastic to biomolecules. Apart from PE, the conversion of PLA into valuable compounds, such as amino acid, is also the promising route for plastic upgrading. Unfortunately, there is no traceable literature focusing on PLA transformation into biomolecules. A traceable work was reported by Yan et al.[126] who realized the conversion of lactic acid to alanine. In this case, photogenerated holes were in charge of converting lactic acid into pyruvic acid. Then, alanine was obtained through an electron-induced reduction pathway with the presence of ammonia.

4.3 | Selective photooxidation of plastic

Analogous to the plastic mineralization process, selective plastic oxidation also takes the advantage of photogenerated holes but aims to convert the plastic wastes into commodity chemicals. As for the nonselective plastic oxidation process, the oxidation potential of catalytically active species is usually ignored by researchers, thus leading to the formation of mixed products or overoxidation of plastics into CO_2, which brings about the loss of plastic intrinsic value to some extent. Therefore, tunning the oxidation level of active species is vital for selective oxidation of plastic wastes into value-added products.

The issues concerning the selective plastic oxidation to desired chemicals may be addressed by designing or selecting appropriate catalysts that can generate mild oxygenous radicals that are capable of avoiding the deep plastic oxidation. Several typical examples extracted from the previous reports concerning the selective oxidation of plastic wastes were presented.[127,128] Using the research by Xiao et al. as an example,[91] several solid acids have been found to enable the PS transformation into benzoic acid, formic acid, as well as acetophenone under light irradiation. It was mentioned that organic solvent adopted in this system not only favored the PS dissolution but also was a contributor to the catalytic performance. Specifically, the solvent could determine the selectivity of the desired chemicals, in which trace amounts of products were gained in the ill-suited solvent like benzene and acetone, while higher yields were obtained when benzene/CH_3CN was employed as solvent. In this case, PS was successfully converted into related products by using p-toluenesulfonic acid monohydrate as a catalyst and a mixed benzene/CH_3CN (V/V:1/1) solution as a solvent, obtaining 50% and 67% yields to benzoic acid and formic acid, respectively. Notably, the real-world PS waste also could be upgraded into desired chemicals, and the yield of products increased along with the molecular weight of PS. To shed light on the reaction pathway, scavenger experiments, and radical quenching measurements were carried out. The results implied that singlet oxygen generated from oxygen was the primary radical oxide species for PS upgrading. During the conversion process, the critical step to drive the partial oxidation lay in the $^1O_2$-mediated hydroperoxidation, which was beneficial for the following C–C bond cleavage in PS. Nevertheless, the initial generation of oxygenous intermediates upon the electron transfer between the catalyst and oxygen molecule might hamper the reaction rate to some extent. Therefore, an efficient route via the hydrogen atom transfer pathway was proposed, which could directly oxidize plastic to desired chemicals.[129] For example, a series of organic semiconductors were employed to efficiently upgrade PS under mild conditions (Figure 8A).[92] As expected, fluorenone could motivate the selective oxidation of pure PS and PS foam into benzoic acid with a yield of $36 \pm 4\%$ and $36 \pm 2\%$, respectively (Figure 8B,C). The change in fluorescence spectra provided evidence for the oxidation process via the hydrogen atom transfer pathway. In this case, the peroxyl radical intermediate was generated followed by a hydrogen extraction process from the polymer that was reckoned as the rate-limiting step during PS upgrading. After that, the resulting PS radicals underwent the β-scission process, thus leading to the cleavage of stable C–C linkages and the product formation. Organic photocatalysts could realize the conversion of PS into valuable chemicals, but some drawbacks from the organic molecule, including self-sensitization and limited light absorption, would incur the decreased catalytic activity.[130,131] In light of this, inorganic photocatalysts have been deemed as reliable catalysts owing to their outstanding advantages like controllable structure and strong stability, which render them more suitable for long-term plastic conversion. For instance, the PS deconstruction into value-added chemicals over inorganic photocatalyst was explored by Ma et al.[59] Intriguingly, the temperature parameter might be one of the factors that influence the PS valorization performance, since tiny products were detected under thermal conditions and the thermally-driven PS conversion (4%) was achieved. Whereas, the combination of thermal catalysis and photocatalysis could significantly accelerate PS conversion. The typical photocatalysts, such as TiO_2, ZnS, and g-C_3N_4, have shown their abilities to transform PS into commodity chemicals. Compared with the 46% conversion of PS over g-C_3N_4, TiO_2, and ZnS only gained 13% and 12% PS conversion, respectively, while the selectivity to organic products was calculated to be 60%, 15%, and 64% on g-C_3N_4, TiO_2, and ZnS, respectively. The significant differences in performance among the above-mentioned catalysts may be ascribed to the following reasons: (1) the solvent selection and (2) the adsorption behavior of the substance on the surface of the catalyst. Compared with metal oxides or metal sulfides, polymer semiconductor favors the dissolution in acetonitrile and thus holds the superiority for contacting with PS, thus promoting the efficiency of PS conversion. Notably, the high selectivity to desired products on ZnS was reached, which could attribute to the property of metal sulfide that driven the activation of C–H bonds to form carbon radicals rather than C–C bonds cleavage under light illumination.[132] Furthermore, the desorption ability for intermediate products enabled by photocatalysts serves a vital role in selectivity. Take TiO_2 as an example, TiO_2 with abundant unsaturated-bond coordination was detrimental to the desorption of organics with hydroxyl groups, thus resulting in overoxidation.[133] To investigate the oxidation process, chromatography, and infrared spectroscopy technologies were carried out to investigate the generation of intermediates during photocatalysis (Figure 8D). The results manifested that the molecule weight was slightly increased in the initial stage of photocatalysis, and new absorption peaks were formed, indicating the oxygen-containing compound generation. In conclusion, the PS upvaluing underwent two steps: (1) the incomplete oxidation of PS via the introduction of oxygen-containing groups in the dark conditions (i.e., the C–H activation process); (2) the formation of phenyl products or intermediates through the C–C breaking procedure (Figure 8E). Note that the products mainly consisted of acid- or keto-phenyl compounds owing to the easy conversion of phenolic substance into CO_2. In the end, the final products over PS oxidation were apt to generate benzoic acid and corresponding phenyl chemical or CO_2. To investigate the stability of g-C_3N_4, a circulatory system was applied toward PS upgrading. The steady rate accumulated in 160 h for benzoic acid production could well prove that g-C_3N_4 held long-term

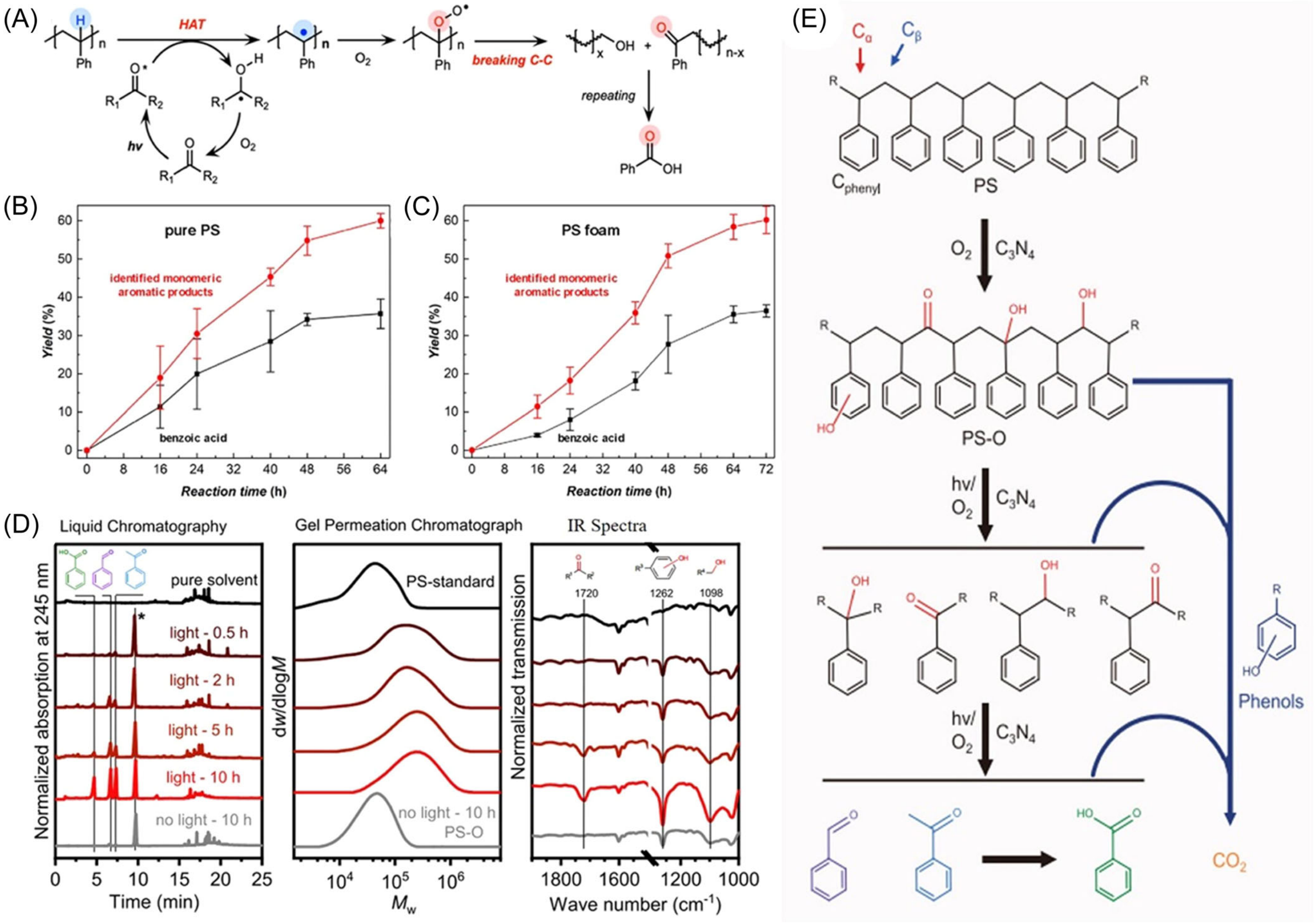

FIGURE 8 (A) The description of the process of converting polystyrene (PS) into benzoic acid via HAT pathways. The yield of products originated from pure PS (B) and PS foam (C) during upgrading. Reproduced with permission: Copyright 2022, American Chemical Society.[91] (D) The liquid chromatography of products under conditions of light and without light, molecular weight distribution, and infrared spectra after diverse pretreatment. (E) The presumed reaction pathways of photocatalytic PS conversion. Reproduced with permission: Copyright 2022, Springer Nature.[59]

stability to PS conversion into benzene. It should be noted that g-C_3N_4 was able to drive BPA degradation.[134] The reasons why g-C_3N_4 can catalyze both BPA degradation and PS selective oxidation are attributed to the differences in the use of solutions during photocatalysis. Specifically, BPA degradation is always carried out in an aqueous solution, which contributes to the formation of hydroxyl radicals and thus results in overoxidation (i.e., degradation), whereas the PS oxidation process is implemented in the water-free acetonitrile solution, in which O_2^- radicals with moderate oxidation ability are generated and utilized to realize incomplete oxidation (i.e., selective oxidation).

Generally, most cases reported recently concerning the selective valorization of plastic wastes focus on PS upcycling, which may be ascribed to the following two points: good solubility of PS in organic solvent and easy identification of product. To begin with, PS can be naturally dissolved in organic solvent without pretreatment when compared with some other widely used plastics (e.g., PE, PP, and PET). Furthermore, the obtained products from PS conversion can be easily identified by using high-performance liquid chromatography owing to their strong light absorption capability. Moreover, the resulting products can be separated via a simple liquid–liquid extraction. However, the valorization of PS cannot catch up with the production rate of plastic wastes, and with the exception of PS, the tunable oxidation of other plastic wastes is rarely investigated using artificial photosynthesis. Some traceable cases concerning upcycling of plastic wastes have been reported using thermocatalysis. As an example of the selective conversion of PLA into alanine,[75] commercial PLA was directly utilized as a feedstock for alanine generation with the aid of ammonium hydroxide that served as the agent for both depolymerization and nitrogen source for PLA upgrading. In another case, the conversion of primary PET into value-added chemicals (e.g., dimethyl cyclohexanedicarboxylates [DMCD]) was developed.[135] During this process, the PET depolymerization was investigated in the presence of methanol, and the obtained product (i.e., dimethyl terephthalate) could be utilized as feedstock for hydrogenation, generating high-value chemicals (i.e., DMCD). The forementioned studies have paved a new avenue for plastic upgrading, in which plastic wastes could be converted into valuable substances. In view of this, artificial photosynthesis can be also expected to photoreduce plastic wastes by using photoexcited electrons.

4.4 | Photooxidation of plastic coupled with hydrogen evolution

Another promising method for plastic upgrading is the oxidation of plastic wastes combined with HER, in which photoinduced electrons drive water splitting into hydrogen and concurrently holes are in charge of the photooxidation of plastic wastes into value-added compounds.[136,137] Such a process seems to be similar to the well-known photocatalytic overall water splitting that consists of HER and OER half reactions.[138] However, OER proceeds through a slow four-electron-transfer process, which impedes the overall efficiency of water splitting. Plus, the as-obtained oxygen enables a low economic value, which necessitates the development of one effective reaction to replace water oxidation. Since the photooxidation reaction of constituent monomers from plastic wastes is thermodynamically and kinetically favored,[139] the plastic oxidation integrated with HER is therefore considered to be a preferable and sustainable technique for converting solar energy into hydrogen while realizing plastic upgrading.

Crucial to enabling plastic photoreforming is the development of photocatalysts with optimal features, including adequate redox potential and effective charge transfer. To achieve this goal, a versatile composite (i.e., ligand-free CdS dots) was fabricated and utilized as the catalyst for gaining H_2 under alkaline conditions from a variety of synthetic polymers, including PET, PLA, and PUR. In contrast, CdS held a weaker oxidation capacity than TiO_2 and a suitable reduction potential for HER, which endowed CdS with the potential for plastic incomplete oxidation coupled with hydrogen generation. Additionally, the thiol group on the CdS surface was proved to be an active center for C–H bond activation to generate carbon radicals, which promoted the selective oxidation process.[140] It was mentioned that ligand-free CdS dots were easily corroded, resulting in the formation of core-shell CdS/CdO_x structure with the corrosion resistance (Figure 9A).[61] In this research, the pretreatment process was carried out in an alkaline solution that helps to undergo the depolymerization of plastic wastes into their component units, as uncovered by ^1H nuclear magnetic resonance spectroscopy (^1H NMR) that demonstrated the generation of the constituent monomers of PET (i.e., ethylene glycol and terephthalate). In the following photoreforming reaction, fourfold enhancement of the HER activity could be seen over CdS/CdO_x using PET hydrolysate as feedstocks as compared to that obtained from the raw PET powders (Figure 9B). On the half-reaction for plastic oxidation, the hydrolysate was then reformed into a series of chemicals (e.g., isophthalate, formate, acetate, glycolate, lactate, and ethanol) by photoinduced holes (Figure 9C). Notably, real-world PET bottle was selected as feedstock for photoreforming, and steady H_2 generation rate over 6 days strongly confirmed the stability of CdS/CdO_x system. In this case, the main drawback is the use of CdS nanodots photocatalyst with easy aggregation and high recombination rate of charge carriers, which led to the reduction of the conversion rate of PET. In light of this, the development of photocatalysts with tunable band structures and high efficiency for surface charge separation turns out to be an option for elevating the efficiency of plastic upgrading. For this purpose, the $Cd_xZn_{1-x}S$ nanosheet anchored with MoS_2 ($MoS_2/Cd_xZn_{1-x}S$) was constructed as a photocatalyst for PET oxidation paired with H_2 evolution.[94] By incorporating Zn atoms, the redox potential of CdS nanosheet could be adjusted. This improved redox potential along with the addition of Zn levels has been shown to be a contributing factor to the reforming of PET. Furthermore, the enhanced photovoltage intensity could be observed after the decoration of MoS_2 on the $Cd_xZn_{1-x}S$ nanosheet, indicating the improved charge transfer that was beneficial for PET upgrading. As a result, the PET hydrolysate as feedstock could be transformed into a range of valuable chemicals (e.g., formate, acetate, methylglyoxal, and glycolate) on $MoS_2/Cd_xZn_{1-x}S$. Through the identification of the oxidation products by ^1H NMR, it was discovered that methylglyoxal was the primary product, indicating the occurrence of the coupling reaction between methanol and glycolate. In addition to the PET granule, the real-world PET bottle was employed to produce hydrogen as well as value-added chemicals, demonstrating a potential practical application in plastic upgrading. In contrast to PET, PLA is recognized as the "green polymer" due to its production from natural biomass and the ability of natural degradation. However, the kinetically slow degradation results in the accumulation of PLA waste in the environment. Alternatively, the solar-driven PLA

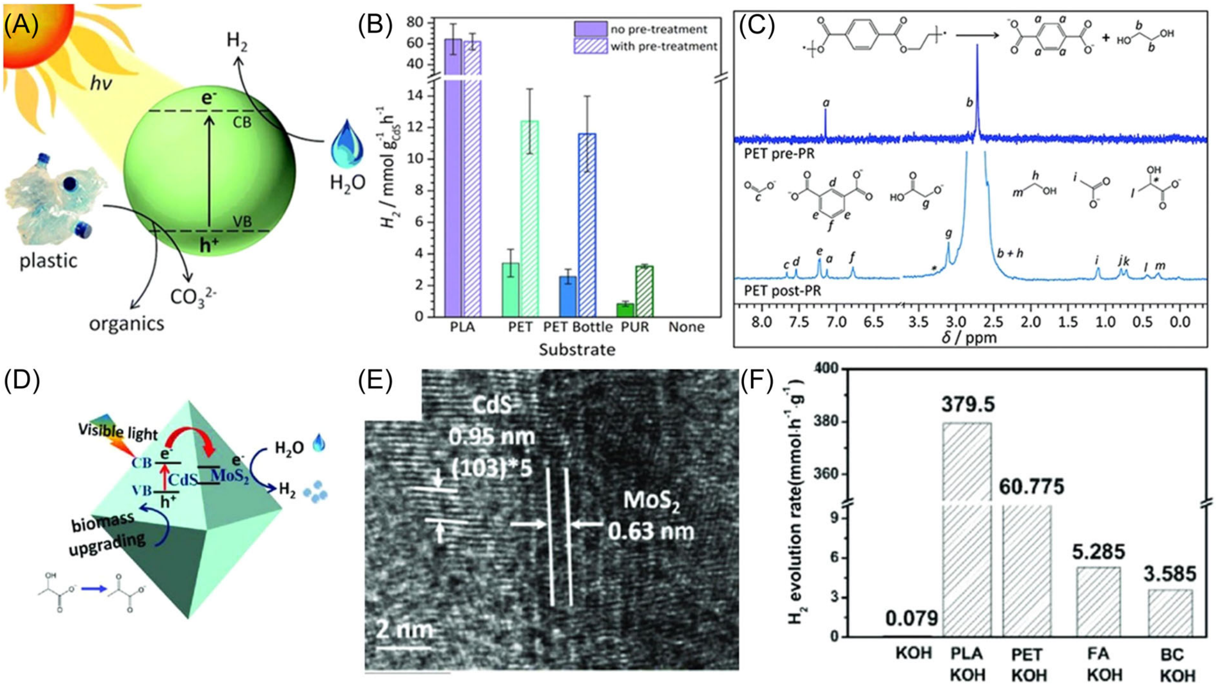

FIGURE 9 (A) The scheme of solar-driven plastic oxidation coupled with hydrogen evolution; (B) The performance of H_2 generation from plastic photoreforming with the aid of CdS/CdO_x photocatalyst. Reproduced with permission: Copyright 2018, The Royal Society of Chemistry.[61] (C) ^1H NMR spectra of polyethylene terephthalate (PET) before and after photocatalysis. (D) The mechanism of polylactic acid (PLA) conversion over CdS/MoS_2. (E) Transmission electron microscopy (TEM) image of tight interface between CdS and MoS_2. (F) photocatalytic hydrogen evolution from plastic wastes. Reproduced with permission: Copyright 2021, Wily-VCH.[97]

transformation seems to be a promising approach for plastic upgrading, which regretfully has been neglected over the past decades. The case concerning PLA upvaluing was reported recently using CdS/MoS_2 as a catalyst that was constructed via an in situ sulfidation over the $CdMoO_4$ (Figure 9D).[97] Such an intimate connection between CdS and MoS_2 provided an electron migration channel from CdS to MoS_2. As depicted in Figure 9E, the lattice fringes of CdS and MoS_2 as well as the apparent interface between CdS and MoS_2 were observed, manifesting the possibility of the efficient interfacial charge transformation. Besides, the enhanced photocurrent response confirmed the rapid separation of photogenerated charge carriers. Afterward, the photocatalytic H_2 performance over CdS/MoS_2 was assessed by using PLA as feedstock, with a superior activity over CdS/MoS_2 as compared with CdS, MoS_2, and their physical mixture (Figure 9F). To deeply understand the PLA oxidation process, the possible intermediate/products should be investigated. As a result, the intermediates, including pyruvate and acetate were observed by ^1H NMR spectroscopy. Besides, CO_2 was detected via the chemical precipitation method using $Ba(OH)_2$ reagent. After having a full knowledge of the intermediates during PLA upgrading, the reaction pathway was proposed. Initially, PLA was hydrolyzed into lactate in the presence of base, which was subsequently oxidized into pyruvate via a deprotonation reaction induced by photogenerated holes. Finally, pyruvate underwent the cleavage of C–C bonds to generate acetate, formate, and CO_2.

Compared with the forementioned polyester plastics dominated with C–O linkages, photoreforming of polyolefin plastics with C–C linkages seems to be a huge challenge owing to the chemically inert C–C bond. A series of chemical methods (e.g., pyrolysis, hydrocracking, and hydrogenolysis) have been implemented to upcycle polyolefin[97,141,142]; however, the severe operation conditions (e.g., elevated temperature and high pressure) means a substantial energy supply. By contrast, artificial photosynthesis may be a desirable approach for the conversion of polyolefins owing to its moderate conditions. In this scenario, the upgrading of PE into valuable products via photocatalysis was explored by Reisner and coworkers (Figure 10A).[99] To begin with, PE plastic was pretreated in diluted nitric acid and then transformed into dicarboxylic acid (e.g., succinic acid, and glutaric acid). Subsequently, pure succinic acid (the primary residue of PE pretreatment) was utilized as the feedstock to initiate the process of PE photoreforming. By utilizing TiO_2 and CN_x as photocatalysts, succinic acid was consequently transformed into gaseous products (e.g., ethane, ethylene, and CO_2), of which CO_2 originated from the decarboxylation of succinic acid over 80 h (Figure 10B). The production of ethane could ascribe to the dual decarboxylation of substrate in the presence of photoinduced holes. Besides, ethylene could be obtained in the CN_x-triggered reforming system, indicating that the ability of catalyst to transfer adsorbed hydrogen to intermediate radicals. In another case, pretreated PE powder was reformed over CdS-based photocatalysts.[100] For accelerating the separation of photoinduced charge pairs, MoS_2 as a cocatalyst was tipped at one end of CdS nanorods (Figure 10C). In this photocatalytic system, hydrogen could be continuously observed when PE hydrolysate was utilized as feedstock (Figure 10D). An isotope-labeled experiment was carried out to identify the hydrogen origination in PE photoreforming, demonstrating the formation of mixed products (e.g., D_2, and HD), which proved the hydrogen originated from water reduction. On the other hand, a range of oxidation products, including methane, ethane, propane, and n-pentane, were detected during the photoreforming of pretreated PE (Figure 10E), of which methane, ethane, and propane were evolved from the decarboxylation of acetic acid, succinic acid, and glutaric acid, respectively. Of note, n-pentane was synthesized by decarboxylation of pimelic acid that stemmed from the photo-Kolbe reaction between glutaric acid and propionic acid intermediate. The cycled photoreforming of pretreated PE over MoS_2/CdS was implemented, with the continuous H_2 evolution over 50 h and insignificant structure change of MoS_2/CdS photocatalyst, which confirmed its durability. Such a strategy toward charge separation behavior would present a viable route to boost the photocatalytic performance (Figure 10F).

To summarize the process described above, the constituent units of plastics were first obtained by chemical depolymerization and were then chemical valorized into value-added chemicals as well as solar fuels via photoreforming. Since polyester plastics (e.g., PET and PLA) feature C–O linkages, it means that their depolymerization into the constituent monomers can be realized at base conditions. Compared with the hydrolysis of easter bonds, the pretreatment of polyolefin via oxidation breaking using corrosive acids usually leads to the generation of CO_2. Given the problems, attention should be directed away from the polyolefin pretreatment using corrosive acids and toward finding a more economically viable solution. Therefore, developing cascade catalysis (e.g., thermal-photocatalysis) may present a feasible pathway for polyolefin reforming.

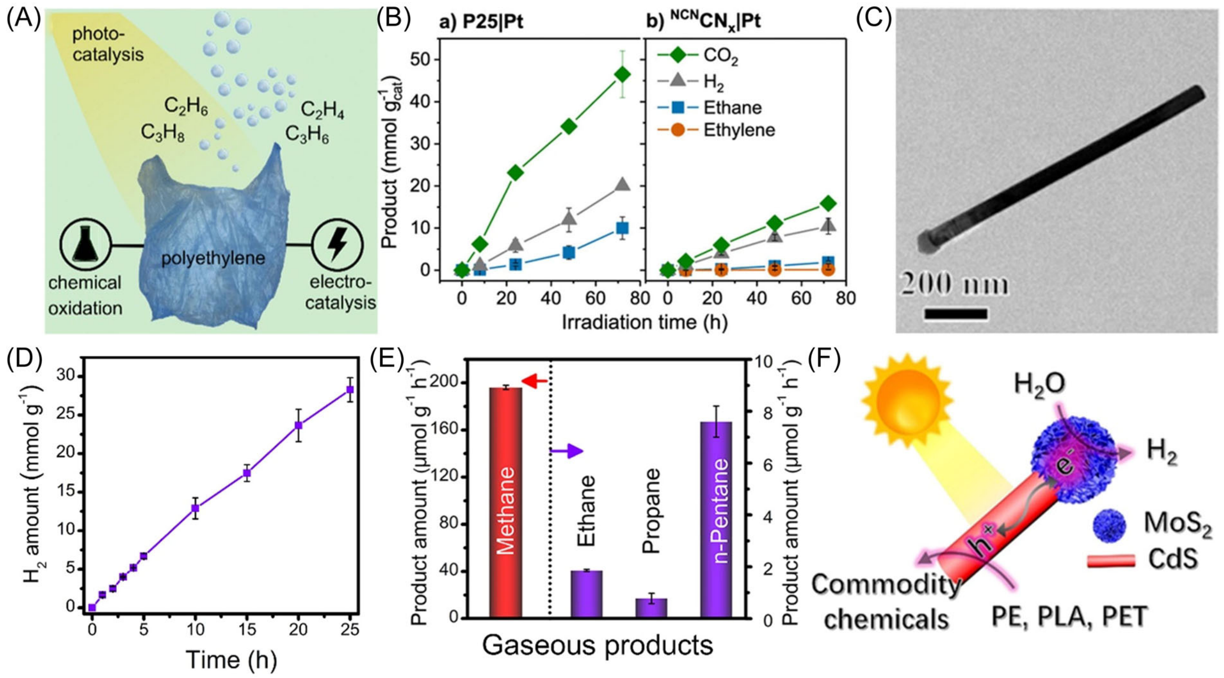

FIGURE 10 (A) PE conversion into gaseous products via photocatalysis. (B) The amounts of products during photocatalysis over P25|Pt and $^{NCN}CN_x$|Pt. Reproduced with permission: Copyright 2021, American Chemical Society.[99] (C) Transmission electron microscopy (TEM) image of MoS_2-tipped CdS nanorod. (D) H_2 generation from pretreated polyethylene (PE) over photocatalysis. (E) The amounts of alkane during PE photoreforming. (F) The schematic diagram of plastic wastes upgrading using CdS/MoS_2 photocatalyst. Reproduced with permission: Copyright 2022, American Chemical Society.[100]

5 | FUTURE PERSPECTIVE AND OUTLOOK

Plastics still serve a vital and irreplaceable role in daily life; nonetheless, their excessive use and accumulation in the environment have harmed our ecosystem owing to their resistance to natural degradation induced by their rigid polymeric nature. Bearing a circular economy in mind, using biodegradable plastics has become a consensus owing to the fact that bioplastics are easily decomposed by microorganisms. However, turning this into reality remains challenging, as no company has industrially commercialized biodegradable plastics. That is, the conventional plastic industry is still the major way to produce plastic for a long time, therefore continuing with plastic disposal in an economically competitive and environmentally friendly way. The management of plastic wastes ranging from plastic degradation to plastic upgrading necessitates the development of technology. Hence, this study highlights the recent advances of solar-driven plastic conversion, with the aim of enlightening the design principle of photocatalysts and the corresponding conversion mechanism towards plastics upgrading. Despite the impressive achievements achieved previously, plastic upgrading is still in the early stage. Some future challenges are presented as follows.

To begin with, the undesirable solar-to-chemicals conversion efficiency is still an important challenge that hinders the large-scale implementation of plastic upgrading by photocatalysis. This may be ascribed to the rapid recombination rate of photogenerated electrons and holes, which is deemed to be the primary challenge to achieve highly efficient plastic conversion. To this end, it is extremely urgent to seek tactics for solving the limitations of charge carries separation and surface reaction efficiency. In this scenario, deposition of dual cocatalyst is believed to be an ideal approach to address this issue. Previously, single atom and metal alloy have been utilized as electrocatalyst for HER and CO_2RR, indicating that these electrocatalysts as reduction cocatalyst favored the maximization of electron utilization efficiency.[143,144] Also, spinel oxide has been devoted to the conversion of alcohol to value-added chemicals via electrolysis, which manifested the ability of spinel oxide for alcohol oxidation.[145] Thus, these electrocatalysts can be selected as cocatalyst for promoting the photocatalytic conversion efficiency via suppressing the fast recombination rate of photogenerated charge pairs.

In addition, the photocatalytic systems developed currently suffers from poor selectivity to valuable C_{2+} product, which is deemed as a bottleneck to implement photocatalytic plastic conversion economically. Constructing a tandem catalysis system may be an effective strategy to improve the selectivity to value-added product. For example, the combination of electrocatalysis and biocatalysis has been presented to be a good solution to convert CO_2 to long-chain compounds with high selectivity, which can be extended to plastic disposal.[125] The high selectivity to short-chain products was obtained by enzyme catalysis, and subsequently the gained products could be upgraded into long-chain compounds via photocatalysis. In parallel, photocatalysis coupled with thermalcatalysis has been investigated in the domain of methane reforming.[146] It has been reported that thermal catalysis could significantly decrease the crystallinity degree of plastic, which rendered the subsequent photocatalytic oxidation of plastic wastes easier. Based on the foregoing considerations, it is feasible to integrate the advantages of multiple strategies to implement the economical and green conversion of plastic.

Finally, artificial intelligence technology, such as smart automation, IR4.0, and machine learning, turns out to be an option for screening high-performance catalysts. Among these, machine learning has been devoted to designing catalysts or predicting the performance of the catalyst. For instance, machine learning was used to predict the catalytic activity for the cleavage of C–C bonds in lignin.[147] After training over the random forest model, high accuracy was obtained, indicating that machine learning could offer a guidance for catalyst design and performance prediction. In addition, smart automation is a tool that can substitute labor to do some dangerous or fine experiment, which can dramatically promote efficiency in the area of screening catalysts. Cooper et al.[148] reported that a mobile robot showed superiority in the area of searching, such as continuous exploring and auto-screening systems. Besides, some state-of-the-art spectroscopy technologies should be applied to uncover oxidation mechanisms. Taking the in situ spectroscopy as an example, the in situ FTIR or Raman can offer vital information about cleavage and generation of chemical bonds, which helps in analyzing the evolution pathway of value-added chemicals during photocatalysis.

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CONFLICTS OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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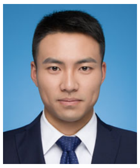

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