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Advancements in catalysis for plastic resource utilization

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The widespread production and utilization of plastic products have become ingrained in our society, resulting in a staggering amount of plastic waste, severe environmental challenges, and resource depletion. To address this issue sustainably, catalytic technology has emerged as a promising approach to break down non-biodegradable polymers into tiny organic molecules for secondary applications. Among these methods, photochemical processes utilizing light as an energy source offer controlled degradation of plastics under mild and environmentally friendly reaction conditions. Considering the pressing issue of plastic pollution, this paper presents a comprehensive overview of novel techniques for recycling waste plastics, delving into the underlying scientific principles of catalytic degradation. Moreover, we propose directions for feasibility studies on managing plastic pollution and advancing the development of plastic products.

Environmental significance

The escalating growth of the plastics industry and widespread plastic consumption have resulted in a grave global environmental challenge: plastic pollution. Conventional methods like landfilling or incineration have proven ineffective in addressing this issue, leading to additional environmental hazards such as landfill degradation and the release of harmful gases. In contrast, plastic resource transformation offers a distinct solution. By breaking down long chains of giant plastic molecules into tiny organic compounds, it presents a two-fold solution: resolving energy concerns caused by dwindling oil supplies while addressing plastic pollution. This dual-purpose approach has captured the attention of numerous researchers, although its implementation poses significant challenges. In recent years, catalytic technology has emerged as a preferred choice for the breakdown and recycling of diverse waste polymers, owing to its remarkable efficiency and selectivity. Notably, the integration of environmentally friendly and sustainable photocatalysis has breathed new life into plastics, offering one of the most promising avenues for achieving high-value utilization of waste plastics. Thus, this study aims to provide an overview of catalytic technologies employed in plastic treatment, along with a comprehensive examination and discussion of catalytic depolymerization mechanisms, as well as the potential for recycling waste plastics. By focusing on these aspects, we strive to contribute to the advancement of sustainable solutions for plastic pollution and foster a better understanding of the immense possibilities catalytic technologies offer in transforming plastic waste into valuable resources.

1. Introduction

Since the 1950s, humans have produced some 9.2 billion tonnes of plastic, 60% of which has been landfilled, incinerated or dumped directly into rivers, lakes and oceans.¹ A report published by the Organisation for Economic Co-operation and Development (OECD) in 2022 states that in the last 20 years, annual global plastic production has soared from 234 million tonnes in 2000 to 460 million tonnes in 2019. Plastic waste has also increased from 156 million tonnes in 2000 to 353 million tonnes in 2019. Global plastic production is expected to reach 1.2 billion tonnes per year by 2060, by which time the amount of plastic waste is also expected to nearly triple.² While plastics have brought convenience to our lives, they have also inflicted severe harm on the natural environment and human health through plastic pollution.^{3–5} In the face of global environmental

pollution and resource depletion caused by waste plastics, the idea of sustainable development and circular economy has been widely accepted by all countries.⁶ However, the development of the global recycled plastics industry is relatively slow and varies greatly from region to region due to the bottlenecks in recycling technology and the lack of economic viability of plastics. As a result, the life cycle of plastics has not yet been formed.⁷

Plastics, mainly composed of high molecular weight synthetic resins, undergo processing with cross-linking agents like plasticizers and antioxidants to acquire their chemical resistance and rigidity.⁸ Consequently, the degradation of plastics in nature alone through light, weathering and microbial bacteria takes a long period of time, while non-degradable plastics such as polyethylene (PE) remain largely unaffected.⁹ Generally, thermoplastic, homogeneous, and relatively clean waste plastics can be physically recycled, while structurally complex and difficult-to-degrade thermoset waste plastics necessitate chemical interventions.^{10–13} The utilization of chemical reagents to break down the long chains of plastic macromolecules can lead to a range of high-value chemical intermediates, thereby offering a sustainable approach

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to treating plastic waste in the long run (Fig. 1).^{14–16} It is crucial, however, to address the issue of secondary pollution during the chemical degradation and recycling processes.^{17,18} As a result, traditional methods like open burning, which lead to significant environmental harm, are being phased out.^{19,20} Emerging, green, efficient, and low-cost methods of plastic recycling and treatment are becoming a vibrant area of research at present.

Given the pressing need to combat plastic pollution, it is imperative that we pursue sustainable solutions that mitigate environmental impact, foster efficiency, and offer affordability. The exceptional stability of plastics poses a challenge when it comes to their degradation and recycling, as it requires surmounting the energy barrier associated with breaking long polymer chains.²¹ Chemical oxidation serves as an effective means of degrading plastics through incineration or gasification, yielding heat or energy feedstocks such as syngas.²² Alternatively, chemical cracking transforms waste plastics into fuel oil and chemical feedstocks through thermal or catalytic processes.²³ Among these methods, catalytic technology stands out by promoting or accelerating reactions through a reduction in activation energy. This advantageous feature enables rapid reaction rates and high selectivity in product formation.²⁴

Catalytic treatment of waste plastics minimizes the energy requirements for degradation while selectively harnessing the carbon, hydrogen, and oxygen present in the plastics.^{25,26} This approach not only converts plastics into alternative fuel or small molecule monomers but also yields high-value products and chemical raw materials, effectively turning waste plastics into valuable resources. Various catalytic strategies, utilizing different energy sources such as thermal cracking catalysis, biocatalysis,

electrochemical catalysis, and photocatalysis, are demonstrating feasibility and showcasing their respective advantages in waste plastics treatment. For instance, environmentally friendly, energy-driven photocatalytic strategies facilitate the release of hydrogen from plastic decomposition or enable selective depolymerization of plastics into liquid hydrocarbon fuels of appropriate molecular weight through hydrogenolysis. However, catalytic technologies also face challenges in terms of efficiency, necessitating further improvement.^{27,28} This paper provides a comprehensive overview of catalytic technologies employed in the treatment of plastics, shedding light on the degradation process of plastic macromolecules from both a structural and catalytic mechanism perspective. Additionally, a brief analysis of the issues encountered by catalytic technologies is presented to elucidate more ecologically and naturally beneficial catalytic strategies. Through a deeper understanding of catalytic processes and their potential drawbacks, we aim to contribute to the advancement of efficient and sustainable solutions for plastic treatment, paving the way for a greener future.

2. Molecular structures of hard-to-degrade plastics and their resource recovery technologies

The ease of plastic degradation is heavily influenced by its molecular structure.²⁹ It is well known that plastics are polymers with a large relative molecular mass, exhibit a crucial parameter known as molecular weight. A higher molecular weight signifies a longer molecular chain composed of monomers, resulting in enhanced resistance against

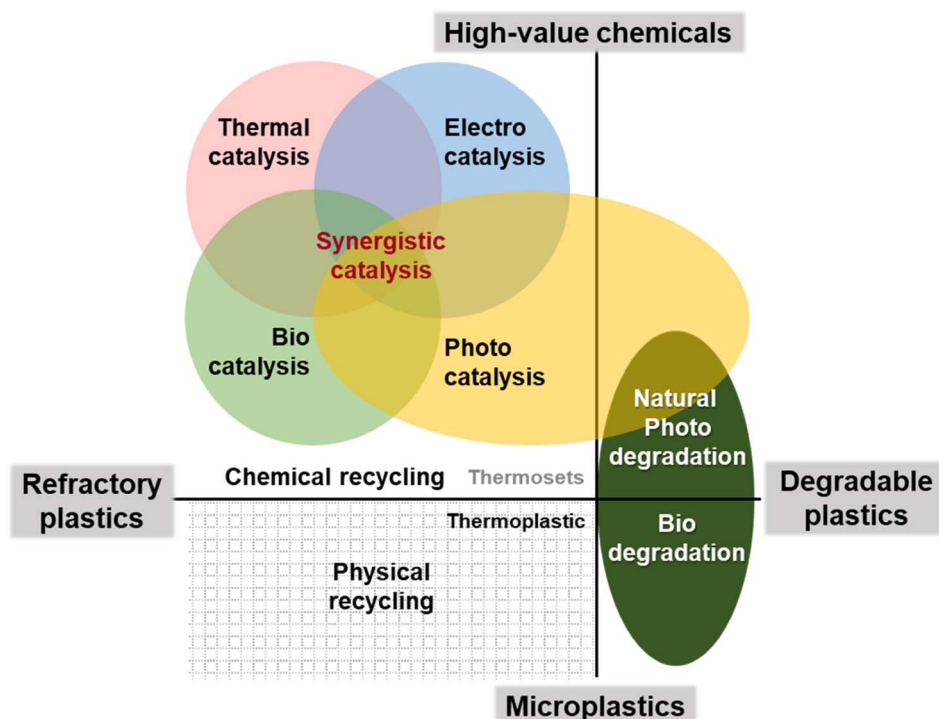


Fig. 1 Schematic diagram of the idea to apply catalytic technology in the resource recovery of waste plastics.



corrosion. Variations in functional groups within the plastics molecular structure distinguish different types of polymers, consequently affecting the mechanical, thermal, and chemical resistance of the plastic. Hence, selecting an appropriate degradation method is imperative, considering the plastic's molecular structure. Table 1 presents various common types of challenging-to-degrade plastic structures alongside their corresponding resource recovery technologies.

2.1 Structural analysis of hard-to-degrade plastics

To date, there is a wide range of nearly a hundred different plastic materials known. Depending on their behavior in nature, plastics

can be categorized into two main groups: degradable plastics and non-degradable plastics.^{30–33} Degradable plastics can be further classified into several types. First, there are photodegradable plastics that are infused with photosensitizers, enabling them to break down under the influence of light. Second, biodegradable plastics can be decomposed by microorganisms, facilitating their natural degradation over time.³⁴ Lastly, there are water-degradable plastics that are water-soluble, allowing them to dissolve when exposed to water.

In contrast, non-degradable plastics mostly possess a highly stable polymer structure, making them resistant to natural degradation. Examples of non-degradable plastics include PE,

Table 1 Molecular monomer structure and molecular weight information of commonly consumed plastics

Plastics	Polymer	Monomer	Molecular weight	Aggregation method	Recovery technology
Poly(amide)		—	341.5	Ring opening polymerization	—
Poly(carbonate)		—	290.3	Ring opening polymerization	Biocatalysis
Poly(ethylene)		CH ₂ =CH ₂	10 000–100 000	Addition poly-merization	Thermocatalysis Microwave catalysis
Poly(ethylene terephthalate)		—	20 000–30 000	Ring opening polymerization	Thermocatalysis Electrocatalysis Biocatalysis Photocatalysis
Poly(lactic acid)		—	60 000	Ring opening polymerization	Photocatalysis
Poly(propylene)		CH ₃ -CH=CH ₂	500–8000	Addition poly-merization	Photocatalysis
Poly(styrene)		C ₆ H ₅ CH=CH ₂	80 000–150 000	Addition poly-merization	Photocatalysis
Poly(urethane)		—	80 000–150 000	Ring opening polymerization	Thermocatalysis
Poly(methyl methacrylate)		C ₅ H ₈ O ₂	80 000–200 000	Addition poly-merization	—
Poly(vinyl chloride)		CH ₂ =CHCl	50 000–110 000	Addition poly-merization	Photocatalysis



poly(vinyl chloride) (PVC), poly(styrene) (PS), poly(urethane) (PU), and poly(methyl methacrylate) (PUMA). These plastics are synthesized through addition polymerization or condensation polymerization processes, wherein multiple monomers are linked together to form long-chain molecules, resulting in a three-dimensional network structure.³⁵ Addition polymers, such as PE, form strong carbon-carbon bonds within the polymer, making them chemically inert. Such polymers are also referred to as “full carbon-backbone polymers”. On the other hand, condensation polymers are more susceptible to hydrolysis at high temperatures and in humid environments.^{36–39} Another significant factor influencing plastic degradation is the organization of their molecular structure. Thermoplastics can exhibit either semi-crystalline or amorphous properties. Semi-crystalline polymers, like PE, poly(acetal), and nylon, undergo a distinct solid-to-liquid transition at specific temperatures.⁴⁰ Amorphous polymers, such as PS and polycarbonate (PC), do not melt but rather soften when heated above their glass transition temperature.^{41,42} Additionally, semi-crystalline plastics generally exhibit greater resistance to organic chemicals compared to amorphous plastics. For proper degradation and recycling, plastics require macroscopic fragmentation and intramolecular depolymerization. Precisely breaking the bonds between monomer molecules is the key to depolymerization reactions.

2.2 Waste plastics resource technologies

2.2.1 Plastics recovered as energy. The molecular structure of waste plastics primarily consists of hydrogen, carbon, and oxygen—the key elements present in fossil fuel molecules. The combustion of waste plastics yields a calorific value comparable to that of fuel oil, approximately 40 MJ kg^{-1} , making it a viable supplementary fuel source.^{43,44} By effectively harnessing the heat generated from plastic combustion or the syngas produced through plastic molecule vaporization, the energy value of plastic recycling can be fully utilized.⁴⁵ While waste plastics can be incinerated without the need for pre-treatment or separation from municipal waste, excessive burning can have detrimental environmental effects, including the release of substantial amounts of greenhouse gases.^{17,19} Depending on the plastic type and combustion conditions, the burning of plastics generates not only carbon dioxide and water but also harmful compounds like polycyclic aromatic hydrocarbons, acidic compounds, carbon monoxide, hydrogen chloride and heavy metal compounds.⁴⁶

To protect the environment, direct incineration for energy recovery is not considered feasible. Instead, researchers have turned to thermochemical technologies to indirectly repurpose plastics as an alternative to fossil fuels. These technologies involve converting plastic waste into liquid fuels through processes like pyrolysis and gasification.^{47,48} However, the efficiency of large-scale thermochemical treatment for plastic waste is still limited.^{49,50} To enhance the conversion efficiency of waste plastics, Hu *et al.* introduced chemical cyclic redox technology into the thermochemical treatment process.⁵¹ They employed a cyclic process involving Fe and Fe_2AlO_x to achieve a syngas concentration of

92.84%. Additionally, they designed a two-zone reactor to facilitate thermal cracking and oxidative hydrolysis of plastics, resulting in a carbon conversion rate of 81.03% (Fig. 2a and b). In addition to direct heating methods, the rapid heating capabilities of microwaves have shown promise in transforming waste plastics into energy. Wan Mahari *et al.* have successfully utilized microwave-induced high-speed heating to obtain high-quality liquid oils and combustible gases from waste plastics within a short time-frame.⁵² It appears that if the macromolecular chains in waste plastics can be broken down through thermochemical means, further control of the reaction conditions may enable the production of high-value chemicals with different properties.

2.2.2 Plastics into high-value chemicals. The composition of waste plastics is often complex, containing numerous fragments that can be recycled. Cibwe *et al.* conducted targeted chromatography on 21 plastic samples from Canadian recycling companies and identified over 280 recyclable chemicals (Fig. 2c).⁵³ However, they also observed that current recycling methods still generate unintended trace contamination. Recycling methods for converting waste plastics into high-value chemicals are typically classified into cracking and depolymerization processes. Thermal cracking encompasses techniques such as thermal, catalytic, and hydrocracking, while depolymerization includes hydrolysis, alcohol, and solvent decomposition.⁵⁴

Thermal cracking is a straightforward process based on free radical reactions. Strong heat is applied to break C–C and C–H bonds, generating free radicals that subsequently combine to form monomers or low molecular compounds.^{55,56} Recent research has focused on utilizing pyrolysis to convert waste plastics into valuable carbon nanomaterials like graphite or graphene. Smith *et al.* successfully transformed commercial poly(propylene) (PP) into carbon materials using conventional fused deposition modeling (FDM) with 3D printing.⁵⁷ Wyss *et al.* proposed a method for rapid production of 1D graphite materials from waste plastics by optimizing the heat source with flash joule heating (FJH).⁵⁸ In just a few milliseconds at temperatures above 3100 K, the plastic polymer rapidly reconstitutes into highly ordered sp^2 heterogeneous flakes, bypassing the need for lengthy chemical vapor deposition processes. On top of thermal cracking, catalysis can further enhance the efficiency and product selectivity of plastic cracking, as will be highlighted in the next section.⁵⁹ Catalysis can further enhance the efficiency and selectivity of plastic cracking.

Chemical depolymerization, on the other hand, can break down waste plastic polymers into monomers without the need for a catalyst. Dong and colleagues achieved selective depolymerization of PP and poly(ethylene terephthalate) (PET) into monomers using a far-from-equilibrium thermochemical plastic depolymerization method.⁶⁰ Their strategy involved employing an electrified space-time heating (STH) unit, which prevents random breaking of C–C and C–H bonds and avoids the formation of by-products (Fig. 2d and e). The choice of reagent in depolymerization reactions significantly affects the treatment of waste plastics. For instance, if organic acids are selected as reagents for breaking long-chain plastics, it is possible to completely depolymerize PU waste's main chain at room temperature using acyclic acetal units of glycerol. This process, referred to as cyclization-triggered chain



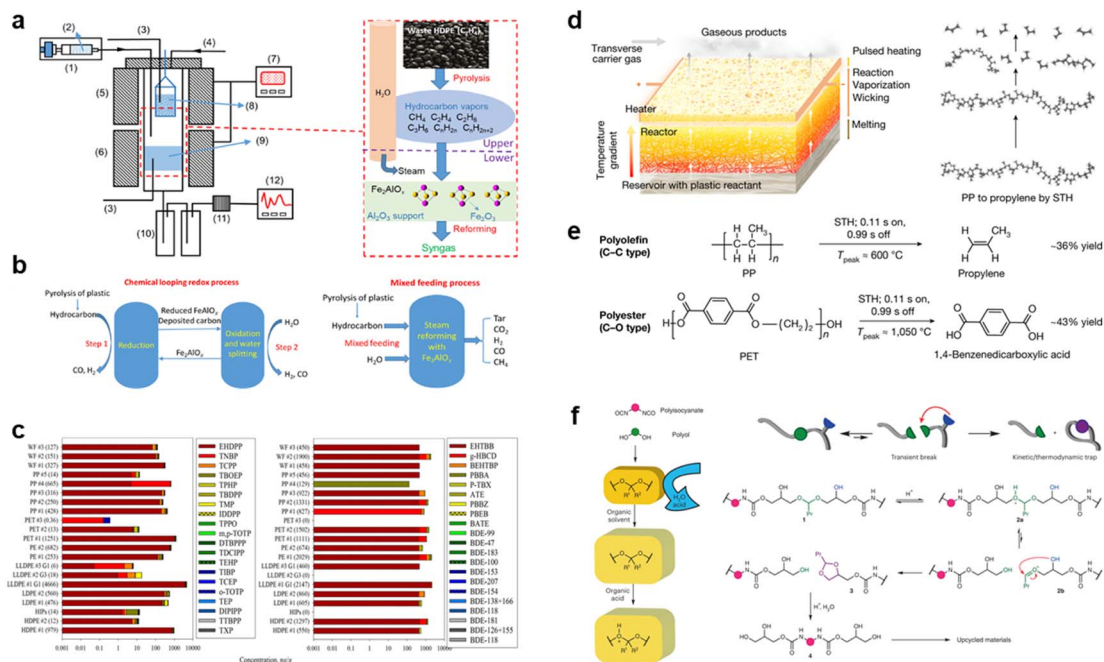


Fig. 2 (a) Display of the experimental system and reaction process. (b) Schematic of the chemical looping redox process and mixed feeding process for plastic conversion. Reproduced with permission from ref. 51 Copyright 2022, ACS. (c) Chemical distribution (stacked bar, x-axis) of the targeted organophosphate ester plasticizers and flame retardants and halogenated flame retardants. Reproduced with permission from ref. 53 Copyright 2023, ACS. (d) Schematic demonstrating the STH process in the bilayer configuration and the molecular transformation from polymer to monomer using PP as a model plastic. (e) The depolymerization reactions of PP (as a model polyolefin) and PET (as a model polyester) to their monomers by STH. Reproduced with permission from ref. 60 Copyright 2023, Springer Nature. (f) Polyurethanes and proposed CATCH cleavage. Reproduced with permission from ref. 61 Copyright 2023, Springer Nature.

(CATCH) cleavage by Morado *et al.*, demonstrates promising applications not only for PU but also for other types of waste plastics (Fig. 2f).⁶¹

3. Catalytic technology for waste plastics resource recovery

In principle, the desired characteristics of plastic materials for both service and recycling are inherently contradictory. They must possess stability and durability during their useful life, while also undergoing rapid and complete degradation under mild conditions for effective recycling. Consequently, innovative technologies are needed to overcome the kinetic and thermodynamic barriers associated with plastic decomposition and manage the existing pollution caused by non-degradable plastics.⁶² Catalysis plays a crucial role in this context by reducing the activation energy of reactions and altering the reaction pathway, thereby enhancing reaction rate and selectivity.⁶³ Various energy-driven catalytic processes, such as thermocatalysis, electrocatalysis, biocatalysis, field energy catalysis, and photocatalysis, have shown promising results in transforming waste plastics into valuable resources.^{64,65}

3.1 Thermocatalysis strategies

The incorporation of catalysts into the thermal cracking process offers significant benefits in terms of alleviating harsh reaction conditions for waste plastic depolymerization.

This not only improves the efficiency of the reaction but also enhances product distribution, ultimately increasing its value.⁶⁶ However, the thermal stability of the catalyst poses a major challenge due to the elevated temperatures involved in waste plastic thermal cracking. Yu *et al.* employed a calixarene $\text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ precatalyst to effectively deconstruct medical waste plastic materials into carbon nanotubes and hydrogen at 850°C .⁶⁷ Remarkably, even after 10 consecutive high-temperature cycles, the catalyst maintained the highest yields of carbon nanotubes ($245 \text{ mg g}_{\text{cat}}^{-1}$) and hydrogen ($24.92 \text{ mmol g}_{\text{cat}}^{-1}$) for waste plastic treatment. Through varying the reaction temperature and pre-catalyst composition, they identified the Fe/Co ratio in the pre-catalyst as a key factor in enhancing reactivity and product selectivity. In another study, Dong and colleagues achieved the decomposition of waste plastics and conversion of hydrocarbons using ZSM-5 catalysts at 500°C .⁶⁸ Over time, the reaction products exhibited exceptional selectivity for short-chain olefins, aromatics, alkanes, hydrogen, coke, and methane (CH_4) due to the unique pore structure of ZSM-5 and appropriate reaction conditions (500°C , 1 atm).

Moreover, the use of a precious metal platinum (Pt) catalyst further reduced the cracking temperature of waste plastics.^{69,70} Li *et al.* developed a Pt nanoparticle ($\text{Pt}@S-1$) catalyst encapsulated by β -zeolite and silica molecular sieve-1, achieving an impressive 89.5% naphtha yield at 250°C with 96.8% selectivity for C_5 – C_9 hydrocarbons using a tandem catalytic reaction (Fig. 3a).⁷¹ The suitable acidity of the zeolite catalyst and the size

effect of the Pt nanoparticles facilitated rapid breaking of C–H/C–C bonds in the waste plastic molecules and effectively controlled the narrow distribution of alkanes. Additionally, Zhang *et al.* directly converted various grades of waste PE plastics into liquid alkyl aromatics ($\sim C_{30}$) at low temperatures by solidly loading Pt onto γ -alumina (Fig. 3b).⁷² Notably, they overcame the thermodynamic barrier to obtain long-chain alkane products by modulating the barometric pressure during the reaction. Too low pressure was insufficient for plastic hydrolysis, while excessive pressure led to aromatic hydrogenation. Considering the wide range of plastic types, each waste plastic exhibits distinct thermal decomposition temperatures and chain-breaking mechanisms, leading to the continuous emergence of new thermocatalysts.^{73–75}

3.2 Electrocatalysis strategies

Electrocatalysis is a powerful method of accelerating reactions through charge transfer at the interface of electrodes and electrolytes.⁷⁶ Since 2021, Zhao's research group has been at the forefront of green electrocatalytic reforming of PET waste plastics to co-produce formic acid and hydrogen. Their initial focus was on converting ethylene glycol (EG) derived from waste plastics into formate using copper-based nano-wire catalysts, which exhibited high selectivity.⁷⁷ Density functional theory (DFT) calculations demonstrated that the CuO catalyst facilitated the breaking of C–C bonds, leading to the production of the glyoxal intermediate. Building upon their success, the group further optimized the electrocatalyst design and synthesized $NiCo_2O_4$ electrocatalysts that

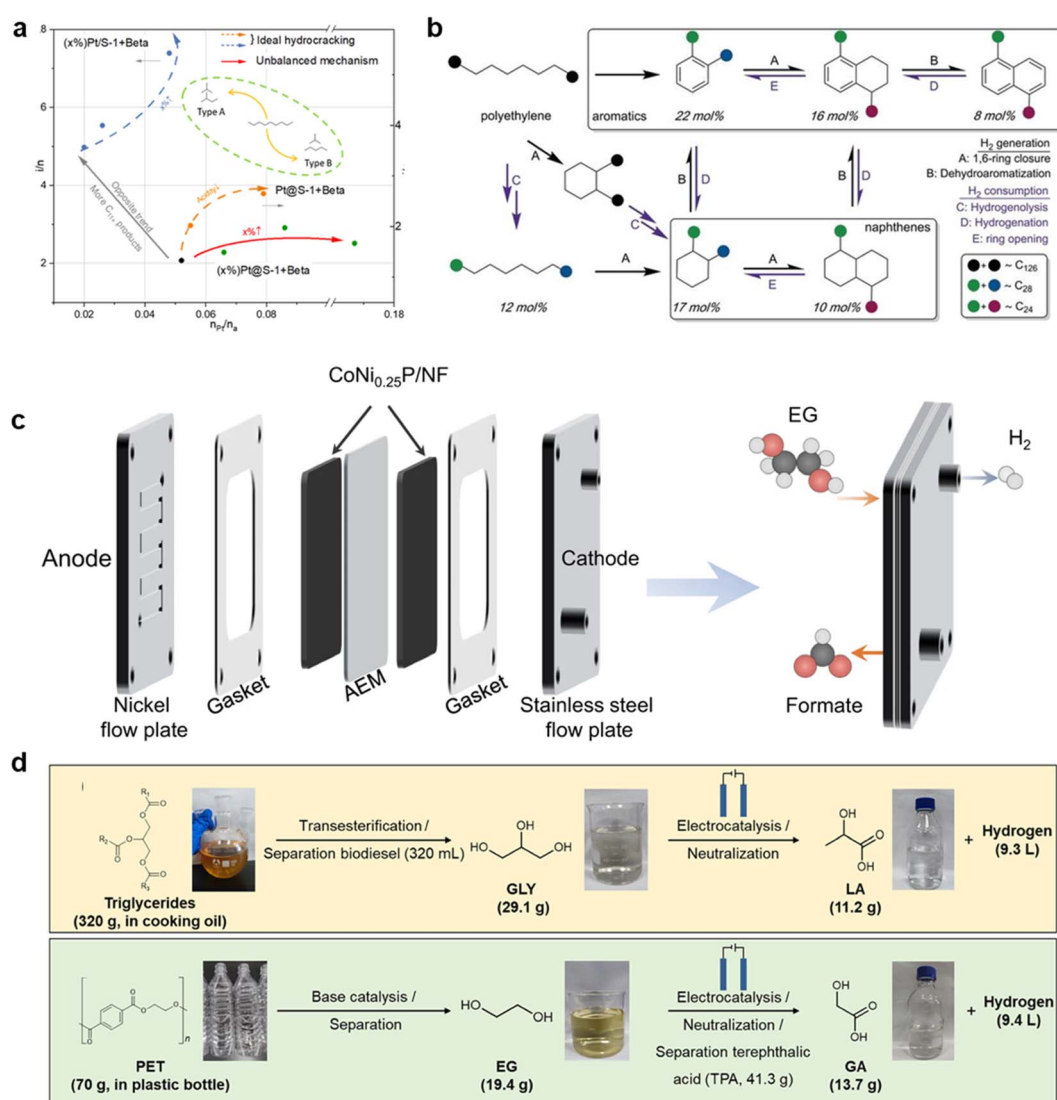


Fig. 3 (a) Relationship between isomer/normal (i/n) and Pt/Brønsted acid sites (n_{Pt}/n_a) over different catalysts. Reproduced with permission from ref. 71 Copyright 2023, ACS. (b) Overall PE conversion to alkyl aromatics and alkylnaphthene, and proposed mechanism of tandem polyethylene hydrogenolysis/aromatization via dehydrocyclization. Reproduced with permission from ref. 72 Copyright 2020, AAAS. (c) Membrane-electrode-assembly (MEA) for EG oxidation and the MEA setup for paired HER(–)/EG oxidation(+). Reproduced with permission from ref. 85 Copyright 2021, Springer Nature. (d) Schematic illustrations of the electrocatalytic upgrading process of triglycerides and waste PET bottles. Reproduced with permission from ref. 87 Copyright 2023, ACS.

efficiently hydrolyze PET, resulting in formic acid with a Faraday efficiency of up to 90%.⁷⁸ To make the process even more sustainable, photovoltaics were employed as an energy source to drive the electrocatalytic cracking of plastics, enhancing the value of formic acid production while generating hydrogen (H₂).⁷⁹ Solar energy not only served as an electricity source but also promoted charge separation on the catalyst, thereby enhancing the reaction efficiency.⁸⁰ Through the introduction of Fe₂O₃/Ni(OH)_x photoanode catalysts, photoelectrocatalysis (PEC) technology achieved the conversion of PET to formic acid with a Faraday efficiency of approximately 100%.⁸¹ Light played a crucial role in exciting electron-hole separation on the anode catalyst, thereby improving the selectivity for degradation products of waste plastics. It is worth noting that photocatalysis itself is also employed in waste plastic degradation management, which will be discussed in detail in the subsequent section.

In the electrocatalytic recovery of waste PET, transition metal Co- and Ni-based catalysts have exhibited high selectivity for formate.^{82–84} Zhou *et al.* developed nickel (Ni)-modified cobalt phosphide (CoNi_{0.25}P) electrocatalysts as membrane electrodes, achieving selectivity above 80% for formate products (Fig. 3c).⁸⁵ Behera *et al.* utilized a one-dimensional (1D) coordination polymer based on cobalt (Co) as an electrocatalyst, resulting in a 100% yield of terephthalic acid (TPA) and 80% selectivity of potassium dicarboxylate (KDF) at a low starting potential of 1.27 V.⁸⁶ Furthermore, besides formic acid, other valuable compounds can also be obtained from waste PET. Yan *et al.* successfully cleaved glycerol from PET waste, yielding lactic and glycolic acids by employing gold (Au) loaded on nickel hydroxide (Fig. 3d).⁸⁷ The selectivity of these products was attributed to the formation of alcohol salts through interactions between adjacent OH groups on the intermediate molecule, resulting in an increased local current density facilitated by Au.

3.3 Biocatalysis strategies

The biocatalytic treatment process for plastics primarily relies on enzymatic catalysis.⁸⁸ Nature harbors a vast array of active enzymes and microorganisms that possess the capability to break down plastic copolymers, including PET enzyme (PETases), keratinases, and hydrolases.^{89,90} In the case of PETases, Kalathil *et al.* discovered that *Ideonella sakaiensis* (*I. sakaiensis*), a PETase, can completely mineralize PET into carbon dioxide, water, and adenosine triphosphate (ATP) when exposed to oxygen. Under anaerobic conditions, PET is broken down into acetic acid and ethanol (Fig. 4a).⁹¹ *I. sakaiensis* also exhibits the ability to generate electricity from waste plastic, especially when co-cultivated with the electrogenic *Geobacter sulfurreducens*. Naturally, enzymes are found within organisms as well as in the natural environment. Eiamthong *et al.* identified highly active MG8 enzymes in the human salivary metagenome for PET hydrolysis, surpassing the degradation efficiency of hydrolases used in both nature and industrial production.⁹² They genetically recoded the MG8 gene fragment to obtain a covalent binding agent that could facilitate the bio-functionalization of PET.

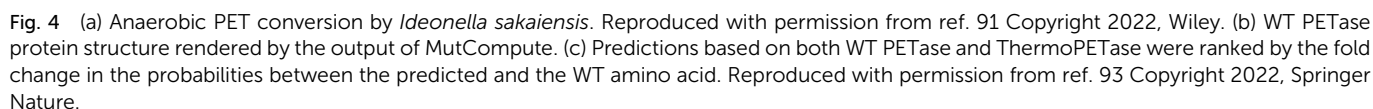
However, the uncontrolled survival of enzymes in nature and their lack of stability during catalytic reactions with waste plastics pose challenges. Moreover, the diverse range of enzymes in nature makes it difficult to fully comprehend their survival requirements and performance. To address this, researchers conducted a comprehensive analysis of waste plastic hydrolysis enzymes using machine learning algorithms (Fig. 4b and c).⁹³ Their findings revealed that the FAST-PETases effectively enables a closed-loop recycling process for PET. By studying native enzymes, genetic engineering techniques can be employed to develop specific enzyme catalysts for the degradation of waste plastics.⁹⁴ Zhu *et al.* developed a BIND-PETases derived from the original enzyme, which exhibits a 30 day survival period at 4 °C and can directly degrade PET microplastics in wastewater without becoming inactivated.⁹⁵ Alternatively, in combination with inorganic nanomaterial Fe₃O₄, the enzyme achieves nearly 100% microplastic removal and degradation efficiency.⁹⁶ Apart from enzymatic catalysis, the use of bio-based materials in catalytic depolymerization has proven effective in breaking down plastic molecules. Saito and his colleagues experimented with vanillin derivatives as bio-based feedstocks, which offer high purity of recovered PC monomers without causing chemical secondary pollution to the environment.⁹⁷ Overall, biocatalytic degradation of waste plastics is a viable approach, but it necessitates better control and design of enzyme catalysts to enhance its efficacy.^{98,99}

3.4 Other catalysis strategies

Organocatalysis has emerged as an effective method for decomposing waste plastics, serving as a valuable complement to transition metal-based and biocatalysis.¹⁰⁰ Given that plastics are inherently organic polymers, organic reagents offer distinct advantages for recycling waste plastics based on the principle of similar solubility. Organocatalytic degradation can be categorized into alcoholysis, phosphate ester, and alcohol-amine reactions, depending on the specific reagents employed. Furthermore, it can be combined with organic polymerization to establish closed-loop recycling pathways for plastics.^{101,102} In the study by Yang *et al.*, a modular series of dinuclear organoboron catalysts was designed for the synthesis of chemically recyclable poly(cyclopentene)carbonate (PCPC) and its subsequent depolymerization after use.¹⁰³ The catalytic efficiency of PCPC polymerization achieved remarkable results, with a metal-free organocatalysis achieving a high yield of 1.0 kg PCPC g_{cat}^{−1}. The depolymerization of PCPC involved simple random chain cleavage and unchaining pathways. This intriguing monomer-polymer-monomer cycle demonstrates the potential of organocatalysis in plastic recycling.

Moreover, researchers have been exploring the use of field effects as an energy source to catalyze the decomposition of waste plastics. The thermal effect of microwave fields, for instance, enhances the efficiency of hydrogen production from waste PE. The Fe₁Co₁Al₂ catalyst's structure benefits from the field effect during the reaction process, facilitating charge transfer from hydrogen to iron within the waste plastic.¹⁰⁴ When the catalyst is capable of absorbing microwaves, the





plastics.^{114–116} Photocatalysts are mostly semiconductor materials. When the absorbed energy is greater than or equal to the band gap photon, the photocatalyst is excited to produce photogenerated electron–hole pairs that leap to the conduction band and remain in the valence band. The photogenerated electron–hole pairs migrate to the catalyst surface under the action of an electric field and react with the adsorbed material on the surface in reduction and oxidation reactions respectively.¹¹⁷ The fundamental concept of photocatalysis involves utilizing light to generate electron–hole pairs in semiconductor materials, which subsequently produce active radicals for various desired redox reactions. Moreover, the photogenerated radicals can be incorporated into macromolecular polymers, allowing the production of plastic products that facilitate photodegradation.¹¹⁸ Accordingly, photocatalysis offers a comprehensive approach to tackle plastic pollution, encompassing both end-of-pipe recycling and source treatment challenges.^{119,120}

4.1 Photocatalytic degradation of microplastics

In their natural state, waste plastics undergo environmental aging and are degraded by sunlight into microplastics (MPs) and nanoplastics (NPs), which then enter the soil or water.¹²¹ Solar irradiation causes certain waste plastics to break down into dissolved organic carbon (DOC), which can potentially be assimilated by bacteria.¹²² However, not all waste plastics can be completely degraded by natural light alone. Small-size waste plastic molecules (1–100 μm) can only be fully mineralized by specific microorganisms. Otherwise, they remain as micro-pollutants that are difficult to detect by humans. Liu *et al.* conducted an analysis of the aging process of PS plastics under light exposure using ionophore mass spectrometry (spICP-MS).¹²³ The findings revealed that PS produces significant amounts of MPs and NPs during aging, posing a long-term chronic toxicity risk to organisms and a “hidden” ecotoxicological threat. Additionally, the natural photodegradation of

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plastics by light also generates substantial quantities of volatile organic chemical pollutants (VOCs), contributing to air pollution (Fig. 5a and b).¹²⁴

The natural photodegradation of waste plastics primarily relies on the activity of reactive oxygen species (ROS), particularly oxidative free radicals.¹²⁵ In photocatalytic reactions, a diverse array of photogenerated radicals is commonly employed for the mineralization of organic pollutants.^{126,127} To facilitate the rapid and complete photodegradation of waste plastics, photocatalysis can be employed to treat microscopic plastic particles.¹²⁸ Uheida and colleagues utilized glass fibers embedded with zinc oxide (ZnO) nanorods (NRs) to capture and degrade PP microplastic particles.¹²⁹ Under visible light, ZnO NRs catalyze the efficient formation of carbonyl and hydroxyl groups on waste plastics, effectively reducing the particle size of PP microplastic waste. While natural aging of waste plastics primarily occurs under UV light, the choice of light for the photocatalytic degradation process is typically based on the photoresponse of the photocatalyst. Ma *et al.* designed FeO_x/g-C₃N₄ and Fe₂O₃/g-C₃N₄ photocatalysts with visible light activity for PET degradation.¹³⁰ These catalysts exhibit a significant breaking effect on the ester bonds present in PET over a broad wavelength range of 200–800 nm.

4.2 Value-added conversion of waste plastics under photocatalysis

The light-driven reprocessing of waste plastics for recycling can be referred to as photo-reforming. The catalysts that facilitate

this process are mostly precious metal or cadmium (Cd)-based photocatalysts.¹³¹ Uekert *et al.* conducted a study where they prepared CdS/CdO_x quantum dots for efficient photo-reformation of three commonly used plastic molecules: poly(lactic acid) (PLA), PET, and PU.¹³² They achieved this in alkaline aqueous solutions, resulting in high-purity H₂ as well as organic products such as formate, acetate, and pyruvate. To address the photo-corrosive properties of CdS, they designed a carbon nitride/nickel phosphide (CN_x/Ni₂P) photocatalyst, which controlled the toxicity and cost of the catalyst.¹³³ Under alkaline conditions, CN_x/Ni₂P was capable of converting PET and PLA into H₂ and various organic small molecule compounds. The catalytic recovery reaction system was scalable up to 60 times and could be extended to polyester fibers and plastic waste contaminated with oil (Fig. 6a and c).

Cd-based photocatalysts can also be modified by defective and heterojunction means. This modification led to the development of d-NiPS₃/CdS waste plastic photo reformation catalysts with high H₂ yields ($\sim 40 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and excellent stability over 100 hours.¹³⁴ The photocatalytic decomposition of waste plastics is feasible in both alkaline and acidic environments as long as the photocatalyst can produce stable reactive oxygen radicals. Huang *et al.* developed an acid-catalyzed system for the degradation of plastic waste. They achieved visible light selective acid-catalyzed oxidation of PS without a photosensitizer by adjusting the ratio of acid and solvent.¹³⁵ The [PS-acid] adduct formed during the acid-catalyzed reaction between PS and acid was found to act as the true photosensitizer. In the presence of light, this adduct generated singly linear oxygen (¹O₂) to oxidize PS, forming formic acid, benzoic acid, or acetophenone (Fig. 6d). Additionally, other radicals with oxidizing properties could be employed for the decomposition of waste plastics. Oh *et al.* utilized chlorine radicals generated by FeCl₃ under white light irradiation to capture hydrogen atoms from waste plastics, resulting in the degradation of PS into benzoyl compounds.¹³⁶ They demonstrated the feasibility of this method for gram-scale waste plastics treatment using flow chemistry.

Compared to thermal catalysis, photocatalysis provides the ability to recycle plastics and convert them into high-value chemicals. The key difference lies in the milder reaction conditions and the special high selectivity of photocatalysis for waste plastic products.^{137,138} Cao *et al.* achieved the oxidation of PS to aromatic compounds by g-C₃N₄ in visible light catalysis, showing a high selectivity for benzoic acid in the liquid phase product (Fig. 6e).¹³⁹ This selectivity was attributed to the precise activation of C–H and C–C bonds on PS by photogenerated radicals, leading to the further oxidation of hydroxyl and carbonyl groups on its main chain, forming aromatic oxygenated compounds. In terms of efficiency, composite photocatalysts prepared using the porous MOFs material UiO66-NH₂ encapsulated with ZnO contribute to improved electron-hole separation, enhancing photocatalytic efficiency.^{140,141} This, in turn, accelerates the catalytic conversion of PLA and PVC to acetic acid. The widespread application of light has also encouraged the photocatalytic cracking of plastics beyond the recycling of waste plastics, even extending to lithography

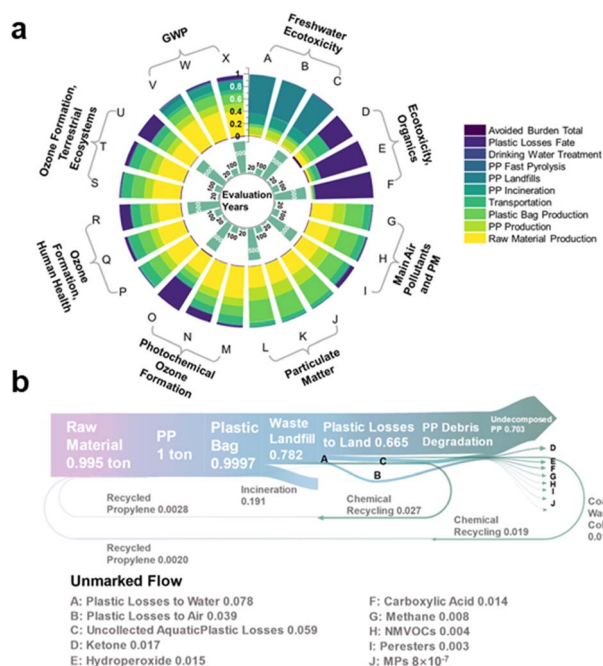


Fig. 5 (a) Environmental profile based on various environmental indicators in 20, 100, and 500 years. (b) Mass flow distribution across the entire life cycle in 500 years shows the mass flow rates in tons from raw material and resource extraction to the photo-degradation products as graves. Reproduced with permission from ref. 124 Copyright 2023, ACS.



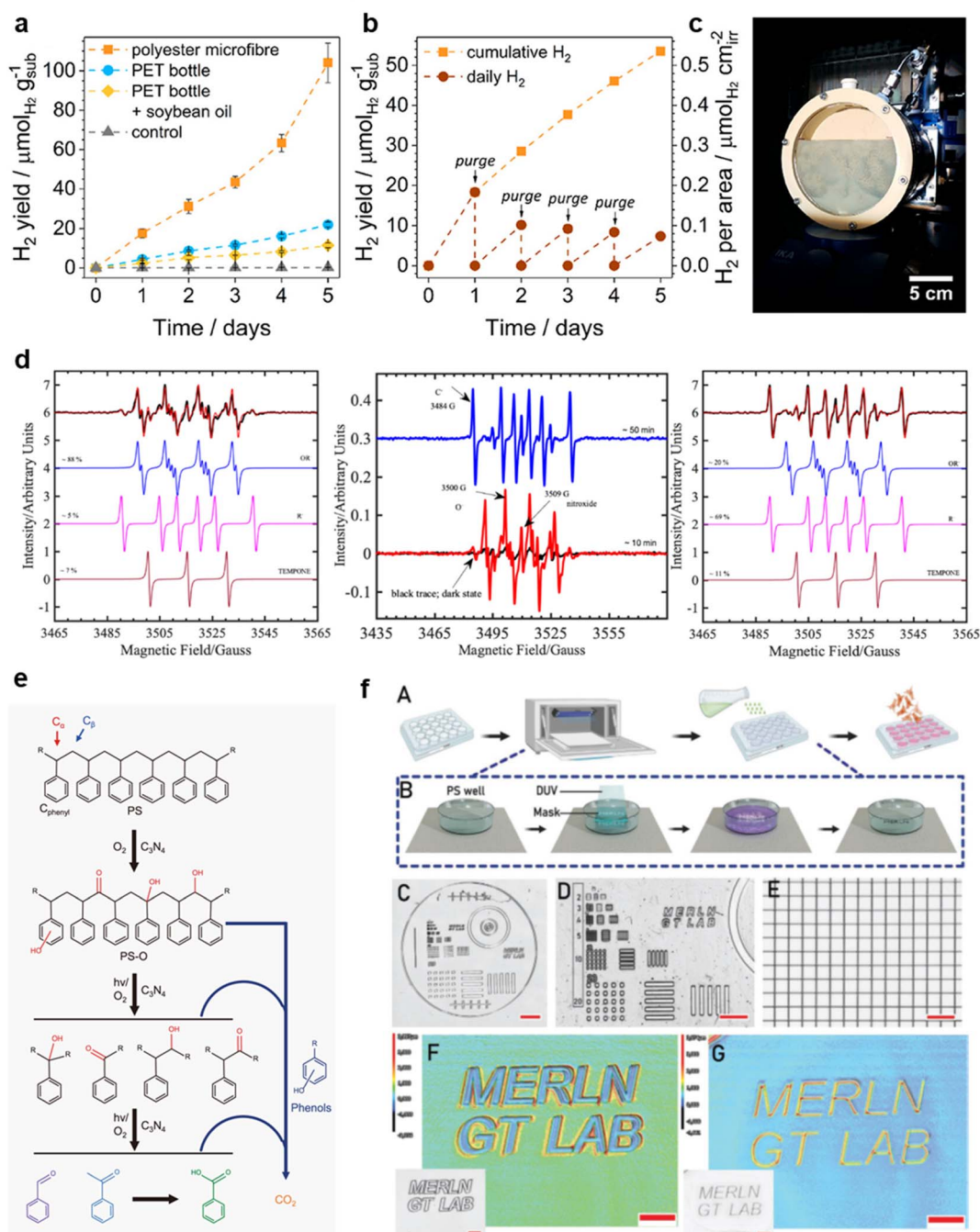


Fig. 6 (a) Long-term photo reforming of polyester microfibres, a PET bottle, and an oil-coated PET bottle. (b) Upscaled photo reforming of polyester microfibres; the sample was purged every 24 h. (c) Photograph of the batch reactor in use. Reproduced with permission from ref. 133 Copyright 2019, ACS. (d) EPR spectra from *in situ* irradiation at 405 nm (1 mW LED) of PS and a pTsOH·H₂O solution with 4-oxo-TMP and DMPO spin traps (1 : 4). Center: experimental spectra measured after 10 min (red) and 50 min (blue) irradiation. Left and Right: Simulated spectra of three separate components of nitroxyl, a carbon-centered DMPO adduct, and an oxygen-centered DMPO adduct. Reproduced with permission from ref. 135 Copyright 2022, ACS. (e) Proposed reaction pathway of polystyrene photo-oxidation reaction. Reproduced with permission from ref. 139 Copyright 2020, Springer Nature. (f) Direct microstructure fabrication on bulk TCP. Reproduced with permission from ref. 142 Copyright 2022, Wiley.

processes. Samal *et al.* capitalized on the controlled reaction conditions of photocatalysis to directly build subcellular microstructures on PS using deep ultraviolet light in a short period. This simple lithography technique does not require

expensive equipment or specific reagents, making it easily accessible even to non-experts (Fig. 6f).¹⁴² It significantly expands the possibilities of photocatalytic degradation in plastics.

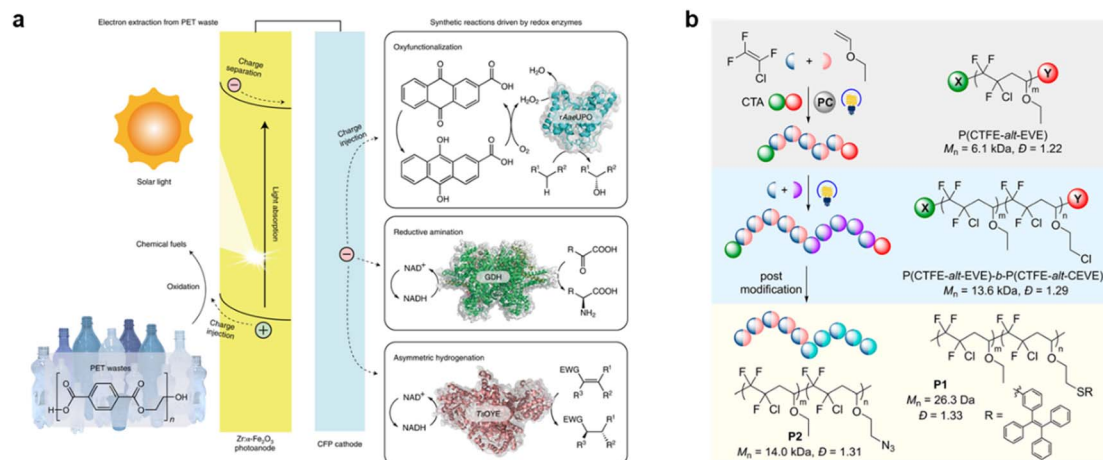


Fig. 7 (a) CFP-based cathodes reduce O_2 to H_2O_2 for biocatalytic oxyfunctionalization and NAD^+ to NADH for enzymatic amination and asymmetric hydrogenation. Reproduced with permission from ref. 152 Copyright 2022, Springer Nature. (b) Synthetic schemes of the two-step photopolymerization and post-modification. Reproduced with permission from ref. 155 Copyright 2020, ACS.

4.3 Photo-thermal/electro/biocatalytic synergy

The efficiency of carrier separation, light utilization, and quantum efficiency in photocatalytic reactions has been a significant barrier to the industrialization of photocatalysis.^{120,143} To enhance the conversion of light energy into chemical energy, thermocatalysis, electrocatalysis, and biocatalysis are often integrated into the photocatalytic process, leveraging synergistic effects to improve the cleavage efficiency of waste plastic molecules.^{144,145} Moreover, the addition of photocatalysis can enhance the selectivity of degradation products in waste plastic, complementing the aforementioned catalytic technologies. In a study by Liu *et al.*, integrated Co single site (Co SSCs) catalysts were introduced into a photo-thermal catalytic system to promote the conversion of carbonyl groups in waste polyester plastics and optimize the nucleophilic addition elimination process.¹⁴⁶ The photothermal synergy significantly increased the conversion of PET and the yield of bis(2-hydroxyethyl) terephthalate by 5.4 and 6.6 times, respectively, compared to thermal catalysis alone. Electrocatalytic enrichment, on the other hand, offers even greater effectiveness in separating photogenerated electron-hole pairs due to the directional charge transfer, thereby enhancing the performance of photocatalytically degraded plastics.¹⁴⁷ And to conserve energy resources, piezoelectric materials can be utilized as a source of electricity.^{148,149} The combination of piezoelectric-photocatalysts has demonstrated the ability to inhibit the rapid recombination of photogenerated charges, exhibiting unique advantages in plastic waste treatment.¹⁵⁰

The integration of biocatalysis and photocatalysis holds great promise for achieving complete degradation of waste plastics, transforming large molecules into smaller ones and ultimately achieving complete mineralization. Ye *et al.* developed a bio-photocatalyst system by assembling *Methanosarcina barkeri* (*M. b.*) and carbon dot functionalized polymerized carbon nitride (CDPCN) catalysts.¹⁵¹ This system successfully degraded PLA into CH_4 in five consecutive cycles, achieving

a selectivity of up to 100%. Furthermore, Kim *et al.* combined electrocatalysis, biocatalysis, and photocatalysis in a photo-electrochemical biosynthesis reaction of PET waste plastic (Fig. 7a).¹⁵² In this system, Zr-doped hematite served as a photoanode to extract electrons from the waste PET and transfer them to the bioelectrocatalytic site, while carbon material acted as a cathode to receive the electrons and activate hydrolytic enzymes for the plastic cracking reaction. This comprehensive approach involving all three technologies presents a more promising and efficient pathway for the treatment and recycling of plastics.

4.4 Photochemical green preparation of degradable plastics

Plastics continue to play a significant role in manufacturing and daily life, creating a growing need for biodegradable plastics to replace environmentally harmful alternatives.¹⁵³ Photoexcited photocatalysts generate oxidation-reduction intermediates that aid in the synthesis of plastics through a process called reversible deactivation of radical polymerization (RDRP).¹⁵⁴ Simply put, RDRP allows for precise control over the molecular weight, molecular weight distribution, and polymer structure of plastics when there is a uniform and adequate light source.

Jiang and colleagues have introduced a groundbreaking technique called photoorganocatalytic reversible deactivation, which applies to vinyl chlorotrifluoroethylene (CTFE) and vinyl ethers (VE) in alternating radical copolymerization (Fig. 7b).¹⁵⁵ This method enables the controlled synthesis of main-chain fluorinated alternating copolymers at room temperature and atmospheric pressure. The “activation-deactivation” cycle allows for continuous switching of CTFE molecules, facilitating chain growth and enabling free growth and post-synthesis modification of the copolymer. By incorporating photosensitizers into the polymerization system, recyclable plastics with photodegradable properties can be obtained, thus establishing a more comprehensive recycling chain for the environmentally friendly use of plastics.

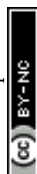


Table 2 Summary of catalytic technologies for recycling of waste plastic resources

Catalytic technology	Driving force	Eco-friendliness	Economy
Thermocatalysis	Thermal energy	Low	Middle
Electrocatalysis	Electrical energy	Middle	High
Biocatalysis	Bioenergy	High	Middle
Photocatalysis	Light	High	High
Microwave catalysis	Microwave field	Middle	Middle
Organic catalysis	Free energy	Middle	High

5. Summary and perspectives

Polymers are the building blocks of plastics, forming long, complex molecular structures with a carbon skeleton and various functional groups branching out from the carbon elements. These versatile materials have revolutionized consumer goods, but unfortunately, they have also led to the persistent problem of plastic pollution that can endure for decades or even centuries. Waste plastics, which are difficult to degrade, exist in a multitude of forms, ranging from hard to soft, and they resist easy melting and transformation. Presently, waste plastics pervade our environment, infiltrating the soil, infiltrating rivers, and spreading through untouched regions with rainfall. Urgent action is required to address this issue and find suitable methods for treating and recycling waste plastics. Conventional disposal approaches like landfilling, incineration, and mechanical cracking are no longer viable in the face of the current plastic pollution crisis.

Catalytic technology offers a promising solution for recycling and reusing plastics, but it is not without its challenges (Table 2). Thermocatalytic processes can effectively lower the thermodynamic requirements for breaking down waste plastics through thermochemical cracking. Ideally, waste plastics should be crackable at lower temperatures and atmospheric pressure, while also enhancing selectivity for desired products. Electrocatalysis, commonly used for energy conversion, can also contribute to waste plastic treatment. However, its industrial implementation necessitates the optimization of reaction cells, and the environmental impact of power supply greening must be considered. Enzyme-driven biocatalytic processes closely mimic natural degradation of waste plastics, with autogenous enzyme activity and catalyst efficiency being crucial factors. Photocatalysis, on the other hand, faces challenges in terms of catalytic efficiency. Enhancing the utilization of visible light and the oxidation capacity of photocatalysts through catalyst modification proves to be an effective strategy. It is vital to effectively prevent secondary pollution during the treatment of waste plastic, making green photocatalysis technology crucial in this regard. Thus, based on photocatalysis, harnessing multiple catalysts working in synergy to leverage their respective strengths may emerge as a powerful approach for rapidly eliminating plastic pollution.

Author contributions

Yao Chen: conceptualization; writing-original draft & editing; Lele Bai: resources; writing-original draft; Dening Peng:

resources; writing-original draft; Xinru Wang: resources; writing-original draft; Meijun Wu: resources; writing-original draft; Zhenfeng Bian: writing – review & editing.

Conflicts of interest

The authors declare no competing financial interest.

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