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Cite this: *RSC Sustainability*, 2025, **3**, 4866

Shining light on waste: photochemical strategies to reduce and transform plastic pollution

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DOI: 10.1039/d5su90049b

rsc.li/rscsus

Introduction

Plastic products are cheap, versatile, and abundant, with over 400 million tons manufactured each year; however, the accumulation of plastic waste poses a critical environmental threat.¹ While combustion can be used to degrade plastics, this approach is energy-intensive and unproductive, generating greenhouse gases and nonspecific products. As an alternative, photochemical C–H activation can be used to valorize plastics into energy-dense, oxidized small molecules, which are valuable as chemical feedstocks and sustainable fuels.^{2–4} Photochemical strategies operate at mild temperatures, offering improved energy

efficiency and reduced greenhouse gas emissions. In this approach, C–H bond activation uses radical intermediates to break the challenging C–C bonds of nonbiodegradable plastics for sustainable upcycling.⁵ Photochemical plastic degradation reflects a recent and evolving research frontier. This essay highlights recent technical advancements that address United Nations Sustainable Development Goals and identifies key obstacles in scaling light-activated reactions for sustainability outcomes. This photochemical strategy directly converts plastic waste into valuable materials, helping to alleviate the global pollution crisis and support a transition to a circular economy.

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Current limitations of plastic waste management

Plastics are a diverse class of polymers with attractive features including low cost, high durability, light weight, and easy manufacturing. These properties are useful across large sectors of industry, such as healthcare, packaging, and automotive.⁶ Plastics represent a major global commodity, with the production of plastics growing at a rate of 5% each year,⁷ and a total of over 8.3 billion tons of virgin plastic material having been produced.⁸ However, plastic manufacturing and end-of-life both render significant environmental impacts. Plastic manufacturing accounts for 3.8% of global greenhouse gas emissions and approximately 6% of the

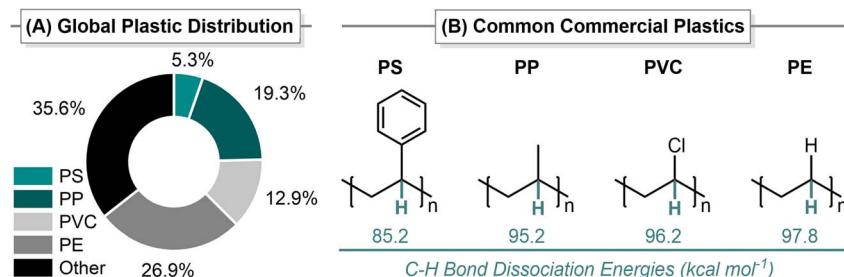


Fig. 1 (A) Nearly two-thirds of the plastic products manufactured each year are comprised of four nonbiodegradable polymers: polystyrene (PS), polypropylene (PP), poly(vinyl chloride) (PVC), and polyethylene (PE). Data obtained from Plastics Europe.¹² (B) The chemical structures of these plastics, along with their corresponding C–H bond dissociation energy values ($\text{BDE}_{\text{C}-\text{H}}$), are shown. Data obtained from Li *et al.*¹⁴

world's oil consumption,^{9,10} while over 6.3 billion tons of total plastic products have been discarded as waste.⁸ To address these concerns, researchers explore strategies to recover useful materials from plastic waste. One approach, known as chemical upcycling, aims to convert plastic waste into high-value products that can be utilized in chemical manufacturing and renewable fuels.

Plastic degradation requires cleaving structurally essential bonds along the polymer backbone or cross-links. This is straightforward in materials that contain labile C–X (X = O, N) bonds, such as polyesters and polyamides, which are readily fragmented into monomers or oligomers for chemical recycling.¹¹ In contrast, commercial plastics with structural C–C linkages represent a major hurdle in chemical recycling. As shown in Fig. 1A, global plastic manufacturing is dominated by four commodity polymers: polystyrene (PS), polypropylene (PP), poly(vinyl chloride) (PVC), and polyethylene (PE), each of which feature C–C bond backbones.¹² The strength of these plastics is valuable for commodity applications but presents barriers for waste management and recycling. While combustion can be used to break these bonds, the high energy input typically produces low-value mixtures containing gases, liquids, and coke.¹³

Photocatalytic oxidation for plastic upcycling

In recent years, photocatalysis has emerged as a powerful tool for driving

difficult chemical reactions.^{15,16} Synthetic organic chemists have identified a broad range of earth-abundant organic and transition metal catalysts that selectively cleave C–H bonds under light activation and mild conditions. This strategy has been adapted to convert commercial plastics into oxidized small molecules under ambient and O₂ atmospheres. The initial step in this process involves breaking a C–H bond, with the C–H bond dissociation energy values (BDE_{C–H}) provided in Fig. 1B. Upon light activation, the photosensitizer enters an excited state and cleaves the indicated C–H bond to generate a carbon-centered radical. This radical reacts with oxygen to form an alkylperoxy radical, which rapidly decomposes into unstable alkoxy radical species. These alkoxy radicals promote radical rearrangement and adjacent C–C bond cleavage through repeated β -scission, ultimately producing oxidized small molecule products.^{17,18} This is a promising strategy to upcycle nonbiodegradable plastics using catalysis; however, the effectiveness of this strategy depends on the polymer's chemical structure.

The photocatalytic oxidation of polystyrene (PS) into benzoic acid has the most precedent among these plastics due to its relatively weak C–H bond strength and the stabilization of radical intermediates. This approach has been explored using transition metal photocatalysts, including FeCl₃ and UO₂²⁺,^{19–23} as well as a broad range of organic additives, including *p*-toluenesulfonic acid (*p*-TsOH), fluorene, anthraquinone, and *N*-bromosuccinimide (NBS).^{18,24–26} Several investigations illustrate that light-driven

chemical recycling protocols operate successfully at the gram scale, achieving 23–40% yields as benzoyl products under an O₂ atmosphere.^{18,21}

By comparison, there are relatively few reports which demonstrate photocatalytic oxidation of the three other nonbiodegradable plastics. Photochemical oxidation of PP, PVC, and PE has been achieved using VO(acac)₂ (acac = acetylacetone) catalysts and Nb₂O₅ layers. In the presence of a 2 mol% loading of VO(acac)₂ in CH₂Cl₂, these three polymers were irradiated under a white LED light source in an O₂ atmosphere for 5 days. This resulted in the evolution of CO₂ and the production of formic acid (for PP, PVC, and PE) and acetic acid (for PP), with isolated yields ranging between 9.2–29.6%.¹⁴ In other work, the complete photodegradation of PP, PVC, and PE was observed upon irradiation with a Xe lamp for 40 to 90 hours in the presence of Nb₂O₅ and H₂O.²⁷ While CO₂ was the major product, continuing irradiation drives a cascade photocatalytic reaction to acetic acid without requiring a sacrificial reductant. Still, only trace amounts of acetic acid were detected (0.07 mg per 150 mg of PE).¹³

Scaling up photochemical plastic upcycling for global impact

Large-scale photoreactors are necessary to scale photochemical reactions for global implementation. As photochemical strategies have become widely adopted, industrial photochemical reactors can adapt bench-scale reaction strategies to kilogram-to-ton scales.²⁸ Photochemical reactions typically suffer due to the attenuating effect of light traveling through space (inverse square law) and media (the Bouguer–Lambert–Beer law).²⁹ By tailoring the number, length, and diameter of reaction channels, it is possible to increase the reaction efficiency and thermal dissipation driven by a fixed light source. This approach is valuable for photoreforming plastic waste under mild conditions, aiming to leverage fixed LED sources or solar light



to make circular recycling protocols more affordable and accessible.

Flow photoreactors are popular tools that scale photochemical reactions with sustainability benefits. This equipment features long, coiled sample channels driven by a liquid pump and maintained under controlled temperature, ensuring uniform irradiation with efficient heat and mass transfer.^{30,31} A simplified diagram of the flow setup is provided in Fig. 2. Flow setups offer decreased reaction times, reduced catalyst loadings, and controlled gas injection or removal, which provides the operator with greater control than batch chemistry protocols. In practice, flow setups have successfully generated gram-scale oxidized products from commercial plastic waste using LED irradiation, establishing that this approach is a practical strategy for waste remediation.^{21,25}

Utilizing sunlight could improve the sustainability gains of this work and eliminate the need for high-energy LED lamps. Solar photoreactors use ambient light to drive challenging chemical reactions at a reduced operational cost. Despite these advantages, most photocatalytic systems for plastic degradation use ultraviolet light, with few examples powered by visible light.^{21,25} Because visible and near-infrared light comprise a majority of the usable solar spectrum, this motivates the design and discovery of new photocatalysts that operate with low-energy light sources.

Research and technological deficits

One constraint to this approach is the limited scope of polymers that have been valorized through photooxidation, with studies commonly degrading PS. While challenging, identifying strategies to degrade PP, PVC, and PE offers significantly greater sustainability benefits. To create better catalysts, the fundamental structure–function relationships that govern intramolecular photoactivation, commonly utilizing ligand-to-metal charge transfer, are still in the early stages of understanding and development.^{22,32–35} These investments will identify methods to optimize light harvesting and photolytic quantum yields, overcoming the low light efficiency and slow reaction rates that currently plague these efforts. Finally, effective polymer degradation requires dissolving the materials, which restricts this reactivity to soluble reaction systems. Adapting these approaches to sustainable media, including saltwater or other aqueous conditions, would incorporate green chemistry strategies at a reduced environmental cost.

Both fundamental and technological investments are required to develop the infrastructure needed to translate this research into practical sustainability solutions. Here, we discuss how flow photoreactors interface with earth-abundant photocatalysts offer a green approach to convert persistent plastic

waste into valuable materials, thereby supporting global sustainability efforts. This essay highlights growing trends in harnessing photochemical activation for efficient plastic degradation. It proposes that continuing investment will translate these fundamental discoveries into sustainable solutions that benefit our communities and support a circular economy.

Conclusions

Current progress and ongoing challenges in adapting photochemical oxidation strategies to decompose plastic waste are summarized. Converting commercial plastic into targeted small molecules, such as benzoic acid, formic acid, and acetic acid, facilitates waste degradation and offers new life to this material as upcycled chemical feedstocks. In a world of mounting environmental issues from accumulating plastic waste, designing sustainable and scalable strategies to break and reuse this waste addresses essential global concerns. The widespread availability of light, oxygen, and earth-abundant photocatalysts makes this approach a powerful and practical solution for transforming plastic waste into value-added materials.

Conflicts of interest

There are no conflicts to declare.

Data availability

There is no additional data associated with this article.

Acknowledgements

No AI was used in the preparation of this essay.

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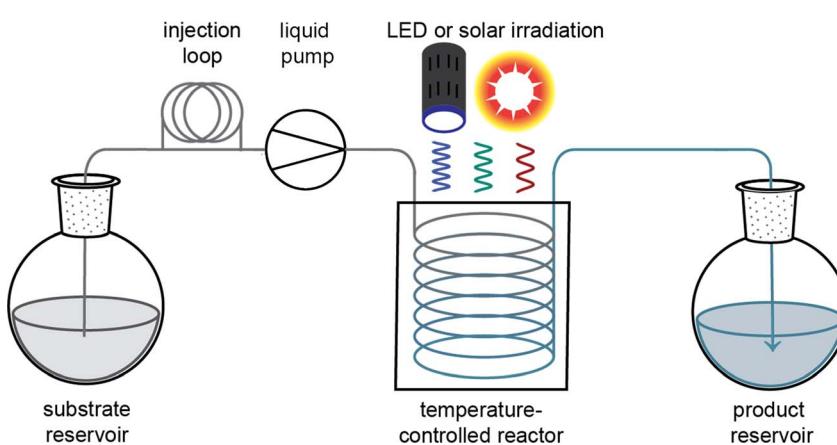


Fig. 2 A simplified diagram of a flow photoreactor setup. Flow reactions provide increased operational control for large-scale reactions, which is desirable for sustainable photocatalysis.



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