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Visible-light-driven photocatalytic depolymerization of post-consumer PET to terephthalic acid *via* cerium catalysis with batch-to-flow scalability†

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Polyethylene terephthalate (PET), as one of the five major engineering plastics with an annual production exceeding 80 million metric tons, has created escalating environmental challenges. Currently, approximately 79% of discarded PET is treated through landfill or incineration, while conventional chemical recycling technologies (*e.g.*, hydrolysis and alcoholysis) require harsh conditions such as high temperature, high pressure, and highly corrosive media, leading to issues including high energy consumption, severe equipment corrosion, and secondary pollution. This study pioneers a cerium-based photocatalytic system, achieving for the first time the efficient depolymerization of PET waste under visible-light-driven conditions. At ambient temperature and pressure, the cerium trichloride (CeCl₃)

photocatalyst activates visible light to depolymerize post-consumer PET (including plastic bottles and textile fibers) into high-purity terephthalic acid (PTA) without requiring strong alkali pretreatment, overcoming the equipment corrosion challenges inherent in conventional photocatalytic reforming technologies that rely on concentrated alkaline solutions. An innovatively designed microchannel reactor system leverages its high surface-to-volume ratio to enhance light utilization efficiency while resolving optical path decay issues, providing an engineered solution for large-scale processing. This breakthrough establishes a sustainable pathway for PET circular economy, addressing critical limitations of existing physical and chemical recycling methods.

Green foundation

1. Global production of non-degradable petrochemical plastics poses urgent environmental challenges. Our approach combines microfluidic and photocatalytic technologies to enable efficient plastic recycling, simultaneously addressing pollution mitigation and carbon reduction.
2. The developed process reduces the reaction time from 24 hours to 45 minutes while operating at room temperature, achieving energy conservation and emission reduction. This temperature–time optimization facilitates industrial scale-up potential.
3. Subsequent research focuses on optimizing the reaction system using greener alternatives while maintaining process scalability. The methodology demonstrates technical feasibility for transforming plastic waste streams through energy-efficient depolymerization pathways.

Introduction

PET, as one of the five major engineering plastics with an annual production exceeding 80 million tons, has created escalating environmental challenges due to its widespread use in

beverage bottles and textile fibers.^{1,2} Currently, approximately 79% of discarded PET is treated through landfill or incineration,^{3,4} while conventional chemical recycling technologies (*e.g.*, hydrolysis and alcoholysis) require harsh conditions such as high temperature (>150 °C), high pressure (>2 MPa), and highly corrosive media (18.4 M sulfuric acid/5 M sodium hydroxide), leading to issues including high energy consumption, severe equipment corrosion, and secondary pollution (Fig. 1a).^{5–7} The recycling and upcycling of polymeric materials have emerged as a transformative technological paradigm,^{8–11} particularly manifesting in catalytic hydrogenolysis and photoreforming strategies for PET (Fig. 1b). This methodology employs either homogeneous Ru-based systems^{12–14} or heterogeneous catalysts^{15–20} to selectively cleave C–O bonds in PET backbones. Nevertheless, current

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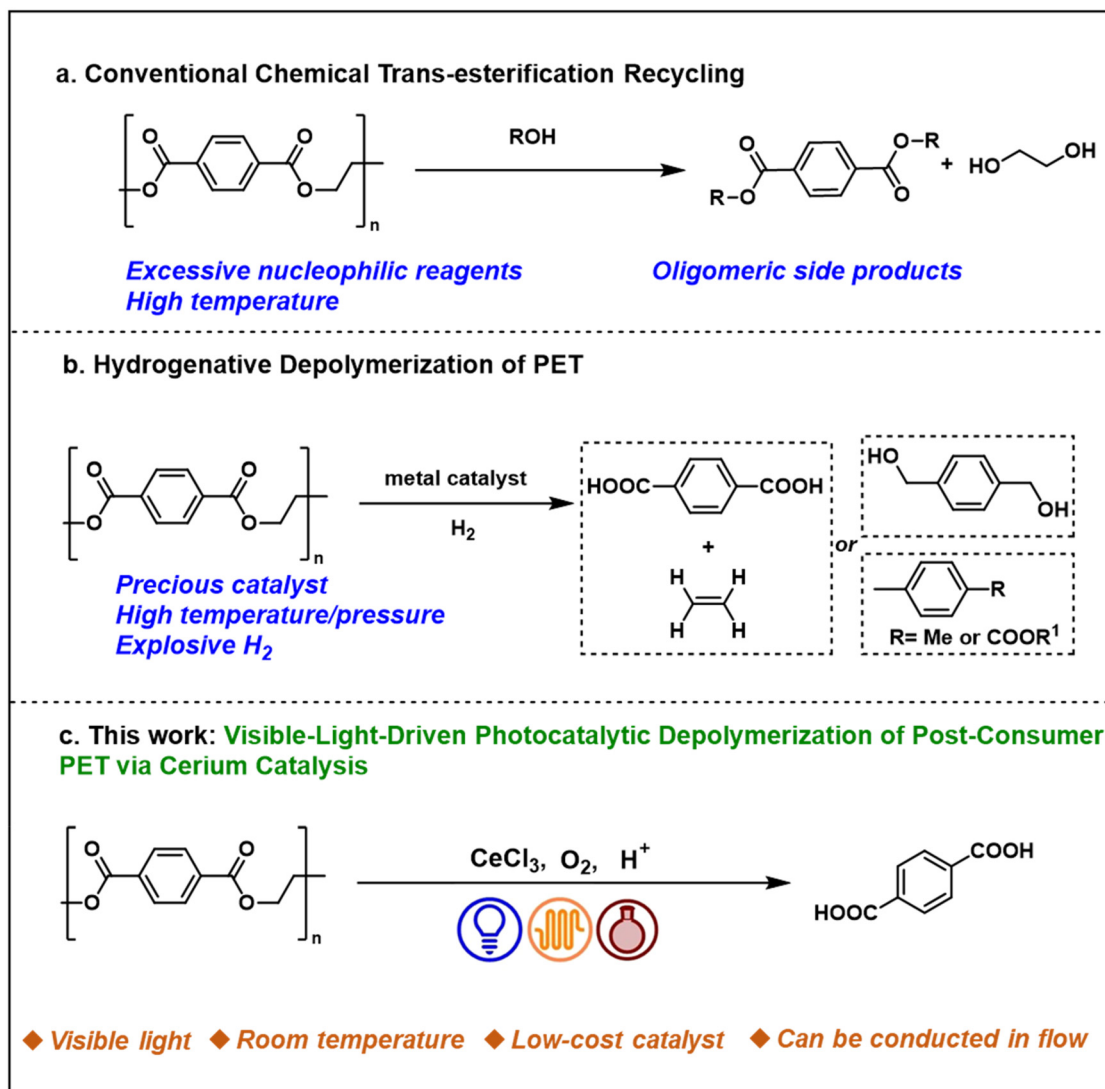


Fig. 1 Polyethylene terephthalate recycling. (a) Chemical *trans*-esterification recycling. (b) Hydrogenative depolymerization of PET. (c) Visible-light-driven photocatalytic depolymerization of post-consumer PET via cerium catalysis.

implementations require operationally demanding conditions, including elevated temperatures (>120 °C) and/or high-pressure hydrogen environments (>5 bar), and precious metal-based catalytic systems.

Photocatalytic conversion, driven by solar energy, presents a promising sustainable option. Unlike traditional photodegradation, it enables selective conversion of plastics into high-value chemicals by precisely activating chemical bonds, offering a pathway for efficient plastic upcycling under ambient conditions.²¹ However, such reactions often require acid or alkaline pretreatment, elevated temperatures, or UV lamp irradiation.

To address the global plastic waste crisis, we propose a photocatalytic strategy for the degradation of waste PET under ambient conditions. Recent advances highlight rare earth complexes as cost-effective and accessible catalysts for such transformations.^{22,23} Cerium-based systems, derived from the

most abundant rare earth element, are particularly attractive due to their unique redox versatility (Ce(III)/Ce(IV) interconversion) and tunable photophysical properties.^{24,25} These characteristics have positioned cerium catalysts at the forefront of photoinduced organic synthesis.²⁶ While cerium-based catalysts have achieved remarkable progress in photocatalytic activation of sp³ C–H bonds in small molecules,^{27–29} their application in polymer depolymerization—particularly for plastic waste valorization—remains underexplored to date. Building on cerium-mediated ligand-to-metal charge transfer (LMCT) processes—a mechanism leveraged in diverse light-driven reactions—we report an efficient photocatalytic protocol for PET depolymerization. Our method employs a low-loading cerium catalyst, molecular oxygen, and hydrochloric acid under mild conditions to achieve high-yield recovery of PTA, even from blended PET substrates.

Results and discussion

The study commenced with commercial PET ($M_w = 15$ kDa) as the model substrate, utilizing hexafluoroisopropanol (HFIP) as the solvent due to its superior room-temperature solubility for PET (Table 1). Under ambient conditions (25 °C), a reaction system containing the CeCl_3 catalyst, HCl, and O_2 , irradiated with a 450 nm LED, achieved a 91% yield of PTA. To mitigate the environmental risks associated with HFIP (a fluorinated compound with bioaccumulative and recalcitrant properties), the solvent was efficiently recovered after the reaction *via* rotary evaporation, leveraging its low boiling point (58–60 °C). Experimental results demonstrated that the recycled HFIP maintained an 85% product yield in subsequent reactions, confirming its stability and reusability. This recovery strategy not only reduced the emission risks of fluorinated solvents (aligning with wastewater treatment protocols for distillation-based recovery) but also significantly lowered experimental costs. Furthermore, process optimization (*e.g.*, precise control of distillation temperature and pressure) could enhance both the purity of recycled HFIP and overall reaction efficiency.

Control experiments elucidated critical reaction dependencies. Trace product formation (<5%) occurred in the absence of CeCl_3 , suggesting that HCl may initiate structural disruption of PET through crystal lattice breakdown and dissolution/swelling phases, enabling limited photochemical depolymerization under O_2 and light (entry 2). Conversely, omitting HCl, O_2 , or light irradiation entirely suppressed PTA formation (entries 3–5). Catalyst screening revealed inferior performance for alternative cerium species and the reported FeCl_3 catalyst (Table S1†), yielding PTA ranging from 49% to 58%, underscoring the unique efficacy of CeCl_3 . We screened light sources of different wavelengths and found the highest PTA yield under 450 nm irradiation (Table S2†). We also attempted to reduce

the amount of hydrochloric acid. When using 0.25 equivalents of HCl, the yield of PTA decreased to 81%. Therefore, we ultimately chose to use 0.5 equivalents of HCl (Table S3†). The HCl stoichiometry screening revealed an optimal PTA yield at 0.5 equivalents of HCl, with further increases in HCl loading resulting in diminished product formation (Table S4†). Temporal optimization studies demonstrated negligible yield improvement upon extending the reaction duration beyond 24 hours (91% at 24 h *vs.* 92% at 36 h), thus establishing 24 h as the operationally optimal timeframe (Table S5†).

To systematically evaluate the engineering applicability of this strategy, we optimized the reaction system in a microchannel reactor (Table S6†) and successfully achieved continuous-flow depolymerization of various beverage bottles and polyester fiber waste (Fig. 2). Results demonstrated that these types of complex plastic waste could be efficiently converted into target products within 45 minutes. This outcome validates the industrial scalability advantages of the proposed strategy in shortening reaction cycles, enhancing process controllability, and reducing energy consumption.

Given the inherent complexity of real-world PET waste—such as post-consumer polyester–cotton textiles and packaging bottles contaminated with impurities (*e.g.*, dyes, non-PET polymers)—we applied our optimized catalytic system to authentic substrates (Fig. 2).

Remarkably, diverse PET-based materials, including colored beverage bottles (tea, coffee, water), milk bottles, storage containers, lids, and vegetable packaging boxes, were efficiently depolymerized to PTA with yields of 78–95% under standard conditions after minimal pre-processing (shredding *via* high-speed milling). Furthermore, blended fabrics (100% PET fiber; PET–cotton hybrids: 65–80% PET; PET–rayon–spandex composites: 74.5% PET, 21.5% rayon, 4% spandex) also exhibited robust compatibility, achieving PTA yields of 78–95%.

Table 1 Optimization of reaction conditions^a

Entry	Modification of reaction conditions	Yield ^b (%)
1	None	91 (85) ^c
2	Without CeCl_3	Trace
3	Without HCl	n.d.
4	Without 450 nm LEDs	n.d.
5	Without O_2	n.d.
6	CeF_3 instead of CeCl_3	51
7	CeO_2 instead of CeCl_3	58
8	$\text{Ce}(\text{SO}_4)_2$ instead of CeCl_3	49
9	Reaction time was 8 h	21

^a Reaction conditions: polyethylene terephthalate (0.25 mmol), CeCl_3 (1 mol%), HCl (50 mol%), HFIP (2.0 mL), O_2 (1 atm), irradiation under 450 nm LEDs, 24 h, 25 °C. ^b The yields were calculated based on isolation. n.d. = no detected. ^c Use of recycled HFIP.

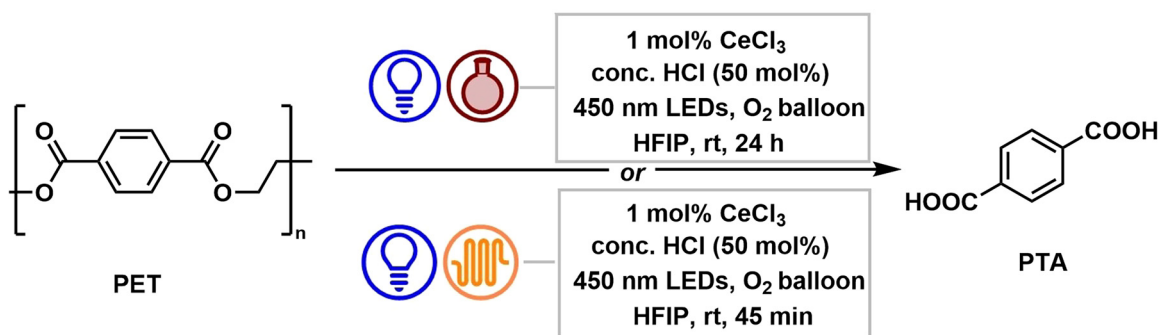


Fig. 2 Oxidative depolymerization of PET materials in batch^a and flow^b. ^aPolyester material (0.25 mmol, accounting for the repeat unit), CeCl₃ (1 mol%), HCl (50 mol%), HFIP (2.0 mL), 1 atm of O₂, irradiation under 450 nm LEDs, 24 h, 25 °C. The yield was calculated based on isolation. ^bPET (0.5 mmol), CeCl₃ (1 mol%), conc. HCl (50 mol%), HFIP (10.0 mL) at room temperature (25 °C), blue LEDs (450 nm, 50 W), isolated yield.

These results validate the system's tolerance to structural and compositional heterogeneity in practical PET waste streams.

To elucidate the reaction mechanism, preliminary mechanistic studies were conducted. The addition of radical scavengers (TEMPO or BHT) to the standard reaction system completely inhibited product formation (Fig. 3a and b), strongly suggesting

the involvement of radical intermediates. Furthermore, to probe the fate of the ethylene glycol moiety within the PET polymer chain during oxidative degradation, post-reaction mixtures were treated with 1.5 equiv. of aniline to trap potential oxidation products. Subsequent high-resolution mass spectrometry (HRMS) analysis unambiguously detected formamide (Fig. 3c), indicat-

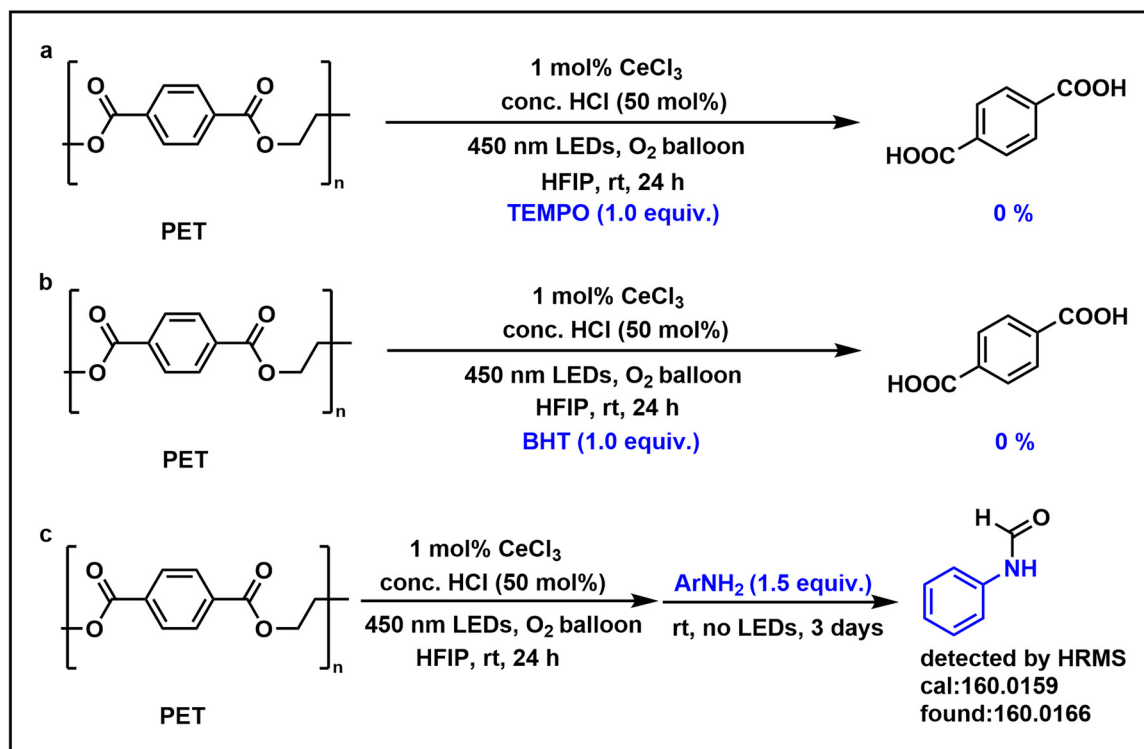


Fig. 3 Mechanistic studies.

ing that the methylene groups in PET underwent deep oxidation to generate formic acid. Finally, to evaluate changes in surface hydrophilicity during the depolymerization process, we measured the water contact angles of pristine PET and its degradation products (Fig. S5†). After 24 hours of degradation, the contact angle decreased significantly from 77.4° to 59.6° , indicat-

ing that oxidative cleavage of the polymer backbone led to substantial generation of hydrophilic functional groups, such as hydroxyl and carboxyl moieties.

Based on experimental evidence and prior literature,²⁹ we propose a plausible reaction mechanism (Fig. 4). Photoexcitation of Ce(IV) initiates LMCT, generating a chlorine radical (Cl^\cdot) and

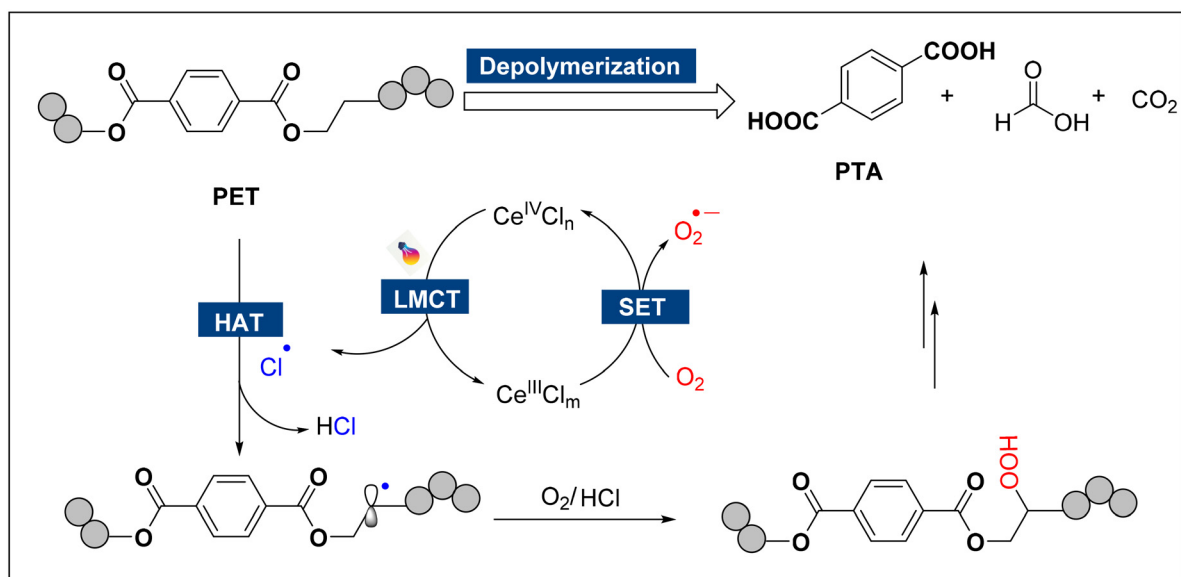


Fig. 4 Plausible mechanism.

reduced Ce(III). Hydrogen atom transfer (HAT) then happens from an sp³ C–H bond within the PET polymer chain to the chlorine radical, forming an alkyl radical intermediate. This intermediate subsequently reacts with molecular oxygen (O₂) to yield a peroxide species. Under acidic conditions (HCl), the peroxide undergoes cleavage, depolymerizing into low-molecular-weight products such as PTA and formic acid. Concurrently, single-electron transfer (SET) from Ce(III) to oxygen regenerates the active Ce(IV) species, closing the catalytic cycle.

Conclusions

We have developed a highly efficient oxidative depolymerization process for PET using an earth-abundant cerium-based catalyst (CeCl₃) at ultralow loading (≤1 mol%) under ambient-temperature and visible-light conditions. This system enables the selective conversion of both pristine commercial PET and post-consumer PET waste (e.g., textiles, packaging) into high-value PTA with near-quantitative yields. Preliminary validation in a continuous-flow microchannel reactor underscores its industrial scalability. By integrating resource-efficient catalysis with scalable reactor design, this work provides an innovative solution for establishing a closed-loop PET recycling framework, offering significant environmental benefits through reduced energy consumption and plastic pollution mitigation.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interest.

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