

Micromachines for Microplastics Treatment

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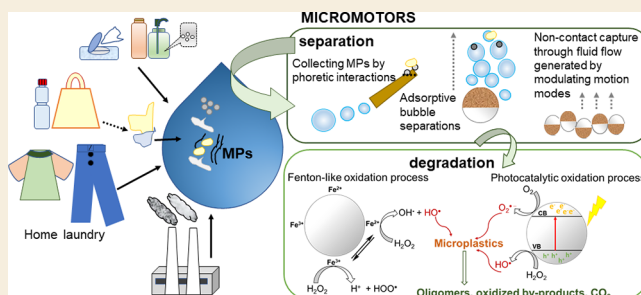
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ABSTRACT: The increasing accumulation of persistent non-degradable microplastics in the marine environment represents a global environmental problem. Among emerging approaches to tackle microplastics are micro- and nanomotors, tiny devices capable of autonomous propulsion powered by chemical fuels or light. These devices are capable of on-the-fly recognition, capture, and decomposition of pollutants. In the past, various micromotors were designed to efficiently remove and degrade soluble organic pollutants. Current effort is given to the rational design and surface functionalization to achieve micromotors capable of capturing, transporting, and releasing microplastics of different shapes and chemical structures. The catalytic micromotors performing photocatalysis and photo-Fenton chemistry hold great promise for the degradation of most common plastics. In this review, we highlight recent progress in the field of micromotors for microplastics treatment. These tiny self-propelled machines are expected to stimulate a quantum leap in environmental remediation.

KEYWORDS: microplastics, micromotors, microrobots, degradation, catalysis, nanorobots



1. INTRODUCTION

Microplastics (MPs) are significant waste contaminants that persistently remain in aquatic environments. They are considered as solid plastic particles (1 μm to 5 mm)¹ and are a result of both commercial product development (primary origin) and the mechanical fragmentation of larger plastic waste (secondary origin).² In addition to being pollutants themselves, MPs are extensively discussed and studied as possible vectors of chemical additive transport with a negative impact on ecosystems and human health.³ Through their occurrence in edible aquamarine animals, such as shellfish species, they can enter the food web and, consequently, affect food security.⁴ Considering the plastic market volume production, the largest volume commodity thermoplastics can be mostly detected as the main candidates in MP populations.⁵ An analytical study of MPs floating along the coastline of the Mediterranean Sea showed that low-density polyethylene (LDPE) and high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PS)-based MPs dominate (80%) among the collection of samples.⁶ All of these plastics consist of long polymer chains and are precisely engineered and processed to be functional for a prolonged period. In addition to their polymeric structure, the plastics' additives and stabilizers provide MPs with stability against oxidation, which means lack of functional groups cleavable by hydrolysis and/or enzyme action.⁷

Among the treatment technologies for MP pollution, membrane separations that combine filtration-based technologies are most successful in wastewater treatment plants to

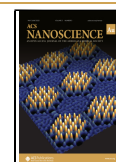
collect and remove MPs,^{8–11} followed by microbial and/or chemical treatment to induce their degradation. Among advanced water remediation approaches, micromotors have received much attention as an emerging tool for enabling environmental sensing and pollutant removal or degradation.¹² This new generation of artificial devices is purpose-made to be capable of converting local chemical energy or the energy of external fields (magnetic, electric) or light into autonomous motion¹³ and to perform specific tasks in aqueous environments.^{14,15} Typically, micromotors have been designed with various geometrical shapes including nanowires with helical, tubular, and spherical Janus-like shapes.¹⁶ For various water remediation tasks, chemical- (hydrogen peroxide) and light-driven micromotors have been extensively studied.¹⁷ Compared to static counterparts, the micromotors through autonomous propulsion induce a micromixing effect, which promotes the mass transfer in their microenvironment and enhances removal of targeted pollutant molecules in the solution.¹⁸ The work of Wang's group proved the positive contribution of H₂O₂-driven tubular micromotors with oxygen bubble propulsion to enhanced decontamination of organophosphate nerve agents without the need for external stirring.¹⁹

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Scheme 1. Micromotors as Efficient Tools for Microplastics Separation and Degradation

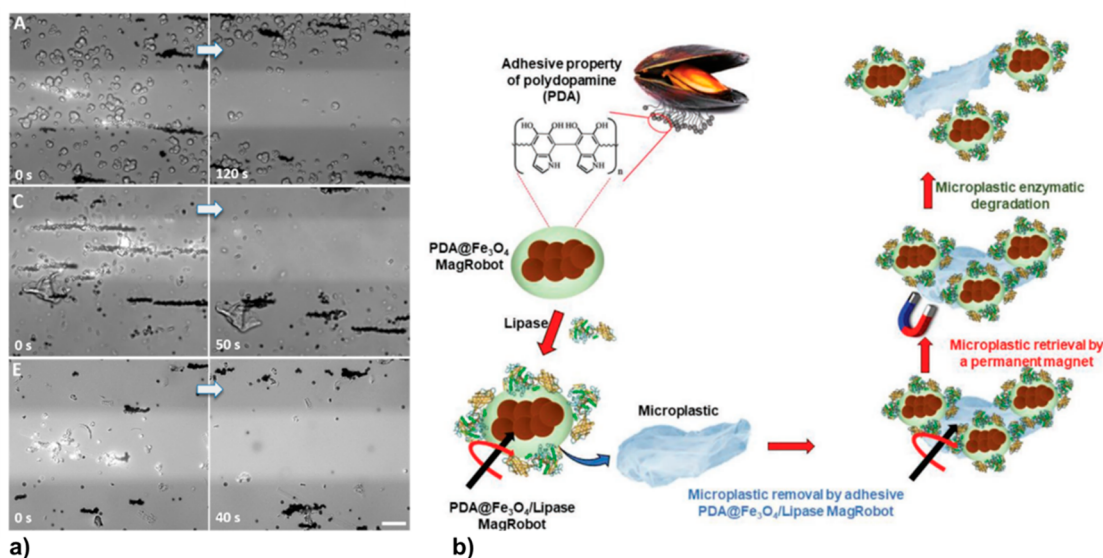
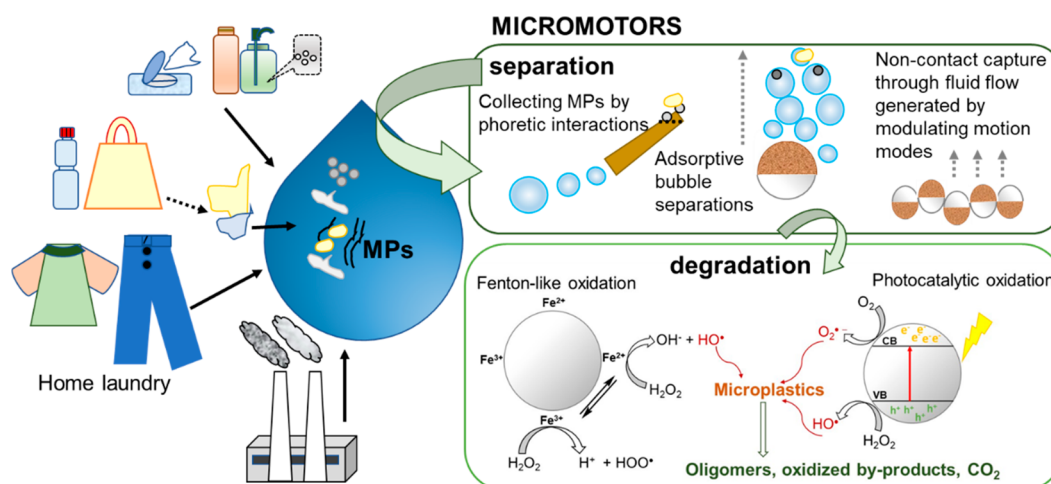


Figure 1. Capture of microplastics with active microrobots. (a) Mechanical removal of microplastics with photocatalytic microrobots. Magnetic Au@Ni@TiO₂ chains remove different extracts under the magnetic field in different conditions: (A) washing powder in 0.1% H₂O₂ under 63 mW UV light; (C) face cleansing cream sample in 0.2% H₂O₂ under 63 mW UV light; and (E) microplastic sample from Warnow River in H₂O₂ under 315 mW UV light. Reprinted from ref 38. Copyright 2019 American Chemical Society. (b) Magnetically powered microrobots containing mussel inspired adhesive for “gluing” microplastics. Reprinted with permission from ref 45. Copyright 2021 Wiley-VCH GmbH.

In addition to a microstirring function, the catalytic micromotors can act as environmental microcleaners as H₂O₂ is recognized as a green oxidant for wastewater treatments.²⁰ Tubular biotemplated Fe₃O₄–MnO₂ micromotors were shown to decompose H₂O₂, generating both oxygen bubbles for self-propulsion (up to 615 μm·s⁻¹) and hydroxyl radicals for rapid removal of organic dye from real wastewater.²¹

An additional advantage of micromotors lies in the versatility of their composition and possibility to functionalize and/or modify their surface to achieve adsorption capability or targeted pollutant recognition. With the introduction of *n*-alkanethiols with different chain lengths, the micromotors' surface can be modified to be superhydrophobic and hence to capture hydrophobic pollutants with an “on-the-fly” mechanism. The study of Guix et al. proved the superhydrophobic layer-coated Au/Ni/PEDOT/Pt microtubes as efficient oil adsorbents (PEDOT = poly(3,4-ethylenedioxythiophene)).²² By versatile fabrication technologies, micromotors can be

designed to perform Fenton reactions, UV–vis illumination combined with the Fenton reaction, and heterogeneous photocatalysis.^{23–25} This makes the catalytic micromotors promising tools that can be integrated with advanced oxidation processes^{26–28} in wastewater treatments to reduce operational cost. Moreover, micromotors can assemble into a swarm, performing collective behavior, and by following a chemical gradient or under magnetic and light fields, they can move to the targeted area, which is difficult to reach.²⁹ This provides the micromotors with a great promise to resolve complex environmental tasks in real-world wastewater. The review highlights current research in micromotors designed to load and/or degrade MPs as persistent solid pollutants in a water environment (Scheme 1).

2. MICROMOTORS FOR MICROPLASTICS SEPARATION

Catalytic micromotors based on manganese dioxide (MnO_2) have received considerable attention due to their low cost, facile synthesis, the possibility of being prepared with various geometrical designs, and efficient bubble propulsion up to $\sim 1600 \mu\text{m}\cdot\text{s}^{-1}$ in solution with hydrogen peroxide as a fuel.^{30,31} The dual capability of performing both adsorptive bubble separations (ABS) of dyes and solids as well as the catalytic degradation of various organic dyes makes these micromotors promising candidates for treatments in wastewater remediation.³² MnO_2 is among the transition metal oxides that perform Fenton-like reactions; due to the combination of ABS and catalytic degradation, the MnO_2 micromotors were shown to remove 90% of organic dye in 60 min.³³ Moreover, the degradation of organic dyes is enhanced under alkaline conditions.³⁴ Considering the occurrence of such alkaline fields in activated sludge, the micromotors could have utilization for the treatment of organic pollutants in aeration and sedimentation tanks.³⁵

The combination of MnO_2 and ferromagnetic materials provide micromotors with bubble propulsion owing to hydrogen peroxide decomposition and the capability to be recovered by magnets and even magnetically steered by an external magnetic field. Magnetic $\text{Fe}_3\text{O}_4\text{-MnO}_2$ and $\text{Fe}_2\text{O}_3\text{-MnO}_2$ micromotors with core-shell geometry were fabricated by hydrothermal reaction and heat treatment methods.³⁶ When added to a dye solution, most dye molecules were removed by the ABS mechanism at the beginning. Based on the UV-vis measurement of dye solution absorbances, it was shown that the amount of 0.1 g/L $\text{Fe}_2\text{O}_3\text{-MnO}_2$ micromotors reached more than 90% dye removal efficiency in 2 days. In addition to ABS at the beginning, continual catalysis of dye degradation occurred based on an oxidative radical mechanism. Moreover, through the ABS mechanism, $\text{Fe}_2\text{O}_3\text{-MnO}_2$ micromotors collected about 10% of the suspended PE microplastics (5 g/L) of irregular shape and porous surface from simulated wastewater. This separation occurs due to hydrophobic interactions; suspended plastic microparticles in aqueous medium are generally vulnerable to adhere to air microbubbles that vertically flow in the vessel.³⁷ Considering the fact that the majority of MPs are hydrophobic, they can be selectively collected by this way and floated to the water's surface.

Photocatalytic Janus-like Au@Ni@TiO_2 -based micromotors are actively propelled both in water ($\sim 15 \mu\text{m}\cdot\text{s}^{-1}$) and in 0.1% H_2O_2 solution ($\sim 66 \mu\text{m}\cdot\text{s}^{-1}$) under UV illumination.³⁸ The performance of the micromotors to load MPs was studied on commercially supplied polystyrene microparticles, primary MPs isolated from products of personal care, and MPs collected from the Baltic Sea and Warnow River (Figure 1a). Individual micromotors were shown to collect primary MPs of various shapes from extracts by performing phoretic motion in hydrogen-peroxide-enriched solutions. More importantly, when micromotors were assembled into long chains, they were able to collect MPs by the shoveling effect under UV illumination and external magnetic field. The chains resulted from the magnetic attraction between Ni components of individual micromotors.

The removal of MPs by an adsorption utilizing adsorbents means an important approach in wastewater treatment.³⁹ To achieve efficient capturing performance of adsorbents or

filtration membranes, mussel-inspired surface engineering is one of the highly emerging strategies.⁴⁰ This approach is inspired by the strong adhesion of marine mussels' foot to various surfaces including plastics like inert Teflon.^{41,42} The binding mechanism to plastics is explained mostly by hydrophobic interactions, which was proved by the strong adhesion of mussel foot protein to CH_3 -terminated surfaces,⁴³ with a contribution of cation- π interaction and π - π benzene stacking in the case of PS.⁴⁴ Mussel-inspired magnetic micromotors were fabricated by deposition of polydopamine coating onto the surface of Fe_3O_4 particles.⁴⁵ The polydopamine layer was synthesized by oxidative polymerization of monomeric dopamine in alkaline solution. Under exposure to a transversal rotating magnetic field, the micromotors were propelled following a linear trajectory and collected PCL and PP-based MPs of a broad range of sizes and irregular shapes. Moreover, a lipolytic enzyme was immobilized in the polydopamine surface of the micromotors, providing them with the capability to degrade model bioplastic PCL after polymer capturing (Figure 1b). This proof-of-concept suggests that, in the case of cutinase-like enzymes,⁴⁶ the micromotors could become a promising tool for the capture and degradation of PET-based MPs.

Taking inspiration from nature, sunflower pollen grains were utilized as scaffold structures to achieve hollow hedgehog-like micromotors ($\sim 30 \mu\text{m}$ diameter) with the capability of adsorbing floating oil.⁴⁷ Pollen grains are natural microcapsules with excellent intrinsic properties for wastewater treatments as they are highly oleophilic.⁴⁸ By introduction of a nickel layer into the micromotor structure, it was possible to assemble single micromotors into chains performing wobbling and rolling motions under an external magnetic field. Consequently, symmetric and asymmetric fluid fields were created, enabling the push and release of polystyrene particles (100 μm) as a model cargo. Micromotors were further tested for removing MPs extracted from a face cleansing cream sample, achieving a removal efficiency of $\sim 75\%$. In the case of micromotors tested for MPs captured in sea wastewater, the removal efficiency was $\sim 70\%$. In addition to solid particles, the micromotors collectively captured and transported oil droplets (200 μm), and in the case of the water/oil interface, the oil adsorption at the micromotor's spinning was up to $9 \text{ g}\cdot\text{g}^{-1}$. To summarize, these micromotors have potential for wastewater treatments owing to their low-cost and available sources, resistance to low and high pH fields, and recyclability by ethanol washing and drying for up to six cycles.

3. MICROMOTORS FOR MICROPLASTICS DECOMPOSITION

3.1. Photocatalytic Micromotors

Micro- and nanomotors containing a semiconductive material component with a well-established band gap are considered as light-harvesting machines, autonomously propelling in a water and H_2O_2 -enriched environment by taking advantage of the photocatalytic reaction.⁴⁹⁻⁵¹ These micromotors are essentially asymmetrically designed as either Janus-like spheres or microtubes to gain thrust from local concentration gradients or to autonomously propel through bubble recoil, respectively. Principally, by excitation of the photocatalytic part of micromotors through light (UV, NIR, visible) illumination, electron-hole pairs are generated. These pairs are assumed to react with water and oxygen molecules adsorbed on the

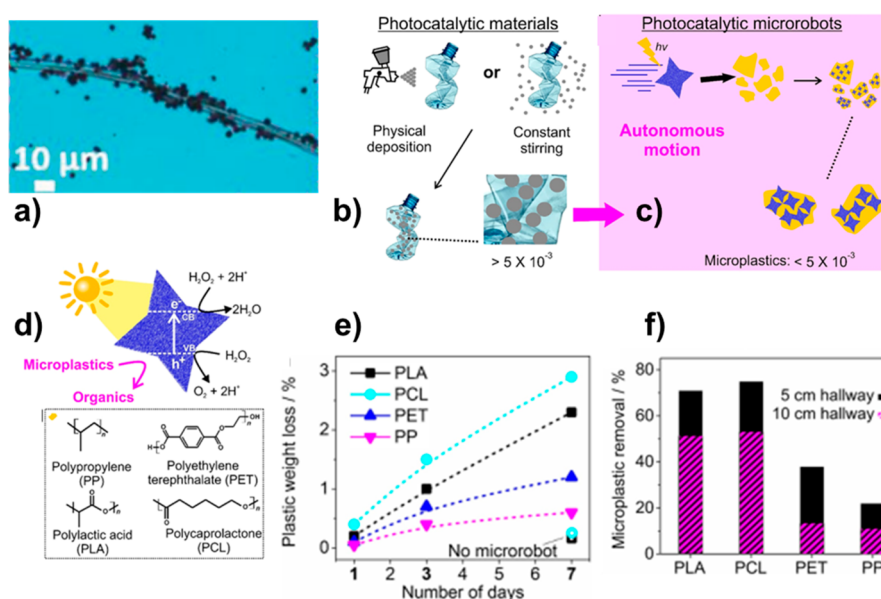


Figure 2. Light-driven microrobots photocatalytically degrading microplastics. (a) Bi_2WO_6 light-driven microrobots swarming on polymer textile fiber and degrading it. Reprinted with permission from ref 54. Copyright 2020 Wiley-VCH GmbH. (b) Conventional methods providing maximum contact between BiVO_4 microrobots and waste as physical deposition and constant stirring techniques. (c) Autonomous motion of BiVO_4 microrobots (blue) under sunlight to attach to floating microplastics (yellow). (d) Self-propulsion of BiVO_4 microrobots and the polymeric (micro)plastic waste investigated. (e) Weight loss of microplastics after 1, 3, and 7 days of treatment by microrobots in 7 mL of aqueous solution (0.01 wt % H_2O_2). (f) Efficiency of the collection of different microplastics including PLA, PCL, PET, and PP in 5 (black) or 10 cm (magenta) channels. Reprinted from ref 57. Copyright 2021 American Chemical Society

micromotors' surface, yielding charged species. Because of the Janus-like design, H^+ ions accumulate on the semiconductor's hemisphere, while electrons accumulate on the opposite, typically noble-metal-based hemisphere (Au, Pt) of the micromotor. The resulting charge separation builds up a local electrical field around the semiconductor/metal micromotors, thereby inducing their self-electrophoretic locomotion.⁵²

Among Aurivillius-based compounds, bismuth tungstate (Bi_2WO_6) has been extensively studied as an attractive visible-light-activated photocatalyst for environmental remediation.⁵³ The fabrication of perovskite-like Bi_2WO_6 micromotors consisted of nanoparticle self-assembly into 3D microspheres, which through the Ostwald ripening process afforded the resulting 3D structures ($\sim 7 \mu\text{m}$) with a heterogeneous surface.⁵⁴ The resulting micromotors autonomously propelled at the rate $1.9 \pm 0.3 \mu\text{m}\cdot\text{s}^{-1}$ under visible light illumination in aqueous media. Moreover, under prolonged illumination, individual micromotors agglomerate and move together due to chemical gradients resulting from asymmetric distribution of ionic species released during photocatalytic reaction.⁵⁴ Considering the high oxidizing potential of these species, the micromotors were studied to degrade commercial baby wipes as a representative of wet wipe fabric composed of PP, modified cellulose, and additives. Wet wipes and sanitary towels are among personal care textile products which, after being flushed down toilets, become an important source of waste MP fibers in aquatic systems.⁵⁵ After 50 h of prolonged light illumination, the micromotors actively attached to the surface of textile fibers (Figure 2a) to degrade them, as evidenced by their cracking and the development of larger holes. The occurrence of oxidative degradation reactions was evidenced by both identifying newly developed aldehyde, ketone, and carboxyl functional groups onto treated textile

fibers and by releasing CO_2 as a final mineralization product during the interaction between micromotors and fibers.

To achieve the capability of magnetic separation, visible-light-driven BiVO_4 micromotors with a star shape⁵⁶ were decorated with Fe_3O_4 nanoparticles (Figure 2b–f).⁵⁷ Micromotors were shown to adsorb on the surface of PLA and PET pieces ($\sim 70\%$ coverage) during their phoretic motion in a Petri dish and successfully removed about 70% of dispersed PLA and PCL-based MP pieces in a 5 cm long channel. The micromotors initiated the oxidative degradation process on polymer pieces as evidenced by the occurrence of newly formed oxygen functional groups and polymer mass loss. This is particularly important for the recycling of PLA, the degradation of which in artificial seawater and realistic seawater environments was found to be almost negligible from 180 days to even 1 year of exposure.⁵⁸ With the micromotor treatment, the mass loss of PLA to 3% was achieved in 1 week. The removal of microplastics was also tested in microchannels to simulate confined environments.

The photocatalytic degradation of plastics has been gradually proved as an efficient approach among existing microplastics treatments.⁵⁹ The semiconductor material is excited under proper wavelength with the yield of photo-generated pairs of electrons and holes $e_{\text{CB}}^-/h_{\text{VB}}^+$ (CB = conduction band, VB = valence band). Valence band holes h_{VB}^+ react with adsorbed molecules of water and hydroxyl groups on the surface of heterogeneous photocatalyst, producing hydroxyl radicals ($\text{HO}\cdot$).⁶⁰ At the same time, electrons e_{CB}^- reduce O_2 in the solution to form superoxide anion ($\text{O}_2^{\cdot-}$), which undergoes reaction with water, affording hydroperoxyl radicals ($\text{HOO}\cdot$). Subsequently, hydrogen peroxide results from the coupling of two hydroperoxyl radicals. Both hydroxyl and superoxide anions⁶¹ are considered

as two of the most important radicals in free radical chemistry and can effectively oxidize organic compounds and plastics.⁶²

Current knowledge on the mechanisms of microplastics' oxidative degradation by photocatalysts has been summarized by Ricardo et al.²⁸ Hydroxyl radicals attack the C–H bonds of polymer chains and, by abstracting H atoms, generate carbon-based alkyl radicals that immediately react with O₂ to form peroxy radicals (–COO•). Peroxy radicals turn into hydroperoxides by abstracting H atoms from other polymer chains. By cleavage of the –O–O– bond, hydroperoxide dissociates to hydroxyl and alkoxy radicals, which can then undergo β-scission to fragments with aldehyde, ketone, and vinyl end groups.^{63,64}

3.2. Micromotors Performing Fenton-like Oxidation of Microplastics

The Fenton reaction, first reported in 1894, concerns the generation of hydroxyl radicals (HO•) by the reaction of hydrogen peroxide with Fe²⁺ or, less frequently, Fe³⁺ cations in the presence of a catalyst in an acidic environment.^{65,66} Because Fe²⁺ ions are oxidized during the reaction, their regeneration should be maintained to prevent their depletion. During the photo-Fenton process, Fe²⁺ ions are photochemically regenerated, and then the reactions continue like in the conventional “dark” Fenton process.⁶⁷ Principally, photo-Fenton reactions utilize light energy (visible light/UV light irradiation) to accelerate the reduction of accumulated Fe³⁺ cations or to promote the ligand-to-metal charge transfer in [Fe(OH)]²⁺ complexes, yielding in both cases Fe²⁺ cations. Despite their efficiency, conventional, homogeneous Fenton and photo-Fenton reactions are limited due to the requirement of acidic conditions and removal of Fe-based precipitates, which represents additional pretreatment and post-treatment steps in wastewater remediation. Micromotors performing Fenton-like oxidation can be considered as heterogeneous Fenton catalysts acting mostly on the surface of bulk material.⁶⁸ For hematite (α-Fe₂O₃), it was shown that Fe²⁺ ions confined on the hematite facets can significantly enhance OH• radical generation compared to materials with unconfined counterparts.⁶⁹ Moreover, iron ions leaked out from the solid catalyst could contribute to a homogeneous Fenton process, enhancing the whole degradation process.^{70,71} Current state-of-the-art heterogeneous Fenton catalysts, including mechanism pathways of OH• generation, were thoroughly reviewed by Pillai et al.⁷¹

The hydroxyl radical (HO•, 2.8 V vs normal hydrogen electrode) is considered as one of the most powerful oxidizing agents in nature, capable of attacking and degrading various organic pollutants including plastics in the environment.^{72–74} The effectiveness of photo-Fenton chemistry for microplastics degradation was proved on chemically activated polymers previously. Sulfonated virgin PE and PE waste (LDPE, HDPE),⁷⁵ sulfonated PS,⁷⁶ PP, and PVC⁷⁷ were shown to undergo partial oxidation after FeCl₃ grafting, producing low-molecular-weight organic molecules and CO₂.

Hematite (α-Fe₂O₃) is a known n-type semiconductor with a band gap energy of about 2.0 eV that has emerged as a photocatalyst for photoelectrochemical water splitting.⁷⁸ It is recognized as a catalyst of Fenton and photo-Fenton reactions in which hydroxyl radicals are produced by light, iron, and hydrogen peroxide. Moreover, hematite nanoparticles are among the most promising metal oxides with the capability of organic dye adsorption and inorganic impurity removal in

water remediation application.⁷⁹ Hematite peanut-shaped micromotors displayed self-propulsion under blue light and self-organized into ribbons with a positive phototaxis in H₂O₂ solution.⁸⁰ Because of their biocompatibility and the possibility of their actuation by an external magnetic field, the micromotors were studied for issues regarding cell manipulation and patterning.⁸¹

Janus-like hematite–metal micromotors were fabricated by a hydrothermal reaction followed by physical vapor deposition of gold, gold–palladium, or platinum–palladium.⁸² The micromotors efficiently captured polyethylene glycol (PEG) due to the attraction between their positive charged surface (+64 mV) and negatively charged PEG (–27 mV). PEG is a widely utilized water-soluble polymer in cosmetics and lubricants. Because its biodegradation starts to occur when it has molar mass below 440 g·mol^{–1}, the degradation of PEG longer chains is an important issue to be addressed in wastewater.⁸³ The magnetically navigated hematite micromotors were proven to degrade PEG chains of 4000 g·mol^{–1} under UV light irradiation to 1000 g·mol^{–1} and less in 1 wt % H₂O₂ (Figure 3).⁸²

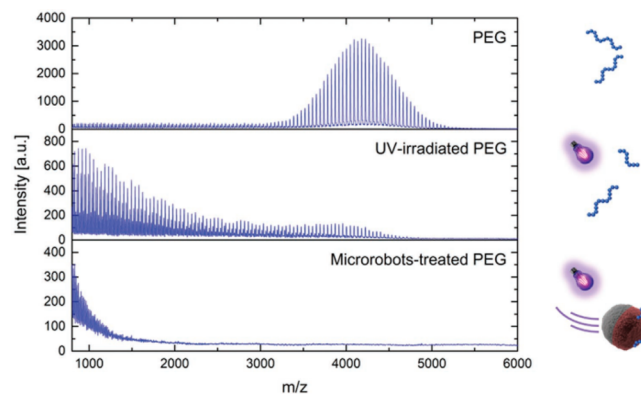


Figure 3. Magnetic photocatalytic hematite microrobots for photo-degradation. From top to bottom, MALDI-MS spectra of untreated PEG, PEG treated for 24 h under UV light irradiation in 1 wt % H₂O₂, and PEG treated for 24 h with hematite/Pt–Pd Janus microrobots under UV light irradiation in 1 wt % H₂O₂. Reprinted with permission from ref 82. Copyright 2021 Wiley-VCH GmbH.

4. CONCLUSION

The added value of micromotor applications to existing microplastics treatment technologies can be seen from several perspectives. One is the low-cost micromotor fabrication, for example, the availability of constructing materials, which have a high surface area and a broad spectrum of surface functional groups. Moreover, mass production of micromotors with desired shape can be achieved due to the progress in manufacturing methods.

Another benefit lies in the possibility to transport single micromotors into barely accessible places and make them arrange subsequently into swarms. The incorporation of magnetic materials (iron oxides) provides the catalytic micromotors with the possibility of assembling into long chains for efficient microplastics collection and removal. Moreover, the possibility of recovering micromotors by magnetic attraction would reduce material inputs into the microplastics treatment process.

Through versatile chemistry of the carrier and the surface, micromotors can be fabricated as mobile chemical platforms, performing Fenton-like or photocatalytic oxidation reactions. During propulsion, they are capable of capturing variously shaped microplastics and initiating their degradation through a variety of oxidized radical intermediates up to CO₂. The degradation performance of micromotors can be intensified by rational material design to yield a dual catalyst, synergistically combining the heterogeneous Fenton-like process with photocatalysis.

However, future effort should be aimed at the modification of micromotors to make them independent of surfactant presence or relatively high concentration of hydrogen peroxide fuel to achieve massive bubble propulsion in real-world settings. In the future, rationally designed micromotors and microrobots could represent a new strategy for plastic waste recycling with the achievement of added-value compounds. By judiciously selected material design and construction, advanced recoverable and pH-insensitive micromotors can be fabricated either with the capability of selective microplastics collection according to their chemical origin or shape or with degradation capability.

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Notes

The authors declare no competing financial interest.

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