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Micromotors for Environmental Applications. A Review

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This frontier article reviews recent advances in the use of self-propelled micromotors in the environmental field. It illustrates how mobile reactors or receptors can greatly improve the efficiency and speed of environmental remediation and monitoring processes. The new capabilities of synthetic micromotors that enable such exciting environmental applications are discussed. Current opportunities and challenges for using such functional nanomotors for improving diverse environmental applications are discussed.

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ARTICLE

Micromotors for Environmental Applications. A Review

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Self-propelled micromotors represent a new paradigm in the environmental field, greatly enhancing the efficiency of traditional operations due to the actively moving matter phenomena. This review highlights current opportunities and challenges in the use of micromotors for enhancing pollutant degradation and removal, accelerating bacterial killing or enabling dynamic environmental monitoring. Such studies exemplify the wide range of potential environmental applications of dynamic micromachines associated with their continuous motion, force and functionality. We will conclude with the challenges of moving these exciting advances from the bench scale to larger-scale field applications.

Micromotors and the environment

The rapid pace of industrialization has resulted in excessive emissions of hazardous pollutants into our water and air resources. To protect the human health and the environment, adequate contaminant management is required either by biological, physical or chemical treatment. Yet, the efficiency of these processes is limited by diffusive mass transport, and external means of agitation are required for enhancing the yields. Emerging applications of nanotechnology have added a new dimension to environmental remediation processes.[1] In particular, self-propelled micro- and nanomotors, capable of converting energy into movement and forces, hold considerable potential to overcome the diffusion limit of treatment operations by employing actively moving matter.[2-9] The continuous movement of such microscale objects imparts significant mixing without external stirring, leading to higher efficiencies and shorter clean-up times.[10] Since early pioneering studies on self-electrophoretic and peroxide-driven micromotors,[11] research efforts have been aimed to explore alternative propulsion mechanisms based on Marangoni effect,[12] photoinduced motion,[13] electromagnetic,[14, 15] thermal,[16] light[17-19] or ultrasound fields[20-22] and even biohybrid motion.[23, 24] The efficient propulsion and motion control of modern micromotors have been coupled with additional capabilities, including facile functionalization, cargo towing or collective and chemotactic behaviors. Such impressive capabilities of microscale machines have been exploited for improving diverse operations in diverse fields, including enhanced drug delivery,[25, 26] analytical sensing,[27-29] energy generation[30] or assisted fertilization.[31]

The new capabilities of synthetic micromotors have opened also a new horizon in the environmental field. Recent proof-of-concept studies have demonstrated that micromotors can have a profound impact upon the environmental field, with applications ranging from water-quality screening to the degradation and removal of pollutants. Early studies on micromotor-based environmental applications, initiated by Wang's group in 2009, exploited the pollutant effect upon the micromotor speed for motion based-detection of silver ions (**Figure 1**).[32] This pioneering work has laid the foundation for future micromotor-based sensing protocols, which will be reviewed in the following sections. The same group reported in 2012 on the first application of functionalized tubular micromotors for dynamic removal of oil from water.[33] Subsequently, Sanchez and Schmidt employed rolled-up Fe/Pt tubular micromotors for degrading organic pollutants in water via the Fenton oxidation process.[34] These early efforts represent the first proof-of-concept applications of micromotors for water cleaning. Since then, the number of papers reporting on environmental applications of micromotors has risen exponentially. Such studies relied primarily on the use of hydrogen peroxide as fuel. While hydrogen peroxide is often used as oxidative reagent in water treatment and is naturally decomposed in time, its widespread applications may be limited. A logical step in the field (since 2014) has been the design of water-fueled micromotors or the exploration of environmental-friendly fuel-free propulsion mechanisms such as light or ultrasound.[35] In parallel, recent efforts have aimed at improving the overall efficiency of micromotor-based remediation protocols by exploiting new nanomaterials such as graphene. Yet, some key issues, crucial to the translation of these major advances for practical environmental applications, remain unexplored. These demand future studies concerning scale-up issues toward coverage of large contaminated areas or deeper toxicity studies.

The aim of the present review is to highlight recent advances and prospects in the application of self-propelled micromotors for environmental applications. As several reviews have covered early progress in the field,[36-38] we will focus here on recent developments over the last 3 years. We will illustrate first how the movement of functional micromachines adds a new dimension to environmental monitoring processes with shorter analysis times and *on-site* monitoring capabilities. We will also discuss the use of micromotors for adsorptive removal and advanced pollutant degradation. Novel bacteria killing applications will be also covered. These recent studies exemplify the wide range of potential environmental applications of mobile micromachines towards dynamic remediation and sensing activities. A brief overview is summarized

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in **Table 1**, which we hope will help the reader to follow the contents of this comprehensive review.

Table 1. Summary of self-propelled micromotors for environmental application

Motor	**Pollutant**	**Ref.**
Environmental sensing and monitoring		
Motion based pollutant detection		
Au/Pt nanowires	Silver	32
PEDOT/Au-catalase tubular micromotors	Hg, Cu, NaN_3, aminotriazole, nerve agents	45, 46
CdTe/PEDOT/Pt tubular micromotors	Hg	50
Fluoresceinamine loaded Si/Pt Janus micromotors	Sarin and soman simulants	51
MIP-PEDOT/Pt/Ni/Pt tubular micromotors	Phycocyanin	53
Catalase-polycaprolactone micromotor	HCl, NH_3	47
Selective pollutant isolation and detection		
Lectin modified Au/Ni/PANI/Pt tubular micromotors	Escherichia Coli	55
Assisted electrochemical detection		
Mg/Au Janus micromotors	Nerve agents, phthalates	57, 58
Adsorptive removal of pollutants		
SAM modified Au/Ni/PEDOT/Pt tubular micromotors	Oil droplets	33
Marangoni propelled capsule millimotor	Oil droplets	12
Water driven Mg/Au/SAM micromotors	Oil droplets	62
	Heavy metals	72
$MnFe_2O_4$ Janus micromotors	Oil droplets	60
Activated carbon/Pt Janus micromotors	Heavy metals, explosives, nerve agents, azo-dyes	65
Zeolite/Ag Janus micromotors	Chemical and biological warfare agents	69
Zr/rGO/Ni/Pt tubular micromotors	Chemical warfare agents	67
rGO/Ni/Pt tubular micromotors	Heavy metals	68
rGO/Pt Janus micromotors	Persistent organic pollutants	66
Carbonic anhydrase functionalized PEDOT/Pt tubular micromotors	CO_2	70
GO/PtNPs rolled-up micromotors	Oil droplets	61
Pollutant degradation		
Advanced oxidation		
Fe/Pt rolled-up micromotors	Azo-dyes	34, 73
PEDOT/Pt tubular micromotors	Chemical warfare agents	78
rGO/Prussian blue hydrogel micromotor	Azo-dyes	75
Ti/Fe/Cr rolled-up micromotors	4-nitrophenol	80
MnO_2 Janus micromotors	Azo dyes	79
CoNi@Pt mesoporous nanowires	Azo dyes, 4-nitrophenol	81
Ag/ZIF Janus micromotors	Rhodamine B	77
Biocatalytic degradation		
SDS-based enzyme-releasing motors	Phenolic pollutants	82
Plant (radish) based enzymatic motors	Phenolic pollutants	83
Photocatalytic degradation		
TiO_2/Mg Janus micromotors	Chemical and biological warfare agents	86
Au/TiO_2/Pt Janus micromotor	Azo dyes	89
TiO_2/Pt and Pt/TiO_2 tubular micromotors	Rhodamine B	88
CdS/PANI/Pt tubular micromotors	Bisphenol A	90
TiO_2/Pt Janus micromotors	Rhodamine B	92
Light driven TiO_2/Au Janus micromotors	Dyes	94
Light-Driven Au-WO_3@C Janus micromotors	Dyes	19
Bacteria killing		
US propelled lysozyme modified nanowire motors	*Micrococcus lysodeikticus*	22
Mg/chitosan Janus micromotors	*Escherichia Coli*	96

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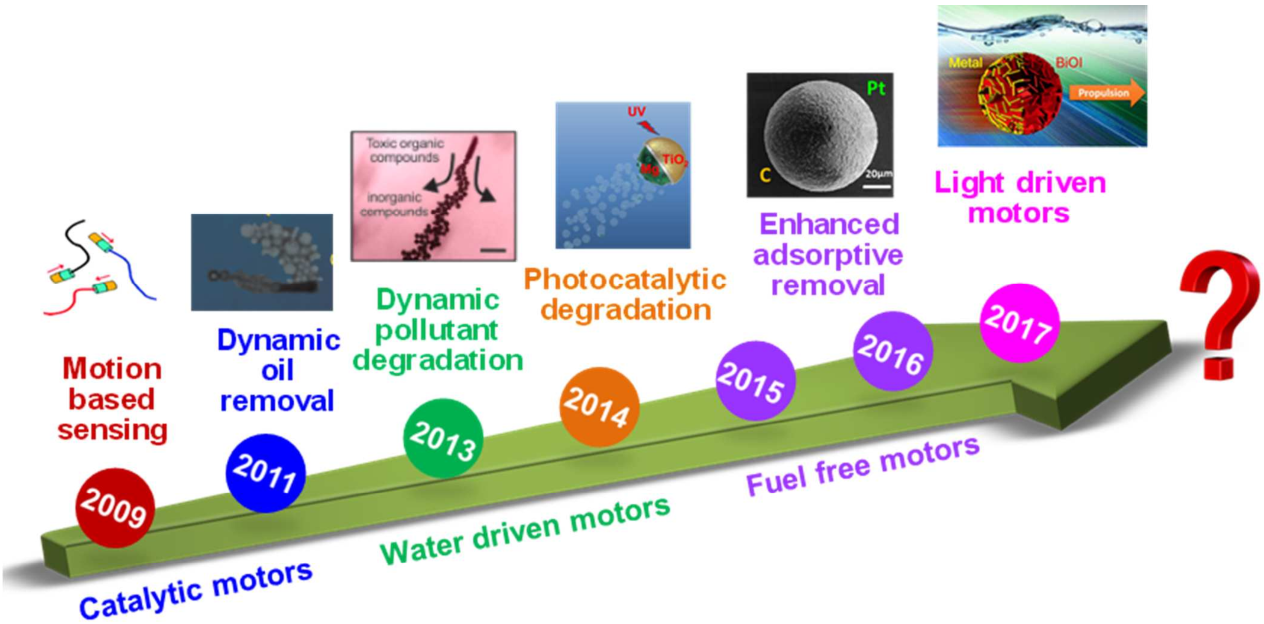

Fig. 1. Time-line showing the progress on the use of self-propelled micromotors for environmental applications. Reproduced with permission from ref. 33 (top part in 2011), copyright 2012 American Chemical Society; ref. 34 (top part in 2013), copyright 2013 American Chemical Society; ref. 65 (top part in 2016), copyright 2015 Wiley and ref. 17 (top part in 2017), copyright 2017 American Chemical Society.

Micromotors for *"On the move"* environmental sensing and monitoring

Self-propelled micromotors represent a new paradigm for real-time environmental monitoring, holding considerable promise for detecting sudden changes and incoming threats or monitoring continuously remediation processes or inaccessible environments with minimal sample preparation. One early and effective strategy relies on the changes in the swimming behaviour of catalytic micromotors in the presence of hazardous chemicals. Catalytic micromotors can display a chemotactic behaviour in the presence of a gradient of the fuel concentration, with a directed movement and increased speed toward higher peroxide concentrations.[39] Polymeric microsphere motors based on embedded Pd nanoparticles display chemotactic movement (with increasing speed) toward higher pH region, indicating promise for environmental pH monitoring.[40] Micromotors could use chemotactic search strategies to track chemical plumes to their source. For example, bimetallic nanowire motors display dramatic and specific acceleration in the presence of silver ion. Such acceleration reflects the underpotential deposition of silver onto a platinum segment that increases the catalytic activity. Such motion based sensing protocols are highly selective and sensitive (down to the nanomolar level) with the speed or distance providing the quantitative information.[32, 41] The silver-based acceleration has formed the basis for a motion-based detection of DNA hybridization in connection to silver nanoparticle tags.[42] Iridium-based Janus micromotors, powered by low levels of hydrazine, display a well-defined fuel-concentration/speed dependence that indicates considerable promise for tracking hydrazine plumes.[43, 44] Inspired by life fish toxicity test, catalase-powered tubular micromotors (see **Figure 2**) display diminished speeds and lifetime in the presence of toxic pollutants (e.g., heavy metals, pesticides), nerve agents [45],[46] or HCl and NH_3 gases.[47] Such motion-based toxicity screening protocols rely on the toxin-induced inhibition of the catalase enzyme powering the micromotor.[46] Similar strategies using enzyme-free micromotors rely on the poisoning of the Pt catalytic layer in the presence of certain pollutants that leads to diminished speeds. For example, Pumera employed Cu/Pt tubular motors for selective monitoring of lead in the presence of cadmium ion. Such selectivity is based on the different adsorption rates of each metal ion on the Pt catalyst.[48] A similar protocol was applied for detecting dimethyl sulfoxide and amino acids or peptides containing thiol groups that can poison the Pt catalyst.[49]

The coupling of micromotors with fluorescent dyes or nanoparticles, such as quantum dots, represents an attractive and convenient way for designing advanced mobile environmental microsensors. This strategy relies on rapid binding-induced changes (quenching/recovery) in the fluorescence intensity. **Figure 2A** illustrate an example for detecting heavy metals ions based on the use of quantum dots (QDs) embedded tubular micromotors. The micromotors were fabricated by integrating CdTe QDs on the outer surface of PEDOT/Pt micromotors through a positively-charged (poly(diallyldimethylammoniumchloride) layer. The motion accelerated binding of trace Hg^{2+} to the QDs selectively quenches the fluorescence emission and leads to effective *"on-the-fly"* discrimination between the two most relevant mercury species, Hg^{2+} and CH_3Hg^+, and other co-existing ions.[50] Silica/Pt Janus micromotors loaded with fluorescein amine have been used for *"on-off"* detection of diethylchlorophosphate, a simulant for sarin and soman chemical threats.[51] The fluorescence quenching of micromotors has been attributed to the interruption of the fluorophore's conjugation upon the release of the HCl by-product of the diethylchlorophosphate-fluorescein amine phosphoramidation reaction. Tubular graphene micromotors modified with a specific ricin B aptamer, tagged with fluorescein amidine dye offer considerable potential for *"off–on"* fluorescent detection of chemical agents such as ricin.[52] Molecularly imprinted-based tubular micromotors, fabricated using phycocyanin as the imprinting molecule and employing Pt and Ni as catalytic and magnetic layers, have been applied for detecting phycocyanin in water samples.[53] The native fluorescent emission of such cyanobacteria associated protein allowed for water quality assurance against pathogenic bacteria.

The transmission of infectious diseases via contaminated water and microbial pathogen contamination represents a major global risk to public health. Thus, isolation and identification waterborne pathogens is extremely important for meeting environmental monitoring requirements. Self-propelled functionalized micromotors have shown to be extremely useful for the direct selective isolation of target analytes from untreated samples.[54] **Figure 2B** illustrates an example of lectin-modified Pt based tubular micromotors for direct isolation of *Escherichia Coli* bacteria from untreated seawater and drinking water samples.[55] *Bacillus globilli* antibody-functionalized micromotors have been shown to selectively recognize, capture, transport and destroy deadly *Bacillus globigii* spores in environmental matrices.[56] Another promising example reported on the utility of Mg/Au Janus micromotors to assists electrochemical measurements in strip-based micro-volume electrodes. Micromotors can act both as "autonomous stirrers" toward greatly enhanced mass transport and as "artificial enzymes", inducing localized pH gradients for the degradation of the target analytes **(Figure 2C)**. In this example, the micromotors, confined onto the surface of sensor strips, serve as "artificial" enzymes toward the alkaline hydrolysis of paraoxon into readily detectable p-nitrophenol.[57] In a similar strategy, Mg/Au Janus micromotors have been used for the degradation of the non-electroactive persistent organic pollutant diphenyl phthalate (DPP) into readily detectable phenol.[58] Recently developed multi-stimulate responsive micromotors - prepared by screen-printed technology - incorporating specific responsive materials capable of colour-changes in response to variety of environmental stimuli (e.g., temperature, pH and light) indicate considerable promise for highly efficient naked-eye 'on-the-fly' water quality monitoring.[59]

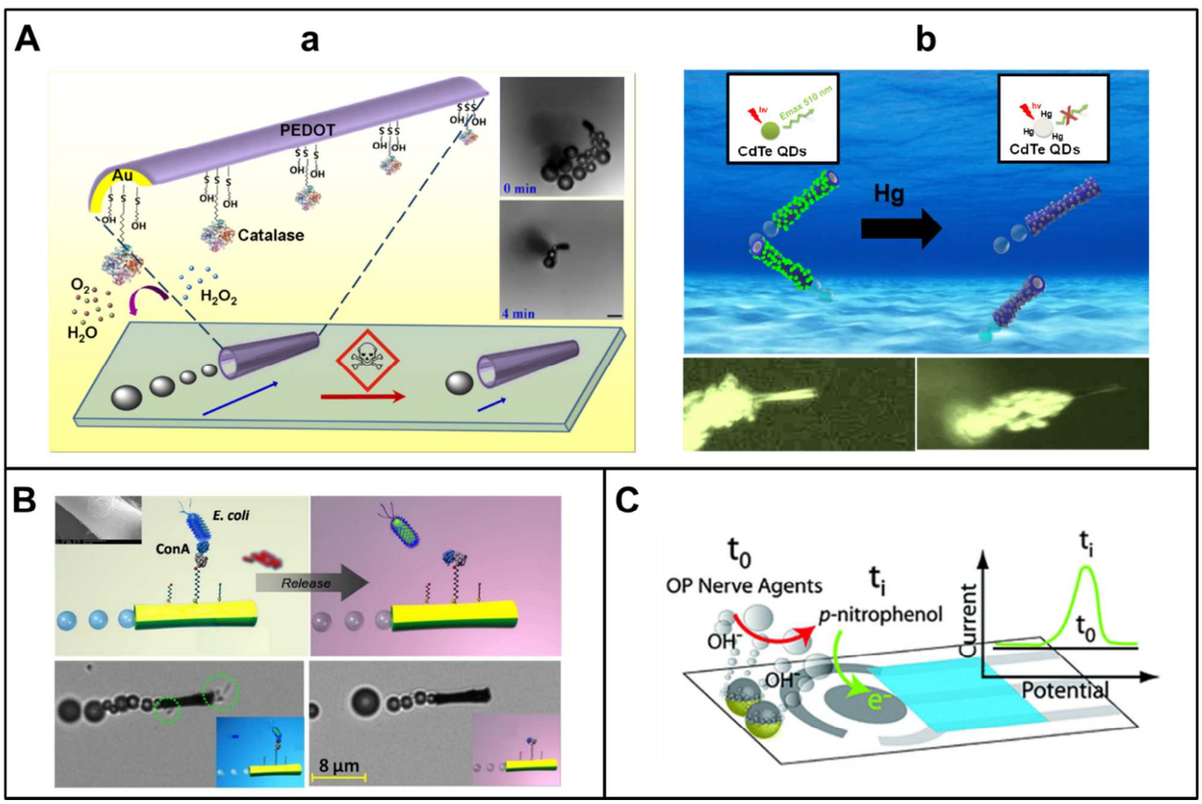

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Fig. 2. (A) Motion-based pollutant detection using self-propelled micromotors: (a) Biocatalytic PEDOT-Au-catalase micromotors for heavy metal ion screening. The scheme illustrates the pollutant effect on the micromotor speed through inhibition of the catalase biocatalytic layer; (b) CdTe-QDs modified micromotors for selective mercury detection based on the Hg-induced fluorescence quenching of the QDs immobilized on the micromotor surface. (B) Lectin-modified PEDOT/Pt micromotors for selective pick-up, transport and release of *Escherichia Coli* bacteria in environmental samples. (C) Mg/Au Janus micromotors assisted detection of non-electroactive nerve agents in sensing strips. Localized OH ions generated by Mg/Au micromotors, along with convection forces, result in the degradation of organophosphate (OP) nerve agents into readily detectable nitrophenol. Reproduced with permission from ref. 46 (A, a), copyright 2013 American Chemical Society, ref. 50 (A, b), copyright 2015 Royal Society of Chemistry, ref. 55 (B), copyright 2012 American Chemical Society and ref. 57 (C), copyright 2015 Royal Society of Chemistry.

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Micromotors for enhanced adsorptive removal of pollutants

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. Regarding micromotors and the environment, research aims have been directed towards the design of micromotors functionalized with adequate (bio)-ligands or composed by high surface area materials such as graphene or activated carbon. A great deal of attention has been given to dynamic oil removal using micromotors as efficient way to fight against petroleum spills. Guix et al.[33] employed alkanethiol-modified PEDOT/Pt tubular micromotors to clean oil-contaminated water via adhesion and permeation onto the alkanethiol coating (**Figure 3A**). Judicious optimization of the alkanethiol chain length and navigation time allowed for efficient capture and transport of multiple oil droplets. In addition, the micromotors can be further reused after releasing and degrading the captured oil droplets for future practical applications. Later on, hydrophobic $MnFe_2O_4$@oleic acid pot-like bubble propelled micromotors were directly used for environmental oil remediation without any further surface modification because of the hydrophobic surface endowed by the pre-existed oleic acid long chains.[60] Similarly, hydrophobic graphene/Pt tubular micromotors, prepared by rolled-up process assisted with wax-printed membranes, were successfully applied for collecting oil from water samples. The high surface-to-volume ratio associated with the graphene along with self-propelled micromotor movement offer favourable conditions to collect oil droplets present in water through hydrophobic interactions.[61] Yet, to avoid the use of peroxide fuel, Pumera et al.[12] employed millimeter-sized dodecyl sulfate/polysulfone polymeric capsule motors powered by Marangoni effect. The capsule repels the oil droplets over several centimetres and merge several oil droplets, effectively cleaning the water surface. A more biofriendly approach rely on seawater-powered Au/Mg micromotors modified with self-assembled monolayers of long-chain alkanethiols.[62] The spontaneous redox reaction of Mg particles upon contact with chloride-rich water (via galvanic and pitting corrosion processes) results in efficient hydrogen bubble generation and enhanced propulsion whereas the strong hydrophobicity of the modified gold layer result in effective *'on-the-fly'* collection of oil droplets. The incorporation of a Ni layer allowed for efficient recovery after dissolution of the Mg core.

Carbon allotrope-based catalytic micromotors, combining the high surface area of such nanomaterials along with the efficient fluid mixing imparted by micromotor movement, hold considerable promise for efficient removal of a myriad of pollutants.[63, 64] **Figure 3B,a** illustrate self-propelled activated-carbon micromotors prepared by asymmetric deposition of a Pt patch on the surface of 80 µm activated carbon microspheres. The coupling of the high adsorption capacity of carbon adsorbents with the rapid movement of catalytic Janus micromotors results in a highly efficient moving adsorption platform for the fast isolation of heavy metals, nitroaromatic explosives, organophosphorus nerve agents and azo-dyes.[65] Yet, graphene is the most exploited carbon allotrope for adsorptive removal of pollutants. For example, reduced graphene oxide coated silica/Pt Janus magnetic micromotors display enhanced removal capabilities of persistent organic pollutants (polybrominated diphenyl ethers and triclosan) from water. The micromotors can be reused in 4 consecutive cycles without change in its adsorption properties.[66] Reusable zirconia/graphene oxide/Pt hybrid micromotors have shown to display remarked efficiency for *"on-the-fly"* nerve agent capture, with its outer zirconia nanostructures being responsible for effective and selective binding of organophosphate compounds.[67]. Inspired by graphene micromotor works, Sanchez's group employed graphene oxide-based micromotors for active capture and remove lead ions, followed by micromotors reusability after the chemical detachment of lead from their surface (see **Figure 3B, b**).[68] Apart from carbon allotropes, zeolites, which display high retention capacity associated with their microporous inner structure, have been exploited for micromotor preparation. Thus, zeolite/Ag micromotors have proven to be extremely useful as dual-function 'fighters' towards highly efficient nerve agents adsorption and, as will be described in a following section, for killing of bacteria .[69]

Recent efforts have explored the coupling of enhanced movement with highly efficient (bio) catalytic remediation agents. For example, addressing growing concerns regarding the build-up of greenhouse gas, Uygun et al. described an effective mobile CO_2 scrubbing platform coupling the biocatalytic activity of carbonic anhydrase (CA) with the autonomous movement of peroxide-fuelled micromotors **Figure 3C**). The CA enzyme bounded to the micromotor surface catalysed the hydration of CO_2 to form bicarbonate that was mineralized as $CaCO_3$. The continuous movement of the immobilized CA and enhanced the mass transport of the CO_2 substrate, lead to significant improvements in the sequestration efficiency and speed compared to the stationary immobilized or free enzymes.[70] DNA functionalized gold/platinum tubular micromotor have been applied for the removal of mercury ions from water. The highly specific and strong binding of Hg(II) to T-T mismatched pairs in DNA sequences confers the adsorption capability for Hg(II) on these mobile microtubes.[71] A most environmental friendly strategy which avoids the use of hydrogen peroxide is depicted in **Figure 3D**. Mg/Au micromotors, incorporating a dithiol (2-mercaptosuccinic acid) chelating layer, have been used for highly specific Zn, Cd and Pb ions chelation. While propelling in the sample, the Mg core is dissolved (see SEM images in the figure), propelling the micromotors while trapping the heavy metals in the thiol layer. The shell gold layer, with the heavy metals, float to the water surface for convenient disposal.[72]

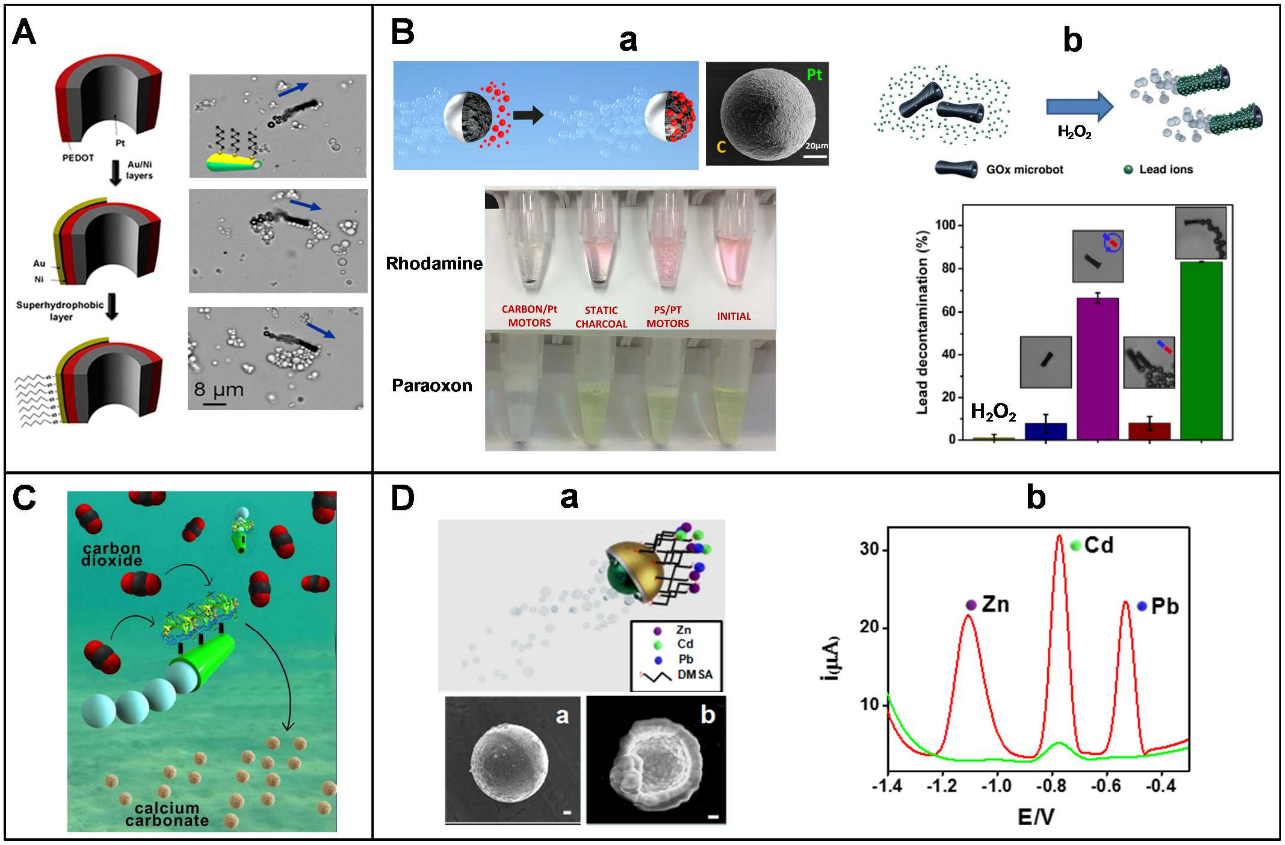

Fig. 3. (A) Dynamic oil removal using SAM modified Au/Ni/PEDOT/Pt tubular micromotors: Schematic of the functionalization and time-lapse images of hexanethiol-modified micromotors transporting a payload of multiple oil droplets (11, 50, and 73 s, respectively). (B) Carbon based micromotors for adsorptive removal of pollutants: (a) schematic of activated carbon/Pt Janus micromotors for removal of heavy metals, explosives, nerve agents, azo-dyes and photographs of different coloured polluted water solutions before and after micromotor treatment; (b) graphene/Pt/Ni tubular micromotors for lead removal. Graph bar showing the removal efficiency of the micromotors (in green) compared with control experiments (moving and magnetic control in red; micromotors under magnetic stirring; purple, static, blue and peroxide). (C) Self-propelled carbonic anhydrase PEDOT micromotors for CO_2 sequestration. (D) Thiol-modified Mg/Au Janus micromotors for heavy metal removal: (a) Schematic of the chelation mechanism and SEM images of the micromotor before and after water treatment and (b) stripping voltammograms of a water contaminated solution before (in red) and after 5 min treatment (green) with the ligand-modified micromotors. Reproduced with permission from ref. 33 (A), copyright 2012 American Chemical Society; ref. 65 (B, a), copyright 2015 Wiley; ref. 68 (B, b) copyright 2016 American Chemical Society; ref. 70 (C), copyright 2015 Wiley and ref. 72 (D), copyright 2016 Royal Society of Chemistry.

Micromotors for accelerated pollutant degradation and bacteria killing

Self-propelled micromotors in advanced oxidation processes for pollutant degradation

Advanced oxidation processes refer to a set of chemical treatments designed to remove organic and inorganic threats in water by oxidation through reactions with hydroxyl radicals, ozone, hydrogen peroxide (H_2O_2) or UV light. In this context, peroxide driven micromotors offer a new dimension to advanced pollutant removal since peroxide act here as strong oxidizing agent, which has been widely used by the environmental and defence communities for the degradation of harmful organic substances. The drag on the mixture by the micromotor movement enable better contact and mixing between the active reactants and the pollutant, resulting in more efficient degradation processes compared to static counterparts. Some examples are illustrated in **Figure 4**. For example, taking advantages of the peroxide fuel, rolled-up Fe/Pt tubular micromotors hold considerable promise for degrading organic pollutant via the Fenton oxidation reaction. In the presence of peroxide fuel and in acidic conditions (pH 2.5), the outer iron layer of the micromotor gradually dissolves into ferrous ion which in connection of peroxide fuel drives the Fenton reaction. Thus, the hydroxyl radicals generated reacts with rhodamine 6G as model pollutant, breaking down it organic rings into oxidized product and gradually into CO_2. Active micromotor motion result in *ca.* 12 times faster pollutant removal rate compared to their static counterparts.[33] In addition, as shown in the figure, the degradation efficiency can be increased by increasing Fe thickness. Further studies by the same research group using 4-nitrophenol as model pollutant revealed that the micromotors can swim for more than 24 hours and be stored more than 5 weeks during multiple cleaning cycles, revealing thus its potential for future full-scale applications.[73] Similarly, multifunctional zero-valent-iron/platinum Janus micromotors powered by peroxide fuel acts have used as mobile Fenton-like catalyst for the degradation of methylene blue after 60 min of treatment.[74] Recent efforts have exploited the replacement of Pt catalyst or the use of adsorptive-degradation configurations to improve the overall efficiency of Fenton micromotor schemes. For example, Prussian blue-reduced graphene oxide moving hydrogels[75] and platinum-free cobalt ferrite micromotors[76] have been described for Fenton mediated removal of methylene and antibiotics, respectively. Also, **Figure 4A, b** shows a schematic of a zeolitic imidazolate metal organic framework (ZIF)-Zn-Fe-Ag micromotor for the degradation of Rhodamine B (RhB) by Fenton-like processes. Upon peroxide addition, efficient micromotor movement and bubbles evolution result in an enhanced adsorption of RhB into the ZIF-Zn-Fe micromotor matrix. At the same time, OH radicals are generated due to the catalytic decomposition of peroxide in the Ag catalytic sites, which oxidize the RhB present in the matrix and in solution.[77]

A pioneering work from Wang's group demonstrated the accelerated oxidative detoxification of organophosphorus nerve agents using bubble-propelled polymer/platinum composite micromotors (see **Figure 4B**).[78] Hydrogen peroxide was used as both oxidation agent and fuel whereas $NaHCO_3$ or NaOH acted as peroxide activators. *In-situ* generation of peroxyl anions (with no external stirring) result in the conversion of the nerve agents into p-nitrophenol. The forced convection and enhanced mass transport of the remediation agents with the micromotors is the principal cause of oxidative decontamination. Later efforts illustrate the efficiency cost-effective MnO_2 moving microspheres for the degradation of methylene blue pollutant in a similar fashion, using peroxide as remediation reagent.[79] Current efforts of the micromotor community are exploring the use of sodium borohydrate as an alternative remediation agent and fuel. **Figure 4C** displays a highly efficient wastewater-mediated activation micromotor strategy for 4-nitrophenol (4-NP) degradation. Rolled-up Ti/Fe/Cr micromotors decorated with Pd nanoparticles were used in connection with $NaBH_4$ as reductant. The catalytic reduction of 4-nitrophenol (as fuel) by Pd particles in the presence of $NaBH_4$ drives the micromotor while degrading it into 4-aminophenol. The enhanced intermixing ability of these micromotors caused a removal of the pollutant about 10 times faster when compared with non-motile counterparts.[80] Magnetic mesoporous CoNi@Pt nanorods display enhanced movement and effective azo-dyes degradation capabilities in $NaBH_4$ rich solutions.[81]

Self-propelled micromotors for biocatalytic pollutant degradation

Enzyme-assisted pollutant removal is a natural, less harmful and effective way to remove pollutant. Yet, despite of its potential promise only few studies have been devoted to this topic. On a first study, Marangoni-effect powered biocatalytic motors, fabricated by filling commercial pipette tips with SDS and laccase solution, were used for highly efficient removal of eriochrome black-T and 2-amino-4-chlorophenol. The simultaneous release of laccase as decontamination agent and SDS as propellant into the contaminated solution, led to greater mobility and to a faster biocatalytic decontamination process through the efficient dispersion of laccase.[82] Enzyme-rich tissue based motors, prepared using unmodified *Raphanus Sativus* radish tissues, containing the enzymes catalase and peroxidase, displayed efficient motion and decontamination activities for 2-amino-4-chlorophenol, catechol, and guaiacol pollutants within 3 min.[83]

Chemical and light-driven micromotors for photocatalytic pollutant degradation

The use of light source (UV, VIS, etc.) to assist water purification processes is a convenient and biofriendly approach for microbial water treatment and pollutant removal. Photolysis can be considered as another advanced water oxidation processes in which light is used in connection with a semiconductor metal oxide as catalyst. In some cases, an additional oxidizing reagent (peroxide) should be also present to generate radicals for subsequent pollutant oxidation.[84] The use of light to power or improve the efficiency of micromotor in environmental remediation schemes entails several advantages such as the use of renewable energy source that does not require a physical connection to the motor, precise control of movement and reaction rates and the absence of toxic waste products.[17, 18] The first generation of micromotors rely on the use of catalytic propulsion (using Mg or catalytic layers for peroxide fuel decomposition) combined with UV light irradiation for photocatalytic degradation of a myriad of pollutants. Such initial configurations rely on TiO_2 as base material for micromotor fabrication, which is a highly efficient semiconductor. Upon light irradiation, TiO_2 adsorbs a photon with energy higher than the band gap energy and the negative electrons transferred from the valence band to the conduction band, creating positive holes. The photo-induced electron–hole pairs either recombine and release heat or interact with other molecules such as peroxide, resulting in the generation of OH radicals as powerful oxidizing reagents.[85] A fully biocompatible and environmental-friendly early approach is based on TiO_2/Au coated Mg microparticles for the degradation of chemical and biological warfare agents (see **Figure 5A**). UV irradiation of the TiO_2 shell thus generates the essential oxidative species for pollutants mineralization. The Mg core imparts an efficient propulsion and significant mixing during the photo-catalytic decontamination process toward a remarkably effective photocatalytic cleaning microsystem. Nearly complete degradation of the nerve agent's simulants methyl paraoxon (see **Figure 5A**) and bis(4-nitrophenyl) phosphate has been achieved using the micromotors. Further bacteria killing applications will be described in a following section.[86]

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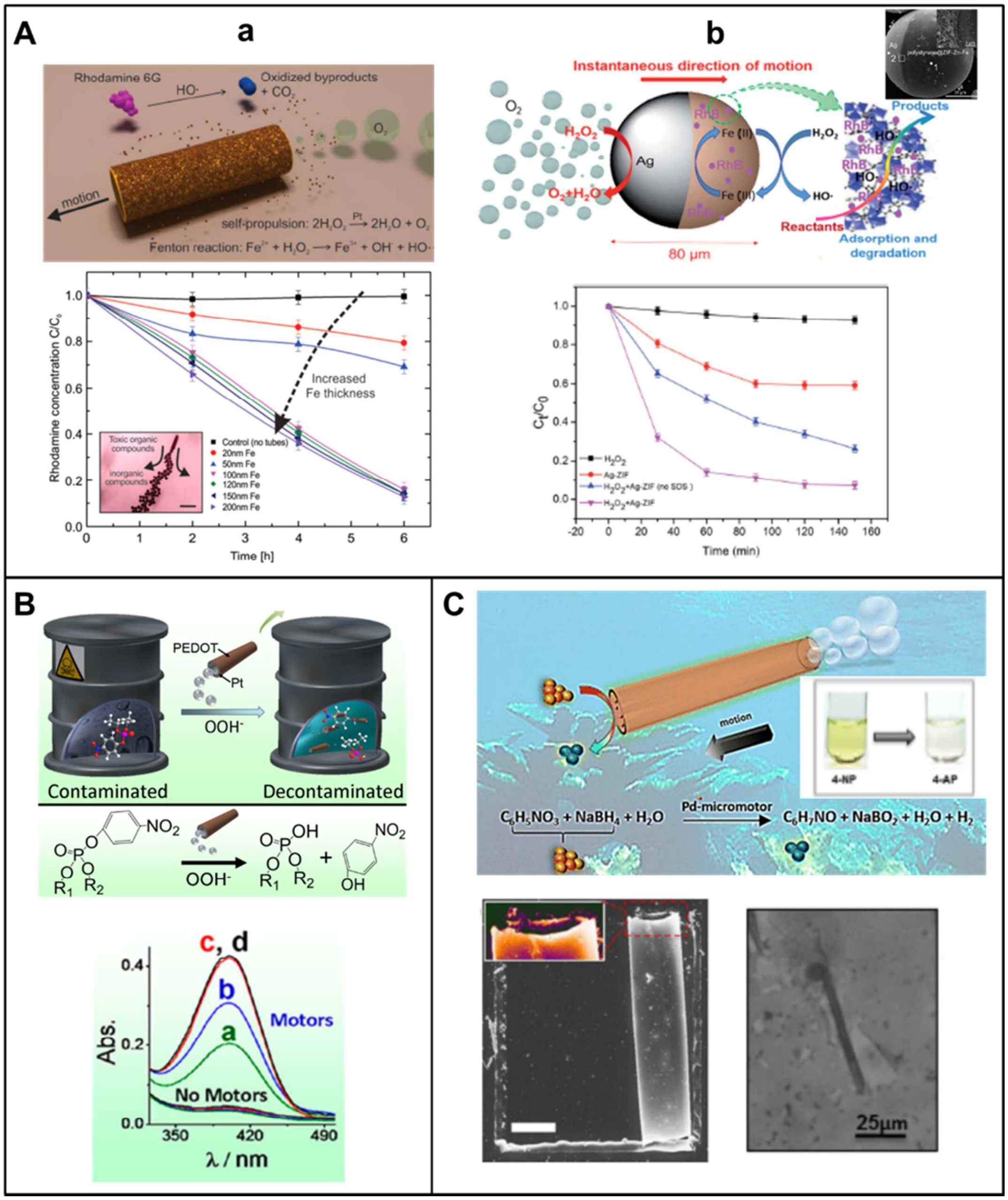

Fig. 4. (A) Micromotors-based advanced pollutant oxidation: (a) Tubular Fe/Pt rolled-up micromotors for destroying organic contaminants based on the Fenton reaction. The micromotors contain double functionality with an inner Pt layer for the self-propulsion and the outer Fe for the in-situ generation of Fe ions. Bottom part shows the influence of Fe thickness upon the Rhodamine removal; (b) Self-propelled metal–organic framework/Ag Janus micromotor for adsorptive removal/Fenton degradation of Rhodamine 6G. (B) Micromotor-based accelerated oxidative detoxification of nerve agents and schematic of the degradation process. (C) Wastewater activated Pd/Ti/Fe/Cr rolled-up micromotors for 4-nitrophenol degradation using $NaBH_4$ as reductant and fuel. Bottom part shows SEM and propulsion images of

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Another interesting strategy rely on coaxial TiO_2-PtPd-Ni nanotubes for water remediation under UV light, visible light, and natural sunlight. Such hybrid structures display a 100% degradation of rhodamine B under visible light and natural sunlight irradiation. The multicomponent design enables to efficient propulsion and actuation using magnetic or acoustic fields as external energy sources or peroxide fuel.[87] Other configurations rely on the use of peroxide as co-reagent along with light irradiation and micromotor movement. **Figure 5B** shows a schematic of two different tubular TiO_2 micromotors, one with Pt nanoparticles decorated on the inner surface and the other with Pt nanoparticles decorated on the outer surface. The micromotors can propel at low peroxide levels (0.05 %) without the aid of any surfactant owing to the superhydrophilic wetting behaviour of TiO_2. Efficient degradation of rhodamine B upon UV light irradiation demonstrates the intermixing and photocatalytic ability of the two micromotor systems.[88] A similar approach is depicted in **Figure 5C** and relies on TiO_2-based microshells decorated with AuNPs and PtNPs (by template-assisted, aqueous phase synthesis method) as the outer and inner layers, respectively. Under anaerobic conditions and using H_2O_2 as fuel, the plasmonic micromotor can efficiently propel by O_2 and efficiently degrade methylene blue, rhodamine B, and methyl orange under artificial solar light irradiation. The AuNPs in the TiO_2 shell lead to a high electron-hole separation efficiency and to the absorption for strong photocatalytic activity.[89] CdS quantum dots have also been explored as alternative photocatalyst to TiO_2. Thus, peroxide-driven CdS/polyaniline Pt tubular micromotors are extremely efficient for solar light photocatalytic degradation of bisphenol A as model persistent organic pollutant. In this case, active oxygen species such as OH and superoxide radicals are the key active intermediates for the efficient degradation. Photons with energy higher than CdS are absorbed onto its surface. Thus, the valence band electrons are excited to the conduction band, leaving a positive charged hole in the valence band. Subsequently, valence and conduction band electrons can react with water or a hydroxyl groups to produce the above mentioned degradation radicals.[90]

A second generation of motors employ light both for degradation and as external stimuli for micromotor propulsion towards environmental friendly schemes. TiO_2 microtubes arrays prepared by electrochemical anodization of Ti sheets can propel under UV light irradiation by diffusiophoresis.[91] Water-fuelled TiO_2/Pt Janus display aggregation and separation behaviours that can be wirelessly and remotely controlled by regulating *"on/off"* switch, intensity and pulsed/continuous irradiation mode of UV light. Efficient motion in water is governed by the light-induced self-electrophoresis under the local electrical field generated by the asymmetrical water oxidation and reduction reactions on its surface were exploited for Rhodamine B degradation.[92] Similarly, water-driven TiO_2/Au Janus micromotors have been used for the degradation of dye pollutants under UV irradiation. Interestingly, under the presence of the dyes methyl blue, cresol red and methyl orange there is an enhanced motion and improved micromotor velocity, which can be attributed to a self-electrophoresis mechanism induced by the photocatalytic degradation of the dyes on the asymmetrical surface. Valence band electrons of TiO_2 are excited to the conduction band under UV light, facilitating the electron transfer TiO_2–Au, suppressing the recombination of electron–hole pairs and enhancing their lifetime. The separated electron–hole pairs trigger the formation of reactive superoxide radicals, which reacts with the dye molecules inducing their oxidative degradation to mineralized products.[93, 94] Also, as depicted in **Figure 5D**, light-driven Au–WO_3@C Janus micromotors were used for the rapid photocatalytic degradation of sodium-2,6-dichloroindophenol and Rhodamine B. In this case, however, a diffusiophoretic effect is the dominating driving force for the micromotor propulsion. Indeed, the higher concentration of photodegradative products around the WO_3 side in comparison with the Au side, and the nanosized porous structure of WO_3@C microspheres facilitates the diffusion of reactive products, leading to an osmotic flow from low to high solute concentration regions on the surface of Janus particles which propels the micromotors forward. This is accompanied by a generation of oxide radicals for the dye mineralization.[19] AgCl based star-like micromotors were used for the degradation of different organic dyes and the simultaneous inhibition of the bacteria growth. The reduction of Ag ions into metallic silver from the AgCl particles takes place upon the UV light irradiation. This leads to the generation of a local electrolyte gradient for self-diffusiophoretic motion.[95]

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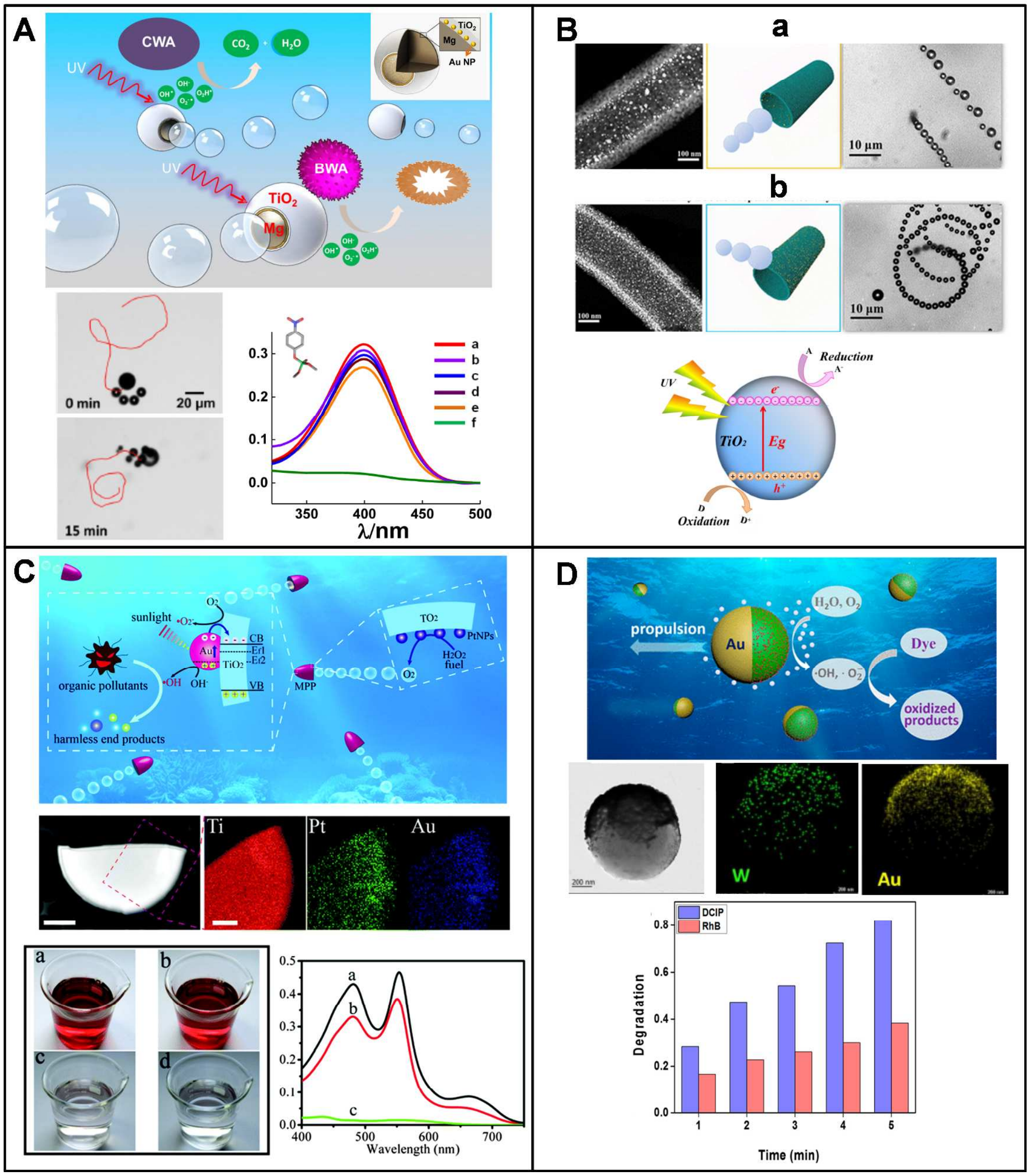

Fig. 5. (A) Water-powered TiO_2/AuNPs/Mg Janus micromotors for photocatalytic degradation of chemical and biochemical warfare agents: Mechanism and time lapse image of the micromotor navigation in 15 min period. UV/VIS spectra show the degradation of methyl paraoxon using the micromotors (in green) and control experiments. (B) Internally (a) and externally (b) propelled TiO_2/Pt tubular microengines for photocatalytic degradation of azo-dyes. (C) Plasmonic motor for the sunlight photocatalytic degradation of organic pollutants, schematic of the operation and corresponding SEM and EDX images. Bottom part shows the decontamination ability of a mixture of azo dyes before (a, b) and after (c, d) treatment with the micromotors (D) Light-driven Au-WO3@C Janus micromotors for rapid photodegradation of dyes. Down images show the STEM characterization and element distribution on the micromotor body and degradation experiments. Reproduced with permission from ref. 86 (A), copyright 2014 American Chemical Society; ref. 88 (B), copyright 2017 American Chemical Society; ref. 89 (C), copyright 2016 Royal Society of Chemistry and ref. 19 (D), copyright 2017, American Chemical Society.

Self-propelled micromotors for killing of bacteria

The quest for efficient microbial antibacterial treatments has led to the development of novel micromotor based strategies. **Figure 6A** shows an excellent example of the use of chitosan–Mg Janus micromotors for *Escherichia coli bacteria* inactivation in contaminated seawater and freshwater. The chitosan-coated Mg micromotors swim through water sample, contact and damage the bacteria cell through the activity of its outer chitosan layer. Such bacteria death is facilitated by mechanical interaction between the chitosan layer, present on the micromotor structure, and the bacteria.[96] A particular attractive and environmental friendly approach relies on the use on lysozyme-modified ultrasound propelled nanowire motors. The antibacterial properties of lysozyme, associated with the cleavage of glyosidic bonds of peptidoglycans present in the bacteria cell wall, have been combined with the rapid movement nanomotors, resulting in a greatly enhanced bacteria-killing capability. Rapid and effective killing of the Gram-positive *Micrococcus lysodeikticus* bacteria (69–84%) can be achieved within 5 min, thus offering great promise for future nanotechnological water purification schemes (see **Figure 6B**).[22] The TiO_2/Mg micromotors described previously can efficiently inactivate *Bacillus globigii* spores (anthrax simulants).[86] Mg/Fe micromotors decorated with Ag nanoparticles can kill bacteria through the silver bacteria effect.[97] The micromotor motion enhanced the transport of the released Ag^+ ions, while the inner iron magnetic layer offered remote guidance and convenient micromotor removal. Similarly, zeolite/Ag micromotors, described in previous section, are useful for *"on-the-move"* killing of *Escherichia Coli* bacteria.[69] (see **Figure 6C).**

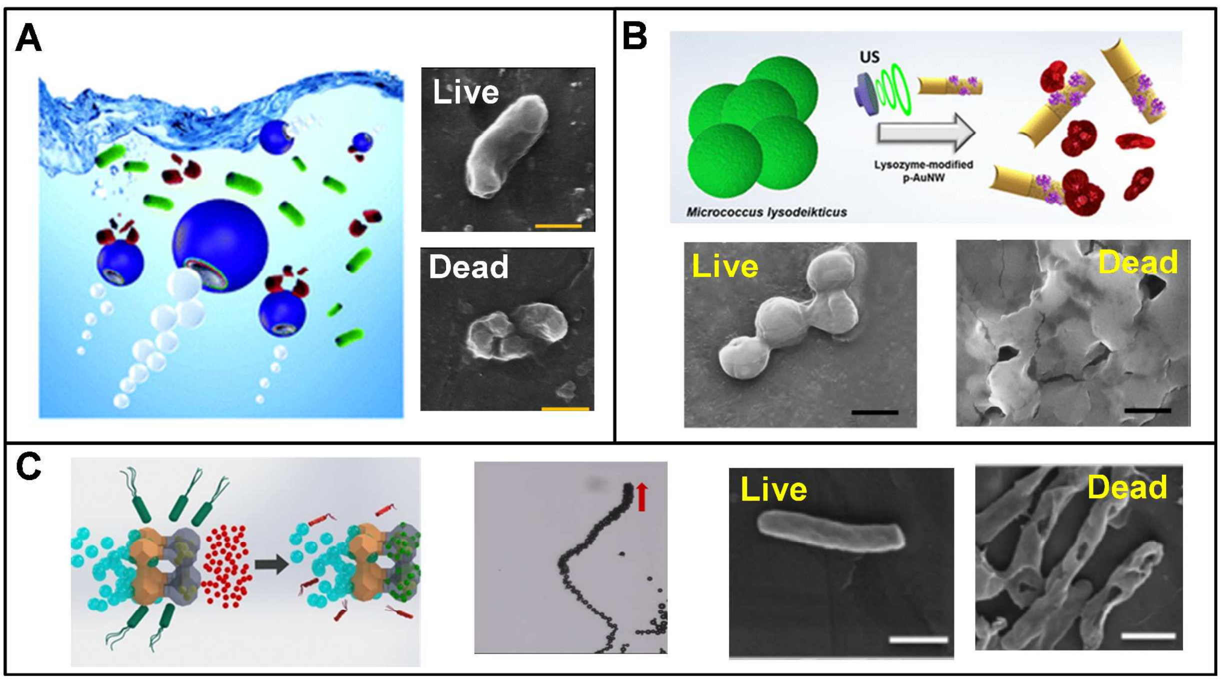

Fig. 6. (A) Water-powered Mg/Au/PLGA/Alg/Chi micromotors for *Escherichia Coli* bacteria killing. Right part shows SEM images of the bacteria before (live) and after micromotors treatment (dead). (B) Ultrasound propelled lysozyme nanowire motors for killing bacteria. (C) Zeolite/Ag Janus micromotors for biological warfare agent's detoxification: schematic of the operation, propulsion and effective *Escherichia Coli* killing. Reproduced with permission from ref. 96 (A), copyright 2017 Royal Society of Chemistry; ref. 22 (B), copyright 2015 American Chemical Society and ref. 69 (C), copyright 2015 Wiley.

Conclusions

The new capabilities of synthetic micromotors have opened a new horizon in the environmental field. Self-propelled micromotors represent a new paradigm in the environmental field, greatly enhancing the efficiency of traditional strategies due to the actively moving matter phenomena. This review highlights current and previous prospects and challenges for translating such recent advances into practical applications (see **Table 1**). Since early developments of micromotors almost a decade ago, micromotors have shown considerable opportunities in the environmental field, ranging from water-toxicity screening to accelerated remediation processes. We have illustrated first how the ability of micromachines to modify its motion upon the presence of different contaminants can be used for environmental assurance. From early motion-based detection schemes to novel configurations involving fluorescent nanoparticles and dyes, micromotors hold considerable potential for *on-site* detection of threats and to monitor remediation processes and most importantly, inaccessible environments. A second important core of the review has been devoted to the application of micromotors as mobile reactors for water cleaning, mainly via adsorptive removal and enhanced pollutant degradation. Since pioneering *proof-of-concept* applications for oil removal and micromotor-assisted Fenton oxidation, we have witnessed a rapid growth on studies devoted to such exciting topic. Recent trends in micromotor adsorptive pollutant removal are exploring the use of high surface area nanomaterials such as graphene or the combination with highly efficient biocatalyst for greenhouse gas capture. Micromotor-based advanced pollutant schemes are experiencing a tremendous research activity with some studies addressing the scalability and reusability concerns, towards practical future applications. Yet, as many of these strategies still rely in the use of environmentally-unfriendly peroxide fuel or on water-powered (Mg, Zn) motors with limited lifetimes, new environmentally friendly propulsion mechanisms based on light or ultrasound have been explored. In particular, substantial progress has been achieved in light-driven micromotors in which UV or solar light exerts a dual role as external input for micromotor propulsion and for generating radicals used for pollutant degradation. Another promising topic is illustrating the remarkable capabilities of dynamic micromotors as bacteria fighters.[98]

Yet, future efforts should be aimed to translate such exciting advances into practical environmental applications, which will require close collaboration with environmental scientists and engineers, along with new technological breakthroughs and greater sophistication of micromotor, ultimately contributing further to the environmental benefits of nanotechnology. Thus, future studies should address scale-up issues toward coverage of large contaminated areas and large volumes of wastewater.[99,100] A convenient solution relies on the coordinated action of swarms of numerous micromotors for dynamic action over larger scales and for transporting larger payloads of remediation agents. Attention should be also given to the influence of the environmental media upon the propulsion behaviour. For example, in highly polluted water or oxidation based-schemes, part of the micromotor body can be quickly consumed resulting in a short lifetime, not to mention micromotors based on reactive particles. Highly turbid polluted waters can deactivate light-driven motors and catalytic sites of bubble-propelled motors, thereby deactivating them. Finally, potential toxicity issues need to be evaluated to prevent potential adverse environmental impacts. This can be accomplished by using self-degrading materials to construct the micromotor body and by removing the micromotors after decontamination by incorporating magnetic materials (e.g., Fe), allowing also for future reusability and cost-effective processes.

Where we are heading? The maturity of micromachines to address environmental problems is just beginning to be explored. While major progress has been accomplished over the past decade, significant efforts are required to translate these innovative micromotor-based proof-of-concept studies into large-scale environmental applications. In the not-so distant future, we anticipate seeing self-regulated multifunctional micromachines, capable of performing multiple tasks, "sensing, isolating and destroying" toxic pollutants and chemical threats, searching for sources of hazardous chemicals, or delivering nanosensors to remote hostile locations. Swarms of micromachines could be assembled in response to hazardous conditions, used for mapping the spread of a toxic pollutant over large areas or for accelerating environmental cleanup. We hope that the present review will stimulate extensive research efforts in environmental applications of micromotors.

Conflicts of interest

There are no conflicts to declare

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Micromotors and the environment.
Image illustrating the efficient operation of carbon-based micromotor for water purification