Photocatalytic TiO_2 micromotors for removal of microplastics and suspended matter

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ABSTRACT: Environmental contamination is a major global challenge and the effects of contamination are found in most habitats. In recent times, the pollution by microplastics has come to the global attention and their removal displays an extraordinary challenge with no reasonable solutions presented so far. One of the new technologies holding many promises for environmental remediation on the microscale are self-propelled micromotors. They present several properties that are of academic and technical interest, such as the ability to overcome the diffusion limitation in catalytic processes and their phoretic interaction with their environment. Here, we present two novel strategies for the elimination of microplastics using photocatalytic Au@Ni@TiO_2 -based micromotors. We show that individual catalytic particles as well as assembled chains show excellent collection and removal of suspended matter and microplastics from natural water samples.

KEYWORDS: Photocatalytic micromotors, magnetic assembled chains, microplastics, removal

Micromotors, being self-propelled nano/microscale devices, have attracted considerable attention in the last decade, owing to the fascinating physics as well as the envisioned applications in different fields, including biomedical[1–7] and environmental[6–12] applications. Particularly, micromotors hold huge potential for environmental remediation, such as organic degradation,[13–17] oil removal,[18-20] and heavy metal removal.[21–26] Microbial contamination could be detected and remediated,[27,28] and a general assessment of water quality via micromotors was presented.[29,30] Compared to traditional chemically catalytic micromotors, photocatalytic micromotors bear the additional advantage of employing water as non-toxic fuel and light as renewable energy source.[31,32] Light is easily controllable and does not lead to any waste products during the propulsion, thus extending the benefits of micromotors in the diverse environmental applications.[10,11] Especially, for water purification, photocatalytic micromotors display exceptional contributions.[16,17,33,34]

Among the problems of water contamination, plastic contamination attracts global attention owing to its persistence and damage for marine organisms.[35] As one of the main environmental pollutant, microplastics are defined as fragments less than 5 mm in size,[36,37] which do not easily sediment and frequently pass by filtration systems. Fish and other marine creatures confuse these microplastics with food, and since humans are a part of the food chain, we are also influenced by the microplastics. Recently, microplastics also have been found in human stools[38,39] for the first time proving that the threat is ubiquitous, not only endangering to the marine organisms. Fortunately, many countries are starting to tackle the problem, for instance, by banning the

production of personal care products containing plastic microbeads.[40–42] However, due to the persistence of micoplastics, the threat will still be here for long time even if all the countries banned the microbeads products.[40]

In this manuscript, we present a photocatalytic TiO_2 based micromotor, Au@Ni@TiO_2 for microplastics removal. This catalytic micromotor can move efficiently both in peroxide and water under UV illumination owing to the photocatalytic reaction occurring on the particles. Moreover, novel assembled chains can be formed by individual particles under external magnetic field. Phoretic interactions induced by photocatalytic activity of individual micromotors show collective properties with passive particles, and assembled chains display shoveling effect under magnetic field. Here, both catalytic individual swimmers and multiparticle assemblies exhibit exceptional collection properties for passive particles. Subsequently, we show on real life samples the suitability to the collect microplastics and suspend matter based on these two strategies.

RESULTS

Photocatalytic propulsion

We initially prepared the TiO_2 particles by a modification of our previously published method.[43] To obtain magnetic Au@Ni@TiO_2 micromotors, TiO_2 particles were coated with a 10 nm nickel layer and then with 30 nm layer of gold. This photocatalytic micromotor can move efficiently in both, water and peroxide when irradiated with UV light, based on photocatalytic chemical reaction. As shown in the scheme of photocatalytic propulsion of micromotor in water (Figure 1A), under UV illumination, photo-excitation process takes place within TiO_2, creating conduction band electrons and valence band holes. Holes involve in the oxidation reaction of water at TiO_2 hemisphere, which produces protons. Electrons are transferred to metal cap and involve the

reduction of protons at metal cap hemisphere. The consumption of protons leads to a fluid flow toward the metal cap, thus contributing the photocatalytic propulsion of Au@Ni@TiO_2 micromotors. Similar to the case in water, the catalytic decomposition of H_2O_2 via oxidation-reaction mechanism occur on the micromotors in H_2O_2 solution (Figure 1B), propelling the micromotors. It can actively self-propel with the speed of 14.72 μm s^{-1} in H_2O and 65.52 μm s^{-1} in 0.1% H_2O_2 solution with UV light, as shown in the Figure 1A, B (Video S1, S2). The motion tracklines for micromotors during 2 s are displayed. Just as noted earlier with Au@TiO_2 micromotors, the micromotors achieve faster speeds in H_2O_2 compared to H_2O, but steady motion in both fuels.[43]

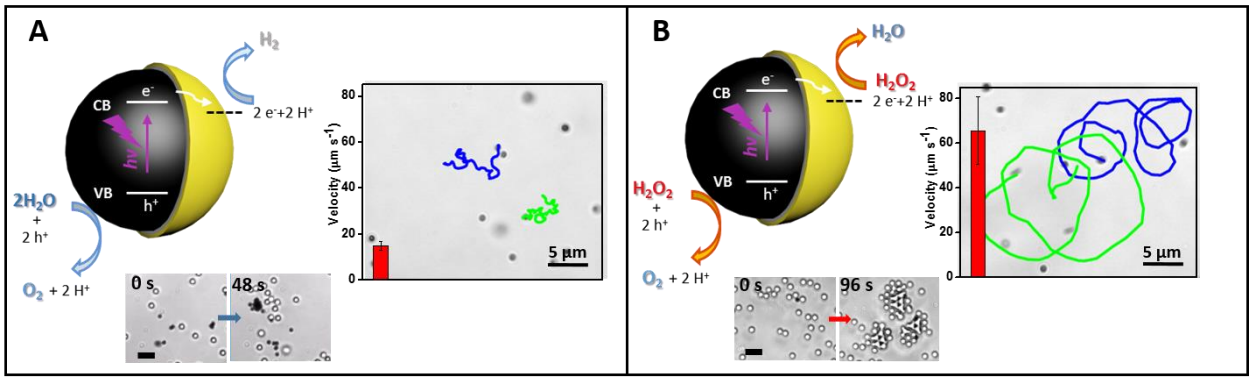

Figure 1. (A, B) Scheme of photocatalytic propulsion of Au@Ni@TiO_2 micromotor, tracklines and speed of micromotors during 2 s in H_2O and 0.1 % H_2O_2 solution with 315 mW UV light, respectively. The insets are the optical images of active-passive particles behaviours based on activity induced interaction in water and H_2O_2 solution. Scale bar, 5 μm.

Interactions

The interaction between passive SiO_2 particles and active metal capped swimmers induced by photocatalytic activity was studied previously[44] and in our earlier work.[43] We found that the interactions between micromotors with passive particles differ among the swimming modes, which

leads to different behaviours in different fuels. For instance, as shown in the insets of Figure 1A, in the mixture of active ($Cu@TiO_2$) and passive (SiO_2) particles in water, it exhibited little interaction between single active and passive particles. In peroxide solution (Figure 1B), passive particles can be collected based on phoretic interaction, forming certain patterns.[43] Here, for the magnetic $Au@Ni@TiO_2$ particles, we also find that the interactions between catalytic micromotors with passive particles exist and behave similar to the $Cu@TiO_2$ micromotors. Especially pronounced in H_2O_2, phoretic interactions with passive particles enable assembling of larger motile structures as well as motion of passive structures (see the model in Figure 2), similar behaviour has been reported in very different systems[45,46] and origins of this behaviour and the differences among the fuels are currently under research and to be considered in a separate work. Herein, this phoretic interaction induced by photocatalytic activity, which displays collective behaviours for passive particles, provides huge potential for environment pollutants, microplastics, collecting and removal.

We use polystyrene (PS) passive particles as a model system for microplastics. As displayed in Figure 2 (Video S3), in the mixture of individual catalytic $Au@Ni@TiO_2$ micromotors and PS particles, micromotors can accumulate PS particles very efficiently through phoretic interactions, and move together with them. This behaviour provides a promising strategy using these magnetically controllable individual micromoyors for microplastics removal based on phoretic interaction.

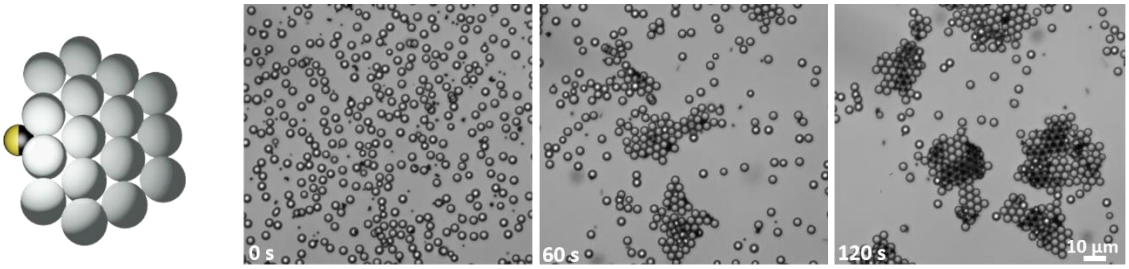

Figure 2. Scheme of phoretic interaction between Au@Ni@TiO_2 micromotors and PS particles; time-lapse optical images illustrating Au@Ni@TiO_2 micromotors collecting PS particles by phoretic interaction in 1.67% H_2O_2 solution with 315 mW UV light.

Microplastics

In order to study the occurrence of microplastics in our daily life and test our system on these, diverse personal care products, which might have microplastics, were extracted by vacuum filtration. These products include washing powders, toothpastes and face cleansing creams. SEM images of different extracts from products are shown in Figure3 A-C (more see in Figure S1). Further analytical methods including Zetapotential measurements, IR and Raman spectra are used to identify the composition of the extracts. Details of the individual samples can be found in the SI.

From the selection of available products we checked, it seems that the EU guidelines have been successfully banning microbeads, and in most of the European products abrasive components have been replaced by other (inorganic) materials, such as silica and zeolites. However, in imported product, namely sample 13 (Figure 3C), we could still identify microplastic compounds. The analytical identification resulted in a mixture of polyethylene and synthetic wax (more details see in Figure S2).

Moreover, to get a better estimate of the occurrence of microplastics in the environment, the extracts from river and sea were investigated by Raman microscopy (see details in the experimental section). SEM images of extracts from Baltic Sea and Warnow River are shown in Figure 3D and Figure 6F, respectively. According to the Raman spectra, microplastics are present in the extracts. For instance, for the extract from Warnow River, there are 8 microplastics out of

1542 particles, including polypropylene (PP), polyethylene (PE), polystyrene copolymer, polytetraflouroethylene (PTFE), polyethylene terephthalate (PET) and pigments (more details in table S2).

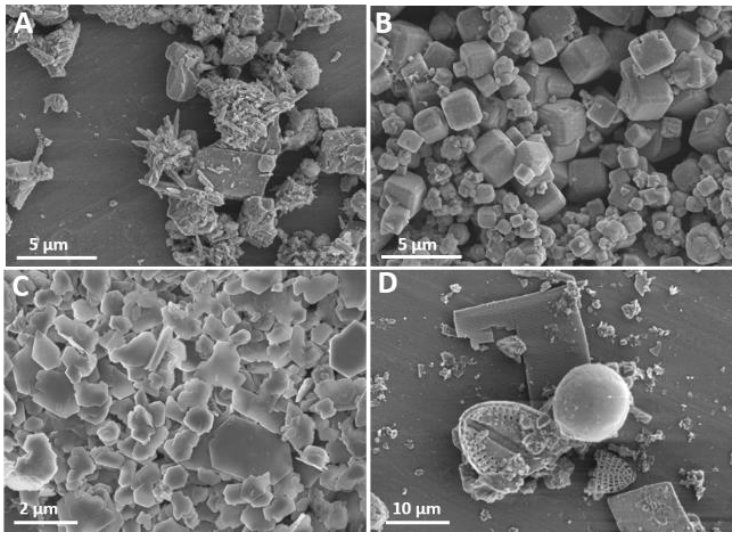

Figure 3. SEM images of extracts from (A) toothpaste (sample 5); (B) washing powder (sample 11); (C) face cleansing cream (sample 13) and (D) Baltic Sea.

Removal by phoretic interactions

To test the applicability of the phoretic interaction for removing the remnants of the personal care products, individual catalytic micromotors are mixed with the extracts. As displayed in Figure 4 (Video S4), the extracts from sample 11 consisting of zeolite, are collected rapidly by micromotors in 0.1% H_2O_2 solution with UV light illumination. This indicates that the phoretic interaction can be applied to collect not only laboratory synthetic sample but also real samples from daily life.

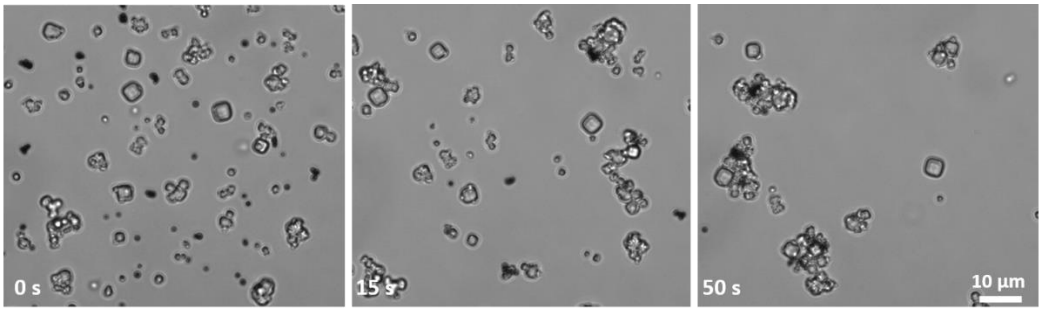

Figure 4. Removal of personal care product (washing powder sample 11) in 0.1% H_2O_2 solution with 315 mW UV light.

However, despite the promising results employing phoretic interactions for microparticles removal, adding peroxide is not ideal for environmental applications. Therefore, another removal strategy independent of the employed fuel is highly desired. Generalizing, one can say that the effect achieved by phoretic interactions strongly resembles pushing the passive particles. Here we want to test the hypothesis, that we can achieve efficient 'pushing' independent from the phroetic interaction origin in peroxide, and that we can still remove passive particles by this pushing effect.

Removal by shovelling

Therefore, we developed a magnetic and motile assembly of catalytic particles, i.e. magnetic micromotor chains. These assembled chains can be controlled and perform direct pushing effect (shovelling) under magnetic field, thus can remove microplastics by shovelling independent of the fuelling.

Magnetic chains are formed through the interaction between magnetic Ni layers inside the Au@Ni@TiO_2 micromotors under external magnetic field.[47] The scheme in Figure 5 A shows the formation of the chain under magnetic field. Correspondingly, the SEM image (Figure 5B) shows the assembled chain formed by individual Au@Ni@TiO_2 micromotors. These assemblies can move directionally in both, H_2O and H_2O_2 solution under magnetic field. As shown in Figure 5C,D

(Video S5, S6), the assembled chain can move directionally at a speed of 7.35 μm s^{-1} in H_2O, and at a speed of 26.96 μm s^{-1} in 0.1% H_2O_2 solution with UV light under magnetic field. Despite being slower than single micromotors, the assemblies benefit from the larger area covered by the chain and can achieve considerable shovelling effects, thus holding greater potential for microplastics removal in real environmental filed.

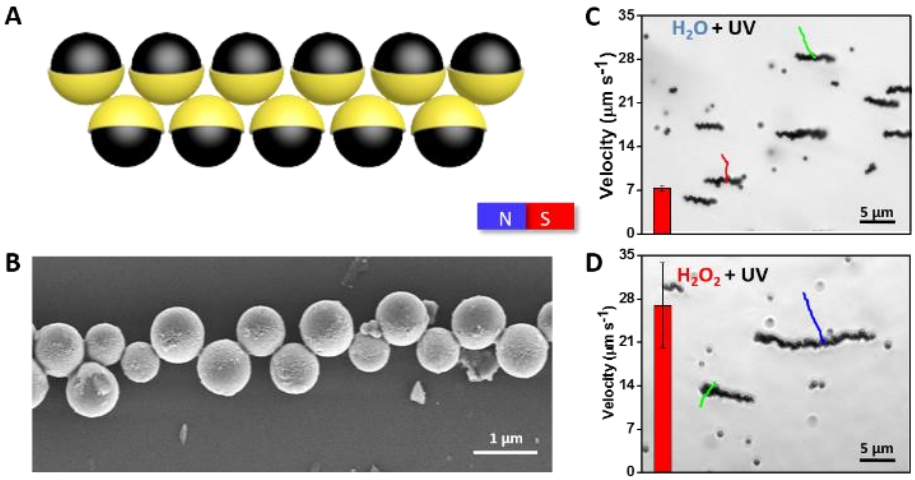

Figure 5. (A) Scheme and (B) SEM image of chain formation of magnetic Au@Ni@TiO_2 micromotors under magnetic field; (C, D) Tracklines and speed of Au@Ni@TiO_2 micromotors chains during 2 s in H_2O and 0.1% H_2O_2 under 315 mW UV light and magnetic field, respectively.

To verify the shovelling effect on microplastics and suspended matter removal by assembled chains independent of fuel under magnetic field, different experiments have been carried out in H_2O_2 solution and H_2O.

Firstly, removal of suspended matter is performed in H_2O_2 solution. This suspended matter consists of zeolites, which extracted from washing powder sample 10. SEM is shown in Figure 6B inset. In order to observe the removal effect more intuitively, the area of the UV light is limited. As displayed in Figure 6A (Video S7), in 0.1% H_2O_2 solution, the suspended matters are collected and shovelled by assembled chains under magnetic field. After 120 s, most of suspended matters

are removed from UV illumination area. The removal efficiency is about 77% by the quantification of microparticles in the irradiated area before and after removal (Figure 6B).

Then the removal of microplastics, extracted from face cleansing cream sample 13, is also successfully carried out in 0.2% H_2O_2 solution. Similar to microscale zeolites, the microplastics are also removed efficiently by the motile assembled chains under magnetic field (Figure 6C, Video S8), and the removal efficiency is about 71% (Figure 6D). Those two cases elucidate that this novel magnetic assembled chains performed excellently by shovelling effect in H_2O_2 solution.

Moreover, the shovelling effect also exhibits exceptional removal for microplastics in pure H_2O. These microplastics are from Warnow River. As displayed in Figure 6E (Video S9), during 40 s, 12 out of 18 microplastics are shovelled from UV area by magnetic assemblies under magnetic guiding, which achieves a removal efficiency of 67% (Figure 6F). Overall, the successful removal of suspended matter and microplastics from both, H_2O_2 solution and H_2O suggests that shovelling effect can work independent of the fuelling system under magnetic guiding.

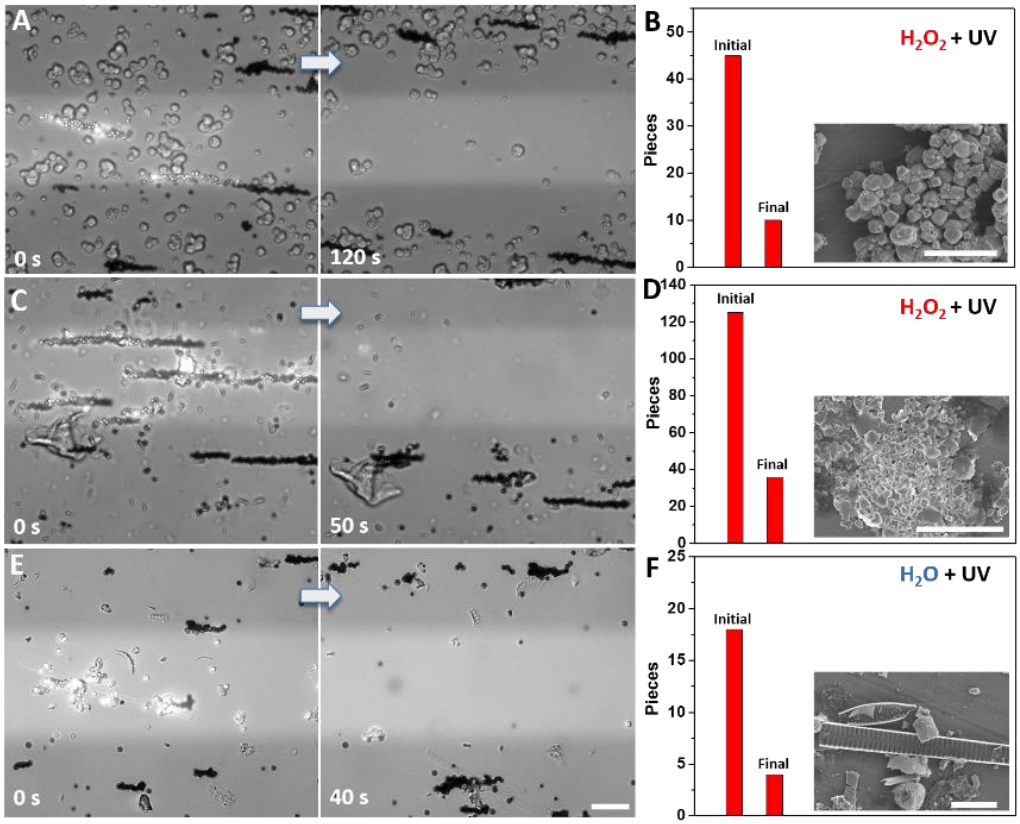

Figure 6. Magnetic Au@Ni@TiO_2 chains remove different extracts under magnetic field in different conditions: (A) washing powder sample 10 in 0.1% H_2O_2 under 63 mW UV light; (C) face cleansing cream sample 13 in 0.2% H_2O_2 under 63 mW UV light; and (E) microplastics sample from Warnow River in H_2O under 315 mW UV light. (B, D, F) amount of microparticles in the initial (before removal) and final (after removal) state. The insets are the SEM images. Scale bar, 10 µm.

DISCUSSION

Since the international attention has been focusing on the plastic problem, in central Europe many individuals are aware of the hazard and avoid products containing added microplastics. An easy to use control of the ingredients of individual products can be achieved by different apps.

European care products were found to rarely contain microplastics. However, the international market still has several products in use containing large proportions of added microplastics. Additionally, degrading plastic based clothing, storage containers and waste products remain a massive source of microplastics and plastic based microfibers. For this it is only natural, that in open waters, such as Warnow River and Baltic Sea, the suspended matter regularly contains microplastics. We extracted and analyzed these microscale matters and showed that in the laboratory scale, we can select the areas and reliably remove them.

We developed photo-catalytic micromotors, and employed either individual micromotors in peroxide or larger assembled chains under magnetic guiding for microplastics removal. The first removal strategy works through non-selective phoretic interactions of the catalytic swimmers that lead to large patterned passive structures around individual photocatalytic microswimmers. The fact that we can use a wide variety of materials with random properties shows the robustness of these phoretic attraction. However, for the here used system the phoretic interactions have the drawback that the presence of low concentration of peroxide is required, which is it not ideal for many water cleaning applications.

A way around the addition of peroxide is the use of shoveling, which would be rather inefficient using single microswimmers. For this, we introduced catalytic chains of magnetic assemblies that form spontaneously when a magnetic field is applied to these magnetic particles. These chains move as a collective and form kind of a barrier that displaces all microscale obstacles that come into their way. Employing this strategy, we were able to remove the extracted microplastics and random suspended matter from Warnow River, achieving about 67% of clearage efficiency in pure water. Also this effect is very robust and material independent. A faster elimination can be

achieved by adding a low percentage of peroxide, but the same sample can also be used in pure water and still achieves a very good output.

The versatility and robustness of the observed effects are clearly a plus for both systems, but also directly cause their biggest drawback: a lack of selectivity. Despite the fact, that especially the phoretic interaction is currently under intense mechanistic investigation, an in depth understanding is yet to be achieved. However, it might pave the way to ‘smarter collector particles.

CONCLUSIONS

We have developed a novel passive particle removal system formed by photo-catalytic Au@Ni@TiO_2 micromotors and characterized both, the motion of individual particles and assemblied chains in different fuels, namely H_2O and H_2O_2. Two strategies for removal of microplastics and suspended matter have been proposed. Few microplastics were found in recently bought products, but their presence in environmental water samples was confirmed. Both suspended matter and microplastics from personal care products and extracted from open waters could be removed from selected areas by individual micromotors and assembled chains. The removal was caused by phoretic interaction with individual micromotors and shovelling when the chained assemblies were used. The latter system works efficiently independent of the fuelling system: in dilute peroxide solution and water, which provides huge prospect for microplastics removal in practical environment. The greatest challenge for the future is to increase the selectivity and enable the micromotors to recognize microplastics as environmental pollutant in the variety of suspended materials, in order to improve the microplastics removal efficiency.

METHODS

Materials and reagents

Titanium (IV) iso-propoxide (TTIP) was purchased from Alfa Aesar Co. Ltd. Dodecylamine (DDA) was purchased from Fluka. Polyvinylpyrrolidone (PVP, K-30), 2,2′-azo-bis(isobutyronitrile) (AIBN), acrylic acid, and styrene were obtained from Sigma Co. Ltd. Personal care products including toothpaste, washing powder and face cleansing cream were bought from supermarket. All other reagents including ethanol, methanol and acetonitrile were of analytical grade and used as received without further treatment.

Synthesis of magnetic Au@Ni@TiO_2 micromotors

700 nm TiO_2 particles were synthesized via hydrolysis and condensation reaction of TTIP.[43] In brief, 0.18 mL of water was added to mixture solution of 105 mL methanol and 45 mL acetonitrile. Then 0.28 g of DDA was dissolved in the mixture under stirring. After stirring for 10 min, 1 mL of TTIP was added dropwisely and stirred for 12 h. Then the particles were washed with methanol three times and were calcined in tubular furnace under nitrogen flow for 2 h at 600 °C, and then the black TiO_2 particles were obtained. For the magnetic Au@Ni@TiO_2 particles, the monolayers of TiO_2 particles were prepared first by dropping 200 μL of suspension onto glass slides. Then 10 nm of nickel layer was first deposited on the top of TiO_2 particles via thermal deposition. Then 30 nm of Au layer was deposited. Finally, the magnetic Au@Ni@TiO_2 particles were released by ultra-sonication.

Extractions of suspended matter and microplastics from personal care products, river and sea

For the extraction from personal care products, 1 g of products was dissolved in 200 mL water. Then, vacuum filtrated device was used to filter the products solution. During the process of filtration, filter membrane with 0.2 μm holes was used. After the filtration, the extracts were

washed with water three times by vacuum filtrated device. The final extracts were obtained after dried with vacuum oven for 4 h.

Environmental microplastics samples from Warnow River and Baltic Sea were extracted using an enzymatic and chemical purification protocol.[48] Parts of the extracts were filtered using Si filters (10 μm holes).[49] The residues onto the Si filter were analysed by Raman microscopy. Subsequently they were dispensed with MilliQ-water for SEM investigations and removal experiments. Measurement details (Zeta Potential, SEM, FTIR and Raman) are described in the SI.

Motion of individual micromotors and assembled chains

Motion of individual Au@Ni@TiO_2 micromotors and assembled chains in water and H_2O_2 solution were investigated by an optical microscope (Carl Zeiss Microscopy GmbH, Germany) equipped with a Zeiss Colibri lamp. The UV light (385 nm, 315mW) was used to experiments. For the directional motion of magnetic assembled chains, magnet was set up for the controlling of the formation and motion.

Removal of carboxylated polystyrene bead (PS-COOH) by individual Au@Ni@TiO_2 micromotors

3 μm carboxylic polystyrene particles were synthesized by dispersion polymerization.[50,51] In brief, 1.35 g of PVP was dissolved in 102 mL of ethanol and 10 mL of water in a 250 mL round-bottom flask under N_2 gas flux with stirring at 280 rpm. Then 0.3 g of acrylic acid was added. The mixed solution containing 0.3 g of AIBN and 15 g of styrene was added to the previous solution. After N_2 gas flux for 30 min, the solution was heated to 70 °C for 24 h in oil bath and stirring lasted for 24 h. The obtained particles were washed with ethanol and water three times.

For the removal of PS-COOH particles, 5 μL of active particles, 5 μL of PS-COOH (1 mg mL^{-1}, 3 μm) particles, and 5 μL of 5 % H_2O_2 were mixed on the cleaning slide.

Removal of microplastics and suspended matter from water by Au@Ni@TiO_2 micromotors.

For the removal of suspended matter by individual micromotors, 7 µL of active particles, 2 µL of extract solution (2.5 mg mL^{-1}) and 1 µL of 1% H_2O_2 solution were mixed on the cleaning slide. For the removal of suspended matter and microplastics by assembled chains, the light area was limited and magnet was set up to form assembled chains and to control the motion direction. No H_2O_2 solution was added when carried out in water. The ratio of removed microparticles was determined by quantification of microparticles in the irradiated area before and after removal by counting all particles with light microscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications websitr at DOI:

Additional figures and tables of extracts from personal care products and Warnow River (PDF)

Video S1, Video S2, Video S3, Video S4, Video S5, Video S6, Video S7, Video S8, Video S9

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

J.S. and LL.W. thank the Volkswagen foundation for the Freigeist fellowship (grant number 91619), as well as the Kärcher foundation. LL.W. would like to acknowledge the China Scholarship Council (CSC) for the financial support. The help with the extractions performed by S. Görke are greatly acknowledged. A.K. thanks for financial support by the BONUS MICROPOLL project funded jointly by the EU and BMBF (03F0775A). The environmental microplastics samples (river Warnow, Baltic Sea) were taken within the Leibniz Competition project MirkOMIK, funded by the German Leibniz Association (grant number SAW-2014-IOW-2). Sampling and purification were done by Sonja Oberbeckmann and Matthias Labrenz (both Leibniz Institute for Baltic Sea Research Warnemünde), what is greatly acknowledged.

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