

Hydrogel-Based Janus Micromotors Capped with Functional Nanoparticles for Environmental Applications

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Janus nano/micromotors have been developed into various sizes, shapes, and functions for a blaze of applications especially in biomedical and environmental fields. Here, a fabrication method of Janus micromotors is reported by capping hydrogel microspheres with functional nanoparticles (NPs). Microspheres are prepared in droplet microfluidics relying on hydrogel polymerization to obtain spheres with diameters from 20 to 500 µm. By solidifying a hydrogel layer onto microspheres, functional NPs of MnO₂ (catalyst of H_2O_2), TiO₂ (photocatalyst), and Fe₃O₄ (magnetic guidance) are adhered onto microspheres resulting in Janus micromotors revealing different functionalities. Dynamics of Janus micromotors (diameter around 250 μ m) are explored by analyzing their trajectories in terms of mean squared displacement when immersed in H2O2 solutions of different concentrations, illuminated by light and guided in an external magnetic field. TiO₂ Janus micromotors perform well for water purification tasks as is exemplarily demonstrated with a degradation of Methylene Blue dye in water. The proposed fabrication method is versatile and enables to achieve adjustable coverage of a microsphere with NPs as well as to realize multifunctional Janus micromotors by adhering different NPs (e.g., MnO2 and Fe3O4) on a sphere. This method provides an attractive way to fabricate multifunctional Janus micromotors in a cost-effective manner for environmental applications.

1. Introduction

Nano/micromotors^[1–3] are designed to be self-propelled in various environment and to accomplish a series of tasks including

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biomedical applications^[4,5] from cargo transportation,^[6-8] drug delivery,^[9-11] biomolecular sensors^[12] to cell sorting,^[13,14] or environmental applications^[15,16] spanning from detection of metal elements,^[17] microbiological detection^[18] to water purification.[19-24] The sizes of nano/micromotors range from a few nanometers^[25] to several hundreds of micrometers.^[2,3,26] Their motion mechanisms can be divided into chemical reaction driven propulsion^[27,28] or other applied physical stimuli driven propulsion, including electric,^[29,30] magnetic,^[7,31] and ultrasound actuation.^[32,33] These motion mechanisms are determined by not only the size of the motors, but also the functional materials and the way they loaded on/in the motors. The sizes and the functional materials of nano/micromotors should be chosen according to the applications.

Among the diverse family of nano/ micromotors, there are many different shapes including wire-shaped,^[34] tubular,^[35] rocket-like,^[36] star-shaped,^[37] helical,^[38] and spherical.^[27,28] Janus nano/

micromotors with spherical shape are very attractive for their easy fabrication and functionalization.^[2,39,40] There are plenty of examples to create these functional layers using physical and chemical fabrication methods. The most well-known method to cap nano/microspheres is physical vapor deposition (PVD)^[6,28] that can half-coat nano/microspheres with functional material layers from top. Based on PVD, glancing angle deposition^[41] can vary the coverages of functional material layers. Microcontact-based approaches enable "stamping" of nanoparticles (NPs) onto spheres.^[42] Adjusting the depth of protection material layers is another strategy to fabricate Janus nano/micromotors with tunable coverage of functional materials.^[43,44] Chemical methods are also widely applied for the fabrication of Janus spheres, including emulsion solvent evaporation,^[45] bipolar electrodeposition,[46] and Pickering emulsion method.[47,48] There are also different techniques like gel trapping technique,^[49] providing the possibilities to tune the coverages level.

Different sizes of nano/micromotors are customized for different applications. Small sizes motors are typically applied in biomedical fields. Larger motors with sizes of several hundred micrometers are useful for environmental applications.^[26,50,51] For example, among environmental applications,

one important branch is degradation of pollutant in water, in which large micromotors (a few hundred micrometers) are of great relevance.^[52] This stimulates the development of fabrication methods to realize large multifunctional Janus micromotors in a cost-effective manner allowing for tunable coverages.

Hydrogel is a type of crosslinked hydrophilic and biocompatible polymers with the capability to retain a large amount of water.^[53,54] Photocurable hydrogel is attractive as a carrier because it can be easily processed into different sizes in spherical shape using high-throughput droplet microfluidics,^[27,55,56] which is cost effective for future mass production.^[52] By now photocurable hydrogels have been used into different applications ranging from drug delivery,^[55,57] cell culture,^[58] and 3D printing.^[59]

Herein, we demonstrate a low-cost and high throughput fabrication method based on photochemical solidification of hydrogel to adhere functional NPs onto hydrogel microspheres with the tunable coverages. We first rely on droplet microfluidics to generate hydrogel microspheres with different sizes ranging from 20 to 500 µm. To address environmental applications where larger sphere sizes are of advantage, we employ 250 µm large spheres for the realization of Janus particles. We explore the fabrication method by adhering different functional NPs (MnO₂, TiO₂, and Fe₃O₄) onto microspheres. After obtaining Janus micromotors, we apply their specific functionalities to propel themselves in various environments (pure water, H₂O₂ solution, and Methylene Blue (MB) solution) and under different stimuli (light and magnetic field). The peculiarities of the motion are studied relying on the quantitative analysis of the motion trajectories in terms of mean squared displacement (MSD). Furthermore, we demonstrate the flexibility of the adopted method by loading two kinds of functional NPs (MnO₂ and Fe₃O₄) on hydrogel microspheres in a single and direct process. Multifunctional Janus micromotors we realized are efficiently propelled in H₂O₂ solution yet can be also guided using external magnetic fields. Moreover, we demonstrate the application potential of TiO₂ Janus micromotors for water purification using Methylene Blue as a prototypical pollutant. This facial and low-cost method provides an alternative and flexible way to fabricate functional NP-capped Janus micromotors at a larger scale with tunable coverages for various applications.

2. Results and Discussion

2.1. Fabrication of Hydrogel Microspheres

Figure 1a illustrates the fabrication of hydrogel microspheres within a glass capillary microfluidic device. The inner fluid is hydrogel precursor and the outer fluid is 5 wt% continuous poly(vinyl alcohol) (PVA) solution. The inlets indicated in green are used to let the hydrogel precursor and the PVA aqueous solution into the glass cappillary device. Both fluids are injected simultaneously from syringes into the needle inlets. The inner fluid (hydrogel precursor) is broken into droplets (blue color) and transported along the tube when these two liquids meet with a typical 0.01 mL min⁻¹ of the inner flow rate, as

shown in the left bottom schematic of Figure 1a. After the first 5 min of UV polymerization (365 nm, intensity 300 mW cm⁻²) turning the hydrogel precursor into a crosslinked hydrogel, we obtain solidified hydrogel microspheres (pink color sphere in Figure 1a and their optical image in Figure 1b). The sizes of hydrogel microspheres are determined by the flow rate ratio of the outer fluid over the inner fluid.^[56] Therefore, the droplet formation is investigated under different flow rates of outer fluid (PVA solution) and the inner fluid (hydrogel precursor) (Figure 1c,d). By finely modifying the flow rate of the outer fluid and the inner fluid, we obtain hydrogel microspheres from around 20 up to 500 µm in diameters. There are three different flow regimes: wetting, jetting, and droplet.^[60-62] No hydrogel droplet is formed in the wetting regime. Droplet regime forms smaller droplets that can be solidified into solid microspheres with diameters from about 20 up to 300 µm (Figure 1e-I-IV). Under the jetting regime, the size of the hydrogel microsphere ranges from about 300 to 500 µm (Figure 1e-V-VIII). For future demonstration, we exemplarily choose particles with the size of about 250 µm which are created at 0.09-0.1 mL min⁻¹ of the outer flow rate and 0.01-0.03 mL min⁻¹ of the inner flow rate.

2.2. Fabrication of Hydrogel-Based Janus Micromotors with Different Coverages

After obtained hydrogel microspheres, we process them into Janus micromotors with different coverages of functional NPs. In this study we use three different types of NPs: manganese dioxide (MnO₂) NPs (50 nm), titanium dioxide (TiO₂) NPs (5-10 nm), and ferroferric oxide (Fe₃O₄) NPs (20 nm). These three functional NPs are widely used in the fabrication of nano/ micromotors as chemical catalyst (MnO₂), ^[26,63] photocatalyst (TiO_2) ,^[64–66] and magnetic material (Fe₃O₄),^[37,67,68] respectively. Every step in this fabrication is exactly the same for each type of functional nanoparticle. The core idea of the fabrication is to adhere functional NPs onto microspheres utilizing photocurable hydrogel precursor. The schematic of the fabricating procedure includes five steps (Figure 2a). First, functional NPs are added on the slice to embed hydrogel microspheres with different coverages. Then, we drip hydrogel precursor on the slice, following with 3 min standing. The next step is to remove all the residuals. It is important to clean the precursor between two microspheres to prevent them from solidifying together in the last step. Finally, the second UV polymerization aims at solidifying hydrogel precursor into solid hydrogel layer, which also adhere functional NPs onto the outermost surface of hydrogel microspheres. Janus micromotors with different coverages can be obtained by finely adjusting the depth of NPs layer at the first step (Figure 2b-I-IV; Figure S1, Supporting Information). Correspondingly, their scanning electron microscopy (SEM) images (Figure 2c-I-IV; Figure S2, Supporting Information) show different coverages of functional NPs distributed on the microspheres. These SEM images indicate that hydrogel microspheres after the second UV polymerization are turned into Janus micromotors with different coverages of functional NPs, such as MnO₂ (Figure 2c-I,II), Fe₃O₄ (Figure 2c-III), and TiO₂ (Figure 2c-IV). We would like to emphasize that the proposed

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Figure 1. Fabrication process of hydrogel microspheres using droplet microfluidics. a) Schematics of the used glass capillary device and the formation process of hydrogel microspheres. b) Optical image of photochemically solidified hydrogel microspheres. c,d) Phases diagrams showing three flow regimes as a function of inner flow rate and outer flow rate. e) Optical images of hydrogel microspheres in different sizes after first UV polymerization. Scale bar: 100 µm.

fabrication method allows producing repeatably and reproducibly Janus particles with defined coverage. To facilitate this statement, we exemplarily show the result of the Janus particles with coverage of 25%, 50%, and 75% repeated for three times (Figure S3, Supporting Information). Furthermore, we note that our fabrication method can be readily extended to fabricate hydrogel-encapsulated Janus micromotors by reinjecting Janus micromotors into the microfluidic device shown in Figure 1a. For further experiments, we collect Janus micromotors and place them in different environments to study their motion. To analyze the motion quantitatively, we use trajectory tracking and MSD analysis.^[69]

2.3. Catalytic-Reaction Driven Motion of MnO_2 Janus Micromotors

We first investigate the motion of MnO_2 Janus micromotors with a coverage of around 25% (Figure 3a,b) in different concentrations of H_2O_2 . The catalytic reaction occurs as follows^[70]

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$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2 \uparrow$$
(1)

The micromotors are driven by O_2 bubbles produced from H_2O_2 splitting with the MnO_2 NPs as a catalyst. Representative trajectories (up to 30 s) of MnO_2 Janus micromotors from the



Figure 2. Fabrication of hydrogel-based Janus micromotors capped with different coverages of functional NPs. Schematic illustration indicating a) the processing method and b) hydrogel microspheres with different coverages of functional NPs. c) SEM images of hydrogel-based micromotors with different coverages: I,II) MnO₂ NPs; III) Fe₃O₄ NPs; IV) TiO₂ NPs. Scale bar: 100 μ m. The boundaries between hydrogel and NPs are underlined by the yellow dotted curve.

tracking videos (Videos S1 and S7, Supporting Information) are color coded to reveal the time progress (Figure 3a). With the increase of the H2O2 concentration, particles evidently have longer displacement, which is characterized by larger MSD (Figure 3b). We only show the first 9 s of the MSD curve based on the data from the trajectories (about 1/4 of the tracking time).^[71] Evidently, the MSD increases with the concentrations of H₂O₂. Note that in pure water, MnO₂ Janus micromotors reveal Brownian motion with a small MSD. The MSD increases and reaches a rather high value of 1.5 mm² at 9 s when the H₂O₂ concentration is set as 30 wt%. A good reproducibility of the catalytic performance is demonstrated in the Supporting Information by quantitatively comparing several trajectories and corresponding MSD curves of nominally same Janus particles propelling in 1 wt% (Figure S4, Supporting Information) and 30 wt% (Figure S5, Supporting Information) H₂O₂ solution.

By tuning the coverage of MnO_2 on hydrogel microspheres, we can achieve different catalytic performance in a solution with the same H_2O_2 concentration instead of various concentrations (Video S2, Supporting Information). In Figure 3c, we investigate the motion of MnO_2 Janus micromotors with different MnO_2 coverages. It is evident that MSD curves are in direct proportion to the coverages. At 9 s, the MSDs start from near 0 (no MnO_2 coverage) and increases to about 5.7 mm² for Janus micromotors with about 60% coverage.

In **Table 1**, we compare the motion performances of MnO_2 Janus micromotors with the literature reports by taking into account the motor size, capping functional material layer, capping coverages, capping method, and motion mechanisms. Typically, two methods are applied to cap micromotors possessing diameters in the range of 100–400 μ m:

- 1. Thin film coating using spluttering^[72] and e-beam evaporation:^[27] When compared to catalytic micromotors fabricated using these methods (2.5, 10 wt% H_2O_2 corresponding to 200, 100 μ m s⁻¹, 50% coverage Pt film), our MnO₂ Janus micromotors (3 wt% H_2O_2 , 135 μ m s⁻¹, 25% coverage MnO₂ NPs) reveals comparable motion performance although we are not using expensive Pt layer and complex vacuum facilities for deposition. In this respect, we are convinced that the capping method developed in the study is a facial and cheap method. Furthermore, we can add multiple kinds of functional nanoparticles in one time to fabricate multifunctional nanoparticle Janus micromotors with tunable coverages.
- Self-assembly method like microfiber confined method^[73] and interface assembly method based on droplet microfluidics,^[21,74] as well as other methods like vortex mixing:^[75]





Figure 3. Motion characterization of MnO_2 Janus micromotors. a) Trajectories of MnO_2 Janus micromotors in different concentration of H_2O_2 taken over 30 s (Video S1, Supporting Information). b) The corresponding MSD curves. Each curve is the average of three MSD curves taken under same condition. c) The MSD curves of MnO_2 Janus micromotors with different MnO_2 coverages in 30 wt% H_2O_2 (Video S2, Supporting Information).

These newly developed methods are closer to our approach. They are very flexible and can work with tunable coverages of multifunctional NPs. However, compared with catalytic micromotors fabricated relying on these microfluidic-based capping methods with alike coverages^[21,74] (20, 30 wt% H₂O₂ corresponding to 127, 100 μ m s⁻¹ using MnO₂ and Ag NPs, respectively), our MnO₂ Janus micromotors show better motion performance yet at much lower concentration of H₂O₂ fuel, with the average speed of 135 μ m s⁻¹ at 3 wt% H₂O₂. The reason for this increase is twofold: On the one hand, the used MnO₂ NPs are located in the surface region and, therefore, offer larger active catalytic surface area. On the other hand, the crosslinked hydrogel, in which the NPs are embedded, allows fuels to go in and get in contact with the NPs buried

Table 1.	Comparison	of the	motion	performance.
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in the polymer matrix, which then attributes faster bubble generation and faster motion.

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2.4. Photocatalytic Motion of TiO₂ Janus Micromotors

 TiO_2 contained nano/micromotors have been vastly explored for applications in photocatalytic degradation.^[76,77] We fabricate TiO_2 Janus micromotors by adhering TiO_2 NPs to a hydrogel microsphere with coverages about 50% and analyze their motion under different conditions. Trajectories (Videos S3 and S6, Supporting Information) and the corresponding MSD are shown in **Figure 4**. Without UV light illuminating, trajectories of TiO_2 Janus microspheres are very similar in different

Spherical Janus micromotor	Capping method	Size [µm]	Coverages [%]	Motion mechanism	Speed [µm s ⁻¹]	Application scenario	Refs.
Pt-hydrogel	Spluttering	≈350	50	Bubble propulsion	≈200 (2.5 wt% H ₂ O ₂)	MRI	[72]
Pt–hydrogel	e-beam evaporation	200	50	Bubble propulsion	≈100 (10 wt% H ₂ O ₂)	-	[27]
Pt-ETPTA	Microfluidic-based microfiber-confined method	≈210	1	Bubble propulsion	\approx 90 (30 wt% H ₂ O ₂)	-	[73]
MnO ₂ NPs-ETPTA	Self-assembly at the interface	280–370	30	Bubble propulsion	≈127 (20 wt% H_2O_2)	Pollutant degradation	[21]
Ag NPs-ETPTA	Self-assembly at the interface	200–300	18	Bubble propulsion	\approx 100 (30 wt% H ₂ O ₂)	Pollutant degradation	[74]
Magnetic-oil droplet	One-step vortex mixing	200–400	-	External magnetic field	<14	Pollutant adsorption	[75]
MnO ₂ NPs-hydrogel	Photocurable hydrogel assisted method	≈250	25	Bubble propulsion	≈135 (3 wt% H ₂ O ₂) MSD: 18 558 µm ² within 1 s	Pollutant degradation	This work





Figure 4. Motion characterization of TiO₂ Janus micromotors. a) Trajectories taken over 30 s in pure water and in 30 wt% H_2O_2 when 365 nm UV light (intensity: 300 mW cm⁻²) is turned on/off (Video S3, Supporting Information). b) The corresponding MSD curves. Each MSD curve is the average of three MSD curves taken under the same condition.

liquids: pure water and 30 wt% H_2O_2 (Figure 4a). The TiO₂ hydrogel microspheres did not move efficiently in pure water even when exposed to UV light (365 nm, intensity 300 mW). Only when placed in 30 wt% H_2O_2 and illuminated with UV light, the TiO₂ Janus micromotors reveal an enhanced motion, which can be seen from their trajectories (Figure 4a) and MSD (Figure 4b). Under UV light illumination and in the H_2O_2 solution, the motion mechanism of TiO₂ hydrogel microspheres is as follows^[78]

$$\mathrm{TiO}_2 + hv \to \mathrm{h}^+ + \mathrm{e}^- \tag{2}$$

$$H_2O_2 + 2h^+ \rightarrow O_2 + 2H^+$$
(3)

$$H_2O_2 + 2e^- + 2H^+ \rightarrow O_2 + 2H_2O$$
 (4)

 O_2 bubbles are generated and thus propel TiO_2 hydrogel microspheres. From MSD data, we can observe that it reaches about 0.4 $\rm mm^2$ in 9 s with the presence of both UV light and $\rm H_2O_2$ solution.

2.5. Catalytic Motion and Magnetic Control of $\mathsf{Fe}_3\mathsf{O}_4$ Janus Micromotors

Various magnetic coatings are typically applied to achieve directed motion control of micromotors, including Fe_3O_4 NPs,^[37] Fe film,^[35] permalloy caps,^[79] and [Co/Pt(Pd)] multilayer stacks.^[7,80] With the same fabrication method, we obtain Fe_3O_4 Janus microspheres with about 50% coverage and explore their autonomous motion in 30 wt% H₂O₂ as well as the directed motion in pure water in an applied magnetic field (Video S4, Supporting Information). Fe_3O_4 Janus microspheres are self-propelled in 30 wt% H₂O₂, with the trajectory about four times longer than the one in pure water, exhibiting a weak catalytic

activity (Figure 5a). Fe $_3O_4$ can decompose the H_2O_2 just like MnO_2, acting as a catalyst

$$2H_2O_2 \xrightarrow{Fe_3O_4} 2H_2O + O_2 \uparrow$$
(5)

In the field of nano/micromotors, the catalytic ability of Fe₃O₄ NPs in H₂O₂ is usually not utilized but the magnetic feature of Fe₃O₄ NPs is the most common applied one.^[37,81] With the application of a small magnetic field (strength \approx 3 mT),



Figure 5. Motion characterization of Fe₃O₄ Janus micromotors. a) MSD curves in pure water and in 30 wt% H_2O_2 and the corresponding characteristic trajectories. Each MSD curve is the average of three MSD curves taken under the same condition. b) Trajectories of Fe₃O₄ Janus micromotors in pure water with applied magnetic field (Video S4, Supporting Information).







Figure 6. Motion characterization of multifunctional MnO₂ and Fe₃O₄ Janus micromotors. MSD curves in 30 wt% H₂O₂ and the corresponding characteristic trajectories with or without applied magnetic field. The MSD curve is the average of three MSD curves taken under the same condition (Video S5, Supporting Information).

 Fe_3O_4 Janus microspheres are oriented and their trajectories show a directionally deterministic motion (Figure 5b). By manipulating the orientation of a bar magnet, we can obtain complex trajectories and even write characters as demonstrated in Figure 5b where "F," "D," and "U" are written.

2.6. Catalytic Motion and Magnetic Control of Multifunctional Hydrogel Microspheres

In previous sections, we applied the fabrication method (Figure 2a) to realize Janus particles with a single functionality provided by either magnetic (Fe_3O_4) or catalytic (MnO₂) NPs. The method is not limited to be used for a single kind of NPs. It can be readily applied if different functionalities should be combined in a multifunctional Janus micromotor. Here, we decorate a hydrogel sphere with two kinds of functional NPs in a single process. For demonstration purposes, we use a mixture of MnO₂ and Fe₃O₄ NPs. The mass ratio of MnO₂ NPs over Fe₃O₄ NPs is 2:1. The coverage degree is chosen to be about 50%. Without magnetic field, MnO₂ and Fe₃O₄ multifunctional Janus microspheres present a Brownian motion as shown with the right bottom trajectory and the corresponding MSD (Figure 6). With the applied magnetic field, MnO_2 and Fe_3O_4 multifunctional Janus micromotors reveal directional motion (Video S5, Supporting Information). Similar to the discussion in Section 2.5, complex trajectories, e.g., square (Figure 6) can be achieved by an appropriate manipulation with a permanent magnet. The activity of these Janus micromotors can be tailored by adding H_2O_2 fuel solution. In the 30 wt% solution of H_2O_2 , the MSD (Figure 6) can be enhanced almost ten times compared to that of Fe₃O₄ Janus micromotors (compare with the data in Figure 5a). The efficient propulsion is assured by the

superior catalytic activity of $\rm MnO_2$ NPs compared to the one of $\rm Fe_3O_4$ NPs.

2.7. Degradation of Methylene Blue using TiO_2 Janus Microspheres

 TiO_2 is recognized to be photocatalytic and effective to purify MB under UV light illumination (wavelength of 365– 368 nm).^[78,82] We explore the degradation performance of our TiO_2 Janus micromotors using MB as an example of a contaminant. To quantify the degradation process, we use a UV– vis spectrophotometer to measure the time evolution of the concentration of MB. The MB concentration in the reference group shows almost no change both under the dark environment and under the UV light illumination (365 nm, intensity 300 mW cm⁻¹), with the peak wavelength locating at 664 nm (**Figure 7**a). The experimental group with TiO_2 Janus micromotors first degrades with its absorption drop from 1.3 to 0.9 and then decreases significantly to near 0 after 60 min of UV light



Figure 7. UV-vis absorption spectra during 120 min dark experiment and following 60 min UV light irradiation of a) MB solution (reference group) and b) MB solution mixed with TiO_2 Janus microspheres (experiment group). c) Photocatalytic degradation curve of the experimental group (red symbols) and reference group (black symbols). Arrows indicate culture pictures corresponding to the dots. Scale bar: 1 cm.



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illumination (Figure 7b). Compared to the reference group, the MB are evidently degraded by TiO₂ hydrogel microspheres (Figure 7c), showing 95.64% degradation after 1 h. A summary comparing the performance of our TiO₂ Janus spheres for water purification to the state-of-the-art reports is provided in Tables S1–S3 in the Supporting Information. We note that the weight ratio (motor mass/MB mass) of our Janus micromotor reaches a small number of 120, showing a promising economic way to use less motors for equal performance of water purification. Compared to the studies where TiO₂ NPs were used,^[83,84] our TiO₂ Janus micromotors can be turned into being recycle if the motors will be prepared from the mixture of TiO₂ and Fe₃O₄ NPs as described in the Section 2.5 above.

3. Conclusions

In summary, we have demonstrated a fabrication method to obtain hydrogel Janus micromotors possessing a diameter of about 250 µm functionalized with different NPs including MnO₂, TiO₂, and Fe₃O₄. Hydrogel spheres are fabricated using a droplet microfluidic device and are decorated with functional NPs relying on a UV polymerization processing. The fabrication method allows to tune the coverage degree of functional NPs on hydrogel microspheres. Furthermore, multifunctional Janus micromotors can be obtained by adding more than one kind of functional NPs (MnO2 and Fe3O4) at the initial step of the fabrication process. The micromotor motion is studied by analyzing their trajectories in terms of the MSD. We demonstrate the performance of TiO₂ Janus micromotors for water remediation tasks using MB. The degradation efficiency of our TiO₂ micromotors in 1 h is at least 5% higher than other TiO₂contained motors (no other chemicals).

Our fabrication method can be used to scale up the production of multifunctional Janus particles by employing larger glass substrate and placing more microspheres onto substrates at one time. The glass device we used is cost-effective, which avoids using expensive thin film deposition equipment. Such low-cost method tailored for large size functionalized Janus micromotors has a promising future in environmental sector and might inspire nano/micromotors for biomedical applications.

4. Experimental Section

Materials: Manganese dioxide (MnO₂) NPs (diameter: 50 nm) were purchased from Bike New Material Ltd. Titanium dioxide (TiO₂) NPs (diameter: 5–10 nm) were purchased from MACKLIN. Ferroferric oxide (Fe₃O₄) NPs (diameter: 20 nm), methacrylic anhydride (MAAn), ethylene glycol dimethacrylate (EGDMA), and 2-hydroxy-2 methyl propiophenone (Darocure 1173) were purchased from Aladdin reagent. Rhodamine B and PVA (M_w 13000–23000, 98% hydrolyzed) were obtained from Sigma-Aldrich. Hydrogen peroxide solution (H₂O₂, 30 wt%) was purchased from Hushi Inc.

Preparation of Glass Capillary Microfluidic Device: The glass capillary device consisted of one glass slide substrate, three capillaries, and three needle inlets (Figure 1a). One side of two cylindrical capillaries (outer diameter of 0.6 mm; inner diameter of 0.5 mm) were tapered to 40 and 300 μ m, respectively. The first cylindrical capillary with a smaller tapered side (inner diameter of 40 μ m) acted as an input capillary for

inputting the hydrogel precursor. The second cylindrical capillary with a larger tapered side (inner diameter of 300 μ m) was used for transporting hydrogel droplets. These tapered sides of cylindrical capillaries were inserted from opposite sides into the third capillary with a square cross-section (inner opening of 1 mm; outer opening of 1.1 mm). The centers of these three capillaries were aligned using an inverted microscope (Nikon TS100). Two needle inlets and one needle inlet were set for injecting of hydrogel precursor and PVA solution, respectively. Using Araldite rapid epoxy adhesive, these inlets were glued onto glass slide together with all the capillaries.

Fabrication of Janus Micromotors with Different Coverages: Hydrogel microspheres were fabricated using a microfluidic setup shown in Figure 1a. Hydrogel precursor was prepared by mixing Darocure 1173 (10 vol%) with MAAn (70 vol%) and EGDMA (20 vol%). The hydrogel precursor (inner fluids) was injected from two needle inlets to the first capillary. PVA aqueous solution (5 wt%, outer fluids) was used as a surfactant, which flows into the device from another inlet. By controlling flow rates of the inner and outer fluids using microfluidic pumps (Harvard Apparatus), different sizes of hydrogel droplets were obtained. Solid hydrogel microspheres were formed on a glass slide after a 5 min UV-polymerization treatment (UV light 365 nm, AC80V-240 V). A typical flow rate setting was inner flow rate (0.005–0.01 mL min⁻¹) and of the outer flow rate (0.06–0.1 mL min⁻¹).

Solid hydrogels microspheres with a diameter of about 250 μ m were used as a template to prepare Janus micromotors by applying different coverages of functional nanoparticles. The processing was done on a glass slide. Hydrogel microspheres were covered with a NPs layer. By adjusting the thickness of the NPs layer, any desired degree of coverage was achieved. To fabricate completely covered hydrogel micromotor, the thickness of the NPs layer was tuned to be larger than the diameter of the hydrogel spheres. Then, the samples were soaked in a drop of hydrogel precursor. After 3 min standing, the samples were washed carefully in pure water for 5 s to remove residuals, following with the second UV-photopolymerization step (5 min). With this, Janus micromotors with different coverage of functional nanoparticles were obtained.

Morphology Characterization: SEM imaging was conducted at 1 kV (Zeiss Sigma SEM) to obtain morphologies of the hydrogel micromotors with different coverages of NPs. Before SEM, Janus micromotors were coated with 5 nm Au by electron beam evaporation for better conductivity. The optical microscope (OLYMPUS BX51) and the Topview software were operated to observe Janus micromotors.

Motion Recording: A stereoscopic microscope (ST6024-B1 Ruihong) equipped with a video camera was used for capturing motion of Janus micromotors (18 frames s^{-1}). Motion studies of individual MnO₂ Janus micromotors were performed in the H₂O₂ solution of different concentrations (0-30 wt%) in a vessel with a diameter of 10 cm. To acquire relevant statistics, the tracking was done for ten nominally identical micromotors. Each video was taken for 100 s. For the motion recording of TiO₂ Janus micromotors, individual Janus particles were put into pure water or 30 wt% H2O2 solution. The particles were illuminated with a UV light (365 nm, AC80V-240 V) to explore the photocatalytic performance of TiO₂ micromotors. Under each condition, three Janus motors were tracked and recorded (each recording lasts 100 s). Magnetic control studies were carried out by putting a permanent magnet 5 cm away from Fe₃O₄ Janus micromotors with the strength of about 3 mT. To address the catalytic performance of Fe₃O₄ Janus micromotors, their motion was studied in pure water and H₂O₂ solution (30 wt%). The data shown in Figure 5 is the result of the averaging over three nominally identical Fe₃O₄ Janus micromotors.

Video Analysis: The image processing package^[85] Fiji (http://fiji.sc/) together with its plugin Trackmate^[86] were used for particle tracking to get trajectories of MnO2/TiO2/Fe3O4 Janus micromotors from videos. The MATLAB per-value class @msdanalyzer (https://tinevez.github.io/msdanalyzer/) and a custom MATLAB script were used to calculate the MSD.^[71,87]

Degradation Analysis of Methylene Blue: MB was used as an organic contaminant to investigate the purification performance of TiO_2



hydrogel microspheres. The reference group was 10 mL (5 mg L⁻¹) MB solution and the experiment group was 10 mL (5 mg L⁻¹) MB solution mixed with 3 mg TiO₂ hydrogel microspheres. The reference and the experiment groups were contained by plastic culture dishes under same environmental conditions during the experiment. These two groups were first put in the dark environment under a gentle stirring at 23 °C. Then, the two groups were irradiated by UV light (365 nm, intensity 300 mW cm⁻¹), with a gentle stirring at 23 °C. The MB concentration was measured by an UV light spectrophotometer (UV-2550, Shimadzu Scientific Instruments, Japan) at intervals of 10 min during illumination. Photos of the culture dishes containing reference group and experiment group were taken by an inset camera (Huawei 8X) every 10 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

catalytic motion, environmental applications, functional nanoparticles, Janus micromotors, photocurable hydrogels

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