Short Communication

A simple method to fabricate metal-oil micromachines

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Received: 16 December 2019 / Accepted: 12 March 2020 / Published online: 21 March 2020
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Abstract
Micromachines have garnered attention for their potential use in various applications, such as the fields of sensing, environmental remediation, and targeted drug delivery. The Janus micromachine that has an asymmetrical structure and important application potentials has received extensive attention. The self-propulsion of the Janus motor is produced by making full use of the solution environment. In this paper, we use a simple method to fabricate metal-oil micromechanics, which is called the Janus droplet micromachine. The Janus droplet micromachine is consisting of liquid olive oil and solid Al particles, which is driven by gas generated due to reaction between Al particles and alkaline solution. The whole motion process of the Janus droplet micromachine is investigated. In addition, direction control of the droplet micromachine with Fe particles added is demonstrated by applying external magnetic field. This solid–liquid composite Janus droplet micromachine has broad potential applications in drug transportation and other areas.

Keywords Micromachine · Metal-oil · Droplet

1 Introduction

The use of micromachines to power micromachines and microrobots is one of the most exciting challenges facing nanotechnology. In the past decade, some research teams have developed powerful nano/microscale motors based on several propulsion mechanisms to meet future potential applications, ranging from targeted drug delivery [1–3] to environmental remediation [4–6]. According to the shape of these motors, they can be divided into wires motors [7, 8], tubular motors [9–12], and spherical Janus micromachines [13–16]. The motions of these micromachines are realized based on different mechanisms, including bubble propulsion [17–19], self-electrophoresis [20], self-diffusiophoresis [21], self-acoustophoresis [22], etc. Among all the micromachines, Janus micromachines have demonstrated a wide range of potential applications due to their asymmetrical structure and various motion behaviors. For instance, Gao's team described a Pd/Al microparticle motor that can move in different fuels: base, acid, or hydrogen peroxide [23]. Moreover, Al–Ga/Ti microparticle motors was manufactured by the same team, and self-propelling in water was exhibited [24]. Dong's group described light-driven TiO_2/Au Janus micromachines which can be powered efficiently by UV light in pure water [25]. Tang's research team demonstrated the photochemical induced actuation of liquid metal marbles and gave an equation describing the principle of this actuation [26]. In addition to these solid Janus micromachines, Sindoro's team successfully assembled the Janus liquid droplets which can be propelled by electric field [27]. And in Wang's team, the self-driving and long-term transmission movement of PVC particles on the water surface [28]. Xu's team also did corresponding research on self-igniting liquid metal motors [29]. In addition, the droplet motor shows a powerful application in coating [30, 31]. Generally, it is necessary for the liquid micromachine to achieve motion under the action of external force [32–34]. In this work, we

✉ Ying Wang, 2006000081@shiep.edu.cn; ✉ Yongsheng Liu, ysliu@shiep.edu.cn | [1]Department of Physics and Mathematics, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 201300, People's Republic of China. [2]Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China.

use a simple method to fabricate Janus droplet micromachine, and it also can be self-propelled without the need of external propulsion.

Herein, Janus droplet micromachine consisting of olive oil droplet and solid Al particles is produced. In an alkaline environment, the Al particles react with alkaline solution to generate bubbles, which push the micromachine to move in opposite direction. We investigated the influence of bubble on the movement of Janus droplet micromachine. The effect of the number of Al particles which covering the surface of and the surfactants used on the locomotion have been studied. In addition, under externally applied magnetic field, Janus droplet micromachine with Fe particles can be achieved directional control. Janus droplet micromachine can achieve self-propulsion and motion direction control, we anticipate that Janus droplet micromachine may have great potential in a variety of practical applications.

2 Experimental

2.1 Materials

Non-ionic surfactants of Triton X-100 and Tween 20, anionic surfactant of sodium dodecyl sulfate (SDS), and sodium hydroxide (NaOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Aluminum (Al) particles with an average diameter of 5 μm and iron (Fe) particles with an average diameter of 5 μm were purchased from Qinghe County Chuangjia Welding Materials Co., Ltd. Oil used in the experiment was olive oil (100% pure, Sinopharm Chemical Reagent Co., Ltd). Deionized water (18.25 MΩ cm) was obtained from a Millipore Mil-li-Q purification system. All the chemicals were of reagent grade and used without further treatment.

2.2 Fabrication methods

Janus droplet micromachine: The olive oil was first put into a glass bottle. And then, the Al particles with a diameter of 5 μm were added. After vibrating the mixture with a lab dancer (VWR Scientific) at the maximum speed of 2500 rpm for 5 min, the particles were dispersed into olive oil uniformly. Then, 0.1 mL of this solution was mixed with 20 ml deionized water solution containing 0.1 mL Triton X-100 aqueous solution (1% v/v). After this, the three-phase mixture was shaken with the lab dancer at 2500 rpm for 30 s. Finally, the mixture was allowed to stand for 40 min.

Janus droplet micromachine with iron particles: Fe particles and Al particles are uniformly mixed at a mass ratio of 1:5. And the other experimental steps are kept unchanged.

2.3 Characterizations

The morphologies of the materials were characterized by field emission scanning electron microscopy (SEM, Zeiss Supra 55).

2.4 Motion investigations

For this study, the oil containing Al particles was first placed in a quartz container containing 1 mol/L NaOH solution. The height of the solution was around 3 mm. The spontaneous motions of the Janus droplets micromachine in alkali solutions were observed by using the upright metallographic microscope (DYJ-980BD). And the images were recorded by CCD camera (DYS-500, DIANCAM). The motion trajectory of the Janus droplet micromachine was analyzed by utilizing the video spot tracker software.

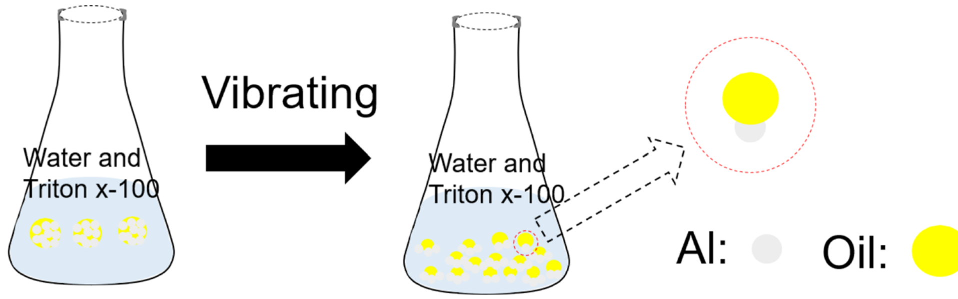
2.5 Magnetic field control

In the preparation of the Janus droplet micromachine with iron particles, a part of the iron particles was mixed in the aluminum particles. The movement of the micromachine was controlled under the guidance of a magnetic field.

3 Results and discussion

The fabrication process of the Janus droplet micromachines is shown in Scheme 1, which is based on the single blend and vibrate technique. The mixed solution containing olive oil and Al particles is dispersed inside the aqueous solution in the presence of the Triton X-100 surfactant. The Janus droplet micromachine is obtained after the mixed solution is dispersed. During the still process, the Al particles accumulates on the bottom surface of the oil droplet due to the gravitational effects.

In the Fig. 1, the Janus droplet micromachine was fabricated by adding Al particles into olive oil with a concentration of 80 mg/mL. The oil containing Al particles was then mixed with NaOH solution. The Fig. 1a–c and Video S1 show the details of the self- propulsion motion of a typical Janus droplet micromachine with a diameter of 115 μm. It is observed that Janus droplet micromachine is suspended in the solution. The pure olive oil droplets usually floated on the surface of the solution because the density of the oil is less than the density of the water. But due to the presence of Al particles, the Janus droplets could be well suspended in solution. In addition, the quality of the aluminum particles plays an important role in the movement of the Janus



Scheme 1 Schematic illustration indicating the fabrication process

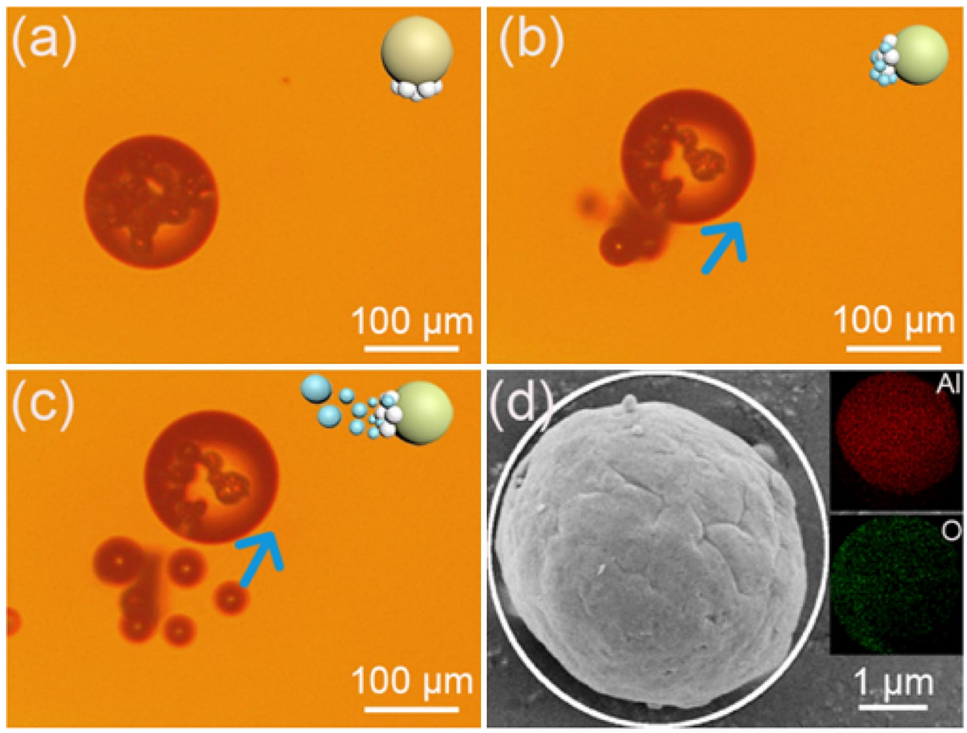


Fig. 1 **a**–**c** Janus droplet micromachine from stationary to moving. Illustration showing the state of the Janus droplet micromachine. **a** Janus droplet micromachine is just put into NaOH solution and no bubble is generated at this time. **b** Bubbles are generated and the Janus droplet micromachine rotates. **c** Janus droplet micromachine is pushed by the bubble. **d** The SEM image of an Al particles, and the EDX mapping of Al particles of Al (red), and O (green)

droplet micromachine. As can be seen from Fig. 1d, the surface of the Al particle is smooth. And the EDX mapping results demonstrate a uniform distribution of O and Al elements in the Al particle, and no other impurity is detected. It is worth noting that the existence of O suggests a native oxide layer on the surface of Al particle.

In order to better explain the moving process of the micromachine, we divide this process into three stages: still, reaction, and promote. First, The Al particles adsorbed by the oil droplets are all concentrated at the bottom of the oil droplet due to the action of gravity, as shown in Fig. 1a. In an alkaline environment, the dense aluminum oxide on the surface of the Al particles reacts with NaOH first (Formula 1).And no obvious experimental phenomenon can be observed during this step.

$$Al_2O_3(s) + 2OH^-(aq) \rightarrow 2AlO^{2-}(aq) + H_2O(l), \quad (1)$$

Then, after the dissolution of aluminum oxide layer, the inner Al is exposed to the alkaline solution.

$$2Al(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow 2AlO^{2-}(aq) + 3H_2(g), \quad (2)$$

The chemical reaction between Al and NaOH (Formula 2) leads to the generation of H_2. And obvious bubbles can be observed on the Al particles surface. The balance of the Janus droplet micromachine is broken due to the generation of surrounding bubbles. As the reaction continues, the bubble becomes larger, and some bubbles begin to break away from the Janus droplet micromachine, as shown in Fig. 1b. Next, the reaction is further aggravated, more bubbles are generated. And bubbles constantly detach from the Janus droplet micromachine, resulting in the propelling of the Janus droplet micromachine, as shown in Fig. 1c.

Obviously, Al particles play an important role in micromachines motion. The power source of Janus droplet micromachine is the generation of bubbles, and the amount of Al particles can remarkably affect bubbles generation. In our experiment, we studied the influence of the concentration of Al particles in oil (40, 80, 120, and 160 mg/mL) on the amount of Al particles on the surface of the oil droplet, and the results are shown in Fig. 2a–d. For the figure, we can clearly observe that the amount of aluminum particles increases. In the statistics shown in Fig. 2e, one may note that the particle number show a remarkable increase when the concentration increases from 40 to 80 mg/mL. While for concentration increase from 80 to 160 mg/mL, the number of Al particles increases slowly, demonstrating a tendency to saturation.

The influences of the Al particle concentration on the motion speed and life time of Janus droplet micromachines are further investigated. In our experiment, 10 individual measurements were conducted for each Al particle concentration to obtain the average speed and life time, and the results are shown in Fig. 3. As the concentration of Al particles increases, the average speed increases first, and then decreases to a constant value. At low Al particles concentration (i.e., < 80 mg/mL), the motion speed increases with the Al particle concentration. When the concentration of Al particles is 80 mg/mL, the average speed reaches a maximum of 32 μm/s. When the concentration of Al particles is larger than 80 mg/mL, more bubbles are generated, but Janus droplet micromachine is not effectively promoted. This indicates that large concentration beyond certain limit can hinder the movement of the micromachine. We consider that there are several factors leading to this phenomenon. First, a small amount of Al particles detach from the oil droplets during the reaction. Secondly, a large amount of gas produces leads

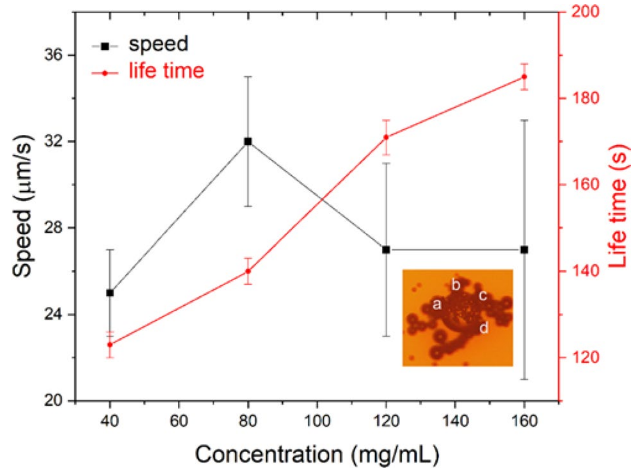


Fig. 3 Dependence of the speed and life time of the Janus droplet micromachine on the Al particle concentration. Inset is a Janus droplet micromachine in NaOH solution, and the Al particle concentrations is 160 mg/mL. a, b, c, d are bubble generation points

the bubbles detached from the oil droplet along multiple locations. The counteract of the thrust forces decrease the motion speed, as shown in the inset of Fig. 3, where a large number of bubbles are generated at four points (a, b, c, and d) simultaneously. Figure 3 also demonstrate that the life time of Janus droplet micromachine increases almost linearly with the concentration of Al particles (red line in Fig. 3). This is because that large Al particles concentration in oil solution lead to a large number of Al particles absorbed, resulting in longer bubble generation time.

Surfactant also play a very important role in the bubble-propelled motion of Janus droplet micromachine. Previous investigation demonstrated that surfactants have an important influence on size and detachment of bubbles. In Wang's works [35], the surfactants and

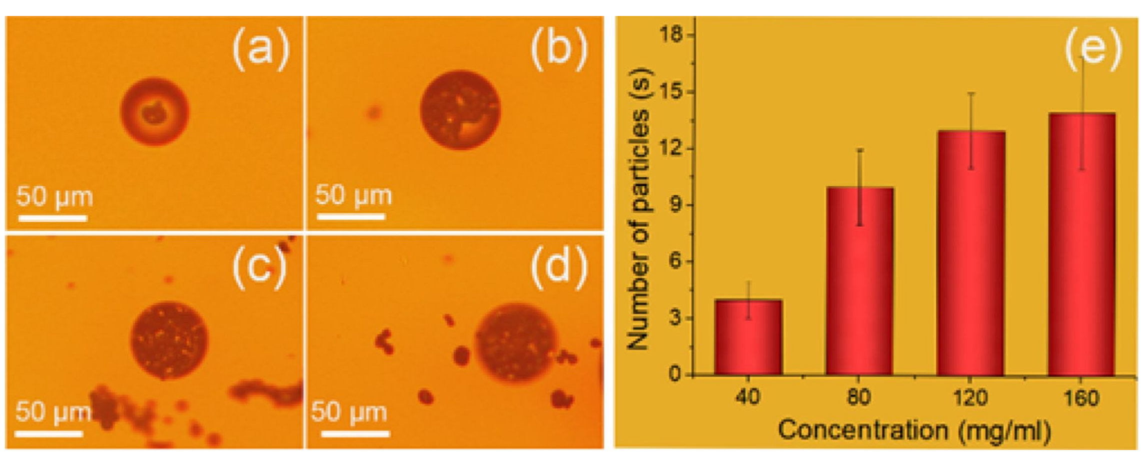


Fig. 2 **a**–**d** Optical microscope images of Janus droplet micromachines made from olive oil with different Al particle concentrations: **a** 40 mg/mL, **b** 80 mg/mL, **c** 120 mg/mL, and **d** 160 mg/mL. **e** The number of Al particle in one droplet as a function of the concentration

their concentrations greatly affected the generation of bubbles. Here, in this work, we also studied the effect of surfactants. Nonionic surfactants (Triton X-100 and Tween 20) and anionic surfactant (SDS) were used in the experiment. In order to exclude the effect of concentration, we chose the same concentration (1% (v/v)) for all three surfactants and the value is above critical micelle concentration (0.3 wt%) [36]. The experimental results are shown in Fig. 4. In the presence of surfactant Tween 20, larger bubbles are still adsorbed on the oil droplet, and the droplets is unable to move (Fig. 4a). Tween 20 is a polyoxymethylene sorbitol ester, and in strong alkaline solutions, the hydrolysis of the ester bond takes places, which leads to function loss of the surfactant [37, 38]. Therefore, no enough driving force can be generated to propel the Janus droplet because the bubble is attached to the droplet. The same situation is also for SDS, as shown in Fig. 4b. But it is founded that a lot of small bubbles are generated and quickly detached from the droplet as in the case of Triton X-100 (Fig. 4c), indicating Triton X-100 is effective in promoting the locomotion of current Janus droplet micromachine.

The movement of Janus droplet micromachine is shown in the video S2. Figure 5a shows the state of the Janus droplet micromachine, and the motion trajectory (yellow line). It is clearly to see that Janus droplet micromachine has a chaotic trajectory and a smaller range of motion. It can be seen from the trajectory that the motion process is random, irregular. In the previous report [9], the micromachine uncontrolled bubble pushes the motor's trajectory to be random. But the Janus droplet micromachine has a smaller range of motion. This particular droplet micromachine moves at an average speed of about 28.22 μm/s. And the video showing the magnetic-control-turning of the self-propelled Janus droplet micromachine with Fe particles is available in Video S3. The motion track is shown in Fig. 5b. And the trajectory clearly shows the linear motion and achieves a 90 degree directional rotation. This particular droplet moves at an average speed of about 22.38 μm/s. This speed is less than the previous value without control, perhaps due to two factors. Firstly, the Fe particles occupy the position of some Al particles and the bubble productivity is decreased. Secondly, the droplet takes a long time to turn, resulting in lower speed.

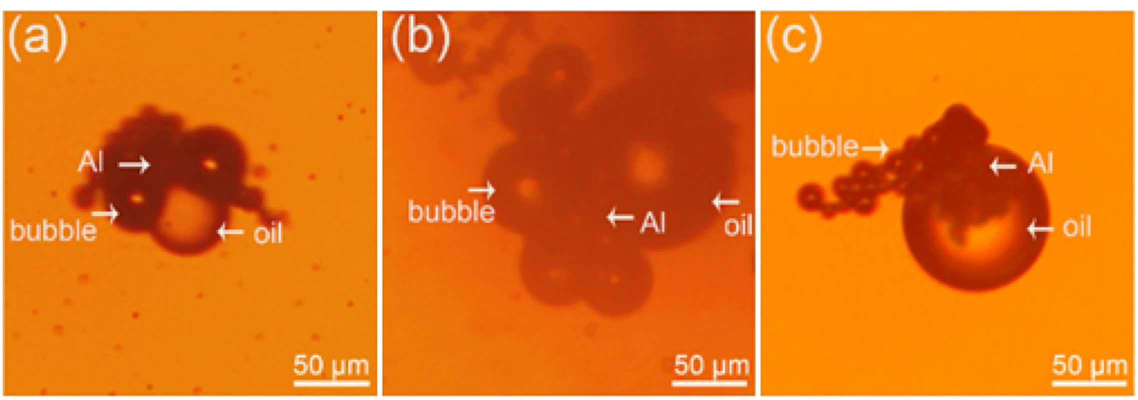
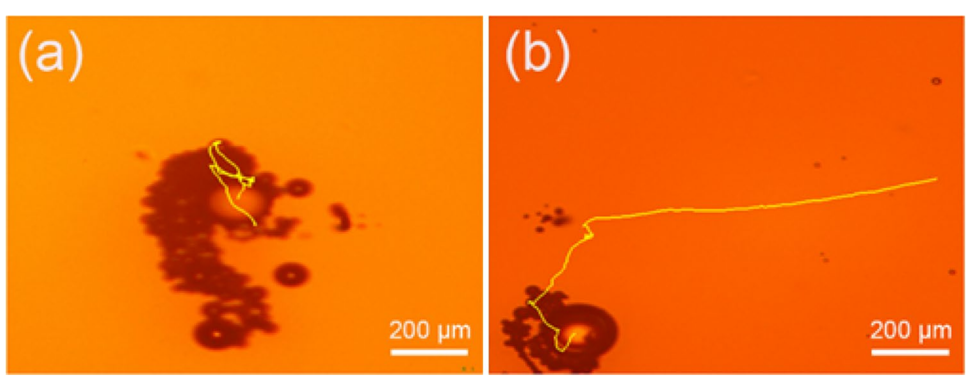


Fig. 4 Effect of surfactants on the motion of Janus droplet micromachine. **a** A Janus droplet micromachine attached with large gas bubble in solution containing 1% (v/v) Tween 20 solution. **b** A Janus droplet micromachine is surrounded by several large bubbles in solution containing 1% (w/v) SDS solution. **c** A Janus droplet micromachine is surrounded by several small bubbles in solution containing 1% (v/v) Triton X-100

Fig. 5 **a** The Janus droplet micromachine (Al particle) moves in 1 mol/L NaOH solution. **b** Under the action of a magnetic field, the Janus droplet micromachine with Fe particles (Al and Fe particle) moves in 1 mol/L NaOH solution. The yellow line is the movement trace of the micromachine



4 Conclusions

We have demonstrated a composite Janus droplet micromachine, which made of oil and Al particles, by using a simple method to fabrication. In alkaline solution, Janus droplet micromachine can achieve better self-propulsion without the need of external propulsion. And, under externally applied magnetic field, Janus droplet micromachine with Fe particles can be achieved directional control. We also noticed that the type of surfactant can affect the motion remarkably. The Janus droplet micromachine may hold considerable promise for the design of practical micromachine toward a wide range of important applications ranging from drug delivery to environmental remediation.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Nos. 51502168, 51475093, 11504227, U1632115, and 51850410502), Science and Technology Commission of Shanghai Municipality (Nos. 19DZ2271100, 17JC1401700), and the Changjiang Young Scholars Program of China. Alexander A. Solovev is very grateful for the financial support from the young "1000 talent" plan of China.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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