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Self-Propelled Droplets for Extracting Rare-Earth Metal Ions

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We have developed self-propelled droplets having the abilities to detect a chemical gradient, to move toward a higher concentration of a specific metal ion (particularly the dysprosium ion), and to extract it. Such abilities rely on the high surface activity of di(2-ethylhexyl) phosphoric acid (DEHPA) in response to pH and the affinity of DEHPA for the dysprosium ion. We used two external stimuli as chemical signals to control droplet motion: a pH signal to induce motility, and metal ions to induce directional sensing. The oil droplets loaded with DEHPA spontaneously move around beyond the threshold of pH even in a homogeneous pH field. In the presence of a gel block containing metal ions, the droplets show directional sensing and their motility is biased toward higher concentrations. The metal ions investigated can be arranged in decreasing order of directional sensing as $Dy^{3+} \gg Nd^{3+} > Y^{3+} > Gd^{3+}$. Furthermore, the analysis of component by an atomic absorption spectrophotometer reveals that the metal ions can be extracted from the environmental media to the interiors of the droplets. This system may offer alternative self-propelled nano/microscale machines to bubble thrust engines powered by asymmetrical catalysts.

Introduction

Droplet-based systems are an important area of research in downscaled reactor techniques and have diverse applications ranging from bioassay[1-4] to high-throughput synthesis of materials.[5-9] Various methods of droplet operation are performed by mechanical, thermal, electrical and magnetic manipulations. Such methods exploiting external power sources allow precise manipulation of droplets.[10-12] The methods, however, results in the limitation of their ability to perform operations beyond the control of external power sources.

Many studies have been devoted to the development of chemical methods to manipulate droplets because of elimination of the need for applying external power sources.[13−31] There are two kinds of chemical methods: the dewetting effect and the Marangoni effect. In the former case, droplets move spontaneously according to a spatial gradient in surface free energy of solid supporting substrate created by a pretreatment process[13,15,17] or self-modifying manner[14,16,18,19] due to chemical reaction between the droplets and substrate. In the latter case, droplets move spontaneously due to convection spontaneously generated by a change in interfacial tension of the droplet interface[20,21,23-26,28-31] or of the liquid substrate i.e. the air-liquid surface.[22,27] In both cases, spontaneous motion arises from a direct conversion of surface free energy of the solid or liquid substrate, or of the droplet interface to kinetic energy. The Marangoni effect exploiting surface free energy of the droplet interface allows functionalized manipulation of the droplets because the droplets freely move without binding on solid or liquid substrate and furthermore chemical reactions with molecules present in the environmental media can be harnessed to provide the droplets with environmentally responsive functions. For example, a pH signal can serve as a chemical signal to trigger a spontaneous motion[31] and its gradient to bias motility toward a desired location.[27]

In our previous study, we have developed self-propelled droplets of oil phase with a pH responsive function.[31] When the initial value of pH in the environmental media exceeded the threshold, the droplets moved spontaneously even in a homogeneous concentration field. In order to make the droplets perform more functionalized tasks, we focused on using two kinds of chemical signals. Although a spatial pH gradient serves as a chemoattractant, the multiple signals have the advantage of inducing various functions; selectivity, molecular recognition and chemical sensing. Furthermore several signals may serve as alternatives if one signal fails to work from some cause.

In this study, we describe a new autonomous extraction device based on self-propelled oil droplets for rare-earth metal ions. The droplet device requires motility, directional sensing and affinity for target metal ions. Two chemical signals were employed for expression of these functions. A pH signal triggered spontaneous motion of the droplets due to generation of spontaneous convective flow induced by a change in interfacial tension of the droplet interface. Metal ions were exploited as a second signal to bias the motility toward the higher concentrations. Furthermore the droplets can extract the target metal ions.

Experimental Section

Reagents and Apparatus. Di(2-ethylhexyl) phosphoric acid (DEHPA), dysprosium(III) nitrate hexahydrate were purchased from Sigma-Aldrich. Phosphate (pH 7.41) and carbonate (pH 10.01) buffers of reagent grade, gadolinium(III) nitrate hexahydrate, yttrium(III) nitrate hexahydrate, and neodymium(III) nitrate hexahydrate were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used without further purification.

Preparation of gel. In order to localize rare earth ions in the aqueous phase, we made a small block of polyvinyl alcohol gel (PVA gel) soaked with the solutions containing the different metal ions. PVA gel was prepared using glutaraldehyde under sulfuric acid catalysis. First, 2.0 M PVA was dissolved in pure water. Next, 0.1 M glutaraldehyde and 0.05 M sulfuric acid were also dissolved in the PVA solution. The solution was kept at room temperature and then turned into gel after 24 hours. The gel was cut into 5 mm squares. The cut gels were washed by pure water in a stirred batch tank to remove acid from the gels, and the washing water was exchanged several times. We continued to wash the gels until the pH in the washing water including the gel equaled to that of pure water. The resulting gels were soaked in water containing rare earth ion at concentration of 0.5 M for 24 hours.

A prepared cubic gel containing one type of metal ion was put 20 mm distance away from the center of a Petri dish (60 mm inner diameter) filled with 10 ml phosphate buffer solution. A 10 μl nitrobenzene droplet containing 100 mM DEHPA was formed in the center of the Petri dish with micropipette one minute after setting the cubic gel. The droplet is heavier than the continuous phase and sinks to the bottom of the buffer solution. We observed the behavior of droplet motion by using the high speed camera (Keyence, VW-6000).

Concentration measurement of dysprosium. In order to investigate the extraction ability of the self-propelled droplets, 300 μL droplets was formed 20 mm apart from the gel containing Dy^{3+} in the phosphate buffer solution. Such large droplets were used for a quantitative analysis of dysprosium concentration inside them. After a given time, 250 μL of the 300 μL droplet was recovered by using a micropipette. This operation was repeated several times. Then the concentration of dysprosium in the recovered droplet phase was measured twice without dilution of the samples by Polarized Zeeman atomic absorption spectrophotometer (Hitachi High-Tech, ZA3700) and then the average concentration was determined.

Results & discussion

In our previous study, we have developed self-propelled droplets of oil phase with pH responsive function.[31] Droplets loaded with surfactant, di(2-ethylhexyl) phosphoric acid (DEHPA) started to move spontaneously even in a homogeneous pH field when formed in buffer solutions for pH higher than 6 at initial condition. Their motion, however, was random and the direction depended on the initial perturbation. In this study, we used the good affinity of DEHPA for metal ions to bias the motility toward a gradient of the metal ions and to make the droplets harvest the metal ions.

First, we explain how to move the nitrobenzene droplets loaded with DEHPA in the aqueous phase of the buffer solution. A driving force for spontaneous motion arises from the Marangoni effect due to deprotonation of DEHPA. As pH is increased beyond the threshold the deprotonation of DEHPA proceeds and decreases interfacial tension. The droplets can move spontaneously and sustainably even in a homogeneous pH field when the initial pH of the continuous phase is adjusted within a range where the interfacial tension decreased significantly at the equilibrium state.[31] The threshold of motility due to the Marangoni effect is determined by the following relation.[28, 31]

$$\Gamma_0 M > \frac{3}{2} k R \eta,$$

where Γ_0 is the equilibrium surface concentration of the surfactant, Marangoni coefficient of the system $M = d\gamma / d\Gamma$ (γ: interfacial tension), k the rate constant of desorption, R radius of droplet and η a prefactor containing the liquid viscosities outside and inside the droplet. When supply of surfactant by the Marangoni effect exceeds the consumption of surfactant by desorption, the resting state becomes unstable and eventually the droplet starts to move spontaneously. In our previous paper, we explored the validation of the mechanism by comparing the onset condition of droplet motion with the linear stability analysis among 6 buffer solutions.[31] We found that the linear stability analysis can predict the threshold of the onset condition of the droplet motion in different buffer solutions except for the phthalate buffer solution. Thus, we believe that the proposed mechanism has high validity. The motility in the experiments of the reference 31 changed from a random to a ballistic motion with the droplet size. For volumes of droplets larger than 5 µl droplets showed a ballistic motion. They, however, moved in any direction.

For directional sensing, the droplets need to detect non-uniform distributions of metal ions. Deprotonated DEHPA is accumulated at the interface between nitrobenzene and aqueous phases with a polar head group of deprotonated DEHPA facing to the aqueous phase. Thus, the droplets are covered with the negatively-charged surfactants which can serve as a receptor for metal ions. When the droplets are exposed to a gradient of metal ions, a DEHPA-metal complex is formed at the interface, following desorption of the complex from the interface. The sequence of events causes a change in the interfacial tension, producing an asymmetric flow field around the droplets. The asymmetric flow field may induce a directed motion of the droplets toward the higher concentration of metal ions. Thus, the droplets can detect spatial gradients using the interaction between DEHPA and metal ions.

When an unwashed metal-free gel was formed at a distance of 20 mm from the center of Petri dish filled with 10 ml phosphate buffer solution, a pH gradient was generated in the solution. We confirmed that self-propelled droplets moved toward the gel. Next, we used the metal-free gel after removal of acid as a target gel. A homogeneous pH field is applied to the continuous phase. The droplets started to move in any direction soon after they were formed. No directional motion toward the gel was observed (upper left panel in Figure 1a). The metal-free gel has no effect on the droplet motility.

Figure 1 shows the trajectory of self-propelled droplets loaded with 100 mM DEHPA in the presence of gels containing 4 metal ions. In the presence of Dy^{3+} the droplets move toward the gel at an arrival rate of about 90% (Center panel of Figure 1A). Even though the droplets started to move from the original point to different directions just after the formation, the motility of the droplets was biased toward the gel (SI Figure 1). After formation of the droplets, “white cloudlike materials”, which are considered to be an aggregated material of metal-phosphate, erupted from the gel and extended in a direction toward the droplets (SI video 1). The white materials wound around the droplets and seemed to pull them nearer the gel. The velocity of the droplets gradually increased as they approached the gel. On the other hand, in the presence of the other metal ions, the droplets hardly headed toward the gel even though the white cloudlike materials moved to the droplets (SI video 2). Interestingly, in the presence of Gd^{3+} the droplets seemed to be pushed away from the gel. In most cases they moved to the opposite side of the gel (Top right panel of Figure 1A). The average speed of droplet motion is shown in SI Figure 2 until the droplets collide with the gel or a wall surface of Petri dish. The droplets exhibit the same speed in all systems. The speed of self-propelled droplets driven by the Marangoni effect depends on the viscosity and the interfacial tension.[32] The interfacial tension varied with pH field.[31] Thus, the speed of the droplet motion does not change with the different metal ions because the phosphate buffer solution keeps a constant pH value except for a portion of the droplet interface. Formation of an asymmetric pH field around the droplet will be discussed later.

Analyzing motility requires the use of a directionality factor, which we define as the cosine of the angle θ between the moving direction and the direction of the gel at a fixed time interval ($\Delta t = 0.0667$ s). A droplet that moves toward the gel has a directionality of 1, whereas droplets moving perpendicular or opposing direction to the gel have directionalities of 0 and -1, respectively. Figure 1B shows a distribution of directionality over the movement. In the presence of Dy^{3+}, a sharp peak of directionality appears near unity, whereas in the presence of Gd^{3+} a peak appears near -1. In the other cases, the frequency of directionality distributes uniformly. The chemotactic index was calculated as the ratio of the directionality larger than 0.5 (corresponding to $-60° < \theta < 60°$) and the total directionality (SI Figure 3). The Chemotactic index of the metal ions investigated can be arranged in decreasing order as $Dy^{3+} \gg Nd^{3+} > Y^{3+} > Gd^{3+}$. Dy^{3+} serves as the most effective chemoattractant to bias the random motion of the droplets toward the gel.

DEHPA can work as an extractant for rare-earth metal ions.[33-35] DEHPA dimers or its reverse micelles extract rare-earth metal ions from the aqueous phase into the organic phase. In order to investigate an extraction ability of the self-propelled droplets, 300 μL droplets was formed 20 mm apart from the gel containing Dy^{3+} in the phosphate buffer solution. Such large droplets were used for a quantitative analysis of dysprosium concentration inside them. The large droplets showed similar behavior to small ones, i.e., reached the target gel in a few second and then moved around the gel. The droplets were recovered by using a micropipette 10 or 30 minutes after the formation of the droplets and then the concentration of Dy^{3+} inside the droplets was measured by an atomic absorption spectrophotometer.

Figure 2 shows the analysis of the atomic absorption spectrophotometer at absorption wavelength of 404.6 nm. The analysis revealed that the self-propelled droplets autonomously extracted Dy^{3+} inside themselves in higher concentrations than the detection limit of the spectrometers, ~1.4 ppb. In the phosphate buffer system (initial pH 7.41), the concentration of Dy^{3+} inside the droplet for an exposure time of 10 min was 29 ppb and for an exposure time of 30 min 71 ppb. Amount of the extraction to the droplets increased with increasing the exposure time. The concentration of Dy^{3+} in the carbonate buffer system (initial pH 10.01) for an exposure time of 30 min was 165 ppb. The increase in pH promotes deprotonation of DEHPA and formation of reversed micelles, enhancing the extraction process like a standard liquid-liquid extraction.[35] However we had a major difficulty in reproducibility of the quantitative extraction experiments based on the self-propelled droplets because it was impossible that the droplets follow the same path and contact with the gel containing Dy^{3+} for the same time in each experiment. There is no doubt that the self-propelled droplets spontaneously extract the rare-earth metal ion.

Let us consider why self-propelled droplets move toward the higher concentration of Dy^{3+}. Directed motion requires an asymmetric convective flow around the droplets. The asymmetric flow can be produced by an imbalance in the forces due to interfacial tension acting on the droplets. The interfacial tension is determined by a surface concentration of the deprotonated DEHPA.[31] If the presence of Dy^{3+} suppresses the deprotonation of DEHPA, then nonuniform distribution of Dy^{3+} can generate nonuniform deprotonation of DEHPA around the droplets, producing an imbalance in interfacial tension. To investigate the suppressing effect of the metal ions on deprotonation of DEHPA, we measured the time evolution of pH in the phosphate buffer solution containing various metal ions at the concentration of 0.1 mM contacting with the nitrobenzene solution containing 100 mM DEHPA in a stirred tank. Detail of the experimental setup is described in Supporting Information (SI Figure 3).

Figure 3 shows the effect of the metal ions on the pH change of the nitrobenzene–phosphate buffer system. First we investigated the pH change without DEHPA. No pH change was observed even though gasses were dissolved from the environment into the solution. The pH in the system with DEHPA decreases exponentially to a constant value. The decrease in pH reflects the increase in the number of hydrogen ions due to the deprotonation of DEHPA. In the absence of metal ions, DEHPA adsorbed at the liquid-liquid interface gradually becomes deprotonated after contacting with the phosphate buffer solution. Some deprotonated DEHPA along with protons transfers from the interface to the aqueous phase, the other DEHPA remains in the interface. Pristine DEHPA is abundant in the nitrobenzene phase and supplied to vacant sites of the interface. A sequence of the processes relaxes to equilibrium. In Figure 3, relaxation time τ of a change in pH in each metal ion system was calculated from the experimental data fitted by $y = a \times \exp(-x/\tau) + b$. The Dy^{3+} system has the longest relaxation time among them. Dy^{3+} reacts with undissociated DEHPA and deprotonated DEHPA adsorbed at the liquid-liquid interface, forming an oil-soluble complex.[35] The presence of Dy^{3+} induces a nonhomogeneous concentration field of the DEHPA, suppressing a decrease in pH due to the deprotonation of DEHPA. For the self-propelled droplets, localized Dy^{3+} induces a nonhomogeneous concentration field of the undissociated DEHPA as well as a nonhomogeneous pH field at a given location of a droplet surface where the reaction between Dy^{3+} and DEHPA occurs. The presence of the undissociated DEHPA diminishes convective flow in the vicinity of the reaction location. The convective flow remaining around the droplet pushes the droplet toward the presence of Dy^{3+}. As a result, directional sensing occurs. Furthermore, the oil-soluble complex also causes extraction of dysprosium from the aqueous phase to the droplet phase. Note that in the experiment, Dy^{3+} has the suppressing effect on the deprotonation of DEHPA even though the concentration of Dy^{3+} is as low as a thousandth part of the DEHPA concentration. This suppressing effect of Dy^{3+} induces the directed motion of self-propelled droplets.

Conclusion

In conclusion, we have demonstrated a new autonomous extraction device based on self-propelled oil droplets. A gradient of the metal ions can bias the random motion toward the target metal ions. The directional sensing of the metal ions investigated is in order as $Dy^{3+} \gg Nd^{3+} > Y^{3+} > Gd^{3+}$. Dy^{3+} serves as the most effective chemoattractant. The order is consistent with the order of the relaxation time of a pH change except for Gd^{3+}. The result shows that the suppressing effect of metal ions on the deprotonation of DEHPA is an element essential to bias the motility of self-propelled droplets. The metal ions act as “antagonists” that bind to a receptor and suppress the signaling processes.[36,37] Furthermore the droplets reaching the gel containing the metal ions can extract the metal ions. The droplet can work as a recovery device, a reservoir of targets and transporter. The concept of self-propelled droplets with environmentally-responsive functions could be readily extended to the extraction and transport of other important target molecules. Such self-propelled matter can fulfill various tasks in response to chemical signals in hazardous areas or limited spaces beyond the control of external power sources. The self-propelled droplets can serve as alternative self-propelled nano/microscale machines to bubble thrust engines powered by asymmetrical catalysts.[38-42]

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Caption

Figure 1. Motion of self-propelled droplets in phosphate buffer solutions in the presence of various metal ions-containing gel. (A) Trajectories of moving droplets until contacting with the target gel or the wall of a Petri dish. The scale bars are 10 mm. (B) Corresponding directionality distribution of self-propelled droplets.

Figure 2. Adsorption spectrum of dysprosium in the recovered droplet phase (A) in the phosphate buffer solution for exposure time of 10 min and (B) 30 min, and (C) in the carbonate buffer solution. Average concentration corresponds to 29 ppb, 71ppb and 165 ppb, respectively.

Figure 3. Time evolution of pH in the phosphate buffer solution containing various metal ions at the concentration of 0.1 mM contacting with the nitrobenzene solution containing 100 mM DEHPA. Relaxation time τ is calculated from the experimental data fitted by $y = a \times \exp(-x/\tau)+b$. The purple solid circle represents the nitrobenzene–phosphate buffer system without DEHPA.