

Self-Propelled Oil Droplets Consuming “Fuel” Surfactant

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Self-propelled droplets have drawn much attention as a primitive type of inanimate chemical machinery, that is, the energy transduction from chemical energy to mechanical energy.^{1,2} When the driving forces of these self-propelled droplets are examined, the droplets can be classified into one of three categories. First, a pentanol droplet³ or a piece of camphor⁴ on a water surface moves in the direction along which the surface tension around the self-propelled object decreases asymmetrically because of the gradual dissolution of the object itself. Second, an oil droplet on a surface of a substrate moves because the surface underneath the droplet is asymmetrically modified and causes the difference in the interfacial energy between the leading edge and the trailing one of the oil droplet.^{5–12} The third category is a new one and it concerns a self-propelled motion of a droplet, being coupled with a chemical reaction that occurs at the interface between the droplet and its surrounding medium. The chemical reaction results in a symmetry-breakage due to the accumulation and release of the products and the droplets swim through the aqueous media without need of an air–water or solid–liquid interface.^{13–15} The self-propelled motion of the third category is sustained until the chemical precursor in a droplet is consumed. Here, we report an experimental system of oil droplets which exhibits a self-propelled motion by consuming a hydrolyzable surfactant as a “fuel”, which is supplied from a bulk aqueous dispersion (Figure 1).

Immediately after mixing an aqueous dispersion of fuel surfactant **1** (*N*-(4-[3-[trimethylammonio]ethoxy]benzylidene)-4-octylaniline bromide), which was synthesized from 4-octylaniline **2** and 2-(4-formylphenoxy)ethyltrimethyl ammonium bromide **3**, with an emulsion of 4-octylaniline **2** containing fluorescent catalyst **4** (see Supporting Information Materials and Methods), most of floating droplets, the diameters of which were in a range of 10–140 μm , moved autonomously (Figure 2).

Their initial speeds of the self-propelled droplets were in the range of 3–40 $\mu\text{m s}^{-1}$. The oil droplets adhered to the glass surface did not show any self-movement. The self-propelled droplets demonstrated unidirectional motion in the three-dimensional space when they were traced precisely with high resolution microscopy. It was found that almost all the self-propelled droplets carried a mass of waste oily droplets with diameters of 1–3 μm on the posterior surface. The waste droplets on the posterior surface of the self-propelled droplet grew or fused together until their sizes reached a certain diameter (ca. 3 μm), and eventually they were released from the self-propelled droplets. The released waste droplets dissolved into bulk water in several seconds (see Supporting Information video). It is to be noted that the sizes of

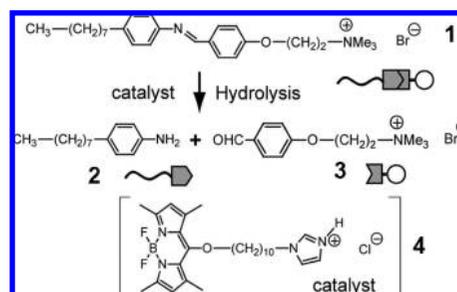


Figure 1. Schematic illustration of the hydrolytic reaction scheme. Fuel surfactant **1** produces lipophilic aniline derivative **2** and hydrophilic benzaldehyde derivative **3** in the presence of catalyst **4**.

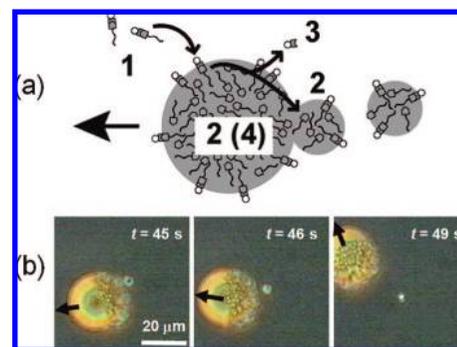


Figure 2. (a) Representative illustration of a self-propelled oil droplet consuming “fuel” surfactant and producing “waste” oily droplets at the trailing edge. The small arrows represent the direction of movement of lipophiles on the surface of the original droplet. (b) Sequential phase contrast micrographs of the release of waste droplets from the posterior surface of the original droplet. The black arrow in each micrograph shows the direction of the motion of the self-propelled oil droplet.

the original oil droplets did not change during the course of the experiment. This is presumably because the surface of the self-propelled droplet is coated with precursor **1** and hydrolyzed product **2** cannot dissolve into the droplet. When the produced waste droplets covered the entire surface of the self-propelled droplets, the self-propelled motion stopped (see Supporting Information video). Fluorescence micrographs revealed that the region covered by the waste droplets fluoresced more weakly than that of the leading end of the self-propelled droplet (see Figure S1). This indicates that the waste droplets do not contain significant amounts of the catalyst, and therefore the catalysis remains localized to the self-propelled droplet and available for further catalysis at the leading end. The convective movement of the internal oil phase is commensurate with the direction of droplet movement as illustrated in Figure S2 and in other experimental models of mobile oil droplets.¹⁵

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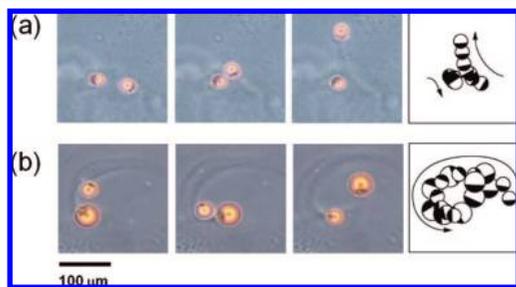


Figure 3. Typical time-course sequential micrographs and superimposed images of two oil droplets repelling each other (a; time interval = 2 s) or those turning together (b; time interval = 4 s).

We speculate that the origin of self-movement consists of three stages. Stage 1: In a dispersion containing fuel surfactant **1**, the hydrolysis of the fuel occurs at the surface of the oil droplet containing the catalyst (see Figure S3). A fluctuation of the rates of hydrolysis leads to the symmetry-breakage of the oil droplet with respect to all the potentially reactive sites on the surface, and hydrolyzed products are accumulated at the most reactive site (see Figure S4).^{12–14} Stage 2: The symmetry-breakage of the oil droplet causes an imbalance in the interfacial tension between the product accumulating site and the nonaccumulating sites, and then the lateral movement of the product is evoked at the surface of the oil droplet. The flow of the product due to an imbalance in the interfacial tension is well documented in systems that possess such a Marangoni instability.^{6,7,12,15} Since the surface of the oil droplet is covered with fuel surfactant, the lipophilic product that is generated by hydrolysis of the fuel does not dissolve into the initial oil droplet, but it is aggregated to form tiny oil droplets as a waste. Therefore, the interfacial energy of the leading edge of the oil droplet becomes lower than that of the waste-covering trailing edge and such a situation induces an interfacial dynamic fluctuation. This fluctuation coupled with the accumulation and directional release of the products from the interface drives the motion of the oil droplet.^{3,5–17} If the flow resulted in equilibration of tension around the droplet, then movement would cease. Stage 3: However the leading edge of the self-propelled droplets takes up additional fuel surfactant and converts it into lipophilic product as the droplet moves. The continued processing of substrates further feeds the interfacial imbalance as described above and activates the internal convection inside of the self-propelled droplet, all likely due to a Marangoni instability (see Figure S5).^{3–11} The convection pushes the waste droplets to the posterior surface of the self-propelled droplets where they are accumulated and then released. This chemical mass transfer, from the adsorption of fuel surfactants to the accumulation and release of waste products, sustains the self-propelled motion of the oil droplet. During the preservation of this asymmetry, the original oil droplet moves unidirectionally (see Figure S6). As long as there is the fuel surfactant in the environment and the catalyst remains active, the droplet sustains its unidirectional self-movement without consuming itself.

We also observed rendezvous of two self-propelled oil droplets which approached each other by chance. Even in close proximity, two droplets did not fuse but changed their directions to avoid collision (Figure 3a). Interestingly, some pairs of approaching oil droplets exhibited a synchronized motion (Figure 3b). In ca. 1 min after the two oil droplets were coupled, one made a turn and the other followed it within the range of ca. 300 μm . Eventually, both oil droplets moved independently of each other. These peculiar behaviors can be interpreted as follows. First, since fuel surfactant **1** dissolves onto the surface of the oil droplet, the surface of the

oil droplets is positively charged. This charge repulsion is likely to suppress the droplet's propensity to fuse, but electrostatic repulsion acts only at relatively short distances and therefore it is unlikely that surface charge plays a critical role in the long distance interactive behavior observed here. Second, there exists a hydrodynamic field of the aqueous media around each self-propelled oil droplet. This field can affect the directional movement of another self-propelled oil droplet due to the effects of fluid dynamics. Third, the amount of the fuel in a zone around the self-propelled oil droplet is likely depleted due to the hydrolysis occurring at this site, and in addition the trail of the droplet is composed of the waste and even less fuel. Since the surface activity of the droplet depends on the local concentration of the fuel, it is likely that a droplet slows or even stops its motion when it moves into a zone that is depleted of the fuel surfactant. The droplet likely turns toward a zone that contains a higher concentration of fuel, exhibiting a sort of chemotaxis. This is consistent with our self-movement model where the local differences in the interfacial tension of the droplet, being caused by the nonhomogeneous distribution of the fuel and the product, affects the self-movement of the system.

In this study, a combined system of self-propelled motion and waste production was constructed using an oil droplet (containing catalyst) and its fuel surfactant. Although no sophisticated molecular architecture is contained in this simple chemical system as opposed to a complicated protein reaction network of a living cell, the whole system is driven by a complex of dynamics exhibited by a composite molecular self-assembly,¹⁸ such as self-organized autonomous movement, fuel-activated chemotaxis, and some degree of interdroplet interaction.

Note Added after ASAP Publication. Errors in the footnotes for author affiliations have been corrected in the version published on the Internet April 8, 2009.

Supporting Information Available: Materials and methods, micrographs of internal convection, and videos and descriptions of self-propelled oil droplets. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Sackmann, E. *Synergetics 29*; Rensing, L., Jaeger, N. I., Eds.; Springer-Verlag: New York, 1985, 153–162.
- (2) Paxton, W. F.; Sundararajan, S.; Mallouk, T. E.; Sen, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 5420–5429.
- (3) Nagai, K.; Sumino, Y.; Kitahata, H.; Yoshikawa, K. *Phys. Rev. E* **2005**, *72*, 041603.
- (4) Kohira, M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. *Langmuir* **2001**, *17*, 7124–7129.
- (5) Brochard-Wyart, F.; de Gennes, P.-G. *C. R. Acad. Sci., Ser. II* **1995**, *321*, 285–288.
- (6) Sumino, Y.; Nagayama, M.; Kitahata, H.; Nomura, S. M.; Magome, N.; Mori, Y.; Yoshikawa, K. *Phys. Rev. E* **2005**, *72*, 041603.
- (7) Sumino, Y.; Magome, N.; Hamada, T.; Yoshikawa, K. *Phys. Rev. Lett.* **2005**, *94*, 068301.
- (8) Domingues Dos Santos, F.; Ondarçuhu, T. *Phys. Rev. Lett.* **1995**, *75*, 2972–2975.
- (9) Lazar, P.; Riegler, H. K. *Phys. Rev. Lett.* **2005**, *93*, 136103.
- (10) Brochard, F. *Langmuir* **1989**, *5*, 432–438.
- (11) John, K.; Bär, M.; Thiele, U. *Eur. Phys. J. E* **2005**, *18*, 183–199.
- (12) Nepomnyashchy, A. A.; Velarde, M. G.; Colinet, P. *Interfacial Phenomena and Convection*; Chapman & Hall/CRC: Great Britain, 2002; Chapter 3.
- (13) Schmid, A. K.; Bartelt, N. C.; Hwang, R. Q. *Science* **2000**, *290*, 1561–1564.
- (14) Toyota, T.; Tsuha, H.; Yamada, K.; Takakura, K.; Ikegami, T.; Sugawara, T. *Chem. Lett.* **2006**, *35*, 708–709.
- (15) Hanczyc, M. M.; Toyota, T.; Ikegami, T.; Packard, N.; Sugawara, T. *J. Am. Chem. Soc.* **2007**, *129*, 9386–9391.
- (16) Kogi, O.; Yuya, K.; Kim, H.-B.; Kitamura, N. *Langmuir* **2001**, *17*, 7456–7458.
- (17) Kovalchuk, N. M.; Vollhardt, D. *Adv. Colloid Interf. Sci.* **2006**, *120*, 1–31.
- (18) Fialkowski, M.; Bishop, K. J. M.; Klajn, R.; Smoukov, S. K.; Campbell, C. J.; Grzybowski, B. A. *J. Phys. Chem. B* **2006**, *110*, 2482–2496.

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