Self-Propelled Motion of a Nitrobenzene Droplet on Au Electrode during Sn Electrodeposition: Factors Creating Imbalance of Interfacial Tension and Marangoni Effect

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A nitrobenzene droplet moves in a self-propelled manner on Au electrode surface during the Sn electrodeposition in H2SO4 solution because the interfacial tension of solid-water interface acting on the front side of the droplet is larger than that on the rear side. The electrodeposition, which increases the interfacial tension, is suppressed by a side reaction such as hydrogen evolution reaction and by adsorbed nitrobenzene molecules. If the electrode surface is non-uniform, the electrodeposition as well as the side reaction takes place non-uniformly on the electrode surface, leading to an initiation of the droplet motion. If the electrode surface is uniform, the motion is initiated when nitrobenzene molecules are adsorbed non-uniformly on the surface. Once the motion is initiated, the imbalance is created spontaneously: the electrodeposition occurs less efficiently at the rear side because it is suppressed by nitrobenzene molecules remaining on the surface. When the electrodeposition is performed in HNO3 solution, the formation of aniline by the reduction of the non-uniformly adsorbed nitrobenzene induces the Marangoni effect and consequently the droplet continually changes in shape and moves like an amoeba. This amoeba-like motion is also self-propelled because nitrobenzene molecules remaining on the rear side are reduced to form aniline molecules.

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Wetting properties of a solid surface, which are of interest from the viewpoint of interaction between liquid and solid phases, can be characterized by the contact angle of a liquid droplet on the solid surface.1–3 The contact angle of an oil droplet placed on a solid surface in a water (aqueous) phase (θ) is defined by the mechanical equilibrium at the interface under the action of three interfacial tensions (see Figure 1a). According to Young’s equation, there is a relationship among interfacial tension of solid-water interface (γ_{SW}), that of the solid-oil interface (γ_{SO}), and that of the oil-water interface (γ_{OW}):

\[ \gamma_{SW} = \gamma_{SO} + \gamma_{OW} \cos \theta \]

Comprehensive studies have demonstrated that a liquid droplet on a solid surface moves spontaneously due to wettability gradients on the solid surface.1–3 As for an oil droplet on a solid surface in a water phase, an imbalance of γ_{SW} (the difference of γ_{SW} between the front and rear sides of the droplet) generates a driving force for the droplet to move spontaneously in the direction of a high interfacial tension, as illustrated in Figure 1b. This motion has a merit that it does not require any power source, while it has a demerit that the production of a wettability gradient surface is often sophisticated and/or costly.

It has been reported15 that the interfacial energy, or the interfacial tension, at Au electrode surface in aqueous solution increases when metals such as Sn, Pb, and Sb are electrodeposited. The increase is attributed to the reaction intermediates of the electrodeposition, i.e., the active adatoms on the electrode surface. When a droplet of oil, e.g., hexane and nitrobenzene, is put on the Au electrode, the increase causes a self-propelled lateral motion of the oil droplet. The driving force inducing the droplet motion is an imbalance of γ_{SW}.15 The droplet moves toward the area where γ_{SW} is relatively high, i.e., where the electrodeposition (M^{2+} + 2e^- → M) occurs relatively efficiently. Once the droplet motion starts to move, the imbalance is created spontaneously: the electrodeposition occurs less efficiently at the rear side because it is suppressed by adsorbed oil molecules remaining on the electrode surface (Figure 2a). There arises a question: how the droplet motion is initiated? If the electrodeposition occurs uniformly on the surface, the droplet cannot move away from its initial position (Figure 2b).

In order to obtain further insight, we have studied the spontaneous motion of nitrobenzene droplets during the Sn electrodeposition (Sn^{2+} + 2e^- → Sn) in H2SO4 solution.14 The study has showed that the imbalance can be caused by the occurrence of a side reaction, namely, hydrogen evolution reaction (HER), near the rear side of the droplet. The HER occurs at the rear side more actively than at the front side (Figure 3a), which is most likely because the surface of the Au electrode is non-uniform. The rate of Sn electrodeposition decreases as that of HER increases, and therefore γ_{SW} becomes lower at the rear side than at the front side (Figure 3b). In other words, the non-uniform surface can be one of the factors that create the interfacial tension imbalance. To confirm this, this present study investigates whether the droplet moves spontaneously on a uniform surface. Interestingly, the droplet motion is initiated without the occurrence of the HER at the rear side, suggesting that there is another factor that causes the interfacial tension imbalance.

On the other hand, an oil droplet put on a solid surface in water phase can move spontaneously without any wettability gradients (that is, without imbalance of γ_{SW}), when there is a hydrodynamic flow due to interfacial tension gradients. This flow, called the Marangoni effect (or the Marangoni flow), is induced by gradients in the interfacial tension of the oil-water interface (γ_{OW}).15–25 We have recently found that a nitrobenzene droplet put on an Au electrode surface moves spontaneously due to the Marangoni effect when the Sn electrodeposition is performed in HNO3 solution. This present study shows how different this motion is from the motion that is induced by the imbalance of γ_{SW}. It also clarifies the origin of the Marangoni effect and provides a deeper insight into the droplet motion during the Sn electrodeposition. These spontaneous droplet motions, the motive force of which are wettability gradients or the Marangoni effect, are of interest from the viewpoint of direct energy conversion of chemical energy to mechanical one because they are driven by simple electrochemical reactions.

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HF solution for 3 minutes, and then immersed in a 0.5 mM HAuCl4 solution for 0.0085 A single-crystalline p-Si (100) wafer (Yamanaka Semiconductor, ca. 18.0 cm2) was used as a substrate, which was etched with a 5% H2O2 solution at 5°C for 2 minutes. The substrate was treated in 0.15 M HF solution at 5°C for 2 minutes. The substrate was treated in an electroless nickel plating bath (MURATA Co., Ltd., EleN-Ni100) at 70°C for 10 minutes. After that, Au was deposited by immersing the substrate in a displacement plating bath (EEJA, LECTROLESS Au1200) at 80°C for 10 minutes. A SEM image of the produced film shows that Au nanoparticles were uniformly deposited on the Si substrate (Figure 4c). Before the measurements, in order to remove organic contaminations, the electrode was exposed to ultraviolet lights (184.9 and 253.7 nm) and ozone gas by using a UV ozone cleaner (Filgen, UV253) for between 30 and 45 minutes.

An Au wire (0.5 mm diameter and ca. 10 mm length), which was sealed in a Teflon tube, was also used as the working electrode. To clean surface, the Au wire was immersed in conc. HNO3 at 60°C for 30 minutes. An Au wire (0.8 mm diameter and ca. 30 mm length) was used as the counter electrode. A saturated mercury-mercurous sulfate electrode (MSE, 0.64 V vs. standard hydrogen electrode (SHE) at 25°C) was used as the reference electrode; however, the potentials are referred to SHE in this study. The motion of the droplet was observed by CCD cameras during Sn electrodeposition in 0.5 M H2SO4 + 5 mM SnSO4 and 1.1 M HNO3 + 5 mM SnSO4. The interfacial tension between nitrobenzene and acidic aqueous solution was measured at room temperature by pendant drop method using an interfacial tension meter (Kyowa Interface Science Co., Ltd, DM-300 and FAMAS analysis software). All the aqueous solutions were prepared using special analytical grade chemicals (Wako Pure Chemical Industries) and purified water (resistivity > 18 MΩ cm) obtained from a Millipore system.

Results and Discussion

Electrochemical measurements.—Figure 5 shows I–E curves for an Au wire electrode in H2SO4 and HNO3 solutions, those containing SnSO4, and nitrobenzene. As can be seen in the top panels, the hydrogen evolution reaction (HER) due to the reduction of H+ (2H+ + 2e− → H2) occurred on Au in the potential region below ca. −0.08 V (see the insets). It should be noted that nitrate ions, NO3−, were hardly reduced on Au electrode (panel b1) because Au is not a good electrocatalyst toward the nitrate reduction.25

When 5 mM SnSO4 was added to the H2SO4 solution (panel a2), the reduction of Sn2+ (Sn2+ + 2e− → Sn0), i.e., the electrodeposition of Sn, occurred below −0.3 V. The HER was not active on Sn compared with Au,27,28 and consequently the reduction current due to the HER was much smaller than that observed without SnSO4. Incidentally, the HER occurred below ca. −0.67 V when a Sn-wire was used as the working electrode (see Figure 3b in the previous paper).14 Thus, in this study, the droplet motion during the Sn electrodeposition was studied at −0.66 V to prevent from the HER on Sn. On the other hand, when SnSO4 was added to the HNO3 solution (panel b2), NO3− was efficiently reduced in the potential region below ca. −0.15 V, which

Experimental Procedure

Electrochemical measurements were conducted by a three-electrode system (Figure 4a) at room temperature (around 25°C). The values of the potential (E) and the current (I) were acquired using a data acquisition system at a sampling rate of 100 Hz, as done before.14 An Au film deposited on a Si wafer of size 15 mm × 25 mm was used as the working electrode. A lead wire was connected to the film and the wafer was sealed with an epoxy resin to be used as the working electrode. A saturated mercury-mercurous sulfate electrode (MSE, 0.64 V vs. standard hydrogen electrode (SHE) at 25°C) was used as the reference electrode; however, the potentials are referred to SHE in this study. The motion of the droplet was observed by CCD cameras during Sn electrodeposition in 0.5 M H2SO4 + 5 mM SnSO4 and 1.1 M HNO3 + 5 mM SnSO4. The interfacial tension between nitrobenzene and acidic aqueous solution was measured at room temperature by pendant drop method using an interfacial tension meter (Kyowa Interface Science Co., Ltd, DM-300 and FAMAS analysis software). All the aqueous solutions were prepared using special analytical grade chemicals (Wako Pure Chemical Industries) and purified water (resistivity > 18 MΩ cm) obtained from a Millipore system.

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Figure 4. Schematic illustrations of (a) the experimental setup and (b) the Au film electrode used as the working electrode. A nitrobenzene droplet, the volume of which is about 5 μL, is put on the electrode. (c) A SEM image of the electrode surface.

corresponds to the potential where under-potential deposition (upd) of Sn occurred. This was probably because Au surface acted as an excellent catalyst toward the reduction of NO₃⁻ when it was modified with upd Sn, in an analogous manner as bimetallic catalysts using Sn and a noble metal such as Pt and Pd.

In the presence of nitrobenzene (the bottom panels), when $E < ca. \ 0.2 \ V$, nitrobenzene was reduced to form aniline ($C₆H₅NO₂ + 6H^+ + 6e^- \rightarrow C₆H₅NH₂ + 2H₂O$) via a two-step reaction: the formation of phenylhydroxylamine ($C₆H₅NO₂ + 4H^+ + 4e^- \rightarrow C₆H₅NHOH + H₂O$) and its consecutive reduction to aniline ($C₆H₅NHOH + 2H^+ + 2e^- \rightarrow C₆H₅NH₂ + H₂O$).

Droplet behavior on uniform surface.— Figure 6 shows the time course of $I$ when $E$ was stepped to $-0.66 \ V$ from the rest potential (ca. 0.3 V) at $t = 0 \ s$ and the snapshots of the droplet (top and side views). Before the potential step, $E$ was kept at the rest potential for several tens of minutes. The current increased (in absolute value) suddenly when $E$ was stepped, and then decayed with time owing to a decrease in the concentration of Sn²⁺ at the electrode surface (top right panel). The contact angle, which was 150° at $t = 0 \ s$, decreased immediately after the potential step (side view). At $t = 0.5 \ s$, the angle decrease stopped at 84°. Then, at $t = 1.0 \ s$, hydrogen bubbles started to evolve from the electrode surface (top view). The reduction current, which was attributed mainly to the Sn²⁺ reduction, was of the order of 1 mA.

In contrast to the previous study (see Figure 3a), the droplet put on the Au film stayed at its initial position though hydrogen bubbles were formed around the droplet. This result, the reproducibility of which was confirmed by repeatedly performing the same experiment, indicates that the interfacial tension acting on the droplet was uniform. This was most likely because the Sn electrodeposition as well as the HER occurred uniformly on the Au film. The film was produced on a Si wafer by electroless plating, and thus its surface was more uniform than the polished surface used in the previous study. However, if $E$ was kept at the rest potential for only a short time, e.g., for a few minutes or less, before the potential step, the droplet moved away from its initial position when the Sn electrodeposition was conducted, as shown in Figure 7. These results clearly indicate that an interfacial tension imbalance was induced by other factors rather

Figure 5. $I$–$E$ curves for an Au wire electrode measured under potential controlled conditions at a scan rate of 0.1 V s⁻¹. The solutions are (left) 0.5 M H₂SO₄ and (right) 1.1 M HNO₃, which contain (middle) 5 mM SnSO₄ and (bottom) 5 mM nitrobenzene (NB).
Figure 6. Time courses of $I$ when $E$ is stepped to $-0.66$ V from the rest potential at $t = 0$ s, and snapshots of the droplet put on an Au film electrode. Before the potential step, $E$ was kept at the rest potential for several tens of minutes. A white arrow in a top view indicates the direction from which the snapshots from the side are taken. The solution is $0.5$ M H$_2$SO$_4$ + $5$ mM SnSO$_4$.

than the occurrence of the HER. It should be noted that hydrogen bubbles were not observed at the rear side of the droplet when the droplet motion was initiated (at $0.7$ s).

What does initiate the droplet motion?—Judging from the above, we postulate that the adsorption of nitrobenzene molecules on Au surface played a role as a factor that initiated the motion, as can be illustrated in Figure 8. When a nitrobenzene droplet was put on an Au film (panel a), it frequently rolled off the film because the film surface was hydrophilic (see the snapshots taken at $t = 0$ s in Figures 6 and 7). For this reason, before conducting the Sn electrodeposition, we put a droplet on the film repeatedly (usually several times), that is, the procedures illustrated in panels b and c of Figure 8 were repeated.

As a result, nitrobenzene molecules should be adsorbed non-uniformly on the film surface at $t = 0$ s (panel d). Therefore, the Sn electrodeposition took place non-uniformly (panel e), which generated the interfacial tension imbalance that initiated the droplet motion. As mentioned in the Introduction, once the motion was initiated, the imbalance was created spontaneously: the electrodeposition occurred less efficiently at the rear side because it was suppressed by nitrobenzene molecules remaining on the surface (panel f). It was likely that the adsorbed nitrobenzene molecules gradually desorbed from the surface with time as mentioned in the previous work, or they were reduced to form aniline molecules because $E$ was more negative ($-0.66$ V) than the potential of the aniline formation. The formed aniline dissolved to the solution bulk, which is discussed in a later section. Note that aniline molecules are protonated to form anilinium ions (C$_6$H$_5$NH$_2$ + H$^+$ → C$_6$H$_5$NH$_3^+$), which are well soluble in aqueous solution.

On the other hand, while $E$ was kept at the rest potential for several tens of minutes, the adsorbed nitrobenzene molecules should desorb completely. Therefore, the Sn electrodeposition as well as the HER occurred uniformly on the Au film, and hence the droplet motion was not initiated (Figure 6).

Amoeba-like motion observed for HNO$_3$ solution.—To obtain further insight into the droplet motion, we performed the Sn electrodeposition using HNO$_3$ solution. Similarly to the above, the droplet stayed at its initial position, when $E$ was kept at the rest potential for several tens of minutes before the potential step (data not shown). Intriguingly, as shown in Figure 9, the droplet moved in a very different manner from the above when $E$ was kept at the rest potential for a short time before the step, i.e., when nitrobenzene molecules were adsorbed non-uniformly on the surface at $t = 0$ s. The contact angle started to decrease at $t = 0$ s. When $t = 4$ s, the angle decrease stopped at $50^\circ$. Then, the droplet continually changed in shape and moved like an amoeba. During this motion, small air bubbles, which were intentionally introduced into the droplet, changed their position from the droplet center, that is, they always moved in the direction of the moving droplet. This clearly indicates that there was a flow inside the oil liquid. We thus can conclude that the amoeba-like motion was driven by a Marangoni flow, that is, a flow due to a gradient in $\gamma_{OW}$, which is discussed later.

During this Sn electrodeposition, the reduction current was as high as several tens of milliamperes (e.g., around $-65$ mA as can be seen in the top left panel) due to the occurrence of the nitrate reduction. More importantly, almost no bubbles were observed during the Sn electrodeposition in contrast to the electrodeposition performed in the H$_2$SO$_4$ solution (compare Figure 9 with Figure 7). This indicates that the nitrate reduction efficiently consumed H$^+$ at the electrode surface. In other words, the nitrate reduction caused an increase in the local pH at the electrode surface. Note that the efficient nitrate reduction required Sn$^{2+}$ ions, as shown above (see Figure 5).
Let us discuss the origin of the amoeba-like motion. The reduction of nitrobenzene occurs on Au electrode, as shown in the bottom panels of Figure 5. At the potential where the motion is observed, –0.66 V, the reaction product is aniline. When the water phase is the H$_2$SO$_4$ solution, the local pH at the electrode surface remains acidic even when the HER occurs at the electrode surface. Therefore, aniline produced at the oil-water interface near the electrode surface diffuses into the water phase (panel a1 of Figure 10). Note that aniline is well soluble in acidic solution.

When the water phase is the HNO$_3$ solution (panel b1), the occurrence of the nitrate reduction causes the pH increase at the electrode surface as mentioned above, and thus aniline dissolves not into the water phase but into the oil phase, i.e., into the nitrobenzene droplet. According to a literature, the interfacial tension between aniline and water (5.9 mNm$^{-1}$) is much smaller than that between nitrobenzene and water (26 mNm$^{-1}$). Thus, the aniline dissolution into nitrobenzene causes a decrease in $\gamma_{ow}$ (panel b2). This can be confirmed by the following fact: the contact angle ($\theta$) decreased to 50°, which was much smaller than the angle during the Sn electrodeposition in H$_2$SO$_4$ solution, i.e., around 80° (compare Figure 9 with Figures 6 and 7).

On the other hand, the dissolved aniline in the droplet reacts with H$^+$ and it is transferred as anilinium ion to the HNO$_3$ solution, resulting in a recovery of $\gamma_{ow}$. The aniline dissolution (and the decrease in $\gamma_{ow}$) occurs at the oil-water interface adjacent to the electrode surface.

**Figure 8.** Schematic of how the imbalance of $\gamma_{sw}$ can be created on a uniform surface by the adsorption of nitrobenzene (NB).
Figure 9. Time courses of $I$ when $E$ is stepped to $-0.66$ V from the rest potential at $t = 0$ s, and snapshots of the droplet put on an Au film electrode. Before the potential step, $E$ was kept at the rest potential for a few minutes. The solution is 1.1 M HNO$_3$ + 5 mM SnSO$_4$.

Figure 10. (left) Schematic cross sections of an edge of the nitrobenzene (NB) droplet in the H$_2$SO$_4$ solution containing SnSO$_4$, and (right) those in the HNO$_3$ solution containing SnSO$_4$. The top panels illustrate how the aniline (AN) dissolution is affected by the local pH at the electrode surface. The bottom panels illustrate how the Marangoni flow is induced in the NB droplet.
whereas the transfer of dissolved aniline (and the recovery of $\gamma_{ow}$) occurs far from the electrode surface (panels b1 and b2). Thus, the aniline dissolution and transfer generate the gradient in $\gamma_{ow}$.

When nitrobenzene molecules were adsorbed non-uniformly on the surface at $t = 0$ s, namely, when $E$ was kept at the rest potential for a short time before the potential step, they were reduced to form aniline molecules. The dissolution and transfer of the formed aniline caused the $\gamma_{ow}$ gradient that produced the Marangoni flow, and thus the amoeba-like motion was initiated (Figure 9). During the amoeba-like motion, aniline molecules were produced at the rear side of the droplet because of the nitrobenzene remaining at the rear side, and hence this motion was also sustained in a self-propelled manner.

On the other hand, when $E$ was kept at the rest potential for several tens of minutes before the potential step, the droplet stayed at its initial position as mentioned above. In other words, the amoeba-like motion was not initiated without the non-uniformly adsorbed nitrobenzene. Further studies are needed in order to clarify the details of the amoeba-like motion.

In order to confirm the aniline transfer, we observed a droplet of a nitrobenzene-aniline mixture which was put on a glass plate. Figure 11 shows snapshots of the droplet in 1.1 M HNO$_3$ solution. When the droplet was put on the plate ($t = 0$ s), the surface of the droplet was not smooth. Immediately, the Schlieren effect, which was ascribed to gradients of the refractive index, started to be observed around the droplet. The effect was observed for more than 180 seconds. On the other hand, when the solution was 0.1 M NaOH, the Schlieren effect was not observed (data not shown). These indicate that the aniline molecules in nitrobenzene were transferred to water phase only when the phase was acidic. Furthermore, the aniline transfer to the acidic solution was also confirmed by a change in the contact angle of the droplet. At the initial stage, the angle (e.g., $131^\circ$ at $t = 20$ s) was smaller than that of a nitrobenzene droplet on a glass plate (about $145^\circ$) because the dissolved aniline lowered $\gamma_{ow}$. It increased gradually and finally became $143^\circ$ (at $t = 170$ s) which was in good agreement with the angle of the nitrobenzene droplet on the glass plate.

![Figure 11. Snapshots of a droplet of a nitrobenzene-aniline mixture (1:1 molar ratio) taken at every 30 seconds. At $t = 0$ s, the droplet is put on a glass plate immersed in 1.1 M HNO$_3$ solution.](image)

**Is marangoni flow induced in H$_2$SO$_4$ solution?**—As for the Sn electrodeposition performed in the H$_2$SO$_4$ solution, the aniline produced at the electrode surface dissolves into the H$_2$SO$_4$ solution (or the solution bulk) as illustrated in panel a1 of Figure 10. The aniline dissolution may cause a change in $\gamma_{ow}$ near the surface, resulting in a $\gamma_{ow}$ gradient along the oil-water interface. It is thus possible that this $\gamma_{ow}$ gradient also produces a Marangoni flow. However, the gradient is not a factor that initiates the droplet motion in the H$_2$SO$_4$ solution.

To confirm this, the interfacial tension between nitrobenzene and H$_2$SO$_4$ solution was measured. When the aqueous phase was 0.5 M H$_2$SO$_4$ solution, the tension was about 26 mN m$^{-1}$. As the concentration of aniline (or anilinium ion) in the H$_2$SO$_4$ solution increased, the tension decreased gradually. When the aniline concentration was about 0.5 M, that is, the solution was saturated with aniline, the tension was decreased to 21 mN m$^{-1}$. During the Sn electrodeposition, the local concentration of aniline near the surface was thought to be much lower than its saturation value. Thus, the $\gamma_{ow}$ gradient was negligible, so that the Marangoni flow was not induced in the H$_2$SO$_4$ solution.

**Other organic compounds.**—When an organic compound such as hexane, chlorobenzene, toluene, or butyl acetate was used as an oil droplet instead of nitrobenzene, the lateral motion of the droplet also occurred due to the $\gamma_{SW}$ imbalance during the Sn electrodeposition in the H$_2$SO$_4$ solution, as mentioned in the previous paper. On the other hand, we think that the amoeba-like motion is specific to nitrobenzene because the reduction product aniline plays an essential role in the motion. Thus, the amoeba-like motion should also occur for an oil droplet that contains some amount of nitrobenzene.

**Conclusions**

A nitrobenzene droplet moves on an Au electrode in a self-propelled manner during the Sn electrodeposition performed in strong acid solutions such as H$_2$SO$_4$ and HNO$_3$ solutions. When the electrodeposition is performed in H$_2$SO$_4$ solution, the driving force of the motion is an imbalance of the interfacial tension of solid-water interface ($\gamma_{SW}$) acting on the opposite side of the droplet, that is, the droplet moves because $\gamma_{SW}$ acting on the front side of droplet is larger than that on the rear side. From the results obtained by this study and previous ones, we can conclude that there are two factors that initiate the droplet motion in H$_2$SO$_4$ solution: the occurrence of the HER at the rear side and the nitrobenzene molecules adsorbed on the electrode surface. These factors can initiate the motion when the surface is non-uniform and uniform, respectively. Once the droplet motion is initiated, the imbalance of $\gamma_{SW}$ is created spontaneously, that is, the motion is self-propelled, because of oil molecules remaining on the rear side.

Furthermore, the adsorbed nitrobenzene molecules create a Marangoni flow inside the droplet that motivates the droplet to move like an amoeba, when the electrodeposition is performed in HNO$_3$ solution. This is because the aniline is produced by the reduction of the adsorbed nitrobenzene and the pH at the electrode surface increases due to the reduction of nitrate ion. The pH increase induces the dissolution of the formed aniline into the nitrobenzene droplet, leading to a decrease in the interfacial tension of oil-water interface ($\gamma_{ow}$). On the other hand, the dissolved aniline is transferred as anilinium ion to the HNO$_3$ solution, resulting in a recovery of $\gamma_{ow}$. The aniline dissolution occurs at the oil-water interface adjacent to the electrode surface whereas the transfer of dissolved aniline occurs at the interface far from the electrode surface. Thus, the aniline dissolution and transfer generate a gradient in $\gamma_{ow}$, leading to the Marangoni flow. The amoeba-like motion due to the Marangoni flow is also self-propelled because nitrobenzene molecules remaining on the rear side are reduced to form aniline molecules.

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References
1. Y. Yuan and T. R. Lee, in Surface Science Techniques, G. Bracco and B. Holst Editors, p. 3, Springer (2013).
2. R. S. Subramanian, in Soft Matter Gradient Surfaces: Methods and Applications, J. Gerzer Editor, p. 407, John Wiley & Sons (2012).
3. M. K. Chaudhury and G. M. Whitesides, Science, 256, 1539 (1992).
4. S. Daniel, M. K. Chaudhury, and J. C. Chen, Science, 291, 633 (2001).
5. S. Daniel and M. K. Chaudhury, Langmuir, 18, 3404 (2002).
6. H. Suda and S. Yamada, Langmuir, 19, 529 (2003).
7. S. Daniel, S. Sircar, J. Gliem, and M. K. Chaudhury, Langmuir, 20, 4085 (2004).
8. S. Daniel, M. K. Chaudhury, and J. B. McLaughlin, Langmuir, 22, 2682 (2006).
9. M. Chakraborty, U. U. Ghosh, S. Chakraborty, and S. DasGupta, RSC Advances, 5, 45266 (2015).
10. A. Shastry, M. J. Case, and K. F. Behringer, Langmuir, 22, 6161 (2006).
11. Y. Sumino, K. Yoshikawa, M. Nagayama, S.-I. M. Nomura, N. Magome, and Y. Mori, Physical Review E, 72, 041603 (2005).
12. Y. Sumino, N. Magome, T. Hamada, and K. Yoshikawa, Physical Review Letters, 94, 068301 (2005).
13. Y. Sumino and K. Yoshikawa, Chaos, 18, 026106 (2008).
14. B. Nanzai, M. Yamauchi, Y. Okawa, K. Wakimoto, and M. Iwata, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 443, 560 (2014).
15. S.-W. Lee and P. E. Laibinis, Journal of the American Chemical Society, 122, 5395 (2000).
16. S.-W. Lee, D. Y. Kwok, and P. E. Laibinis, Physical Review E, 65, 051602 (2002).
17. P. Lazar and H. Riegler, Physical Review Letters, 95, 136103 (2005).
18. S.-W. Lee and P. E. Laibinis, Journal of The Electrochemical Society, 165 (9) H473-H480 (2018)