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Non-oscillatory micromotors “learn” to oscillate on-the-fly from oscillating Ag micromotors†

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The ability to learn new functionalities on-the-fly is highly desired for micromotors operating in a changing environment. Here, we demonstrate how non-oscillatory micromotors transform into spontaneous oscillators, superficially resembling students learning from teachers, via the diffusion then deposition of Ag ions that act as a speed-booster that periodically turns on.

Micromotors, specialized colloids that harvest environmental energy and swim autonomously in liquid,^{1–3} have emerged as a promising candidate as untethered, multifunctional microbots for a wide range of applications.^{4–7} A key requirement in the operation of micromotors is the capability to communicate and coordinate. Recently, a few studies have introduced an interesting strategy for two chemical motors to communicate by modulating speeds.⁸ Specifically, bimetallic microrod motors were found to accelerate significantly in the presence of trace amount of silver ions (Ag⁺).⁹ As a result, a first motor that produces Ag⁺ would, as it moves, accelerate nearby motors of a second type.⁸

Although such Ag⁺-induced acceleration serves as an effective communication scheme between two chemical micromotors, certain applications might require micromotors with changes beyond a variation in speeds. For example, in a hypothetical scenario of targeted cancer therapy, it is beneficial for an advance party of microbots that are activated upon contact with cancer cells to pass on this state of activation to other microbots, so that a large number of them can be activated within a short period of time. This scenario, similar to how the biological immune system or social insects such as bees or ants works, naturally requires micromotors to communicate and, more importantly, to learn from each other.

In this communication, we report an unusual observation where photochemically powered, oscillating micromotors transform

catalytically powered, non-oscillatory micromotors into spontaneous oscillators on-the-fly and without external intervention, bearing a superficial resemblance to students acquiring a new set of skills by learning from teachers.

We begin by briefly introducing the natural behaviors of both the non-oscillatory (student) and the oscillating micromotors (teacher) studied in this article (see Fig. 1 and Video S1, ESI†). Non-oscillatory micromotors here are polystyrene microspheres half coated with platinum (Pt–PS, Fig. 1a and b) and gold–rhodium (Au–Rh) bimetallic microrods (Fig. 1c and d). Their synthesis is detailed in the ESI.† Both types of micromotors are well-studied chemical motors that move autonomously by catalytically decomposing H₂O₂.^{10,11} In either case, solutions of

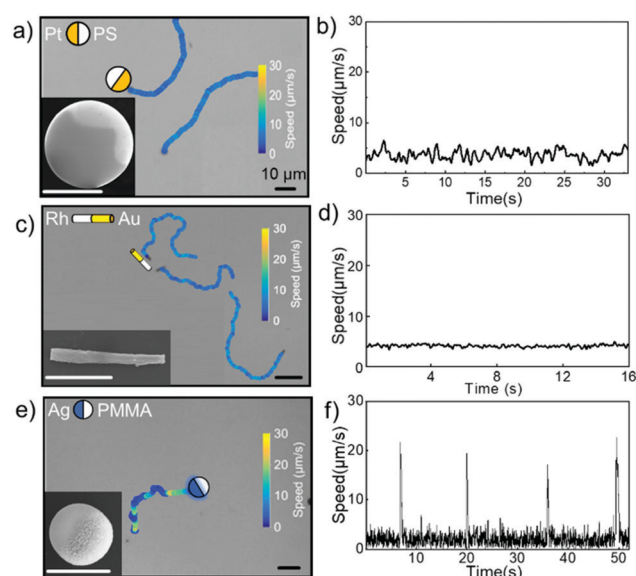


Fig. 1 Typical dynamics of non-oscillatory Pt–PS and Au–Rh micromotors or oscillatory Ag–PMMA micromotors. Their trajectories are color-coded with instantaneous speeds on the left column (a, c and e), while the speed profiles over time are plotted in (b, d, and f). Insets on the left column are scanning electron micrographs of the corresponding particles.

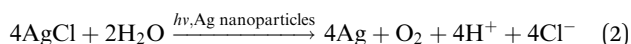
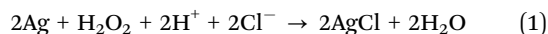
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high ionic strength are known to quench the motor mobility, a feature we shall revisit later in Fig. 4b.^{12,13} In a typical experiment, either type of micromotor move at $\sim 10 \mu\text{m s}^{-1}$ in a tortuous trajectory that is constantly randomized by Brownian motion (Fig. 1a and c). Importantly, their speed profiles are noisy but without periodic fluctuations (Fig. 1b and d).

On the other hand, a few recent studies have discovered that Janus microparticles containing Ag, AgCl or Ag_3PO_4 display striking, oscillatory dynamics (Fig. 1e and f).^{14–17} Specifically, these particles alternate between a fast, directional motion and a slow, Brownian diffusion in the presence of H_2O_2 , KCl and UV light. In the current study, polymethylmethacrylate or silicon dioxide microspheres half coated with Ag (PMMA–Ag or SiO_2 –Ag, respectively) are used as oscillating micromotors. Although a detailed understanding of the operating mechanism is lacking, it is speculated that this unusual dynamic originates from a pair of chemical reactions that spontaneously oscillate on the particle surface:



Collectively, these oscillations give rise to synchronization among a population, as well as traveling waves of activated particles that sweep across the entire population. These observations have been reported in recent studies,^{15,16} and are hallmark features of oscillating micromotors, as we shall see in the following.

Given that the above oscillations originate from a conversion between $\text{Ag}(0)$ and $\text{Ag}(I)$ species on the particle surface, micromotors without Ag, such as Au–Rh and Pt–PS, are not expected to spontaneously oscillate. This is confirmed in their featureless dynamics shown in Fig. 1. However, when mixed with spontaneously oscillating, Ag-containing micromotors, the situation changes dramatically. For example, Au–Rh microrods from Fig. 1a were mixed with PMMA–Ag Janus microspheres from Fig. 1e in a solution of 0.5 wt% of H_2O_2 and 400 μM of KCl (see Fig. S1, ESI[†] for the experiment setup). Upon applying UV light of 365 nm and $\sim 650 \text{ mW cm}^{-2}$, PMMA–Ag micromotors started to pulsate, alternating between a fast motion of $\sim 8 \mu\text{m s}^{-1}$ and a slow, resting stage of $\sim 2 \mu\text{m s}^{-1}$ (essentially Brownian motion). Surprisingly, Au–Rh microrods in the vicinity of a PMMA–Ag microsphere pulsated in the same fashion, with the same frequency and phases, and an even high peak speed (Fig. 2a–c and Video S2, ESI[†]). Similar observations were made for Pt–PS motors mixed with SiO_2 –Ag oscillating micromotors, shown in Fig. 2d–f and Video S3 (ESI[†]), confirming the generalizability of the ability of oscillating micromotors to transform the dynamics of non-oscillatory micromotors.

Importantly, this transformation is most notable for Au–Rh or Pt–PS micromotors in the vicinity (a few body lengths) of an oscillating micromotor. Au–Rh or Pt–PS micromotors farther away could also be transformed and started to pulsate, but often with a much-decreased intensity. This is best seen in Video S4 (ESI[†]), where a cluster of PMMA–Ag oscillating motors periodically activates nearby Au–Rh microrods as it migrates upward.

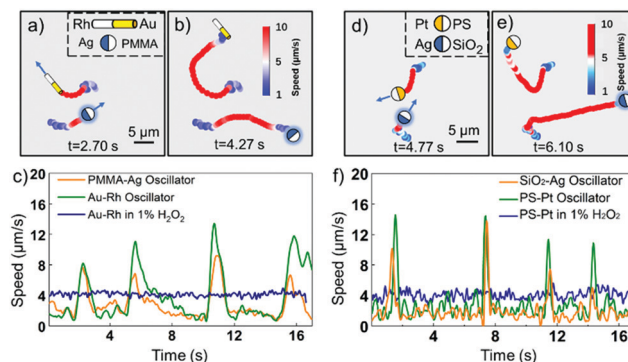


Fig. 2 Oscillating Ag micromotors transform Au–Rh microrod (a–c) and Pt–PS micromotors (d–f) nearby. (a) and (b) Time-elapsed optical micrographs of the actual trajectories, colour coded with instantaneous speeds, of one Au–Rh microrod oscillating near a PMMA–Ag microsphere. (c) Speed profiles of the above two particles over time, compared with that of a non-oscillatory Au–Rh microrod in the absence of any PMMA–Ag motors. (d–f) Same quantification as (a–c), performed on a Pt–PS micromotor moving near a SiO_2 –Ag oscillator.

Naturally non-oscillatory micromotors, now transformed into oscillators, can be repeatedly activated by the propagation of traveling waves of oscillating motors. The propagation of such a wave is illustrated in Fig. 3a (taken from Video S5, ESI[†]), where activated, pulsating PMMA–Ag micromotors at the wavefront are marked in red. The dynamics of one Au–Rh microrod mixed within this oscillating population is highlighted in Fig. 3b and c, with speeds rising and falling as waves passed. We note that an activated Au–Rh rod displays both a significantly larger peak speed and a substantially longer activity than that of a PMMA–Ag motor, *i.e.* the student has surpassed the teacher.

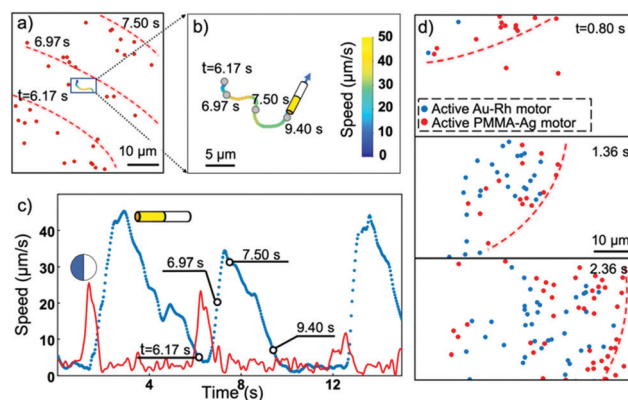


Fig. 3 Au–Rh microrods activated repeatedly by travelling waves. (a) A wave of PMMA–Ag oscillators travels from bottom left to top right. PMMA–Ag motors at the wavefront at three different time instances are marked in red. Au–Rh rods in the suspension are not marked. (b) Trajectory of one Au–Rh microrod (highlighted in (a)) during the propagation of one wave. Its speed was slow when the wavefront was far ($t = 6.17 \text{ s}$), but rose quickly as the wave approached ($t = 6.97 \text{ s}$) and remained high after the wave passed ($t = 7.50 \text{ s}$ and beyond). (c) Speed profiles of the microrod in (b) and one PMMA–Ag oscillator $\sim 10 \mu\text{m}$ away. Time stamps match those in (b). (d) Activated Au–Rh microrods (blue) also formed a wave that propagated together with PMMA–Ag motors (red).

The above experiment represents a situation where a small amount of Au–Rh microrods (student) is mixed with a large number of PMMA–Ag microspheres (teacher), at a rod-sphere ratio of 1 : 1.88, but the results also hold for the opposite case, when the oscillatory micromotors (teacher) are in the minority (rod:sphere = 1:0.73). This is demonstrated by Fig. 3d and Video S6 (ESI†), where waves of activated PMMA–Ag and Au–Rh can still be robustly reproduced. It therefore suggests that only a small amount of naturally oscillating micromotors is required to transform a bigger group of naturally non-oscillatory micromotors.

How does a naturally non-oscillatory micromotor learn to spontaneously oscillate? Fig. 4a illustrates our proposed qualitative mechanism, in which we postulate that PMMA–Ag motors during the oscillation release silver ions (Ag^+) that diffuse (facilitated by local flows) and eventually deposit on the surface of Au–Rh rods. Because it is known that the incorporation of a small amount of Ag greatly enhances the catalytic capability of noble metals such as Pt,^{18,19} the presence of these deposited Ag (likely in the form of nanoparticles, see below) could significantly increase the speed of an Au–Ru micromotor in H_2O_2 , as shown in previous studies of micromotors.⁹ However, [eqn (1)]

suggests that Ag spontaneously oxidizes in the presence of Cl^- and H_2O_2 . Therefore, similar to how the Ag coating on a PMMA–Ag micromotor cycles between Ag and AgCl, the Ag-induced fast propulsion for a Au–Ru micromotor only occurs periodically.

Importantly, an Ag-laden bimetallic rod is still powered by its intrinsic electrophoretic engine, *i.e.* the electrochemical decomposition of H_2O_2 by Au and Rh, and the additional Ag nanoparticles are merely speed-boosters with an intrinsic chemical clock. This clock is periodically turned on and off, boosting the performance of the electrophoretic engine while on, and leaving the motor slow while off. This argument is confirmed by a lack of pulsating motion for particles that are not motors to begin with, such as inert SiO_2 microspheres, or metallic microrods of singular composition (results now shown). This boosting mechanism is fundamentally different from how an intrinsically oscillating PMMA–Ag micromotor moves, where the Ag coating is both the chemical clock and the engine, releasing chemicals and powering the motor *via* diffusiophoresis.^{17,20}

In our crude analogy of education, the above process of “release–diffusion–attachment–transformation” is similar to how a teacher (*i.e.* an oscillating PMMA–Ag motor) passes on her/his knowledge (*i.e.* Ag^+) to a student (*i.e.* a non-oscillatory Au–Rh rod), who upon receiving this knowledge learns what the teacher is capable of (*i.e.* oscillation). Note how a student does not “become” the teacher, but is only modified.

A more robust discussion on this proposed mechanism involves examining if Au–Rh microrods would oscillate in an aqueous solution containing H_2O_2 , KCl and AgNO_3 (but not PMMA–Ag particles) under UV light. This is similar in asking if students are capable of learning with all necessary course materials, but without teachers. A sequence of experiments was then performed, shown in Fig. 4b. Au–Rh rods were first suspended in 1% H_2O_2 , and moved continuously at a speed of a few $\mu\text{m s}^{-1}$. A small amount of AgNO_3 was then added to reach a concentration of $10 \mu\text{mol L}^{-1}$, and rods moved faster at $10\text{--}15 \mu\text{m s}^{-1}$ because the aforementioned Ag-induced acceleration effect. KCl was then added, slowing rods down to Brownian level because of the now elevated ionic strength. Finally, UV light was applied, and rods began to oscillate, and even produced waves (Fig. 4c, taken from Video S7, ESI†) that were qualitatively the same as previous experiments. The results of these experiments show that it is indeed the Ag^+ , not the PMMA–Ag particles *per se*, that are capable of transforming Au–Rh motors into being oscillatory.

We further speculate that Ag^+ deposited on Au–Rh rods as Ag nanoparticles, an argument supported by the following two observations. First, Au–Rh rods after transformation oscillated in trajectories of repeating circles (Fig. 4e), while their natural trajectories in H_2O_2 are more open yet tortuous (Fig. 4d). This change in trajectory seems to suggest that either the shape asymmetry of the rod was broken, or the presence of a Ag nanoparticle made the rod trimetallic, which rotates by an asymmetric chemical gradient. Second, scanning electron microscopy (Fig. 4f) reveals Ag containing nanoparticles scattered on the surface of Au–Rh rods after transformation (see Fig. S4, ESI† for elemental mapping results). These observations, and the earlier report

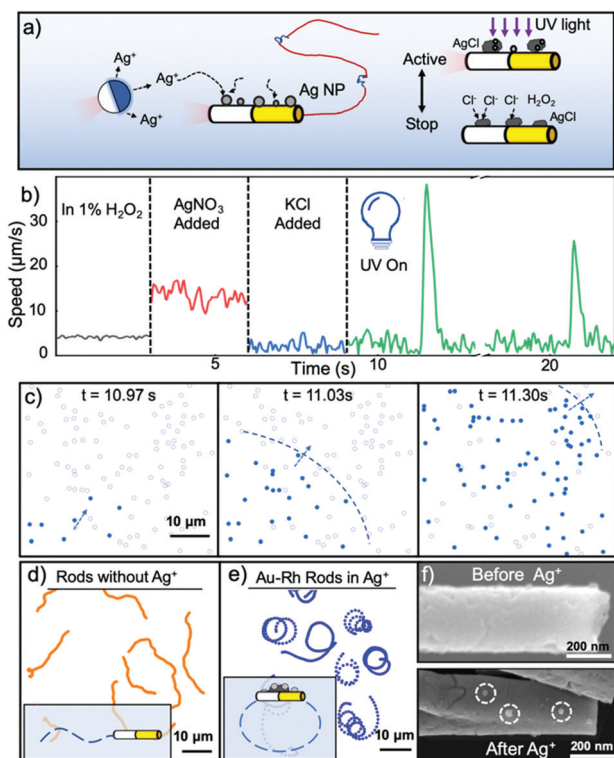


Fig. 4 Understanding the transformation of non-oscillating motors. (a) Pro-posed mechanism on how Ag^+ ions are released from Ag-containing oscillating motors and deposit on Au–Rh rods as Ag nanoparticles. Their conversion periodically boosts the speed of a rod. (b) Speed profile of Au–Rh rod in a sequence of experiments with adding AgNO_3 , KCl and applied UV. (c) Waves of Au–Rh rods (those activated are marked blue) in solutions containing Ag^+ , but without PMMA–Ag micromotors. (d) and (e) Trajectories of Au–Rh rods in the absence (d) or presence (e) of Ag^+ . (f) Scanning electron micrographs of a Au–Rh rod before and after exposing to solutions of Ag^+ . Suspected Ag nanoparticles are circled.

of Ag nanoparticles attached to the surface of Pt-PS motors in the presence of Ag^+ ,⁹ support our proposed mechanism that Ag ions are released from oscillating PMMA-Ag particles, and deposit on the surface of Au-Rh rods as Ag nanoparticles. This deposition could occur *via* under potential electroless plating,^{21–23} as was invoked by Chen *et al.* in their early study.⁸

Finally, it is interesting to note that, just as students tend to forget what they have learned over time, transformed micromotors also have leaky “memories”, in the sense that their oscillating speeds gradually decreased over time (see Video S7, ESI†). Moreover, transformed micromotors do not oscillate well if stripped from the transforming media, *i.e.* when the oscillating Ag-containing micromotors are removed, and Ag^+ is absent from the solution. The analogy is that students perform poorly when they are placed away from the classrooms and books. This is likely because the Ag nanoparticles responsible for oscillation spontaneously oxidized in H_2O_2 following eqn (1). Furthermore, a “student” motor is not capable of teaching other student motors, possibly because the Ag^+ released from a student is too few to affect others that do not already contain Ag.

In conclusion, we have reported an observation where oscillating, Ag containing micromotors transform Au-Rh or Pt-PS micromotors from their natural continuous, tortuous motion to periodic motion of circular trajectories. Control experiments reveal that Ag ions, possibly produced from the surface of an oscillating motor, deposit on the surface of Au-Rh or Pt-PS particles as Ag nanoparticles. They then act as a speed booster that periodically accelerates the bimetallic motors. Our discovery here offers an interesting strategy for a group of micromotors, possibly of different functionalities and dynamics, to communicate, coordinate, and learn from each other, a critical step for the development of microbots in a changing environment.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 J. Wang, *Nanomachines: Fundamentals and Applications*, John Wiley & Sons, 2013.
- 2 T. E. Mallouk and A. Sen, *Sci. Am.*, 2009, **300**, 72–77.
- 3 X. Chen, C. Zhou and W. Wang, *Chem. – Asian J.*, 2019, **14**, 2388–2405.
- 4 M. Safdar, S. U. Khan and J. Janis, *Adv. Mater.*, 2018, **30**, e1703660.
- 5 J. Parmar, D. Vilela, K. Villa, J. Wang and S. Sanchez, *J. Am. Chem. Soc.*, 2018, **140**, 9317–9331.
- 6 X. Chang, W. Tang, Y. Feng, H. Yu, Z. Wu, T. Xu, H. Dong and T. Li, *Chem. – Asian J.*, 2019, **14**, 2357–2368.
- 7 L. Liu, J. Gao, D. A. Wilson, Y. Tu and F. Peng, *Chem. – Asian J.*, 2019, **14**, 2325–2335.
- 8 C. Chen, X. Chang, H. Teymourian, D. E. Ramirez-Herrera, B. Esteban-Fernandez de Avila, X. Lu, J. Li, S. He, C. Fang, Y. Liang, F. Mou, J. Guan and J. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 241–245.
- 9 D. Kagan, P. Calvo-Marzal, S. Balasubramanian, S. Sattayasamitsathit, K. M. Manesh, G. U. Flechsig and J. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 12082–12083.
- 10 W. F. Paxton, K. C. Kistler, C. C. Olmeda, A. Sen, S. K. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert and V. H. Crespi, *J. Am. Chem. Soc.*, 2004, **126**, 13424–13431.
- 11 J. R. Howse, R. A. Jones, A. J. Ryan, T. Gough, R. Vafabakhsh and R. Golestanian, *Phys. Rev. Lett.*, 2007, **99**, 048102.
- 12 A. Brown and W. Poon, *Soft Matter*, 2014, **10**, 4016–4027.
- 13 S. Ebbens, D. Gregory, G. Dunderdale, J. Howse, Y. Ibrahim, T. Liverpool and R. Golestanian, *Europhys. Lett.*, 2014, **106**, 58003.
- 14 M. E. Ibele, P. E. Lammert, V. H. Crespi and A. Sen, *ACS Nano*, 2010, **4**, 4845–4851.
- 15 A. Altemose, M. A. Sanchez-Farran, W. Duan, S. Schulz, A. Borhan, V. H. Crespi and A. Sen, *Angew. Chem., Int. Ed.*, 2017, **56**, 7817–7821.
- 16 A. Altemose, A. J. Harris and A. Sen, *ChemSystemsChem*, 2020, **2**, e1900021.
- 17 C. Zhou, X. Chen, Z. Han and W. Wang, *ACS Nano*, 2019, **13**, 4064–4072.
- 18 F. Gauthard, F. Epron and J. J. O. C. Barbier, *J. Catal.*, 2003, **220**, 182–191.
- 19 A. Wang, X. Y. Liu, C. Y. Mou and T. Zhang, *J. Catal.*, 2013, **308**, 258–271.
- 20 C. Zhou, H. Zhang, J. Tang and W. Wang, *Langmuir*, 2018, **34**, 3289–3295.
- 21 D. He, S. Garg and T. D. Waite, *Langmuir*, 2012, **28**, 10266–10275.
- 22 M. Schaal, A. Pickerell, C. Williams and J. Monnier, *J. Catal.*, 2008, **254**, 131–143.
- 23 J. Wang, N. Marinković, R. Adžić and B. Ocko, *Surf. Sci.*, 1998, **398**, L291–L296.