Micromotors Hot Paper

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Reversing a Platinum Micromotor by Introducing Platinum Oxide

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Abstract: Understanding and controlling the swimming direction of a synthetic nano- and micromotor holds fundamental and applied significance. Here, we focus on platinum-containing Janus colloids that catalytically decompose H_2O_2 into O_2, an archetypical model of chemical micromotor. We discover that platinum oxides (primarily PtO) are produced on Pt films sputter-coated in O_2 plasma, and PtO reverses the motor possibly by self-electrophoresis. Using this knowledge, micromotors moving in either direction were fabricated by intentionally introducing or removing PtO. These findings challenge the conventional wisdom that a Pt micromotor is powered by Pt alone, and open up new avenues for controlling the swimming directions of a micro- and nanomachine.

Over the last two decades, micromotors that harvest environmental energy and move autonomously have received mounting interest for their potential applications in drug delivery, bio-sensing, and environmental monitoring and remediation.[1] One archetypical micromotor is an inert microsphere half-coated with platinum (Pt), which moves by the catalytic decomposition of H_2O_2 on the Pt surface.[2] Such a Pt Janus micromotor is simple in its design and dynamics, and is widely studied by material chemists and soft matter scientists as prototypical microrobots, active colloids and synthetic microswimmers.[3]

Two pillars of conventional wisdoms often hold for Pt micromotors: 1) an asymmetric distribution of Pt is sufficient for self-propulsion; 2) it is Pt, and only Pt, that is present on the metal cap and responsible for self-propulsion. We have challenged the first notion in a recent study by showing Janus microspheres decorated with Pt nanoparticles propel poorly.[4] Here, we challenge the second notion by showing the possible existence of platinum oxide (PtO) from physical vapor deposition, its effect on the speed and directionality of a Pt-coated micromotor, and the intentional control of such an effect. This finding forces us to reimagine chemical micromotors and micro-pumps containing materials previously considered inert, and opens up new venues for controlling the moving direction of chemical micromachines via precise engineering of their material compositions.

A series of SiO_2–Pt Janus microspheres were fabricated by coating SiO_2 microspheres of 5 μm in diameter with Pt of thicknesses ranging from ≈5 nm to ≈100 nm (see Figure S1 for details on thickness measurement). The detail of the sputtering process is worth noting: samples (a monolayer of SiO_2 microspheres) were placed in the chamber of a table-top sputter-coater that was filled with air to begin with, and pumped down to a vacuum level of 3.8×10^{-2} Torr. High energy plasma (primarily from N_2 and O_2) then bombarded the Pt target and produced Pt atoms that deposited on the sample. As we shall see below, the choice of the plasma gas (air vs. argon) is important in determining the direction of a Pt-coated micromotor.

Pt-SiO_2 Janus microspheres fabricated in this way self-propelled in aqueous solutions of H_2O_2 (typically 5 wt %, or 1.47 mol L^{-1}). Importantly, Figure 1 shows that Pt-coated SiO_2 micromotors with a thin Pt coating (e.g. 5 nm) moved pre-dominantly away from its Pt cap (Video S2, part 1), a direction we prescribe as "forward" because it is consistent with the majority of reports of Pt-coated micromotors.[2,5] However, as the Pt coating thickened, micromotors were more and more likely to swim toward the Pt cap, i.e. "in reverse" (Video S2, part 2). Motors coated with 100 nm Pt almost exclusively moved in reverse (Video S2, part 3), at an absolute speed higher than the forward motors. Note that although SiO_2 microspheres are used throughout this article, the choice of the inert microsphere is not a critical factor as we observed qualitatively the same behaviors with poly(methylmethacrylate) (PMMA) and titania dioxide (TiO_2) microspheres (see Video S1, experiments with TiO_2 were performed under ambient light that does not photo-activate TiO_2).

Three factors were suspected to play a role in the reversal of a Pt motor: coating thickness, coating morphology, and material composition. The thickness per se is not likely, because motors always moved forward if sputter-coated in a chamber prefilled with argon instead of air, regardless of the coating thickness (see Figure 2a, Video S3

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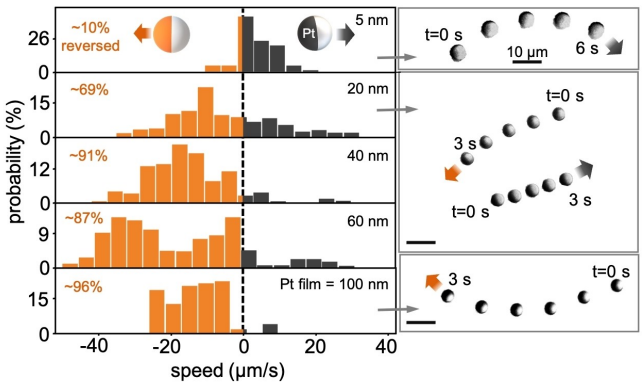

Figure 1. Reversal of SiO_2-Pt micromotors of different Pt thickness sputtered in air. Left: Instantaneous speed distributions of SiO_2-Pt micromotors of different Pt thickness (values labelled). The percentage of motors moving in reverse is labelled in orange. Right: Overlaid optical micrographs of SiO_2-Pt micromotors of 5 nm (top), 20 nm (center) and 100 nm (bottom) Pt. Experiments were performed in 5% H_2O_2, and trajectories of ≈20 motors in each experiment were analyzed. Speeds in the forward and reverse directions are color-coded in black and orange throughout this article, respectively.

and detailed descriptions below). The coating morphology, a common factor that affects motor speed,[6] was also unlikely to reverse a micromotor, because samples heated at different temperatures produced dramatically different coating morphologies, yet this is not correlated to which direction they move in.

That leaves us with material composition as the most likely culprit for the reversal of Pt-coated micromotors. Specifically, we speculate that instead of (or in addition to) Pt, platinum oxide (PtO, Pt_3O_4 or PtO_2) is deposited during sputter-coating, as energetic O_2 plasma bombards the Pt target in an air-filled chamber. This speculation is reasonable because similar sputtering or plasma techniques have been used in earlier studies to prepare platinum oxides.[7] A simple test for this speculation is to instead pre-fill the sputtering chamber with Ar, an inert gas that does not react with Pt to form oxides. The results in Figure 2 clearly shows that only SiO_2-Pt micromotors sputtered with a thick Pt coating in air could reverse, while other samples (e.g. thin Pt films sputtered in air or Ar, or thick Pt sputtered in Ar) did not reverse. Importantly, X-ray photoelectron spectroscopy (XPS, Figure 2c), a common method to detect elemental compositions on the surface of solid samples, clearly shows the presence of PtO in samples sputtered in air (as well as smaller amounts of PtO_2 and Pt_3O_4, see Figure S2 for finer characterizations), while those sputtered in Ar contained primarily Pt. On the other hand, the catalytic capability (Figure 2d), or the surface morphology (Figure 2a inset), of Pt motors sputtered in either atmosphere was comparable with each other, but not correlated with their swimming

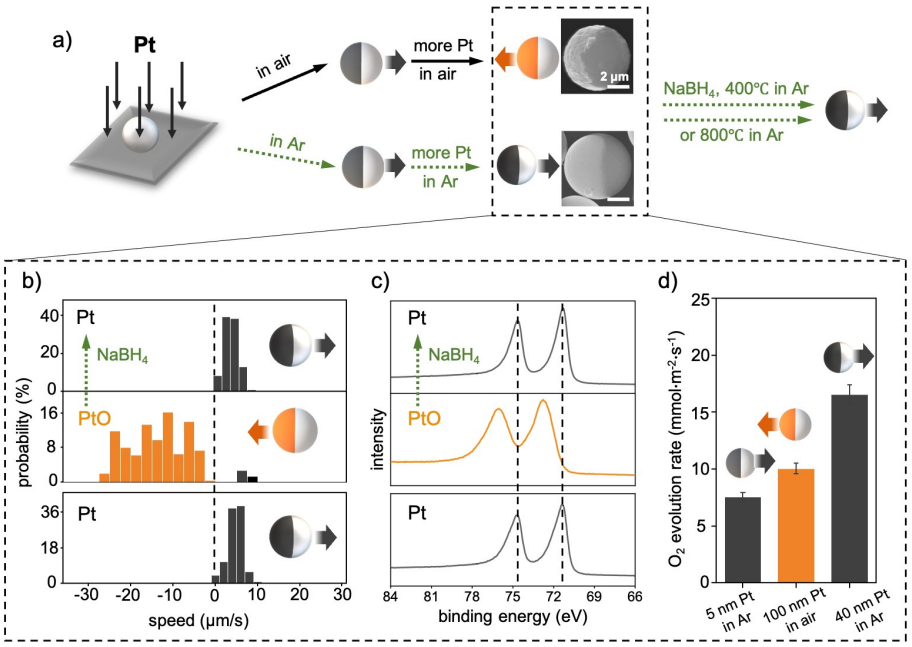

Figure 2. Finding PtO on reversed SiO_2-Pt micromotors. a) Fabrication of motors coated with Pt (indicated by grey or black colors) or PtO (orange). Both move forward after thermal treatment in argon (Ar) or chemical reduction by $NaBH_4$ (see main text for details). b) Instantaneous speed distributions of ≈20 SiO_2-Pt (or PtO) micromotors, fabricated by sputter-coating 40 nm (bottom) or 100 nm (center) of Pt in air. The center sample was then reduced by $NaBH_4$ in Ar at 400 °C to yield the top sample. All motor experiments were performed in 5 wt% H_2O_2. c) X-ray photoelectron spectroscopy of Pt 4f electrons for the samples in (b). Finer designations of each peak are given in Figure S2. d) O_2 evolution rates in 5% (center and right) or 10% (left) H_2O_2 from three samples prepared by labelled conditions, measured by a drainage method (see Figure S3). Error bars represent standard errors from ≈20 independent measurements. Throughout this article, material processing in air and Ar atmosphere is represented with solid black and dashed green arrows, respectively.

directions. These are compelling evidence for the dominant role of PtO in reversing a motor.

If PtO is indeed necessary for reversing a Pt motor, then removing it should make the motor move forward again. This was confirmed by either chemically reducing PtO into Pt by sodium borohydride ($NaBH_4$, a strongly reducing agent), or thermally decomposing PtO into Pt at ≈700 °C in Ar (platinum oxides are known to decompose at elevated temperatures[7b,d,8]). The changes in its swimming direction and in the material composition after chemical reduction with $NaBH_4$ indeed agree with our speculation, as shown in Figure 2b,c and Video S4 (results for thermal decomposition are similar and not shown). See Supporting Information for experimental details.

Taking advantage of the new knowledge of PtO-induced reversal, the swimming directions of a Pt-coated micromotor can be intentionally and systematically controlled by oxidizing Pt into PtO in a furnace (Figure 3). Key experimental parameters include the heating temperatures, the atmospheres in the furnace, or the cooling conditions. In particular, any processing condition that favors the formation of PtO yields a reversed micromotor (path 2 and 5 in Figure 3a, Video S5); otherwise, a forward motor is made (path 1, 3, and 4 in Figure 3a, Video S6). Specifically, we speculate that PtO is only formed when Pt is heated in O_2 and at a temperature above 600 °C (Figure S2). As a result, heating a Pt-coated sample in the absence of O_2 (path 1), or at temperatures below 600 °C (Figure 3b), yielded forward-moving motors that contained primarily Pt. Alternatively, slowly cooling a hot Pt film in an air-filled furnace grants it a second chance to react with O_2 to form PtO (path 2, 5), but not if cooled rapidly ("quenching", path 4), or without O_2 (path 3). Finally, as we mentioned above, chemically reducing or thermally decomposing a PtO film converts it to forward Pt motor (see Figure 3c for the results of heating reversed motors at various temperatures).

The final piece in the puzzle is how PtO reverses a micromotor. To solve this puzzle, we first identified the propulsion mechanism of a PtO motor to be self-electrophoresis, based on the following experimental evidence. First, the sharp decrease in the speeds of both a forward and a reversed motor at high ionic strength shown in Figure 4a suggests that they are both powered by self-generated electric fields.[9] The propulsion mechanism can be further narrowed down to self-electrophoresis, based on the observations that the speeds of both forward and reversed motors are insensitive to their population densities (Figure 4b) and that they form dynamic clusters (Video S7), hallmarks of self-electrophoresis revealed by our recent study.[10]

There are a number of theoretical possibilities of how PtO reverses a motor via self-electrophoresis. For example, preliminary yet inconclusive measurements show that Pt and PtO have different mixed potentials for catalyzing the decomposition of H_2O_2 (Figure S5). As a result, it is possible

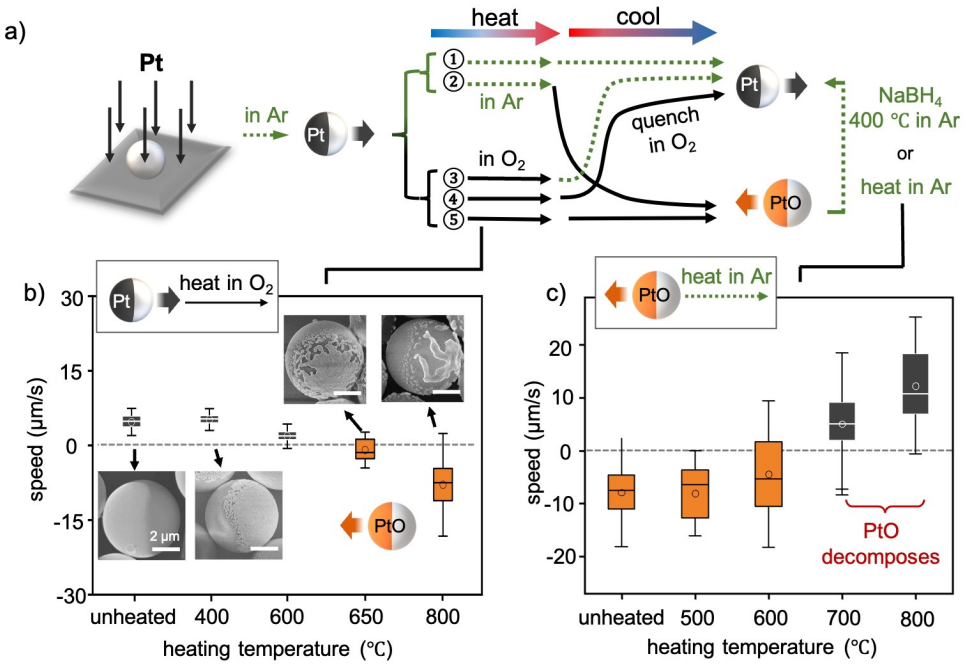

Figure 3. Controlling the swimming directions of SiO_2-Pt micromotors by tuning material compositions. a) Five different ways (path 1–5) to prepare SiO_2-Pt or SiO_2-PtO micromotors. They were all sputter-coated with 40 nm Pt in Ar to begin with. b) Speeds of SiO_2-Pt micromotors prepared by heating in air at different temperatures (corresponding to path 5). c) Speeds of SiO_2-PtO micromotors (prepared by heating SiO_2-Pt motors at 800 °C in air) thermally decomposed in Ar at different temperatures. In all box plots, the circles and lines within a box represent the mean and median speed of ≈20 micromotors, respectively. The top and bottom edge of a box represent the 75% and 25% values of all speed data that are arranged in ascending order, respectively. Error bars represent the standard deviation from ≈20 independent measurements. All experiments were performed in 5 wt% H_2O_2. Throughout this article, material processing in Pt and Ar atmosphere is represented with solid black and dashed green arrows, respectively.

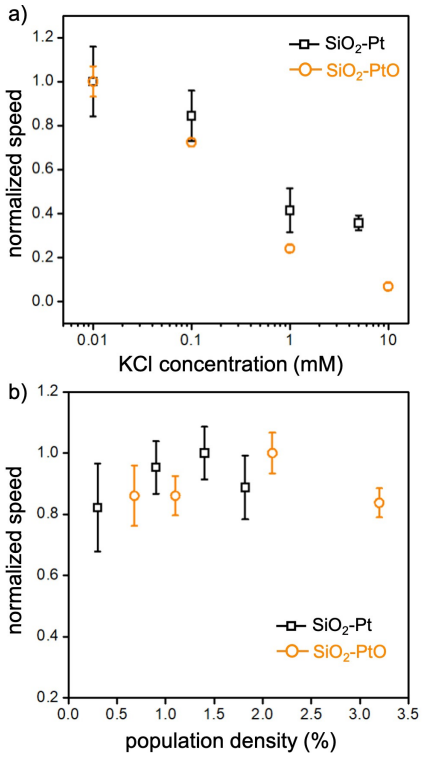

Figure 4. SiO_2-PtO micromotors are powered by self-electrophoresis. a) Normalized speeds of forward-moving SiO_2-Pt and reversed SiO_2-PtO micromotors in KCl solutions of different concentrations. The actual peak speed is 5.5 and 6.6 $\mu m\,s^{-1}$ for SiO_2-Pt and -PtO motors, respectively. b) Normalized speeds of both types of motors at different population densities. The actual peak speed is 7.7 and 12.9 $\mu m\,s^{-1}$ for SiO_2-Pt and -PtO motors, respectively. SiO_2-Pt and SiO_2-PtO motors were made by sputtering 20 nm and 100 nm of Pt in air, respectively. Error bars represent standard errors from 6–23 measurements. All experiments were performed in 5 wt% H_2O_2.

for a thin film containing both species to generate electrochemical currents in the same spirit as a catalytic, bimetallic micromotor or micropump.[11] Depending on the exact configuration of the film, the current could flow in a way that propels a PtO motor in reverse. A second possibility of the reversal is connected to how the *forward* propulsion occurs. A recent hypothesis of how Pt powers a motor is that the oxidation and reduction of H_2O_2 occurs preferentially at different locations on a Pt shell, leading to an electrochemical current and thus self-electrophoresis.[4,5b,9b,12] In the same spirit, a PtO film with thickness variations,[5b,9b,12a] or an access to different amounts of rate-limiting species[12a] across the shell, could generate self-electrophoresis. A third possibility is that, since PtO is much less catalytically active than Pt (see Figure S4 for measurement), its presence on a Pt film essentially inactivates part of the film, potentially leading to qualitatively different propulsion directions. None of the above hypothesis has been confirmed.

Two additional possibilities are unlikely. First, although some species of platinum oxides (such as PtO_2) are known to be photocatalytic,[13] this is unlikely to contribute to powering a motor as we have made the same observations under very weak light (result not shown). Second, it is reasonable to speculate that PtO carries a positive surface charge and therefore reverses a Janus micromotor that was negatively charged to begin with (this is how Cu-SiO_2 motors move toward the metal cap, as the authors of Ref. [14] argued). However, we have measured the zeta potential of PtO nanoparticles, obtained by annealing Pt nanoparticles in air, and found it to be -39.4 ± 5.8 mV and similar to the value of Pt nanoparticles of -29.7 ± 4.2 mV (see Supporting Information for experimental details).

Finally, we note that similar observations of the reversal of Pt-micromotors have also been made by Poon et al, but without explanation.[9a] In addition, the possible oxidization of a Pt film by O_2 plasma has been suggested in the literature to explain the reversal of a bimetallic, catalytic pump.[15] The authors speculated that "the cleaning treatment (by O_2 plasma on the Pt–Au pump) alters the electrochemical properties of the metals by adding some oxygen functionalities to the surface". Our observations and measurements support this hypothesis, and even offered strategies to control the surface compositions and thus the directions of current flows.

To summarize, a SiO_2-Pt micromotor moves in reverse in H_2O_2 if PtO is introduced, either by sputtering a thick Pt film in a chamber prefilled with air, or by annealing a Pt-coated micromotor under proper conditions (see Figure 3 for details). Such a reversed motor moves via self-electrophoresis. A few theoretical possibilities are proposed, but the exact mechanism of reversal remains to be clarified.

The discovery of PtO-induced electrokinetics paves new ways for understanding, designing and fabricating chemically powered nano- and micromotors, gears and pumps of controlled directionality. For example, an interesting application is the fabrication of programmable micropumps by selectively oxidizing regions of a Pt film into PtO (with laser, for example). The pump would then generate flows that can transport cargos in pre-determined patterns and paths. Moreover, our findings highlight the alarming role of Pt oxides in catalysis by materials assumed to be pure Pt, especially with samples prepared by sputtering in low-level vacuum.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Micromotors · Platinum Oxide · Self-Diffusiophoresis · Self-Electrophoresis · Sputtering

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Communications

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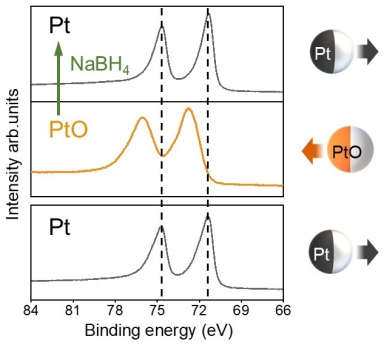
Reversing a Platinum Micromotor by Introducing Platinum Oxide



Platinum oxides (primarily PtO) are produced during the sputter-coating of Pt films by O_2 plasma, and PtO reverses the swimming direction of a micromotor by self-electrophoresis.