Reversing a Platinum Micromotor by Introducing Platinum Oxide

Xianglong Lyu*, Jingyuan Chen†, Jiayu Liu, Yixin Peng, Shifang Duan, Xing Ma, and Wei Wang*

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 H₂O₂ into O₂, an archetypical model of chemical micromotor. We discover that platinum oxides (primarily PtO) are produced on Pt films sputter-coated in O₂ 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 H₂O₂ on the Pt surface.[2, 3] 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.[2, 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 reimage 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 SiO₂–Pt Janus microspheres were fabricated by coating SiO₂ 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 SiO₂ microspheres) were placed in the chamber of a tabletop sputter-coater that was filled with air to begin with, and pumped down to a vacuum level of 3.8 × 10⁻⁵ Torr. High energy plasma (primarily from N₂ and O₂) 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-SiO₂ Janus microspheres fabricated in this way self-propelled in aqueous solutions of H₂O₂ (typically 5 wt %, or 1.47 mol L⁻¹). Importantly, Figure 1 shows that Pt-coated SiO₂ 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, 3] 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 SiO₂ 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 (TiO₂) microspheres (see Video S1, experiments with TiO₂), the motor moving in reverse.

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)
and detailed descriptions below). The coating morphology, a common factor that affects motor speed, 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, PtO$_2$, or PtO$_4$) 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. 

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 show 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 PtO$_4$, 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.
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 \(\approx 700^\circ C\) 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\(_2\)O\(_2\) (Figure S5). As a result, it is possible...
for a thin film containing both species to generate electrochemical currents in the same spirit as a catalytic, bimetallic micromotor or micropump.\textsuperscript{[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$_2$O$_2$ occurs preferentially at different locations on a Pt shell, leading to an electrochemical current and thus self-electrophoresis.\textsuperscript{[4, 5b, 9b, 12]} In the same spirit, a PtO film with thickness variations,\textsuperscript{[9b, 12a]} or an access to different amounts of rate-limiting species\textsuperscript{[12c]} 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,\textsuperscript{[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.\textsuperscript{[14]} argued). However, we have measured the zeta potential of PtO nanoparticles, obtained by annealing Pt nanoparticles in air, and found it to be $39.4 \pm 5.8$ mV and similar to the value of Pt nanoparticles of $29.7 \pm 4.2$ 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.\textsuperscript{[8b]} In addition, the possible oxidation of a Pt film by O$_2$ plasma has been suggested in the literature to explain the reversal of a bimetallic, catalytic pump.\textsuperscript{[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$_2$O$_2$ 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.

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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.

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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\textsubscript{2} plasma, and PtO reverses the swimming direction of a micromotor by self-electrophoresis.