

Beyond Platinum: Bubble-Propelled Micromotors Based on Ag and MnO₂ Catalysts

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ABSTRACT: Autonomous bubble-propelled catalytic micro- and nanomachines show great promise in the fields of biomedicine, environmental science, and natural resources. It is envisioned that thousands and millions of such micromachines will swarm and communicate with each other, performing desired actions. To date, mainly platinum catalyst surfaces have been used for the decomposition of a fuel, hydrogen peroxide, to oxygen bubbles. Here we propose Pt-free, low-cost inorganic catalysts for powering micromotors based on silver and manganese dioxide surfaces. Such Ag- and MnO₂-based bubble-powered micromotors show fast motion even at very low concentrations of fuel, down to 0.1% of H₂O₂. These catalysts should enable unparalleled widespread use of such motors in real applications, as it will be possible to make them in large quantities at low cost.

Self-propelled autonomous micromotors and micromachines are at the forefront of research in micro- and nanotechnology.^{1–6} These autonomous devices have the potential to play vital roles in drug delivery,^{7–9} microsurgery,^{10,11} environmental remediation,^{12–14} and natural resources discovery.^{15,16}

There are three types of mechanisms describing the motion of catalytic micro-/nanomotors: (i) self-diffusiophoresis,¹⁷ (ii) self-electrophoresis,¹⁸ and (iii) bubble ejection.¹⁹ Devices relying on (i) self-diffusiophoresis propulsion decompose asymmetrically the fuel presented in their environment.^{20,21} They move in the direction of the self-generated concentration gradient in their vicinity. The motion of micromotors propelled by self-diffusiophoresis does not involve bubble generation, and the micromotors generally exhibit slow motion.²² (ii) Self-electrophoretic micromotors rely on the simultaneous oxidation and reduction of fuel at the opposite ends of the device. Such redox reactions lead to the flow of the electrons across the device, which is accompanied by a flow of hydronium ions at the surface of the microdevice and consequent propulsion.²³ (iii) A bubble-propulsion mechanism for powering micromotors has become highly popular in recent years.^{24–26} Decomposition of hydrogen peroxide over a catalytic surface, such as platinum, creates bubbles and propels the micromotor forward.¹⁹ The advantages of this mechanism are its high power output, its robust performance, and the very high speed the devices can achieve, dramatically overcoming the velocity of the devices powered by mechanisms (i) and (ii).

To date, despite tens of articles published in the field of bubble-propelled micro-/nanomotors, the vast majority of bubble-powered micromotors have used Pt as catalyst,^{25,27,28} with only a few exceptions. A Communication by Sanchez et al. showed the utility of an enzyme to decompose H₂O₂.²⁹ While the use of enzymes shows ingenuity, the disadvantage is their limited lifetime. Complex Ti/Fe/Au/Ag nanomembrane micro-jet motors were also produced previously.³⁰ Given the significant cost of Pt as catalyst and/or nanomachining as fabrication method, we wish to demonstrate that simple and widely available inorganic materials can be used for bubble-propelled motors. We will demonstrate that simple silver and manganese dioxide particles are highly efficient to decompose H₂O₂ fuel, leading to fast bubble-propelled motion of micromotors. The use of Ag and MnO₂ as potential candidate materials for micromotor fabrication is very attractive because of the excellent catalytic properties, low costs, low concentration of fuel needed, high efficiency, and long lifetime.

First we discuss the silver-surface-catalyzed bubble-propelled micromotors. Figure 1A shows time-lapse images of the movement of a Ag micromotor in 9% H₂O₂ (see also Video 1). Figure S-1 (Supporting Information) shows a tracking image for the path of a Ag catalytic micromotor in 0.5% H₂O₂ over a 2 s time interval. Oxygen bubbles are generated by the catalytic decomposition of H₂O₂ by Ag, and they are released from one side of the motor. Asymmetry is the key to the design of micro-/nanomotors. For spherical Janus motors, the motion is usually attributed to asymmetric generation of bubbles achieved by a partial inert coating, without which no directional movement is achieved due to expected lack of asymmetric bubble thrust.^{1,20} However, the Ag micromotors used here feature inhomogeneity and asymmetry. Bubble generation is closely related to the geometry of the motors, and bubble nucleation on solid surface needs gases to reach heterogeneous nucleation energy, which depends on the gas saturation concentration and the curvature of the surface. Less energy is required for bubble formation on a flat surface than on a convex surface, and even less energy is required on a concave surface.^{31,32} We have conducted experiments in which Ag micromotors were half-covered with Au using sputtering, but little difference in mobility was observed compared to the unspattered ones, showing that the bubble generation is more related to the instinctive morphology of the particles. Three typical kinds of trajectories were found for the motion of the Ag

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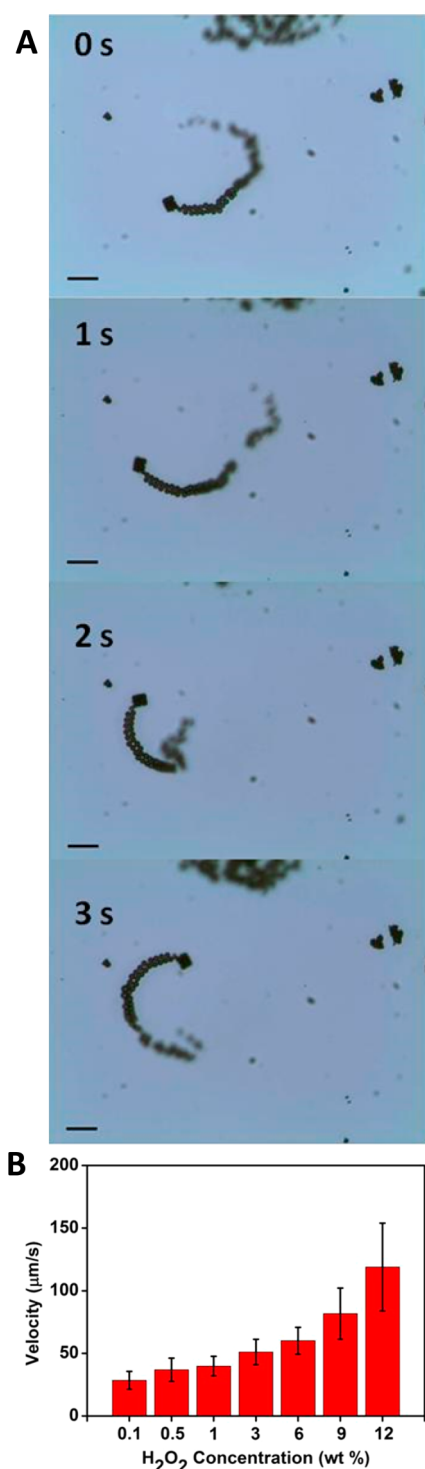


Figure 1. Motion of silver catalytic micromotors. (A) Time-lapse images of a Ag micromotor in 9% H₂O₂ and 0.5% SDS solution (scale bar = 50 μm). (B) Dependence of the average velocity of Ag catalytic micromotors on H₂O₂ concentration at 23 °C. Video 1 shows the moving Ag micromotor motor in 9% H₂O₂.

catalytic micromotors: circular, curved, and self-rotating motions. The different trajectories derive from the differences in size, shape, and geometry of the catalytic micromotor, similar to the case of tubular micromotors.²⁴

The velocity of the Ag catalytic motor is dependent on the H₂O₂ fuel concentration. Figure 1B illustrates the influence of

H₂O₂ concentration on the average speed of the moving Ag micromotors (see also Figure S-2 for velocity expressed in body lengths per second; the size of the particular micromotor shown in Figure 1A is 20 μm). As expected, Ag micromotors show clearly increased velocities with increasing fuel concentration. The percentage of Ag motors exhibiting motion among all the Ag particles and the mobility of the motors depend on the fuel concentration and instinctive morphology of the Ag particles.

There is an obvious increase in the mobility of Ag micromotors with increasing concentration of H₂O₂. Due to the propulsion by vigorous bubbling, the mobility of the Ag catalytic motor is quite high compared to that of the Pt catalytic Janus motors that move by diffusiophoresis, reported previously.^{33–35} Silver micromotors can move at an average speed of ~25 μm/s, even in 0.1% H₂O₂, and the average speed of Ag catalytic motors exhibiting motion can reach over 100 μm/s in the presence of 12% H₂O₂. The high bubble frequency reflects the high catalytic efficiency of Ag for the decomposition of H₂O₂. Given the low costs and good performance, Ag is a promising candidate catalyst for preparation of micro-/nanomotors. However, it should be noted that, with decreasing amount of fuel, the percentage of motors exhibiting motion decreases, as shown in Figure S-3.

Manganese dioxide is another well-known catalyst that can accelerate the decomposition of H₂O₂, and it is much cheaper and more accessible than the noble metal often used in the preparation of micro-/nanomotors. MnO₂ is widely used in industry for cheap carbon/MnO₂ batteries.³⁶ Next we investigate the motion of micromotors based on MnO₂ microparticles in H₂O₂ solution. Similar to Ag particles, MnO₂ micromotors exhibit motion propelled by oxygen bubbles. However, the proportion of moving MnO₂ micromotors is much less than that for Ag particles, and higher concentrations of H₂O₂ are needed for efficient propulsion. Figure 2A shows time-lapse frames from a video of MnO₂ micromotors in 15% H₂O₂. The size of the particular micromotor in Figure 2A is 5 μm. Figure S-4 tracks a MnO₂ motor in the presence of 21% H₂O₂ for 2 s (see also Videos 2 and 3). As illustrated in Figure 2B, the average speed of moving MnO₂ micromotors increases from ~50 μm/s at 12% H₂O₂ to ~120 μm/s at 21% H₂O₂ (see Figure S-5 for velocity expressed in body lengths/s). The proportion of MnO₂ micromotors exhibiting motion also decreases with decreasing H₂O₂ concentration. Nevertheless, the excellent mobility of MnO₂ micromotors demonstrates the potential of MnO₂ to be involved in the preparation of micro-/nanomotors if modified to proper morphology.

Various control experiments, illustrated in Figure 3, were used to confirm the propulsion by oxygen bubbles generated by catalytic decomposition of H₂O₂. No bubble generation was observed for MoO₂ and MoO₃ in the presence of 21% H₂O₂ and 0.5% sodium dodecyl sulfate (SDS) due to the absence of catalytic property of molybdenum oxides. Similarly, no bubble propulsion was observed for MnO₂ and Ag particles in the absence of H₂O₂. In contrast, the mobility of MnO₂ and Ag particles in H₂O₂ reflects the efficient bubble propulsion associated with their good catalytic properties. The mean square displacement (MSD) of Ag and MnO₂ motors showed a parabolic dependence on time (Figures S-6 and S-7, respectively), which indicates that the motion is driven by bubble ejection instead of Brownian motion.^{33,37} The efficiency of the Ag motor in 9% H₂O₂ was found to be 5.81×10^{-8} , while the efficiency of the MnO₂ motor in 12% H₂O₂ was 1.16

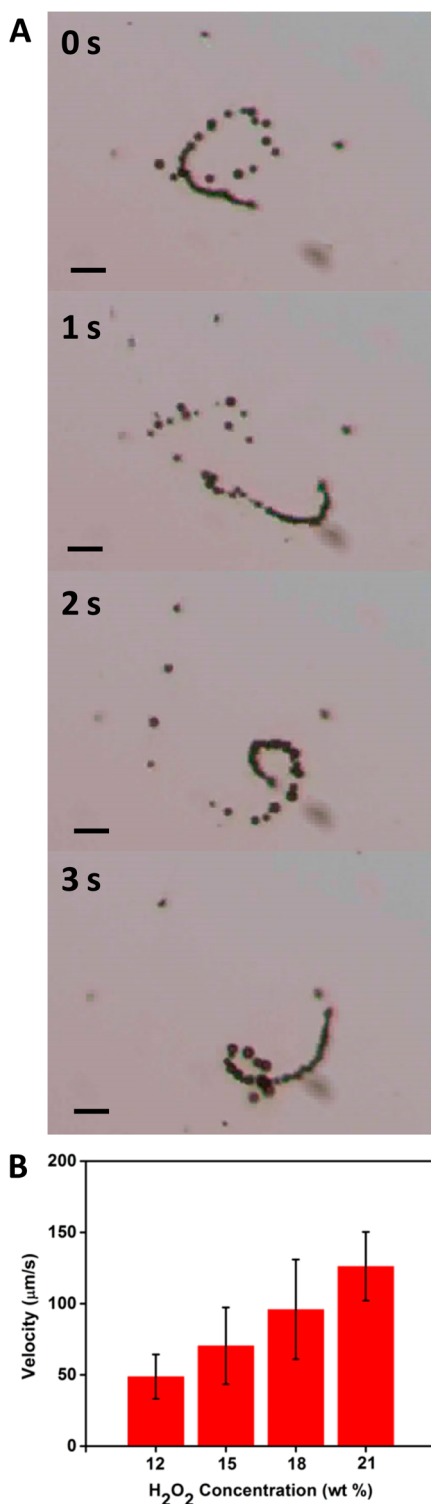


Figure 2. Motion of manganese dioxide catalytic micromotors. (A) Time-lapse images of a MnO₂ catalytic micromotor in 15% H₂O₂ and 0.5% SDS solution (scale bar = 20 μm). (B) Dependence of the average velocity of MnO₂ catalytic micromotors on H₂O₂ concentration at 23 °C. Video 2 shows the moving 5 μm MnO₂ micromotor in 15% H₂O₂. Similarly, Video 3 tracks a MnO₂ micromotor in the presence of 21% H₂O₂ (see Figure S-4).

$\times 10^{-8}$, following the calculation approach previously reported (see Supporting Information for details).³⁸ This compares favorably with previously established efficiencies of other Janus particles that move by diffusiophoresis (efficiency = 5×10^{-10})

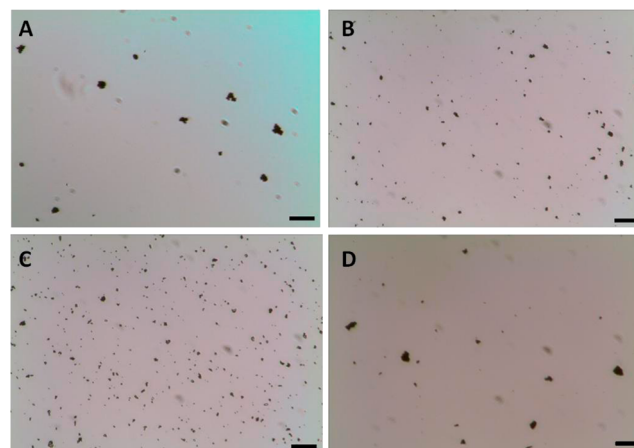


Figure 3. Control experiments: (A) Ag and (B) MnO₂ particles in 0.5% SDS solution and (C) MoO₃ and (D) MoO₂ particles in 21% H₂O₂ and 0.5% SDS solution (scale bars = 50 μm). Conditions: temperature, 23 °C; particle concentration, 1 mg/mL.

and bubble-propelled tubular microjets (efficiency = 2.4×10^{-10}).³⁸

An advantage of Ag and MnO₂ materials over Pt is that they are much less prone to poisoning. It has been previously demonstrated that Pt catalytic bubble-propelled microjet engines are susceptible to thiol poisoning, even at micromolar concentration of thiols.³⁹ We compared the motion of Ag motors in 3% H₂O₂ without and with addition of 10 mM cysteine. No observable difference in the velocity of the Ag motors was found. Similarly, MnO₂ is not prone to thiol poisoning. It should be mentioned that the micromotors reported here are truly catalytic, and their motion stops only when the fuel is exhausted. When fuel is replenished, the bubble-propelled motion of the micromotors resumes, and the micromotors move over the span of the whole experiment with the same agility.

In summary, we have presented new materials for catalytic propulsion of bubble-powered micromotors, silver and manganese dioxide. These Pt-free, Ag- and MnO₂-based micromotors, driven by the bubbles from catalytic decomposition of hydrogen peroxide, exhibited fast motion. The speed of the micromotors can be modulated by changing the concentration of H₂O₂, and efficient propulsion can be achieved even at very low concentration (0.1%) of H₂O₂ fuel. The low costs, high efficiency, and good stability of Ag and MnO₂ (compared to Mg- and Al-based micromotors^{12,40,41}) make them attractive alternatives to the currently popular platinum for prolonged propulsion of micro-/nanomotors in diverse ranges of practical applications. Additional efforts should be devoted to further functionalization and modification of Ag and MnO₂ micromotors for applications in biomedical and environmental fields. It is envisioned that such accessible and affordable inorganic materials will replace the need for Pt in these artificial organisms and contribute to their fabrication in millions and millions of copies.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, tracking of Ag and MnO₂ micromotors, plots of velocities of Ag and MnO₂ micromotors in body lengths/s, MSD analysis, and SEM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

W Web-Enhanced Feature

Videos 1–3 in .avi format are available in the online versions of the paper.

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Notes

The authors declare no competing financial interest.

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