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Self-motile colloidal particles: from directed propulsion to random walk


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The motion of an artificial micro-scale swimmer that uses a chemical reaction catalyzed on its own surface to achieve autonomous propulsion is fully characterized experimentally. It is shown that at short times, it has a substantial component of directed motion, with a velocity that depends on the concentration of fuel molecules. At longer times, the motion reverts to a random walk with a substantially enhanced diffusion coefficient. Our results suggest strategies for designing artificial chemotactic systems.

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The directed propulsion of small scale objects in water is problematic because of the combination of low Reynolds number and Brownian motion on these length scales. In order to achieve an artificial micro- or nanoscale swimmer that is able to propel itself in a purposeful way, one needs both a swimming strategy that works in the environment of low Reynolds number, and a strategy for steering and directing the motion that can overcome the ubiquity of Brownian motion. Common bacteria, such as E. Coli, achieve propulsion by non-time-reversible motion of long flagella, and employ a “run and tumble” strategy to be able to swim towards or away from environmental stimuli.

One possibility for designing propulsion is to devise non-reciprocal deformation strategies that are simple enough to be realizable. Recently, an interesting example of such robotic micro-swimmers has been made using magnetic colloids attached by DNA-linkers, and controlled by an external oscillatory magnetic field. Another possibility is to take advantage of phoretic effects, where gradients of fields such as concentration, temperature, electric field, etc, couple to the surface properties of particles to create slip velocity patterns that could lead to net propulsion.

A particularly appealing strategy for propelling small devices is to take advantage of chemical reactions. In a pioneering experiment, Paxton et al. observed autonomous motion of platinum/gold nanorods, and similar experiments have been performed by Fournier-Bodroz et al who used gold/nickel nanorods and Mano and Heller who used enzymes. One simple strategy for converting chemical energy to mechanical work in such devices has been proposed by one of us and collaborators. In this scheme, a spherical particle is considered with an asymmetric distribution of catalyst on its surface. If the chemical reaction so catalyzed produces more products than it has reactants, then the asymmetric distribution of reaction products propels the particle by a process of self-diffusiophoresis. The experimentally realized swimmers mentioned above are very similar in setup to the one proposed in Ref. However, it seems that the driving mechanism for the propulsion in these experiment is different as it depends strongly on the presence of a (bi-metal or bio-) electro-catalytic structure. It is suggested that the pair of electrochemical reactions at the two poles create a lateral electric field near the particle surface (due to electron transfer) that could move the solvent via electro-osmosis.

Here we have realized the scheme proposed in Ref. experimentally by taking polystyrene spheres with narrow size distributions with a diameter of 1.62µm, and coating one side of the spheres with platinum keeping the second half as the non-conducting polystyrene. The platinum catalyzes the reduction of a “fuel” of hydrogen peroxide to oxygen and water, which produces more molecules of reaction product than consumed fuel. We fully characterize the motion of the artificial micro-scale swimmer using particle tracking, and probe the properties of the motion as a function of hydrogen peroxide concentration. We show that at short times, the particles move predominantly in a directed way, with a velocity that depends on the concentration of the fuel molecules.

FIG. 1: (color online). Trajectories over 25 sec for ×5 particles of the control (blank) and Platinum-coated particles in water, and varying solutions of hydrogen peroxide.
Particle tracking was achieved using a Nikon ME600 ope

In a given solution of hydrogen peroxide, hydrogen peroxide solutions were prepared by subsequent dilutions of 30% Hydrogen Peroxide solution (Perdrogen - Riedel-de Haën). For a given solution of hydrogen peroxide, 100 µl of the microsphere containing stock solution was mixed with 2 ml of the appropriate solution. A cuvette (1 mm optical path length - Hellma, cleaned with Piranha Etch) was rinsed three times with the solution before filling again and sealed using a PTFE stopper. Particle tracking was achieved using a Nikon ME600 optical microscope mounted on an isolation table and fitted with a PixeLink PL-A742 machine vision camera, a ×20 objective (Nikon), and inverted illumination. A movie with a field of view of approximately 120 µm × 120 µm of 3000 frames at a rate of 38 frames per second was recorded for each particle. For each concentration of hydrogen peroxide, approximately 20 separate particles were tracked and analyzed using a Labview (National Instruments) script providing particle trajectory and timing (time, x/µm, and y/µm).

Figure 2 shows particle traces for a Pt-coated bead as well as a control polystyrene bead. While the control particle undergoes a characteristic Brownian motion, the Pt-coated particle shows a systematic enhancement of a directional component in its motion, as the concentration of hydrogen peroxide increases. The motion can be analyzed more quantitatively using particle tracking. From the records of the particle trajectory, we calculate the average value of the squared displacement as a function of time. For a purely Brownian particle of radius R, the squared displacement is linear in time with the slope controlled by the particle diffusion coefficient \( D = k_B T / (6 \pi \eta R) \), where \( k_B T \) is the thermal energy, \( \eta \) is the viscosity of water. The particle will also undergo rotational diffusion with a characteristic (inverse) time scale \( \tau_R^{-1} = k_B T / (8 \pi \eta R^3) \) (also called the rotational diffusion coefficient), with the two stochastic modes decoupled from each other. For a particle propelled with velocity \( V \), the direction of motion is itself subject to rotational diffusion that leads to a coupling between rotation and translation. In this case, one can show that the (2D projection) mean squared displacement is given as:

\[
\Delta L^2 = 4D \Delta t + \frac{V^2 \tau_R^2}{2} \left[ \frac{2 \Delta t}{\tau_R} + e^{-2\Delta t/\tau_R} - 1 \right].
\]

This expression has limiting forms of \( \Delta L^2 = 4D \Delta t + V^2 \Delta t^2 \) for \( \Delta t \ll \tau_R \) and \( \Delta L^2 = (4D + V^2 \tau_R) \Delta t \) for \( \Delta t \gg \tau_R \). At short times, the contribution to the displacement due to the propulsion is linear in time, while
the Brownian displacement is proportional to the square root of time, with these two contributions adding in quadrature. At times long compared to the rotational diffusion time, rotational diffusion leads to a randomization of the direction of propulsion, and the particle undergoes a random walk whose step length is the product of the propelled velocity V and the rotational diffusion time, leading to a substantial enhancement of the effective surface reaction-rate $k_a$. In the vicinity of the particle surface. This gradient creates a slip velocity $V_s = \mu \partial C / \partial \tau$ with the diffusiophoretic mobility given as $\mu = k_B T \lambda^2 / \eta$ where $\lambda$ represents the range of the interaction zone between the solute and the particle [13]. One can then solve the Stokes hydrodynamics around the sphere subject to this local slip velocity pattern on its surface, and find the propulsion velocity. For a particle which is half-coated with a material that can produce excess particles with diffusion coefficient $D_o$ at a rate per unit area $k$, the propulsion velocity is [12]:

$$V = \frac{\mu k}{4 D_o} = \frac{3 \pi}{2} k a \lambda^2,$$

where the hydrodynamic radius of the solute $a$ is introduced by way of the Stokes-Einstein relation.

Since the velocity is directly proportional to the effective surface reaction-rate $k$ [Eq. (2)], the linear initial increase and the subsequent tendency towards saturation observed in Fig. 4a suggests that the Pt-catalyzed break-up of $H_2O_2$ probably occurs in two stages of formation of a Pt($H_2O_2$) complex at a rate per unit area $k_1 [H_2O_2]_{vol}$, in which $[H_2O_2]_{vol}$ has the units of volume percentage, followed by a decomposition into water and oxygen at a rate per unit area $k_2$. This leads to a Michaelis-Menten behavior similar to enzymes [19], as opposed to the kinetics of decomposition in homogenous solution, which is second order and would produce an upward curvature in Fig. 4b. Solving the diffusion-reaction equations with the proposed reaction kinetics, we find

$$k = k_2 \frac{[H_2O_2]_{vol}}{[H_2O_2]_{vol} + k_2 / k_1}.$$
the fitted particle (bare) diffusion coefficient $D$ shown in Fig. 4 has little dependence on the presence or absence of catalyst and the concentration of hydrogen peroxide, and is close to the predicted value from Einstein-Stokes relation (a slight residual dependence on hydrogen peroxide concentration may be a result of a coupling between these two fitting parameters in the analysis of the displacement curves). Figure 4c shows fitted rotational diffusion time. As mentioned above, the long time effective diffusion is substantially enhanced due to the propulsion. For the largest hydrogen peroxide concentration, we find a value of $D_{\text{eff}} = 9.0 \, \mu m^2 s^{-1}$, which is an enhancement over the purely Brownian value $D$ by a factor of nearly 30.

The rotational diffusion time shows a systematic decrease as a function of hydrogen peroxide concentration for the coated particles, with no dependence for the controls. This could be due to the surface reaction imparting a small net angular velocity $\omega$, and we surmise that it might be caused by inadvertent asymmetric Pt coverage during the fabrication. Similar to the translational diffusion coefficient, we would expect a combination $\tau_{R}^{-1} + \omega R^2$ to serve as the renormalized rotational diffusion coefficient. This hypothesis is strengthened by the observation of cycloid trajectories for some samples at high $H_2O_2$ concentrations. At first sight this would seem an unwelcome side effect—an increase in rotational velocity has the effect of decreasing the renormalized diffusion coefficient for the long-time behavior of the propelled particles. But it also raises the intriguing possibility of designing a system in which the linear propulsive and rotational behavior are independently controlled; this would constitute a system in which the step size of a random walk could be controlled by an external parameter, opening up the possibility of designing a system capable of chemotaxis, in a way analogous to the bacteria E. Coli.

By contrast to the existing experimental examples of autonomous swimmers [8, 9, 11, 12], the propulsion mechanism for our platinum/polystyrene particles does not involve electrochemical reactions, and thus they realize a new class of micro- and nano-scale chemical locomotion. We note that for this class of (self-diffusiophoretic) swimmers, spherical geometry is better than a rod geometry, because the velocity for rods is reduced by a factor of the aspect ratio $\frac{L}{R}$ in a way analogous to the bacteria E. Coli.

In conclusion, we show that spatially asymmetric catalysis at the surface of synthetic micron-scale particles can lead to effective autonomous propulsion of spherical colloids. At short times, we observe directed propulsion of the particles with velocities in the $\mu m/s$ range; at longer times the direction of motion of the particles is randomized, and the motion of the particles becomes diffusive in character with an effective diffusion coefficient which is substantially enhanced over the Brownian value. We hope that our quantitative characterization of the motion of the swimmer sheds some light on the fundamental issues involved in designing chemical locomotive systems, and could inspire new directions for their implementation.

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