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Dynamic Interactions between Fast Microscale Rotors

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Nano- and microscale machines were originally envisioned by Feynman, who suggested the possibility of nanomanipulators for device assembly.[1] A significant obstacle to the realization of such nanomachines has been the problem of powering them. Recently, several groups have demonstrated that catalytic reactions can be used to drive the movement of particles on the micrometer and submicrometer length scales.[2−8] Biology provides "living proof" that catalytic machines are scalable to very small dimensions, and indeed, some of the behavior of catalytic motors (e.g., chemotaxis[9] and predator−prey behavior[10]) is biomimetic. The observation of emergent collective behavior suggests that it may be possible to design systems in which synthetic nano- or micromotors could work cooperatively, provided that their interactions are well-understood.

Catalytic motors influence their local environment by generating chemical concentration gradients and fluid flows. These effects have been exploited with stationary catalyst patterns on surfaces to make catalytic pumps.[11] Autonomous motors that rotate without translating represent another interesting class of objects with which to study these effects, because of the possible emergence of cooperative behavior. While several groups have now made rotary catalytic motors,[3,8,12] their movement has been too slow to observe cooperative movement. Here we describe catalytic microrotors that rotate an order of magnitude faster than those described previously, and we analyze the interactions between pairs of rotors that occur over distances of micrometers.

Catalytic microrotors (Figure 1) were fabricated by electrochemical replication of anodic alumina membranes.[2,13] After the Au−Ru bimetallic rods were freed from the membrane, additional Cr, SiO_2, Cr, Au, and Pt layers were sequentially vapor-deposited on one side of each rod [see the Supporting Information (SI)]. The design is similar to that of asymmetric bimetallic rods reported by Mirkin and co-workers,[12] except that the second Au/Pt catalytic bilayer adds a perpendicular force that moves the rod toward the center of the orbit induced by the asymmetric flow. This results in more pure rotary (as opposed to orbital) motion. Higher fuel concentration (15 vs 3%[12]) drives the rotors fast enough for rotor−rotor interactions to become apparent.

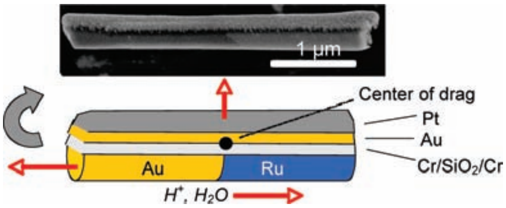

Figure 1. (top) Field-emisson scanning electron microscope image of an electrochemically grown Au−Ru microrod with sequentially deposited Cr/SiO_2/Cr, Au, and Pt layers. (bottom) Schematic drawing of the structure, showing the forces induced by catalytic H_2O_2 decomposition and the resulting rotary motion of the rod.

These microrods rotated rapidly in aqueous 15% hydrogen peroxide solution. The rotation rate averaged 180 rpm, and the fastest rods rotated at ∼400 rpm (Figure 2). This is consistent with the speed expected for Au−Ru bimetallic rods, which have linear velocities of ∼30 μm/s.[13] The velocity at the tip of a 3.5 μm long 180 rpm rotor is 33 μm/s. The direction of rotation (clockwise or counterclockwise) was random. Tracking the position of the center of a rod showed slow Brownian movement (Figure 2c). The microrotor design thus induces fast rotary movement with relatively little translation.

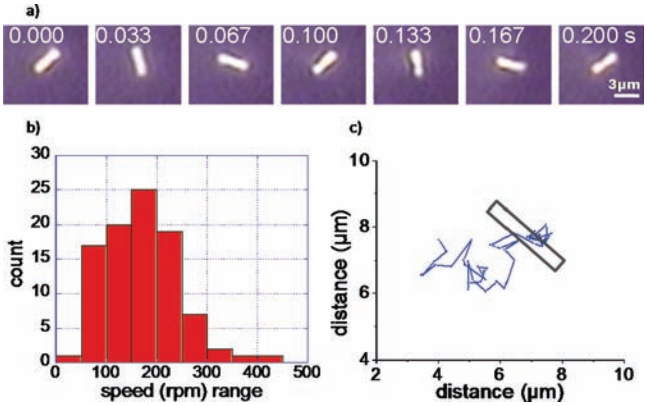

Figure 2. (a) Snapshots of a rotor in 15% H_2O_2. The width of each frame is 8.6 μm, and the rod is 3.2 μm long; each successive frame corresponds to a time delay of 0.033 s. The rod moves in a counterclockwise manner. (b) Histogram of the speeds of rotors in 15% H_2O_2. (c) Rod-center trajectory over 10 s. The motion in (a) and (c) is shown in video I in the SI.

Whitesides and co-workers[14,15] have studied the interactions of macroscopic rotating objects in fluids and found that the flows they generate result in attractive and repulsive forces. It is interesting to consider whether analogous forces might be operative in the low Reynolds number regime of micromotors and to ask about the distances over which they would be larger than the Brownian forces. Figure 3 shows tracking data for pairs of rotors approaching each other along with snapshots taken at their closest center-to-center distance. In the case of unpowered rods (i.e., catalytic rotors in water with no fuel added), the particles can approach closely and orient side-by-side. For powered, rapidly spinning rods, sideways contact is not possible, and the closest possible approach is at a center-to-center distance equal to the rod length, at which point the tips collide. Although such collisions are frequently observed for rods spinning in opposite directions, those rotating in the same direction approach each other to a minimum tip-to-tip distance of ∼1 μm. A histogram of many such co-rotating rod pairs (Figure S3 in the SI) shows an average minimum tip-to-tip distance of 0.9 μm for 3.5 μm long rotors with an average speed of 180 rpm.

Both kinds of apparent interactions between pairs of rotating rods (Figure 3) are interesting. Repulsive interactions between co-rotating rods might be used to form lattices,[14,15] and attractive interactions

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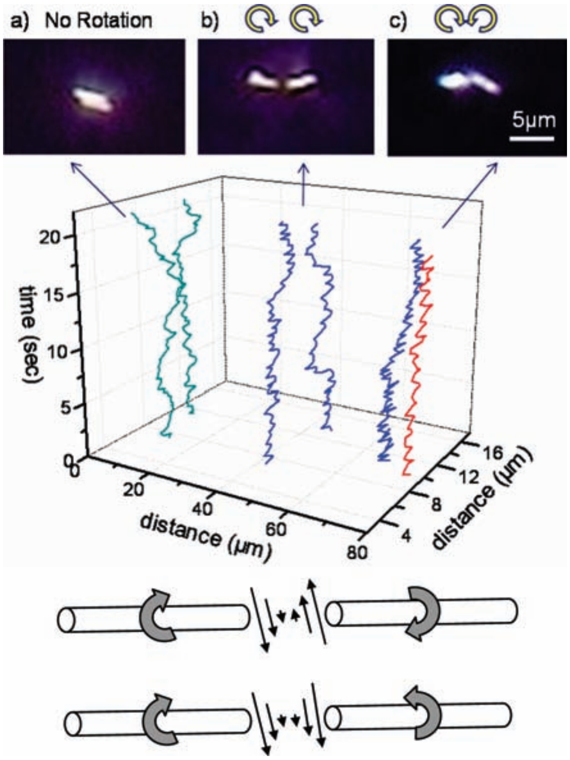

Figure 3. (top) Two-dimensional trajectories of rod pairs and corresponding optical images at their closest center-to-center distances: (a) unpowered rods in deionized water (see video II in the SI); (b) rods rotating in the same direction in 15% H_2O_2 (see video III in the SI); (c) oppositely rotating rods in 15% H_2O_2. The *z* axis represents time, and the *x* and *y* coordinates represent the position of the center of each rod. (bottom) Schematic drawing of the fluid velocity distribution between the tips of the microrotors.

could lead to gearlike synchronization of counter-rotating rods. However, at low Reynolds number ($\sim 10^{-5}$ in this case), the effects of fluid inertia are minimal, and time-reversal symmetry arguments imply that there should be no net force along the line that joins the centers of two rotors.

The shear forces between pairs of co-rotating and counter-rotating rods are different and should cause tip−tip interactions through the fluid. In the case of co-rotating rods, the fluid velocity must be zero at a point midway between the rod tips (Figure 3). At the surface, the fluid velocity must be equal to the tip velocity. The shear stress on the fluid between the rod tips is proportional to the gradient of the velocity (eq 1):

$$\text{shear stress} = \frac{F}{A} = \mu \frac{\mathrm{d}v}{\mathrm{d}x} \qquad (1)$$

where μ is the viscosity, F is the force, and A is the area of interaction of the two surfaces. For co-rotating rods, the velocity gradient and thus the force increase as the rods approach more closely. In contrast, for counter-rotating rods, the shear stress decreases as the rotors approach more closely. It is possible to estimate the magnitude of the shear force by considering an interaction area of $\sim$0.4 μm × $\sim$0.4 μm, these dimensions corresponding to the approximate diameter of the rods. At a tip-to-tip distance of 1 μm, we obtain a force of $\sim$0.01 pN. For cylindrical bimetallic nanomotors, this is roughly the propulsion force at which axial propulsion becomes dominant over random Brownian motion.[2] This force estimate is consistent with the observation that Brownian motion can bring a co-rotating rod pair no closer than a $\sim$1 μm tip-to-tip distance. At that point, fluid shear creates a tangential force on the rotors that alters their trajectory by vertical movement with respect to the line joining their centers.

Another possible contributor to the forces between rotors is the chemical gradient generated by the catalytic reaction. Such gradients contribute substantially to the movement of tracer particles in bimetallic pump systems.[11] Catalytic rotors spinning on the surface of a microscope slide are actually chiral objects when chemical gradients are taken into account. We are currently studying magnetically driven rotors, which have recently been studied as low Reynolds number "swimmers,"[16] in order to separate the effects of chemically generated electric fields and osmotic pressure[17] from the fluid shear forces described above.

In conclusion, we have designed a new kind of fast catalytic nanorotor that is $\sim$10 times faster than previously reported. In these trimetallic rotors, force is generated along two axes that do not intersect at the center of drag. Tracking data for pairs of rotors show that they do indeed interact on the length scale of micrometers, which is consistent with our simple estimate of the forces on the fluid between the tips. The precise mechanism of the interaction is not understood, and it is not yet clear whether chemical gradients also contribute to the forces between catalytic rotors. Finally, we note by analogy to previous experiments on macroscopic rotors[14,15] that it should be interesting to design chiral microrotors, which would have a preferred handedness of rotation. This would allow one to study the cooperative behavior of larger collections of microrotors with finer control over their interactions.

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Supporting Information Available: Details about the preparation and characterization of the microrotors and observation of rotor movement; videos (AVI) showing (I) a spinning microrotor (corresponding to Figure 2a,c), (II) the interaction of two rotors in deionized water (corresponding to Figure 3a), and (III) the interaction of two rotors rotating in the same direction in 15% H_2O_2 (corresponding to Figure 3b). This material is available free of charge via the Internet at http://pubs.acs.org.

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