Molecular Devices

Catalytic Nanomotors: Remote-Controlled Autonomous Movement of Striped Metallic Nanorods**

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Powering nanoscale machinery by nanosized motors that move by in situ conversion of stored chemical energy is one of the most interesting challenges facing nanotechnology. Such a procedure would circumvent the need for an external macroscopic power source. In nature, nanoscale motors typically operate by energy derived from the enzymatic catalysis of spontaneous reactions.[1,2] At the nanoscale, interfacial forces dominate over inertia and, in principle, can be harnessed to move nanoobjects. Indeed, we have recently described the autonomous, non-Brownian movement of platinum/gold (Pt/Au) nanorods with spatially defined zones that catalyze the spontaneous decomposition of hydrogen peroxide (H_2O_2) to oxygen (O_2) in aqueous solutions at the platinum end of the rods.[3] These rods are moved by an interfacial tension gradient resulting from the dissolution of the less polar oxygen in the medium around the platinum end. The sustained catalytic reaction results in the interfacial tension gradient being continuously re-established as the rod moves.

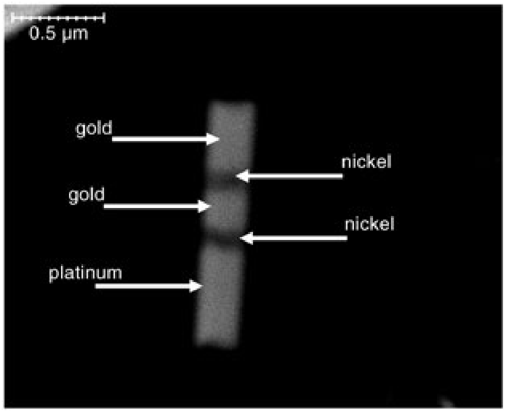

Figure 1. An SEM image at 35 000× magnification of 1.5 µm×400 nm striped metallic rod. Respective segment sizes (nm): Au, 350; Ni, 100; Au, 200; Ni, 100; Pt, 550.

While the above system displayed autonomous movement, the direction of movement was subject to random fluctuations. Directed motion is needed for catalytic nanomotors to be useful in a number of potential applications. Herein, we present a method for controlling the directionality of nanorods by using an external magnetic field. Striped nanorods with platinum, nickel, gold, nickel, and gold segments were employed (Figure 1). The platinum segment serves as a catalyst for the decomposition of hydrogen peroxide, whereas the ferromagnetic nickel segments can be magnetized and used to control the direction of rod movement. Whitesides and co-workers have shown that electroplating nickel segments shorter than the diameter of the rod, results in a rod that could be magnetized transversely rather than longitudinally.[4,5] Furthermore, the nickel segments in our striped nanorods are single domains because their lengths are less than the critical domain size (150 nm).[6]

After fabrication and magnetization of the nickel segments, the rods were imaged by scanning electron microscopy (SEM; Figure 1). Dark-field microscopy was used to observe rod movement in dilute solutions of hydrogen peroxide.[3] We remotely controlled the direction in which the rods moved with a NeFeB magnet that had a field strength of approximately 550 G with respect to the sample, if it is assumed there is a constant field strength for the very small area of observation under the microscope objective (ca. 100 µm). When a magnetic field is applied, a majority of the rods orient themselves perpendicular to the magnetic field lines and move the platinum end forward (Figure 2). This ability to influence rod orientation is expected at 550 G because the rods have a calculated magnetic moment of 1.3×10^{-15} A m^2, which is comparable to that observed for magnetotactic bacteria.[7] At this field strength, the calculated magnetic torque (ca. 7.0×10^{-17} N m) exceeds the rotational thermal energy (2×10^{-21} N m) in the observation plane by over four orders of magnitude.[8]

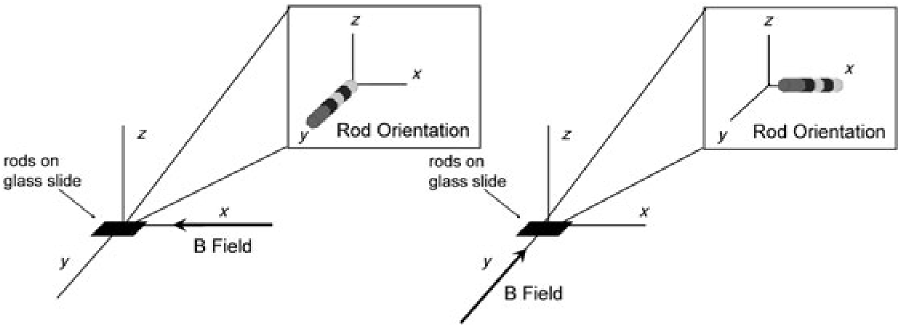

Figure 2. Rod orientation in an applied field, where the Cartesian coordinate axis to the left of the rod represents a sample of rods on the microscope stage and the arrow represents the location of the magnet in the *xy*-plane of the microscope stage.

We measured three different parameters to demonstrate the non-Brownian nature of the movement and, more

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importantly, to show that the magnetic field served to only align the rods and not to statistically alter the speed (see Table 1). The first parameter measured is directionality. Directionality is defined as the cosine of the angle between the direction that a rod is pointed and the actual direction that the rod moves. A value of 1 (cos 0°) indicates a rod is moving in the same direction that it was originally pointed, whereas a rod moving orthogonal or in the opposite direction would have a value of 0 and -1, respectively. The directionality was determined for two time intervals: 0.1 and 2 seconds.

Table 1: Data for Pt/Ni/Au/Ni/Au striped nanorods in pure water and hydrogen peroxide with and without an applied magnetic field.[a]

H_2O_2 [wt%]	Magnetic field	Axial velocity [µm s^{-1}]	Directionality (0.1 s)	(2 s)	Rot. [$^{\circ 2}$ s^{-1}]
5%	off	3.1(8)	0.5(1)	0.6(2)	2000
5%	on	2.4(7)	0.4(1)	0.85(6)	70
0%	on	0.2(2)	0.05(4)	0.3(2)	60
0%	not magnetized	0.1(2)	0.01(6)	0.1(2)	700

[a] The size of the data sets from top to bottom are 22, 19, 21, 20 rods, respectively.

The second parameter, axial velocity, is defined as the product of the directionality (over a 0.1 s interval) and the center-to-center displacement of the rod. The axial velocity essentially drops to zero for rods in pure water, thus demonstrating that only Brownian motion is exhibited. Since Brownian motion also results in a center-to-center displacement, axial velocity rather than speed (displacement/time) is a better measure of movement.

The final parameter measured was the rotational diffusion coefficient $D(\mathrm{rot})$, which is defined as the square of the displacement angle divided by the time interval (1 s). Rods in the applied magnetic field have a lower rotational diffusion coefficient than in the absence of the field (Table 1).

Table 1 shows that axial velocity values are essentially unaltered by the presence of a magnetic field, thereby demonstrating that the field serves to only align the rods and not add an additional driving force for motion. In addition, axial velocity drops almost to zero without hydrogen peroxide present because only the catalytic decomposition of hydrogen peroxide serves to move these rods in solution.

The values of directionality over a short time interval (0.1 s) can be used to distinguish between Brownian and non-Brownian motion. Directionality values at the longer time interval (2 s) helps to distinguish between non-Brownian motion in the absence and presence of an applied magnetic field (Table 1). The directionality is 0.01 for Brownian motion in pure water over a 0.1 s interval, but increases to 0.5 in 5 wt% hydrogen peroxide. The increase in directionality results because the Brownian component of translational velocity becomes less important as the propulsive component increases. At this short time interval, however, it is difficult to quantitatively discern the effect of an applied magnetic field on the catalytically driven movement of the rods. We were able to see the longer term effects of rod orientation in the magnetic field by increasing the time interval from 0.1 to 2 s. Table 1 shows that the directionality of rods in 5 wt% hydrogen peroxide increases from 0.6 to 0.85 when the magnetic field is applied.

The final parameter, the rotational diffusion coefficient, clearly shows that the transverse rotation for rods in 5 wt% hydrogen peroxide ($2000^{\circ 2}$ s^{-1}) is substantially quenched upon the application of a magnetic field ($70^{\circ 2}$ s^{-1}; Table 1). Brownian nonmagnetized rods have a high rotational diffusion coefficient ($700^{\circ 2}$ s^{-1}) versus Brownian magnetized rods ($60^{\circ 2}$ s^{-1}) in the field. Thus, the magnetic field serves to orient magnetized rods with and without hydrogen peroxide. In the absence of an applied magnetic field, the rotational diffusion coefficient is higher for catalytically driven rods than for rods undergoing Brownian motion in pure water ($700^{\circ 2}$ s^{-1}). The latter observation is not surprising because, unlike catalytically driven rods, there is not enough energy to cause large transverse rotations with the Brownian rods leading to a smaller rotational diffusion coefficient. We measured rotational diffusion coefficients for time intervals less than 1 s (not tabulated) and observed an approximate decrease of two orders of magnitude in the rotational diffusion coefficient for the rods in a magnetic field over the range of 0.1 to 1 second. On the other hand, there was no significant change in the rotational diffusion coefficient from 0.1 to 1 second for the rods without an applied field because these rods are merely moving by the catalytic decomposition of hydrogen peroxide with no source of control over their transverse rotation. Rods in pure water also showed a negligible change in rotational diffusion coefficient over the same time range.

The change in directionality for non-Brownian rods in the magnetic field in a two-second interval is shown in Figure 3 (see the Supporting Information). The magnetic field is applied along the "y"-axis, thereby orienting the rods to move horizontally ("x"-axis) over the three-second observation period. Figure 3 also supports the assertion that the magnetic field only orients the rods and not drive them. For example, the direction traveled by one of the rods is opposite to that of the other two. Thus, upon applying a magnetic field the rods will orient, but they will continue traveling in whatever direction the platinum segment was facing before the field was applied. Also, the rods are not appreciably drawn to the magnet, as indicated by relatively horizontal paths. Figure 4 shows the trajectory path of a nanorod spelling PSU and demonstrates the micrometer-scale control over the rods in the presence of a magnetic field while they are moving autonomously in 5% hydrogen peroxide.

In conclusion, we have presented a method to control the direction in which catalytically driven metallic nanorods move. The magnetic field does not influence the rod speed, rather it serves only to direct the nanorods by orienting their net magnetic moments (comparable to magnetotactic bacteria) parallel to the field. The application of the magnetic field results in higher directionality and substantially lower transverse rotation. In principle, tethering these magnetically controlled, catalytically driven "nano/microengines" to other objects using known procedures would result in new classes of nano/micromachines.

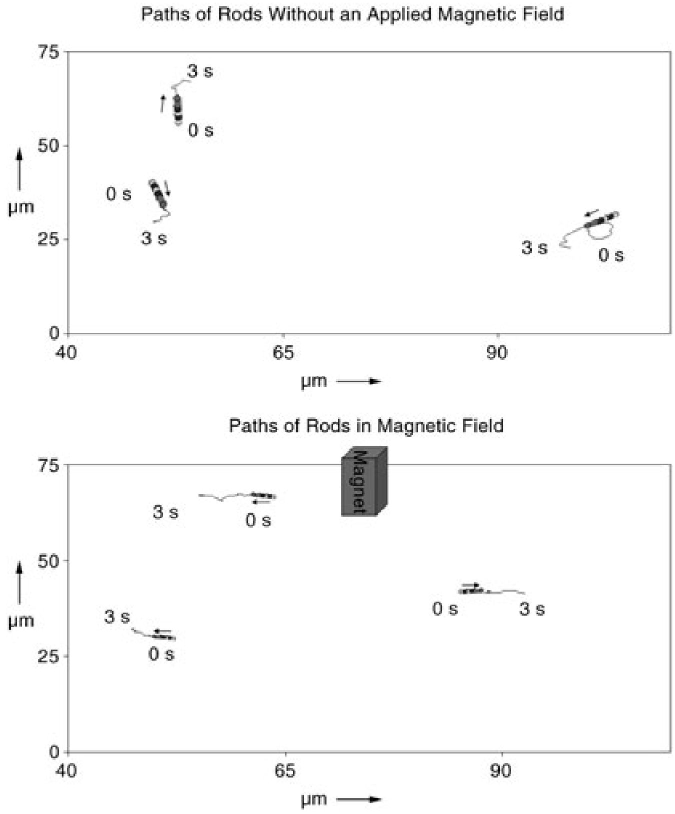

Figure 3. Trajectory paths of rods traveling in a non-oriented fashion before applying a magnetic field (top), where the arrow denotes the direction of the rod along the trajectory, and the same rods traveling in oriented direction in the presence of a field (bottom); the field is a stack of magnets located in the "y" direction along the microscope stage.

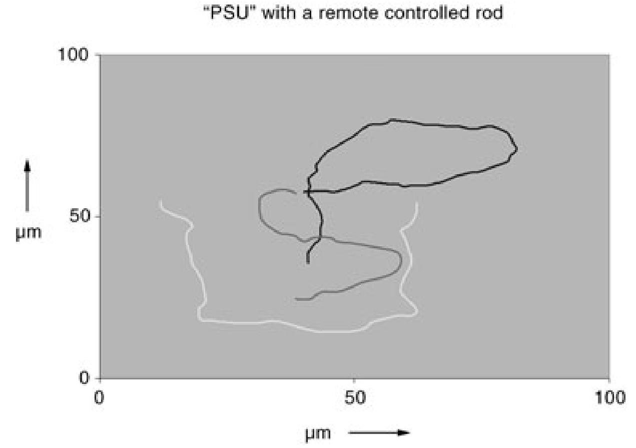

Figure 4. The trajectory path of a Pt/Ni/Au/Ni/Au nanorod spelling the letters "PSU" in 5 wt% H_2O_2.

Experimental Section

The platinum/nickel/gold/nickel/gold (Pt/Ni/Au/Ni/Au) rods were fabricated by using an electrochemical technique with a 0.2-µm pore diameter Whatman Anodisc membrane serving as a sacrificial template.[9] Silver (200 nm) was evaporated onto one side of the Whatman Anodisc membrane. First, the pores were wetted by applying a current density of 0.5 mA cm^{-2} using a Parr 173 potentiostat from Princeton Applied Research. Then the metals were electroplated in succession using commercially available electroplating solutions from Technic. After electroplating, the rods were freed by dissolving the sacrificial silver anode in 5 M nitric acid and the membrane in 5 M sodium hydroxide. Then they were ultracentrifuged and washed four times with water of an approximately neutral pH value to produce the free rods (Figure 1). All SEM images were obtained on a JEOL JSM 5400 instrument at 20 kV. The nickel segments of the rods were magnetized with a NdFeB magnet, as demonstrated previously,[4] and dilute solutions of hydrogen peroxide added to dilute suspensions of the rods. Approximately twenty rods were tracked for each data set in Table 1. Tracking of the rods was done according to the method employed earlier.[3] The magnetic field strength at a certain distance from the stack of NdFeB magnets was determined with a gaussmeter. The stack of magnets was then held in the respective "*x*" or "*y*" directions from the sample on the microscope stage, and this designation is used in assigning rod orientation.

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