Fabrication and Characterization of Catalytic Nanomotors

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Introduction:

Platinum-gold bimetallic nanorods swim autonomously in aqueous hydrogen peroxide solutions. These synthetic nanomotors consist of one platinum (Pt) segment and one gold (Au) segment, each 1 μm long and approximately 200 nm in diameter. The platinum and gold react with the peroxide to form water and oxygen, propelling the nanomotor in the process. A theory called self-electrophoresis has been proposed to describe this movement. In this theory, platinum catalytically oxidizes the hydrogen peroxide to create protons, electrons, and oxygen, and gold catalytically combines the protons and electrons with peroxide to form water. Nanorod locomotion is therefore caused by the asymmetric electrochemical reactions on the platinum and gold surfaces. The charged particles transferred in these reactions generate an electric body force that drives the nanomotor through the surrounding viscous liquid.

In our study, we fabricated nanomotors and attempted to control their direction of motion. This was done by incorporating a nickel (Ni) segment and using magnetic fields to orient them; additionally, alternating current (AC) electric fields were employed to align the nanomotors. We also analyzed the variation of nanomotor velocity with time.

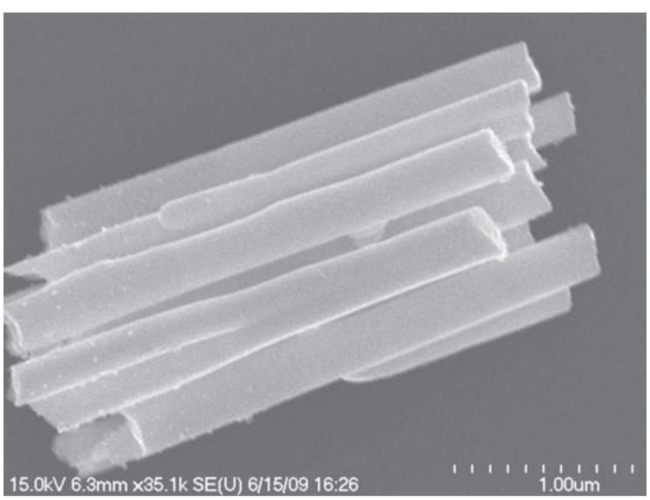

Figure 1: Nanomotors imaged by (FESEM).

Experimental Procedure:

Our nanomotors were fabricated according to the method described elsewhere in detail [1]. Nanomotors were imaged for characterization using a field emission scanning electron microscope (FESEM); see Figure 1. The objective of our first experiments was to directionally control Pt-Ni-Au nanomotors with magnetic fields. The nanomotors were always added to the hydrogen peroxide solution just before the experiment began, and peroxide concentration was always 5 wt%. After the solution was in place in the capillary or microchannel, magnets were placed near the surface to control nanomotor orientation. For the AC electric field experiments, we filled a capillary with nanomotor solution and placed gold electrodes in wells on both ends; we then ran an AC electric field of 200 V/cm at 1 kHz through the capillary to align the nanomotors.

We also studied how nanomotor velocity changed over time for several different volume fractions. Videos were taken of the nanomotors' motion until they appeared to be moving with only Brownian motion, using a Nikon TE-2000 microscope with 60× magnification. Images and videos were captured with a CoolSnap CCD scientific camera.

Results and Discussion:

Upon FESEM imaging of the nickel nanomotors, we discovered that the nickel segments were breaking apart from the platinum segments and were also being etched away, possibly due to the sodium hydroxide (NaOH) rinse step. To remedy this, we shortened the duration of the NaOH rinse and added a short gold segment on either end of the nickel segment. This reduced nickel etching and the nickel segments adhered more strongly to the gold segments, preventing breakage. However, we had some difficulty imaging the nanomotors and controlling the direction of their movement with magnets, without blocking the transmission light source. It was because of these obstacles that we also used an AC electric field to orient the nanomotors. Not only did this method work for Au-Ni-Au-Pt nanomotors, but when 200 V/cm at 1 kHz was applied to Pt-Au nanomotors, they oriented along the electric field as well. Thus, the use of AC electric fields enables directional control of nanomotor movement without the need for nickel segments. Figure 2

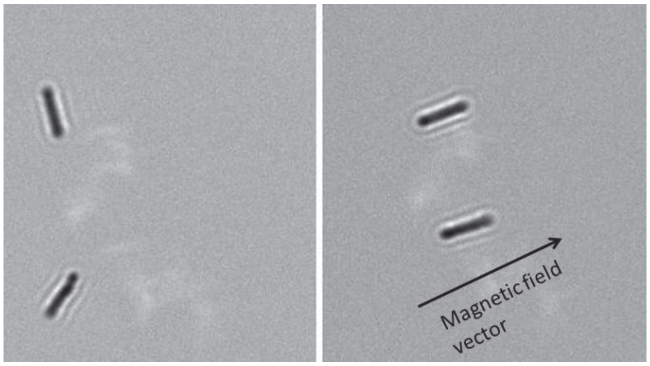

Figure 2: Left, unoriented Au-Ni-Au-Pt nanomotors. Right, nanomotors aligned by magnetic field.

shows a grouping of unoriented Au-Ni-Au-Pt nanomotors, followed by an image of the nanomotors once they had been aligned by magnetic field.

In our study of nanomotor velocity as a function of volume fraction, we found that nanomotors tended to slow down over time. We believe this was due to the local hydrogen peroxide concentration decreasing over time. As the nanomotors remain in peroxide for longer periods of time, the amount of oxygen and water being produced increases and the amount of peroxide left in the solution decreases, causing nanomotor speed to decrease as well.

To support this hypothesis, we considered the advection-diffusion equation for hydrogen peroxide, which is Equation 1 in Figure 3. We assumed that the variation of the total concentration of peroxide with time is more significant than spatial variations of concentration at any given instant in time; therefore the advection and diffusion terms are negligible. For simplicity, we assumed a first order reaction, such that $R \sim -AC$, yielding Equation 2. Integrating this equation resulted in $C = C_0 e^{-At}$. Since we knew velocity to be roughly linearly dependent on concentration [2] (for concentrations up to 5% H_2O_2), such that $V \sim BC$, it followed that velocity decreases exponentially over time according to Equation 3. These free model parameters were adjusted to reproduce the envelope matching the experimental data, which is shown with our velocity/time data for different volume fractions of nanomotors in Figure 4.

In our experimental setup, oxygen bubble formation caused by the decomposition of H_2O_2 into oxygen and water occasionally forced nanomotors to settle to the surface. This made it necessary to move the microscope field of view to a new location to view unsettled nanomotors, which were moving faster due to more peroxide being present locally. This is the cause of the spikes in velocity values over time in the graph.

Equations:

$$(1):\quad \frac{\partial C}{\partial t} + \bar{u} \bullet \nabla C = D\nabla^2 C + R$$

$$(2):\quad \frac{\partial C}{\partial t} = -AC$$

$$(3):\quad v(t) \propto BC_0 e^{-At}$$

Conclusion and Future Work:

Our results suggest that velocity decreases exponentially with time due to depletion of hydrogen peroxide fuel. While we were able to successfully fabricate nanomotors that could be directionally controlled, the experimental method still needs to be modified to ensure more reliable results. Currently, work is being done to observe nanomotors without oxygen bubble interference.

Acknowledgments:

I would like to thank Dr. Jonathan Posner, Jeff Moran, Philip Wheat, and the rest of Posner Research Group for their help and guidance. Thanks also to the National Nanotechnology Infrastructure Network Research Experience for Undergraduates Program, the National Science Foundation, and the Center for Solid State Electronics Research at Arizona State University for research support and funding.

References:

[1] Martin, R.B.; Dermody, D. J.; Reiss, B.D.; Fang, M.; Lyon, L.A.; Natan, M.J.; Mallouk, T.E.; "Orthogonal Self-Assembly on Colloidal Gold-Platinum Nanorods"; Adv. Mater., II, 1021-1025 (1999).

[2] Laocharoensuk, R.; Burdick, J.; Wang, J.; "Carbon-Nanotube-Induced Acceleration of Catalytic Nanomotors"; ACS Nano, II, 1069-1075 (2008).

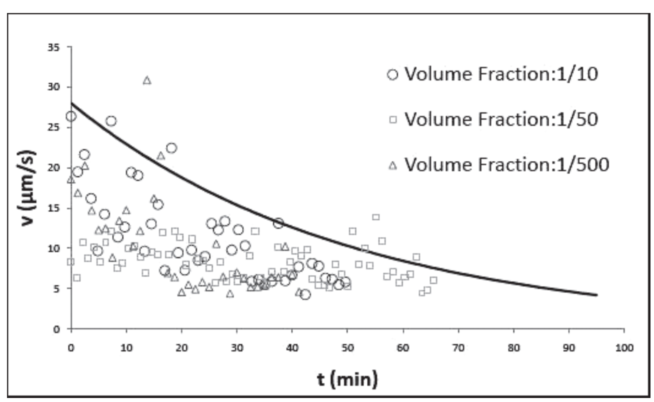

Figure 4: Velocity/time data for different volume fractions of nanomotors.