AUTONOMOUS MOTION OF CATALYTIC NANOMOTORS

A Thesis in
Chemistry
by
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ABSTRACT

In this thesis, I explore and discuss a system that uses the platinum catalyzed decomposition of hydrogen peroxide to induce interfacial effects that result in the autonomous motion of micro-/nanosized particles. Chapter 2 describes the behavior of platinum-gold (PtAu) striped nanorods in hydrogen peroxide and its dependence on a number of factors. Chapter 3 explores several different mechanisms that may contribute to the motion of the PtAu nanorods, and discusses an interfacial tension mechanism for motion in depth. In Chapter 4, I discuss the electrochemical decomposition of hydrogen peroxide involving both Pt and Au and how this bimetallic catalytic process can induce electrokinetic effects to drive the motion of PtAu nanorods in H₂O₂ solutions. In Chapter 5, I describe a switchable catalytic micropump composed of a Pt/Au interdigitated array electrode in contact with H₂O₂ solution, expanding on the concept of catalytically induced electrokinetics discussed in Chapter 4. This work has important implications when considering the development of functional nano- and micromachines powered by catalytic reactions, particularly those that utilize oxidation reduction processes to induce electrokinetic effects.
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Epigraph

“Let us consider a little the nature of true greatness in men. The people who catch hold of men’s minds and feelings and inspire them to do things bigger than themselves are the people who are remembered in history. The cold person who simply propounds some logical position, however important and interesting it may be, cannot do for the Lord’s children what is done by those who stir feelings and imagination and make men struggle towards perfection” (Henry Eyring, *The Faith of a Scientist*, Bookcraft, Salt Lake City, 1967).
Chapter 1

Introduction

Control over the movement of matter on the micron, submicron, and nanometer length scales is an important objective in science and engineering. There is a practical motivation for studying this problem, because it would be desirable for many applications to be able to make tiny machines of different kinds. However, scaling of conventional machine designs to micron and sub-micron dimensions, and providing these machines with power, are both daunting tasks. There is also a fundamental reason for attaining a better understanding of the principles that govern motion on the micron and nanometer regimes in fluids. Although many of these principles are fairly well understood in general, some specific questions about the mechanisms of cell motility, biologically-derived molecular motors, and interfacial phenomena remain unanswered. While there have been several important advances and discoveries in each of these areas, the ability to artificially stimulate and control the movement of individual small objects dispersed in fluids remains a relatively unexplored problem at the interface of many disciplines. Solutions to this problem would accelerate scientific achievement in a variety of fields including biology, medicine, and emerging nanotechnology.

Biological systems produce the smallest and some of the most complex motors known. These protein nanomotors provide the forces that perform many important biological functions that include ATP synthesis, bacterial motility, cell replication, intracellular transport, and skeletal muscle contraction.[1] Some of these biologically
derived motors have been studied extensively as researchers develop useful applications and seek to understand the mechanisms by which they operate. While the mechanisms vary, a common principle is the use of catalysis to convert the chemical free energy of the environment into useful work. Although the work of these motors is coordinated through complicated mechanistic pathways, individual protein motors are able to harvest local chemical energy independent of one another and operate autonomously.

In contrast, most non-biological approaches to moving small objects through fluids involve externally applied fields generated from macroscale sources. Several types of fields have been used in this manner including magnetic,[2],[3] electric,[4] thermal,[5],[6],[7] and concentration fields.[8],[9],[10] While magnetic field gradients act on the body of a magnetic particle, electric, thermal, and concentration fields act on the interfacial region between a particle and the fluid to induce translational movement relative to the surrounding fluid. Anderson’s review of these interfacial forces includes relationships for the observed velocity of a particle moving in response to linear external fields.[11] These types of field-induced movement require either macroscale power supplies or external chemical reservoirs in order to maintain fields sufficient to move small objects. In addition, field-induced effects act on all objects within the field, resulting in an ensemble behavior of similar suspended particles, rather than particles moving independent of one another. These two characteristics make field-induced movement of particles an efficient strategy for sorting of particles based on their behavior in an applied field but unattractive for synthetic autonomous motors.

An interesting question arises when we consider a particle that creates its own gradient by using the chemical free energy of its environment. Macroscale examples of
this type of phenomenon are well known, for example the spontaneous movement of a camphor scraping on water.\cite{12,13} Motion in this case is attributed to the asymmetric dissolution of camphor in water resulting in a concentration-gradient induced surface stress. Sano et al. studied the behavior of mercury drops in acidic potassium dichromate solutions,\cite{14} attributing the observed motion to an asymmetric interfacial tension gradient caused by the reaction of a mercury drop with the oxidizing solution. More recently, Whitesides et al. have used a platinum catalyst to drive millimeter-scale plastic disks across a hydrogen peroxide-containing water surface,\cite{15} and Mitsumata et al. demonstrated the use of chemical gradient-based motion to fabricate a motor powered by the dissolution of a solvent in an aqueous solution.\cite{16} In each case, spontaneous motion was induced by gradients, which were generated by an interaction of the object with its surroundings.

Each of the above examples are the result of chemical or physical reactions in which the moving object supplies the necessary “fuel” required to induce movement, the exception being the Whitesides experiment which used a catalyst as the “engine”. Catalytic engines are attractive for nanoscale devices because they circumvent the need for the moving object to store required fuel “on board”, instead allowing the chemical free energy of the system to be released at spatially-defined catalytic sites. As a result of these localized areas of activity, catalyst particles naturally create chemical gradients due to the consumption of reactants and appearance of the products at the particle/fluid interface. In the case of a symmetrical particle, the net force due to gradients generated by the particle essentially cancels out by symmetry. On the other hand, the active side of an asymmetric catalytic particle (e.g. one that is catalytic on only one side) creates a
gradient by reacting with a substrate “fuel” that is supplied locally. The resulting gradient can then act on the non-catalytic surface of the particle to produce motion.

In this thesis, I discuss and explore a system that uses the platinum catalyzed decomposition of hydrogen peroxide to induce interfacial effects that result in the autonomous motion of small particles. Chapter 2 describes the behavior of platinum-gold (PtAu) striped nanorods in hydrogen peroxide. Chapter 3 explores several different mechanisms that may contribute to the motion of the PtAu nanorods, and discusses an interfacial tension mechanism for motion in depth. In Chapter 4, I discuss the electrochemical decomposition of hydrogen peroxide involving both Pt and Au and how this bimetallic catalytic process can induce electrokinetic effects to drive the motion of PtAu nanorods in H₂O₂ solutions. Expanding on this concept of catalytically induced electrokinetics, in Chapter 5 I describe a switchable catalytic micropump composed of PtAu interdigitated array electrode system in contact with H₂O₂ solution. This work has important implications when considering the development of functional nano- and micromachines powered by catalytic reactions.

1.1 References


Chapter 2

Catalytic Nanomotors: Autonomous Movement of Striped Metal Nanorods

2.1 Introduction

The creation of miniature "engines" that can convert stored chemical energy to motion is one of the great remaining challenges of nanotechnology. Nanoscale motors are ubiquitous in biology, and operate by enzymatic catalysis of spontaneous reactions, such as the hydrolysis of ATP and GTP.\[1,2\] However, nano- and microscale motors driven by catalysis have not yet been demonstrated in non-enzymatic systems. In this chapter, I discuss the autonomous, non-Brownian movement of platinum/gold (PtAu) nanorods with spatially defined zones that catalyze the spontaneous decomposition of hydrogen peroxide in aqueous solutions. Platinum and gold were chosen because platinum is an active hydrogen peroxide decomposition catalyst and gold is not. Whitesides and coworkers have used the same catalytic reaction to propel cm/mm-scale objects on a water surface,\[3\] but movement in that case was in the direction opposite to that observed in our system and attributed to the recoil force of bursting oxygen (O₂) bubbles. This difference in direction of movement suggests that our system operates via a mechanism different from that observed in the Whitesides experiment.
2.2 Platinum and Gold Nanomotors

2.2.1 Synthesis and Characterization of PtAu Nanorods

Striped platinum/gold (Pt/Au) nanorods that are approx. 370 nm in diameter and contain platinum and gold segments, each 1 µm long, were synthesized electrochemically in aluminum oxide (Al₂O₃) templates (Anodisc, Watman) with filtration pores that are 0.2 µm in diameter and subsequently freed by using a previously reported procedure.[4] Specifically, 200 nm of silver was evaporated onto the filtration side of an Al₂O₃ template. The filtration side is the side of the template that the polypropylene ring is attached to, and consists of pores with dimensions given by the manufacturer. Within a few microns, these smaller pores give way to larger continuous parallel pores with diameters 300-400 nm for the bulk of the template. The silver side of the template was assembled in an electrodeposition cell and connected to a potentiostat as the working electrode. A sacrificial layer of silver (using 1025 silver plating solution from Technic) was electrodeposited into the template pores (~12 µm; approximately 1 hour at -1.0 V vs. Ag/AgCl(s)), followed by a small amount of gold (~1 µm; approximately 10 minutes at -1.0 V vs. Ag/AgCl(s) using Orotemp gold plating solution from Technic) and then platinum (~1 µm; plated galvanostatically for approximately 2 hrs. at 1.25 mA using Pt plating solution from Technic). The sacrificial metal was oxidized and dissolved by 5 M nitric acid and the template was rinsed liberally with deionized water. Then, the Al₂O₃ template was subsequently dissolved using 5 M sodium hydroxide. After releasing the AuPt rods from the Al₂O₃ template and rinsing three times with deionized water (DI,
18.2 MΩ·cm), the rods were suspended in DI. The rods were characterized by transmission electron and dark-field optical microscopy (Figure 2-1). In the latter, the gold and the platinum segments were distinguishable due to a difference in color, allowing the direction of motion to be monitored. From TEM micrographs, I measured the dimensions of several PtAu nanorods to determine the average length (2.0 µm) and diameter (370 nm) of the resulting structures.

Figure 2-1: Platinum/gold nanorods composite: Schematic of a platinum/gold nanorod (A). Arrow indicates observed direction of motion in H₂O₂. An optical micrograph (500×) of a platinum/gold rod (B). Transmission electron micrograph of a platinum/gold rod (C).
2.2.2 Autonomous Motion of PtAu Nanorods

A suspension of PtAu rods in aqueous hydrogen peroxide was prepared and a known volume (25 μL) of this mixture was placed in a sealed well on a clean glass slide and topped with a glass cover slip. Rods remained suspended in the fluid above the glass slide due to surface charge repulsions between the rods and glass. I captured real-time video clips (30 frames per second, 240×320 pixels per frame) of the PtAu rods in hydrogen peroxide at 500× magnification using an Olympus BX-60M microscope equipped with a video camera connected to a PC. In general, three video clips at different locations near the center of the deposited droplet were taken for each experiment.

The videos were analyzed using Physvis, a free video analysis program available from Kenyon College, to capture the Cartesian coordinates of both ends (the head and the tail) of a PtAu nanorod in every third frame for 150 frames, or 5 seconds of real-time video. In general, this was repeated for at least 20 particles per video to allow reasonable statistical analysis of rod populations. By extracting the positions of the head and tail of each particle Diffusion coefficients and rod velocities were determined by analyzing captured video clips of each experiment. Briefly, 5 second clips of real-time video were recorded at 30 frames per second (fps), and analyzed using Physvis, a free motion analysis program from Kenyon College (for more details, see appendix A).

In aqueous hydrogen peroxide solutions, the movement of platinum/gold rods is visibly non-Brownian as they move in the direction of their long axis (Figure 2-2) with
the platinum end forward. This direction of movement is in contrast to the Whitesides experiment where the platinum “motor” is at the trailing end of the moving objects. Movement in the axial direction is preferred because the drag force is minimized in this direction[5,6] and the catalytic reaction responsible for the movement takes place on only one end. Although the reaction proceeds with the formation of oxygen, bubbles (on the order of $d > 5 \mu m$) were observed few and far between and did not obscure our view of moving rods over short (<15 min) experiment times.

Figure 2-2: Trajectory plots of three 2 μm long platinum/gold rods identified in (A) over the next 5 seconds (B) in 2.5% aqueous hydrogen peroxide. Axis scale in (B) is microns.
2.3 Motion Analysis of PtAu Nanorods in Hydrogen Peroxide

2.3.1 Diffusion Coefficients of PtAu Nanorods

The observed rod movement can be expressed in terms of diffusion coefficients or center-to-center displacement speeds. Diffusion coefficients were determined experimentally using trajectory diffusion methods and the two-dimensional diffusion coefficient is defined as \( D = \frac{\langle d^2 \rangle}{4 \tau} \), where \( d \) is the center to center displacement in the time interval \( \tau \). At time scales larger than the velocity relaxation time for the rods (>10\(^{-5}\) s) the diffusion coefficient associated with Brownian motion is independent of the time interval. In pure water, PtAu rod movement is Brownian in nature and diffusion coefficients for rods obtained by trajectory analysis are similar to those reported previously (Table 2-1).[7] However, these experimentally determined 2-dimensional diffusion coefficients are notably higher than 0.30 \( \mu m^2/s \) predicted theoretically for similar sized rods. Diffusion coefficients obtained for platinum/gold rods in aqueous hydrogen peroxide are notably different from those obtained for the same rods in pure water or gold rods in aqueous hydrogen peroxide and depend on the duration of the sampling interval, indicating that the behavior of the rods is not due solely to thermal diffusion.
### Table 2-1: Diffusion coefficients (in $\mu$m$^2$/s) for 2 $\mu$m long gold (Au) platinum/gold (PtAu) rods.

<table>
<thead>
<tr>
<th>Sampling Interval (seconds)</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>1.0</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au in H$_2$O$^a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.41</td>
</tr>
<tr>
<td>PtAu in H$_2$O</td>
<td>0.43</td>
<td>0.41</td>
<td>0.40</td>
<td>0.40</td>
<td>0.39</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>PtAu in H$_2$O$_2$</td>
<td>4.13</td>
<td>6.61</td>
<td>9.41</td>
<td>11.6</td>
<td>13.8</td>
<td>23.7</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ From reference [7]. $^b$ In 3.3% hydrogen peroxide.

### 2.3.2 Speed and Axial Velocity of PtAu Nanorods

Analyzing motility using center-to-center displacement speeds requires the use of a directionality factor, which I defined as the cosine of the angle between the rod axis and the direction that it moves (Figure 2-4). Thus, a rod that moves in the axial direction towards the platinum end has a directionality of 1 (cos 0$^\circ$), whereas rods moving perpendicular to the axial direction or backwards have directionalities of 0 and -1, respectively. The product of the directionality and speed yields the velocity component along the rod axis, $v_z$. The Brownian component of translational velocity should become less important as the propulsive component increases, so that directionality increases from 0 to a value approaching 1, as shown in Figure 2-5. In pure water, the directionality is close to zero, as is expected of particles undergoing pure Brownian motion. As shown
in Table 2-2, the directionality and speed both increase with increasing hydrogen peroxide concentration and begin to level off between 3.3% and 5% hydrogen peroxide. For comparison, the average \( v_z \) values for 2 \( \mu \)m pure gold and platinum rods at 3.3% hydrogen peroxide concentration were 0.5 and 2.7 \( \mu \)m/s, respectively. The movement of the platinum rods can be attributed to asymmetry catalytic activity, caused by the asymmetry in the rod geometry. From scanning electron micrograph analysis it appears that each template-grown rod has a concave end and a convex end (Figure 2-3; see also TEM image of PtAu rod in Figure 2-1C). The rougher concave end has higher platinum surface area, which likely results in asymmetric catalytic activity between the two ends.

<table>
<thead>
<tr>
<th>% H(_2)O(_2) (w/w)</th>
<th>Speed ((\mu)m/s)(^b)</th>
<th>Directionality</th>
<th>(v_z) ((\mu)m/s)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>7.7 ± 0.9</td>
<td>0.78</td>
<td>6.6 ± 1.0</td>
</tr>
<tr>
<td>3.3</td>
<td>7.9 ± 0.7</td>
<td>0.75</td>
<td>6.6 ± 0.7</td>
</tr>
<tr>
<td>1.6</td>
<td>5.6 ± 0.6</td>
<td>0.65</td>
<td>4.0 ± 0.8</td>
</tr>
<tr>
<td>0.33</td>
<td>4.9 ± 0.3</td>
<td>0.60</td>
<td>3.4 ± 0.4</td>
</tr>
<tr>
<td>0.031</td>
<td>3.9 ± 0.5</td>
<td>0.19</td>
<td>0.9 ± 0.4</td>
</tr>
<tr>
<td>pure water</td>
<td>3.7 ± 0.3</td>
<td>0.07</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>1.5 (\mu)m Pt</td>
<td>5.0 ± 0.5</td>
<td>0.47</td>
<td>2.7</td>
</tr>
<tr>
<td>2 (\mu)m Au</td>
<td>3.4 ± 0.1</td>
<td>0.10</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^a\) Concentration of rods: 3.3\(\times\)10\(^7\) rods/mL.

\(^b\) Error limits represent 90% confidence intervals.
Figure 2-3: Scanning electron micrograph of two platinum nanorods, approximately 1.5 µm long and 370 nm in diameter. The concavity of the top of the rod on the left clearly demonstrates geometric asymmetry due to rod fabrication procedure. See also Figure 2-1C.
Figure 2-4: $\vec{D}$ gives the displacement of the rod over one time interval ($\Delta t = 0.1$ sec). The directionality is defined by $\cos(\theta)$, where $\theta$ is the initial angle between the rod axis ($\hat{z}$) and the displacement vector ($\vec{D}$). The axial velocity, $v_z = \frac{\vec{D} \cdot \hat{z}}{\Delta t} = \frac{\vec{D}}{\Delta t} \cos(\theta)$. 
2.3.3 Effect of Rod Length

To study the effect of rod length on observed speed in \( \text{H}_2\text{O}_2 \) solutions, I made several batches of PtAu rods with gold segments of varying lengths, and compared the rod length vs. the rod speed in \( \text{H}_2\text{O}_2 \) solutions (Table 2-3). This decrease in rod axial
velocity is consistent with an increase in the drag force for longer rods according to Eq. 2.1:[8]

\[ F_{\text{drag}} = \frac{2\pi \mu L}{\ln\left(\frac{2L}{R}\right) - 0.72} \nu. \]

### Table 2-3: The effect of longer Au segments on the behavior of PtAu rods.

<table>
<thead>
<tr>
<th>Length (µm)</th>
<th>Speed (µm/s)</th>
<th>Directionality</th>
<th>Axial velocity (µm/s)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>7.9 ± 0.7</td>
<td>0.65</td>
<td>6.59</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>2.4 ± 0.2</td>
<td>0.52</td>
<td>1.48</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>2.0 ± 0.8</td>
<td>0.59</td>
<td>1.41</td>
<td>8</td>
</tr>
</tbody>
</table>

### 2.4 Hydrogen Peroxide Decomposition Kinetics

Motion analysis of a different batch (kk3) of PtAu rods, synthesized according to the above procedure, moved with an average axial velocity was 19 µm/s, approximately three times the average axial velocity of the initial PtAu rods reported in Table 2-2. The observed rod speed was related to the rate of the decomposition reaction by monitoring the rate of oxygen evolution for a sample of PtAu rods (kk3) compared to the observed rod speed in suspensions of identical composition.
2.4.1 Set-up and Considerations for Measuring Oxygen Evolution Rate

To measure the rate of oxygen evolution per PtAu nanorod, I placed an aqueous solution containing 10 mL of aqueous hydrogen peroxide solution and 0.1 mL of a suspension containing $2.0 \times 10^8$ rods/mL in a septum-capped tube and purged the system with argon for 10 minutes. The head space was then sampled at regular intervals (every 20 minutes) and the amount of oxygen evolution was measured by gas chromatography (GC), as previously described[9] with one notable difference. The air sampling of the headspace required 0.50 mL in order to give adequate GC signal. This 0.50 mL sample comprises ~3% of the total headspace volume (16.5 mL). The calculated amount of oxygen in the sample assumes that the pressure of each sample is the same, but after 5 samples, the pressure inside the airtight septum-capped tube, and in the air sample, actually drops approximately 14%. The result is that the observed amount of oxygen in the fifth sample is 14% lower than the actual amount. In order to keep the pressure constant inside the septum-capped tube for subsequent samples, I injected 0.50 mL of argon into the septum-capped tube prior to removing 0.50 mL of head space sample.

2.4.2 Procedure for Measuring Rate of Oxygen Evolution

I calculated the absolute amount of oxygen in each sample according to the following procedure: First, I calibrated the GC peak areas due to oxygen and nitrogen to known amounts of oxygen and nitrogen by injecting a 0.50 mL sample of ambient air, and assuming the air pressure was 1.00 atm and the partial pressure of oxygen, $P_{oxygen}$, was 0.20 atm. Next, I injected 0.50 mL samples of the septum-capped tube containing the
reaction mixture (H$_2$O$_2$, deionized water, and PtAu rods) into the GC and recorded the peak area due to oxygen, $A_{\text{oxygen sample}}$. Using the peak area ratio of oxygen to nitrogen in ambient air (0.33), I was able to determine the amount of oxygen in the reaction tube that leaked in from outside the tube and subtract this from the observed oxygen signal to determine the amount of oxygen due to the decomposition of hydrogen peroxide. Then I calculated the absolute amount of oxygen, $n_{\text{oxygen}}$ in the headspace volume, $V_{\text{headspace}}$ at lab temperature, $T$, according to Eq. 2.2, where $A_{\text{oxygen reference}}$ is the oxygen peak area due to a 0.50 mL sample of ambient air for each of the samples and plotted the amount of oxygen evolved vs. time, as illustrated in Figure 2-6. Note that Eq. 2.2 is only valid if the calibration volume is equal to the sample volume, as in the case of these experiments (both are 0.5 mL).

$$n_{\text{oxygen}} = \frac{\left(\frac{P_{\text{oxygen}}}{A_{\text{oxygen reference}}}ight) A_{\text{oxygen sample}} V_{\text{headspace}}}{22.4(L \cdot atm/mol)\left(\frac{T}{273.15K}\right)}\quad \text{2.2}$$
Based on a rod concentration of $2.0 \times 10^8$ rods/mL, these 2 μm long PtAu nanorods produce oxygen at the experimentally determined rate of oxygen evolution from 3.7% hydrogen peroxide was $9.7 \times 10^{-17}$ mol O$_2$/sec per rod. This is approximately 1 order of magnitude lower than that reported in our initial publication due to a calculation error related to the concentration of rods.[10]
2.4.3 Experimentally Determined Rate Compared to Diffusion Limited Rate

The experimentally determined rate of oxygen evolution from 3.7% hydrogen peroxide was compared to the diffusion limited rate estimated from Eq. 2.3, using $D \approx 10^{-5}$ cm$^2$/s as the diffusion coefficient of H$_2$O$_2$, $C_0 = 0.9$ M for the bulk H$_2$O$_2$ concentration, and approximating the PtAu rod as a sphere with $R=1$ µm. As a result, the measured O$_2$ evolution rate was found to be approximately 1/20000 of the limit imposed by the hydrogen peroxide diffusion rate. Thus, the rate of oxygen formation is limited by the turnover rate of the catalyst which, in turn, depends on the surface area of the platinum segment.

\[ J = 4\pi D R C_0 \]  

\[ 2.3 \]

2.5 Conclusions

In conclusion, I demonstrated that it is possible to power the motion of nanoscale and microscale objects by using catalytic reactions. The observed velocities of the PtAu nanorods are comparable to those of flagellar bacteria and similar living organisms: approximately 2-10 body lengths per second. There is a very large number of metals, metal derivatives, and enzymes that catalyze reactions, which can be used to generate gradient-based forces. By appropriate design, these forces can be translated into anisotropic surface forces. Depending on the shape of the object and the placement of the catalyst, different kinds of motion from linear (e.g., Figure 2-2) to rotational (Figure 2-7)
could be achieved. The nano/microengines could, in turn, be tethered or coupled to other objects in spatially defined ways using a variety of known techniques to create a whole new class of catalytically powered nano/micromachines.

Figure 2-7: Cooperative rotational motion of T-shaped assemblies of platinum/gold rods in 2.5% aqueous hydrogen peroxide. Each frame represents 0.1 seconds, and the assembly rotates approximately once per second.
2.6 References


Chapter 3

Mechanisms for Catalytically Induced Chemical Locomotion of Striped Nanorods

3.1 Introduction

Using the platinum catalyzed decomposition of hydrogen peroxide as the principal reaction, I have demonstrated that asymmetric catalytic particles are capable of self-generating forces to propel themselves through solution.[1] In the previous chapter, I described how I electrochemically fabricated metal nanorods consisting of a platinum and a gold segment move in their axial direction at speeds up to 20+ microns/sec when placed in hydrogen peroxide solutions. Interestingly, these nanorods move with the platinum end forward, which is in contrast to the direction of motion in the macroscale experiment of Whitesides et al, in which the platinum catalyst providing the propulsive force was at the trailing end of the moving object.[2] Movement along the long axis of the rods is expected because the catalytic reaction results in an asymmetric concentration gradient along the non-catalytic end of the rod. In addition to the observed linear motion of individual rods, aggregates of two or more rods typically exhibit rotational motion. This rotational behavior was observed for platinum-gold rods (Figure 2-7), and subsequently for nickel nanorods by Ozin et al.[3]
3.2 Possible Mechanisms for PtAu Movement in Hydrogen Peroxide

While it may make intuitive sense that a particle with chemical reactions taking place asymmetrically on its surface would exhibit self-propulsion, the mechanism by which chemical energy is converted to mechanical energy is less obvious. Although it is tempting to attribute the movement to a single source, it is possible that there may be several cooperating and even opposing effects that result in the observed movement. An examination (and estimation, where possible) of these effects should allow us to determine the primary factor(s) responsible for the observed self-propulsion of bimetallic rods in hydrogen peroxide solutions. It could also in principle allow one to design catalytic nanomotors that are propelled by different mechanisms. This chapter explores a number of possibilities, including: differential pressure and bubble propulsion, diffusiophoresis, asymmetric viscosity, and interfacial tension. Self-electrophoresis, another possible mechanism, is discussed in the following chapter.

3.2.1 Differential pressure and bubble propulsion

From the balanced equation for the decomposition of hydrogen peroxide,
\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]
the stoichiometric ratio of products to reactants is 3:2. Because this reaction is fast and takes place only on one end of the rod, it is conceivable that the increase in number of molecules on the catalytic end of the rod could lead to pressure-driven flows, pushing the particle from the region of high pressure (catalyst end) to low pressure. However, this pressure-driven or “thrust” mechanism cannot be the dominant propulsive force because the pressure gradient described would push the rod towards the
gold segment, which is opposite to the movement observed. Furthermore, bubble propulsion, as described by Whitesides et al.[2] cannot be the mechanism responsible for motion because bubbles are not observed and the direction of motion is opposite to that observed.

3.2.2 Diffusiophoresis

Although a pressure gradient is unlikely to be the primary effect, a concentration gradient, and possibly a temperature gradient, would certainly be established. It is well known that chemical,[4],[5],[6] and temperature gradients,[7],[8] can induce diffusiophoretic and thermophoretic movement, respectively, of a colloidal particle. The resulting slip velocity exhibited in these systems can be described as a product of some constant, \( b \), and the undisturbed concentration or temperature gradient.[9] In the simplest case, the PtAu rods in H\(_2\)O\(_2\) most simply and closely resembles a diffusiophoretic system, and I considered the effects of a gradient of neutral solute molecules (O\(_2\)) in generating forces along the axis of the rods. For diffusiophoretic systems (Eq. 3.1):

\[
b = \frac{kT}{\eta} \frac{KL^*}{\eta}
\]

3.1

where \( KL^* \) is a parameter describing the characteristics of the solute. By modeling the dioxygen molecules as hard spheres, this product can be estimated by Eq. 3.2:

\[
KL^* = -\frac{a^2}{2}
\]

3.2
where $a$ is the radius of the dioxygen molecule ($\sim 1 \times 10^{-10}$ m). The oxygen concentration gradient, $dc/dx$, was estimated from Fick’s law for mass flux (Eq. 3.3):

$$\frac{dc}{dx} = -\frac{J}{D}$$

where $J$ is the surface-normalized oxygen evolution rate ($\sim 7.7 \times 10^{-5}$ mol O$_2$/m$^2$, based on measured $9.7(4) \times 10^{-17}$ mol O$_2$/s per rod and a platinum segment surface area of $1.3 \times 10^{-12}$ m$^2$) and $D$ is the dioxygen diffusion coefficient ($2.42 \times 10^{-5}$ cm$^2$/s) to give a concentration gradient at the surface of the rod of $-3.2 \times 10^4$ mol. O$_2$/m$^4$ ($-3.2 \times 10^{-4}$ mol. O$_2$/cm$^4$). Using the expression for slip velocity due to diffusiophoresis, the predicted velocity is 0.4 nm/s along the O$_2$ gradient. Thus, the diffusiophoretic model predicts a velocity much smaller than that observed and in the wrong direction. Ajdari recently suggested that solute concentrations can relax the no-slip boundary condition at the fluid-solid interface resulting in velocity amplification on the order of 10-100.[10] However, even with this enhancement, it is unlikely that diffusiophoresis can account for rods moving over 5000 times that expected for conventional diffusiophoresis (20 µm/s), and is unable to account for the observed direction of motion.

### 3.2.3 Viscosity gradients

Fischer et al. recently proposed that the oxygen concentration gradients emanating from the platinum surface may also result in an asymmetric viscosity in the solution surrounding the PtAu particles.[11] This can be explored by considering the one dimensional diffusion of a PtAu rod that diffuses faster in one direction (forwards) than
in the opposite direction (backwards) due to a difference in viscosity in the respective
directions. The Stokes-Einstein equation (Eq. 3.4) relates viscosity to the diffusion
coefficient:

$$D = \frac{kT}{6\pi \eta a}$$  \hspace{1cm} 3.4

with $D$, $k$, $T$, $\eta$, and $a$, are the diffusion coefficient of the particle, Boltzmann’s constant,
temperature, solution viscosity, and the radius of the particle. All other parameters being
equal, the ratio of forward to backward diffusion coefficients is essentially the ratio of
backwards viscosity to forwards viscosity (Eq. 3.5):

$$\frac{D_{\text{forward}}}{D_{\text{backward}}} = \frac{\eta_{\text{backward}}}{\eta_{\text{forward}}}$$  \hspace{1cm} 3.5

In this simplified viscosity gradient model, the gradient causing motion arises
from the decrease in viscosity on the Pt end by oxygen production at that end, so the
viscosity on the Au end (resisting backwards motion) is the bulk solution viscosity
$\sim 1 \text{ mN} \cdot \text{s/m}^2$. The diffusion coefficient in this backwards direction then is on the order of
the normal diffusion coefficient, about 0.3 $\mu\text{m}^2/\text{s}$. PtAu rods move forward at average
axial velocities up to 20 $\mu\text{m}/\text{s}$, giving it an effective $D_{\text{forward}}$ of 200 $\mu\text{m}^2/\text{s}$ ($\langle x^2 \rangle = 2Dt$ in
1-D). Solving for the effective viscosity in the forward direction from Eq. 3.5, $\eta_{\text{forward}} =
1.5 \times 10^{-3} \text{ mN} \cdot \text{s/m}^2$, thus this analysis predicts a solution viscosity towards the platinum
end that is 10 times less viscous than air ($1.8 \times 10^{-2}$)! This surprising result suggests that
viscosity gradients are not likely to contribute much to the motion of the PtAu rods in
hydrogen peroxide.
3.3 Possible Role of Interfacial Tension Gradients

Interfacial tension gradients that arise due to temperature or chemical gradients offer another interesting possibility. The decomposition of hydrogen peroxide is exothermic ($\Delta H^o$ on the order of $-200$ kJ/mol), creating both oxygen concentration and thermal gradients. Because the source of the gradients is the rod itself (i.e., the platinum end of the rod), the gradients that act on the length of the gold end are continually reestablished as it moves through solution as long as hydrogen peroxide is present. An important question is whether or not the minute changes in temperature and chemical composition are sufficient to generate the forces necessary to move micro and nanoscale objects. The force impelling the rods is balanced by the drag due to movement through a viscous fluid and may be estimated using Stokes drag law for a cylinder (Eq. 3.6):

$$F_{\text{drag}} = \frac{2\pi \mu L}{\ln \left( \frac{2L}{R} \right)} \nu$$

that predicts an opposing propulsive force of $\sim 0.048$ pN for a 2 µm long rod moving 10 µm/s.

The work due to changes in interfacial tension or surface expansion can be expressed in terms of surface area, $\sigma$, and interfacial tension, $\gamma$ (Eq. 3.7):

$$dW = \gamma \cdot d\sigma + d\gamma \cdot \sigma$$

Because the surface area of the particle is constant, we can neglect the first term. By symmetry, $\gamma$ only changes in the x direction, along the length of the Au segment of the
rod, and the force on a thin slice of the cylinder with circumference $2\pi R$ and thickness $dx$ is (Eq. 3.8):

$$dF = \frac{d\gamma}{dx} 2\pi R \cdot dx$$ \hspace{1cm} 3.8

integrated to give (Eq. 3.9):

$$F = \int \frac{d\gamma}{dx} 2\pi R \cdot dx = \Delta \gamma \cdot 2\pi R$$ \hspace{1cm} 3.9

(Note that this neglects the surface area of the rod ends which accounts for $<10\%$ of rod surface area). Using this expression, the interfacial tension difference required to balance the drag force based on experimental data ($R=185$ nm; $F=0.048$ pN) is $4.1 \times 10^{-5}$ mN/m. Thus an interfacial tension difference of only $4.1 \times 10^{-5}$ mN/m (0.041 pN/µm) would be sufficient to move a rod through solution.

### 3.3.1 Estimating Effect of Concentration Gradients on Interfacial Tension

While it is experimentally very difficult to measure the relevant solid-liquid interfacial tensions present in our system, an order of magnitude approximation can be made by what we do know about temperature and chemical composition effects on the interfacial tension at the liquid-vapor interface, and its relationship to the liquid-solid interface through Young’s equation (Eq. 3.10):

$$\gamma_{\text{vapor/Au}} - \gamma_{\text{solution/Au}} = \cos(\theta) \gamma_{\text{solution/vapor}}$$ \hspace{1cm} 3.10

The chemical gradient present arises from the balance of oxygen production and diffusion and may be estimated by solving the convection-diffusion equation for our
system, as done by Crespi and Lammert.[1] The resulting concentration difference from one end of the rod to another may be written as (Eq. 3.11):

$$\Delta C \approx \frac{SR}{2D} \ln \left( \frac{L}{2R} \right)$$  \hspace{1cm} 3.11

where $S$ is the surface normalized oxygen evolution rate, $R$ and $L$ the rod radius and length, and $D$ the diffusion coefficient of oxygen. This concentration difference can be related to interfacial tension as the mole fraction weighted average of the component interfacial tensions (Eq. 3.12):[13]

$$\gamma_{\text{solution}}/X = \sum_i \chi_i \gamma_i/X$$  \hspace{1cm} 3.12

In this equation, $X$ represents the contacting phase (solid or vapor), and the sum is carried out over the $i$ components of the solution. We note that $\gamma_{\text{H}_2\text{O}_2/X}$ is close to $\gamma_{\text{H}_2\text{O}/X}$,[14] and therefore Eq. 3.12 may be written as Eq. 3.13:

$$\gamma_{\text{solution}}/X = \chi_{\text{O}_2} \gamma_{\text{O}_2}/X + (1 - \chi_{\text{O}_2}) \gamma_{\text{H}_2\text{O}/X}$$  \hspace{1cm} 3.13

For $X = \text{vapor}$, $\gamma_{\text{O}_2/X}$ is approximately zero and therefore $\gamma_{\text{solution}/X} \approx \chi_{\text{H}_2\text{O}/\text{H}_2\text{O}/X}$. In order to obtain the solution/Au interfacial tension, we can use Eq. 3.10 in terms of our specific problem (Eq. 3.14):

$$\gamma_{\text{vapor/Au}} - \gamma_{\text{solution/Au}} = \cos(\theta) \gamma_{\text{solution/vapor}}$$  \hspace{1cm} 3.14

Now taking $\gamma_{\text{solution/vapor}} \approx \chi_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}/\text{vapor}}$, and differentiating Eq. 3.14 with respect to $\chi_{\text{H}_2\text{O}}$, we obtain (Eq. 3.15):

$$\frac{d \gamma_{\text{solution/Au}}}{d \chi_{\text{H}_2\text{O}}} = -[\text{H}_2\text{O}] \frac{d \gamma_{\text{solution/Au}}}{d C} \approx -\cos(\theta) \gamma_{\text{H}_2\text{O}/\text{vapor}}$$  \hspace{1cm} 3.15
Combining (Eq. 3.9) and (Eq. 3.15), and taking \( \cos(\theta) = 1 \) for a hydrophilic Au surface, we obtain the force on the rod (Eq. 3.16):

\[
F = -2\pi R \frac{d\gamma_{\text{solution/Au}}}{dC} \Delta C
\]

By setting Eq. 3.16 equal to the drag force calculated from Eq. 3.6, the concentration difference required to move a rod 10 \( \mu \)m/s is found to be \( 3.1 \times 10^{-5} \) M. Based on our observed oxygen evolution rate (\( S = 9.74 \times 10^{-17} \) mol O\(_2\)/sec per rod), the dimensions of our rods (\( L = 2 \) \( \mu \)m, \( R = 185 \) nm), and using the diffusion coefficient for oxygen (\( 2.42 \times 10^{-5} \) cm\(^2\)/s) the molar concentration difference estimated from Eq. 3.11 is \( 6.6 \times 10^{-6} \) M over 1 \( \mu \)m for rods in 3.7% hydrogen peroxide, about 1/5 what is required to move a PtAu rod 10 \( \mu \)m/s according to this model. Modeling the effect of catalytically induced temperature changes on the solution-rod interfacial tension done by Lammert and Crespi predicted surface tension forces indicated that the thermally induced change in interfacial tension generates a net forward force on the order of \( 10^{-4} \) pN, i.e. two orders of magnitude smaller than that required to balance the drag force.[1]

A more straightforward expression for rod velocity can be obtained by combining Eqs. 3.6, 3.11, and Eq. 3.16 to obtain (Eq. 3.17):

\[
v \approx \frac{SR^2 \gamma}{2\mu DL[H_2O]} \ln\left(\frac{L}{2R}\right)[\ln(\frac{2L}{R}) - 0.72]
\]

Eq. 3.17 may be simplified by noting that the two logarithmic terms vary slowly with \( L \) and \( R \). This gives (Eq. 3.18):
which may be used to predict the scaling of the rod velocity with different parameters \((S, R, L, \gamma, \mu, D)\).

### 3.3.2 Experimental Support for Interfacial Tension Gradients

#### 3.3.2.1 Geometric factors

I designed two experiments to test the scaling of the velocity predicted by Eq. 3.18. The first tests the dependence on the geometric factors, \(R\) and \(L\). In these experiments, PtAu nanorods of different lengths and a different radius were prepared by current-controlled electrodeposition so that the thickness of a metal segment could be correlated easily to the electrodeposition time (Table 3-1). The resulting rods were suspended in deionized water and then I measured the average velocities of these rods in \(\text{H}_2\text{O}_2\) (Table 3-2).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Current (mA)</th>
<th>Deposition rate (min/µm)</th>
<th>Expected potential vs. Ag/AgCl(_{(s)}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>-5.0 mA</td>
<td>5</td>
<td>-1.0</td>
</tr>
<tr>
<td>Au</td>
<td>-3.5 mA</td>
<td>10</td>
<td>-1.0</td>
</tr>
<tr>
<td>Pt</td>
<td>-5.0 mA</td>
<td>40</td>
<td>-0.1</td>
</tr>
</tbody>
</table>
3.3.2.2 Effect of ethanol on interfacial tension

The interfacial tension may be modified by adding another miscible component, such as ethanol, to the system. In addition to changing the tension of the fluid at the liquid-vapor (and liquid-solid) interface, ethanol also affects the oxygen evolution rate, but the rod velocity should scale as the product of these two parameters. To test this, I prepared suspensions of PtAu rods that contained 3.7% H₂O₂ and a known amount of ethanol. A sample (25 µL) of these suspensions was placed onto a glass slide bounded by a silicon spacer and topped with a glass cover slip, and the behavior of the rods was monitored and recorded via dark-field optical microscopy, as described in Chapter 1. The

<table>
<thead>
<tr>
<th>Length (µm)</th>
<th>Radius (nm)</th>
<th>Axial velocity (µm/s)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>190</td>
<td>5.6</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>190</td>
<td>2.7(6)(^a)</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>190</td>
<td>2(2)(^b)</td>
<td>47</td>
</tr>
<tr>
<td>8</td>
<td>190</td>
<td>1.0(7)(^c)</td>
<td>64</td>
</tr>
<tr>
<td>2(^d)</td>
<td>50</td>
<td>0.5(4)</td>
<td>20</td>
</tr>
</tbody>
</table>

Distribution of rod speeds was not homogeneous and considerable deviations from the mean were observed. For the different lengths, rods were observed to move as fast as \(^a\) 10 µm/s, \(^b\) 9.8 µm/s, and \(^c\) 18 µm/s. \(^d\) Small diameter rods prepared by Sarah K. St. Angelo.

**Table 3-2: Average axial velocity of PtAu rods of different dimensions in 3% hydrogen peroxide.**
resulting videos were each analyzed using Physvis (a free video analysis program from Kenyon College) to give the average rod speed, directionality, axial velocity, and diffusion coefficient. Table 3-3 compares the data extracted from captured videos to the surface tension and measured oxygen evolution rate (using gas chromatography methods described in Chapter 1). Figure 3-1 shows a plot of average velocity vs. the product $S\gamma$ for a sample of rods in ethanol-water solutions containing hydrogen peroxide. The plot is linear, as expected from (Eq. 3.18). The addition of ethanol also affects $\mu$ and $D$, but according to the Stokes-Einstein equation (Eq. 3.19) the product of these two parameters is approximately constant, and thus these two effects balance each other at constant temperature, $T$.

$$D\mu = \frac{kT}{6\pi R} \quad 3.19$$

<table>
<thead>
<tr>
<th>% ethanol (v/v)</th>
<th>axial velocity (μm/s)</th>
<th>$S\times10^{17}$ mol. O$_2$/s·rod</th>
<th>$\gamma$ (mN/m$^2$)</th>
<th>$S\gamma\times10^{15}$ mol. O$_2$·mN/s·rod·m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19 ± 2</td>
<td>9.7 ± 0.5</td>
<td>72.01</td>
<td>7.0 ± 0.4</td>
</tr>
<tr>
<td>10</td>
<td>8.8 ± 0.5</td>
<td>8.3 ± 0.2</td>
<td>47.53</td>
<td>3.97 ± 0.09</td>
</tr>
<tr>
<td>20</td>
<td>7.2 ± 0.6</td>
<td>6.9 ± 0.2</td>
<td>37.97</td>
<td>2.63 ± 0.07</td>
</tr>
<tr>
<td>33.3</td>
<td>5.6 ± 1</td>
<td>6.0 ± 0.1</td>
<td>32.00</td>
<td>1.91 ± 0.03</td>
</tr>
<tr>
<td>90</td>
<td>2.4 ± 0.4</td>
<td>2.1 ± 0.2</td>
<td>22.72</td>
<td>4.84 ± 0.06</td>
</tr>
<tr>
<td>control</td>
<td>0.3 ± 0.2</td>
<td>0</td>
<td>--</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3-3: Effect of ethanol on axial velocity of PtAu rods in 3.7% hydrogen peroxide, $v_z$, oxygen evolution rate, $S$, interfacial tension, $\gamma$. The final entry represents the apparent axial velocity due to Brownian motion of PtAu rods in pure deionized water. Error limits represent 90% confidence intervals. Axial velocity is plotted as a function of $S\gamma$ in Figure 3-1.
While the interfacial tension effect described above predicts force of the appropriate magnitude, it does not address the direction of rod movement. If this effect is responsible for the observed movement, a hydrophilic rod should move down the interfacial tension gradient in order to minimize the surface free energy of the system. The fact that the rods move with their platinum ends forward suggests that the surface free energy is minimized as the gold end swims up the oxygen concentration gradient, which in turn suggests that the gold is hydrophobic. The hydrophobicity of the gold may

Figure 3-1: The effect of ethanol on axial velocity, $v_z$, where $v_z$ is plotted versus the product of oxygen evolution rate per rod and solution surface tension (i.e. $S \cdot \gamma$). Included is a data point for rods moving in pure water, where the oxygen evolution rate is taken to be zero.
arise from surface impurities\cite{15} or nanoscopic air cavities pinned to the surface of the gold, as reported in the literature.\cite{16,17}

Cao and Mallouk carried out tapping-mode atomic force microscopy (AFM) studies on Au/Pt nanorods to verify the presence of nanobubbles. Rods imaged in air (Figure 3-2) had relatively featureless phase images. Rods imaged under air-saturated water were dotted with 10-50 nm diameter features that showed a negative phase shift (darker regions in Figure 3-3) relative to the background. These images were obtained under tapping conditions where the ratio between set-point tapping amplitude ($A_{sp}$) and the free amplitude ($A_0$) was 0.68. A combined theoretical/experimental study on polymer films by Magonov, et al.\cite{18} shows that at moderate tapping ($A_{sp}/A_0 \sim 0.4-0.7$), more negative phase shift corresponds to softer regions of the surface. Thus the observed phase shift is consistent with identification of the dark features in the phase images as nanobubbles. Similar features were also observed on unmodified silicon surfaces in air-saturated water, which looked very smooth when imaged in air. However, fresh mica surfaces appear smooth in water as well as in air. This is consistent with earlier reports\cite{16} that nanobubbles tend to form on rough and hydrophobic surfaces, but not on smooth, hydrophilic surfaces. It also excludes the possibility that these features come from the influence of the liquid-tip interaction.
Figure 3-2: Tapping mode AFM topography (left) and phase shift (right) images of Pt/Au nanorods in air.

Figure 3-3: Tapping mode AFM topography (left) and phase shift (right) images of Pt/Au nanorods in air-saturated water.
Although Cao and Mallouk were unable to obtain AFM images under conditions of hydrogen peroxide decomposition because of gas evolution in the sample cell, it is important to note that the steady-state concentration of oxygen at the Pt tip, which is on the order of 1 mM, is approximately equal to the maximum solubility of oxygen in water. It is therefore very likely that nanobubble coverage of the rod surface is at least as high as it is in air-saturated water (Figure 3-3). Because of the presence of nanobubbles, two distinct interfacial tensions enter into the calculation of the net force on the nanorod: the interface between bare gold and the solution, and the interface between an oxygen nanobubble and the solution. The nanobubble-derived force scales with $\gamma_{\text{solution/vapor}}$, while the remaining contribution scales with $\gamma_{\text{solution/Au}} - \gamma_{\text{vapor/Au}}$. However, Young’s equation (Eq. 3.10) for the vapor-Au-solution three-phase boundary equates $(\gamma_{\text{vapor/Au}} - \gamma_{\text{solution/Au}})$ with $\cos(\theta)\gamma_{\text{solution/vapor}}$. Therefore, both contributions scale with $\gamma_{\text{solution/vapor}}$. The resulting dependence of the rod interfacial tension on the water mole fraction is thus given by Eq. 3.20, which corrects Eq. 3.15 for partial coverage by nanobubbles:

$$\frac{d\gamma_{\text{solution/rod}}}{d\chi_{H_2O}} = (A - (1 - A)\cos(\theta))\gamma_{H_2O/vapor}$$

3.20

In this equation, $A$ is the fraction of the Au surface that is occupied by nanobubbles. The nanobubble coverage is not known precisely under conditions of hydrogen peroxide decomposition, but $A$ should be sizable judging from AFM images acquired in air-saturated water (Figure 3-3). Taking $A \approx 1$ and $\cos(\theta) \approx 1$, the same force given in (Eq. 3.16) is obtained, but with motion directed towards the Pt end of the rod.
3.4 Conclusions

While there are several potential mechanisms for catalysts to convert chemical to mechanical energy, several can be ruled out for PtAu rods because of their failure to agree with the observed velocity and direction of catalytic rods in hydrogen peroxide. The AFM observations described above, combined with the observed linear relationship between the axial velocity of Pt/Au rods in hydrogen peroxide solutions and the product of oxygen evolution rate and surface tension of the bulk solution seem to account, at least in part, for the high velocity and direction of motion, supporting the role of interfacial tension gradients in rod propulsion. However, these results did not necessarily exclude the possibility of a self-electrophoretic mechanism, described in the next chapter.

3.5 References


Chapter 4
Catalytically Induced Electrokinetics for Nanomotors

4.1 Introduction

One essential aspect of motile biological systems is the ability of individual biomotors and organisms to harness the chemical free energy of their local environment, allowing individual motors to operate independently of one another. Several approaches toward autonomous synthetic motors have been described in the past few years.[1],[2],[3] Understanding the chemically-induced locomotion of micro/nanoobjects or pumping of bulk fluids in these systems is an emerging research area at the interface of many disciplines with potential applications in biomimetics, microfluidics, and nanomachinery.

Among reports of artificial chemical locomotion, Ismagilov and Whitesides et al. were the first to use a non-biological catalytic reaction – hydrogen peroxide (H$_2$O$_2$) decomposition – to power the motion of millimeter scale objects at an air/water interface.[4] Our group later found that the platinum catalyzed decomposition of H$_2$O$_2$ could also be used to power the motion of suspended asymmetric platinum-gold (PtAu) nanorods.[5] By incorporating ferromagnetic nickel (Ni) segments into the nanowire structure, Kline et al. demonstrated that the motion of PtNiAu nanorods could be controlled remotely by using a weak magnetic field.[6] Catchmark and coworkers also demonstrated catalytically driven motion of more complex micromotors by fabricating gear structures that rotate in H$_2$O$_2$ solutions.[7] Other groups have also used this same
reaction to induce motion, such as the spontaneous rotation of nickel-gold nanorods pinned at one end to a silicon substrate, observed by Ozin and others. Later, Feringa et al. used a different approach by functionalizing an otherwise non-catalytic object with a synthetic analog of catalase, a biologically derived H₂O₂ decomposition catalyst.

Although the net decomposition reaction is the same in each of these cases (2H₂O₂ → 2H₂O + O₂), the propulsion mechanisms of the relatively larger systems described by Whitesides and by Feringa and the smaller metallic structures are fundamentally different. The motion of the former may be attributed to the growth and recoil of oxygen bubbles, while the motion of the all-metal particles and structures was initially ascribed instead to differences in interfacial tension generated by the concentration gradient of the products diffusing away from the catalytic product-generation sites. Subsequently, Kline et al. demonstrated that a complementary system consisting of a silver catalyst (for H₂O₂ decomposition) immobilized on a gold surface was capable of pumping fluid surrounding the stationary object. The fluid convection caused by this catalytic micropump was attributed to an electrokinetic mechanism resulting from the electrochemical (rather than purely chemical) decomposition of H₂O₂ involving both the silver and the gold surface, and strongly suggesting that this mechanism might be operative in the PtAu nanorod system. In the previous chapter, I addressed a number of possible propulsion mechanisms for the motion of PtAu nanorods in H₂O₂, including viscosity gradients, diffusiophoresis, and interfacial tension gradients. One final possibility is that of self-electrophoresis resulting from electrochemical hydrogen peroxide decomposition at the platinum and gold ends of a moving rod.
4.2 Concept

4.2.1 Background on Self-generated Electric Fields

The electrokinetic mechanism is a variation of established electrokinetics that describes the effect of an external electric field on the ions in the double layer at an aqueous solution/solid interface. According to classical electrokinetic theory, mobile ions in the electrical double layer migrate under the influence of the electric field and drag solvent molecules as they move, causing a net fluid movement with respect to the solid surface.\[11\] In the case of a fixed surface (such as a capillary or a microchannel), the result is electroosmotic fluid pumping from one electrode to the other. Electrophoresis describes the complementary process for freely suspended particles that migrate in an electric field with respect to the surrounding fluid.\[12\]

Conventional electroosmosis and electrophoresis require an applied electric field from an external source. However, it has been recognized that living cells are capable of transporting charge via transcellular ion channels, and Mitchell suggested this as the basis for a new mechanism of microorganism propulsion.\[13\] If an organism were capable of pumping ions out of its interior in one area and pumping them in at another location, such a cell would be capable of maintaining a dynamic electric field tangential to the cell surface. This gradient would be superimposed over the cell’s equilibrium double-layer by the continuous pumping of ions. Ions in the double layer would migrate in response to this dynamic electric field, resulting in fluid flow in the interfacial region between the cell membrane and the surrounding fluid and a corresponding slip velocity. Anderson recognized the potential of self-generated electric and concentration fields, and proposed
a relationship between velocity, \( v \), and diffusion-induced electric fields arising from cellular processes (Eq. 4.1):[14]

\[
v = -\frac{1}{3} \frac{\varepsilon \kappa}{4\pi \eta k_e} \nabla C_\infty \tag{4.1}
\]

Where \( \varepsilon \), \( \kappa \), \( \eta \), \( \kappa \), \( k_e \), and \( \nabla C_\infty \) are the solution dielectric, the zeta potential of the moving object, the solution viscosity, a constant, the bulk solution conductivity, and the concentration gradient of the electric field-inducing species.

Complementing Anderson’s work, Lammert et al. later put forward a mathematical solution for the velocity of a hypothetical spherical vesicle with an asymmetric distribution of ion pumps on its surface, and agreed that such an object could in principle propel itself through solution electrophoretically with a velocity, \( v_\text{z} \), according to Eq. 4.2:[15]

\[
v = \frac{2}{3} \mu E_x \tag{4.2}
\]

and \( \mu \) is the electrophoretic mobility, a function of object zeta potential and the viscosity and dielectric of the surrounding solution.

### 4.2.2 Self-generated Electric Fields from Bipolar Redox Reactions

In addition to ion pumps, self-generated electric fields may also arise from bipolar redox chemistry on an asymmetric metallic surface, such as H\(_2\)O\(_2\) oxidation and reduction
occurring on opposite ends of a PtAu nanorod. This problem is similar to that of a hypothetical biological cell described above that uses active transport to pump ions into the cell on one end, and out at the other, resulting in a self-generated ion gradient.[15] Similarly, a conducting colloidal particle that catalyzes an oxidation reaction on one end and a reduction reaction on the other would generate its own ion gradient. Consider an asymmetric conducting particle with two ends which catalyze two different electrochemical half reactions. Platinum/gold surfaces take on a negative charge (~ −50 mV) in deionized water, requiring protons from solution to balance the surface charge to preserve electroneutrality of the bulk suspension, thus these reactions proceed at the metal interface under acidic conditions:

\[ \text{A}_{\text{red}} \rightarrow \text{H}^+ + \text{e}^- + \text{A}_{\text{ox}} \quad E_1 \]

\[ \text{B}_{\text{ox}} + \text{H}^+ + \text{e}^- \rightarrow \text{B}_{\text{red}} \quad E_2 \]

such that both oxidized and reduced species are neutral, \( E_1 + E_2 \) is positive (i.e., the reaction is spontaneous), and the overall reaction on the particle surface is fast (Figure 4-1). Note that the reaction would proceed with a flux of electrons inside the particle, as well as the migration of protons outside the particle from one end to the other. In this way, the particle effectively acts as a short-circuited galvanic cell with the electron current (and corresponding ion current) being driven thermodynamically by the net reduction of chemical free energy.
From the balanced half-reactions, the electron current through the particle is equal to the ion current in the fluid surrounding the particle (Eq. 4.3):

\[ i_e = i_{M^+} - i_X \]  \hspace{1cm} 4.3

and the related current densities are then given by Eq. 4.4:

\[ J = \frac{i_e}{A_{flux}} \]  \hspace{1cm} 4.4

where \( A_{flux} \) is the cross-sectional area through which the electrons or ions flow. This area for the electron flux is the cross-sectional area of the particle, and the ion flux primarily occurs in the electrical double-layer surrounding the particle in water (Figure 4-2), the thickness of which is given by the Debye length (Eq. 4.5):

Figure 4-1: Redox active particle capable of generating its own electric field. Species A is catalytically oxidized on one side generating a proton and an electron which are consumed when B is catalytically reduced on the opposite side. The asymmetric production and consumption of ions results in a concentration polarization induced electric field driven by the net reduction of free energy. Ions adjacent to the surface migrate in response to the electric field.
Here $I$ is the ionic strength of the solution and $c$ is the molarity of the dilute electrolyte solution in mol/m³. The electric field, $E$, generated by the flux of electrons or ions, $J$, can then be estimated from Ohm’s Law, $E = J/k_e$, where $k_e$ is the conductivity of the charge transport medium. The conductivity of the metal particle itself is very high ($> 10^5$ S/m for a metal particle), but the conductivity of bulk deionized water is much smaller ($< 10^{-5}$ S/m).
S/m). The conductivity of the double layer will be slightly higher and can be estimated using the Bikerman equation for surface conductivity (Eq. 4.6):

\[
K^{\sigma_d} = \sqrt{8\varepsilon cRT} \left\{ \frac{u_+}{A-1} - \frac{u_-}{A+1} + \frac{4\varepsilon cRT}{\eta F} \left( \frac{1}{A^2} - 1 \right) \right\}
\]

where \( c \) is concentration, \( R \) is the gas constant, \( T \) is temperature, \( u_{+, -} \) are the mobilities of the cation and anion, \( \varepsilon \) and \( \eta \) are the solution dielectric and viscosity respectively, \( z \) is unit charge, \( F \) is Faraday’s constant, and \( A \) is given by the function \( \coth \left( -\frac{zF\zeta}{4RT} \right) \).

Because this conductivity occurs throughout the double-layer, the resulting 2-dimensional conductivity, \( \sigma_d \), the estimated conductivity of the diffuse layer in pure water is on the order of \( 10^{-4} \) S m\(^{-1} \). This, however, disregards the conductivity of the stagnant part of the double layer which may have conductivity as much as 5–10 times higher than the diffuse layer.[16] Regardless of the method to estimate the conductivity of the solution surrounding the catalytic particle, the electric field established in the particle double layer using the most conservative conductivity estimates is \( >10^7 \) times greater than the electric field in the metal particle itself, and may be high enough to cause electrokinetic effects in the solution surrounding the particle.

Because the ions in the double layer migrate with respect to the particle surface in response to this self-generated electric field, by Galilean invariance the particle moves with respect to the fluid. As in the case of external electrophoresis, the observed slip velocity would be a linear function of the electric field, which is a function of the current.
in, and conductivity of, the interfacial double-layer region. Assuming classical behavior, the particle should migrate in its self-generated electric field according to the Hückel equation for electrophoretic slip velocity in the limit of large Debye length, which Lammert showed to be valid for a spherical vesicle generating its own electric field:

\[
v = \frac{2 \varepsilon \zeta E_x}{3 \eta}.
\]

Furthermore, the electric field parallel to the particle surface, \(E_x\), can be written in terms of the ion current density and the 2-dimensional double layer conductivity. Assuming that the dominant charge carriers are cations in the double layer adjacent to the negatively charged metal surface, we obtain:

\[
v = \frac{2 \varepsilon \zeta J_{\text{M}^+}}{3 \eta \sigma_d}.
\]

Using this relation, a particle with a zeta potential of \(-50\) mV requires an ion current density of only \(4 \times 10^{-4}\) mA cm\(^{-2}\) to move 10 \(\mu m/s\). Thus, electrohydrodynamic fluid pumping due to a catalytic redox couple can in principle propel a rod through solution.

### 4.3 Catalytically Induced Electrokinetics for PtAu Nanomotors

Although platinum is an efficient catalyst for the non-electrochemical decomposition of hydrogen peroxide in the absence of another electrode, the electrochemical oxidation of \(H_2O_2\) on a platinum electrode is well documented[17],[18]
and may be coupled to the reduction of \( \text{H}_2\text{O}_2 \) on the polycrystalline Au surface at the opposite end of the PtAu nanorod according to the following reactions:

\[
\begin{align*}
\text{Pt:} & \quad \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \\
\text{Au:} & \quad \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]

If this mechanism were operative on the surface of a PtAu rod, there would be a measurable electron current from platinum to gold. Conservation of charge and the stoichiometry of the decomposition half reactions require that the measured electron current between platinum and gold be accompanied by an ion current in the solution between the electrodes. The resulting ion flux from platinum to gold implies an electric field that can be estimated from Ohm’s Law \( E = J/\sigma \) and brings about particle migration with a velocity that scales as a function of the Helmholtz-Smoluchowski equation (Eq. 4.7):

\[
\nu \propto \frac{\mu_e J_+}{k_e}
\]

where \( \mu_e \) is the electrophoretic mobility of the bimetallic particle (a function of the dielectric constant and viscosity of the solution, and the dimensions and zeta potential of the particle), \( J_+ \) is the current density due to the electrochemical reaction, \( k_e \) is the conductivity of the bulk solution. This relationship predicts that the velocity is proportional to the current, and inversely proportional to the solution conductivity, suggesting strategies by which to test this electrokinetic hypothesis.
4.4 Testing Catalytically Induced Electrokinetics

4.4.1 Confirmation of Electrochemical \( \text{H}_2\text{O}_2 \) Decomposition

The possibility of an electrochemical decomposition pathway was confirmed by measuring the steady-state short-circuit current between a platinum and a gold electrode in contact with reaction mixtures containing hydrogen peroxide. The platinum electrode was prepared by electrodepositing platinum in an aluminum oxide template with a silver backing. Electroplating was stopped before the Pt reached the end of the template pores, allowing for \(~20\, \mu\text{m}\) of open channel between the end of an electrodeposited Pt rod and the top of the \( \text{Al}_2\text{O}_3 \) template (Figure 4-3). This procedure afforded an array of \(2.44 \times 10^9\) individual platinum rods, each with a diameter of 370 nm, and each electrically connected to the silver backing. We incorporated the resulting nanowire array electrode into a solution cell, such that the Pt side of the electrode could be exposed to rinse solution (and later, reaction mixtures), and the dry silver backing could be electrically connected to the ammeter. Prior to using the cell, we filled it with DI water for 24 hours to wash any residual ions from the plating solutions from the template and cell, and then rinsed liberally with DI water. The counter electrode consisted of a 0.5 mm diameter gold wire (Sigma-Aldrich) that was cleaned by soaking it in concentrated nitric acid overnight, and rinsed liberally with DI water prior to use.
The gold electrode was brought in contact with the insulating Al₂O₃ template containing the Pt rod array, and both electrodes were connected to the terminals of the ammeter (Figure 4-3). We then filled the resulting cell containing the Pt rod array electrode with 1.0 mL of reaction solution and measured the catalytically generated steady-state short-circuit current between platinum and gold in contact with reaction mixtures containing either pure deionized water or aqueous hydrogen peroxide solutions. A plot of current vs. time indicates there is a transient current with the addition of new
solution, but this transient current dies off significantly after approximately minute
(Figure 4-4). In practice, we allowed the current to stabilize for three minutes prior to
measuring the current, and the steady state was taken as the average current over the next
100 seconds. Two measurements were made at each H₂O₂ concentration, and the results
are tabulated in Table 4-1.

Figure 4-4: A plot of current vs. time between a platinum nanorod array electrode and a
gold counter electrode. Baseline current in 1.0 mL deionized water was -1.1×10⁻⁸ A
(t = 0-50 seconds). At t = 50 s, the deionized water was replaced with 5% H₂O₂. Initially,
a transient current was observed that decreased significantly after 60 seconds. Steady
state currents reported represent the average current between t = 200 and t = 300 seconds.
It is well known that platinum is capable of decomposing hydrogen peroxide through non-electrochemical pathways in the absence of another electrode. Previously, we observed that the surface area normalized rate of oxygen evolution per PtAu rod due to all decomposition processes was $8.7 \times 10^{-6}$ mol. O$_2$/s·m$^2$ (in 3.7% H$_2$O$_2$). We calculated the electrochemical oxygen production rate from the Eq. 4.8:

$$\text{rate} = \frac{J}{nF}$$  \hspace{1cm}  \text{(4.8)}$$

where $J$ is the measured current density (0.12 to 0.68 A/m$^2$ in 0.6 to 6% H$_2$O$_2$, respectively), $n$ is the stoichiometric number of electrons transferred in the process, and $F$ is Faraday’s constant. Using this approach, we calculated that the current density on the Pt nanorod array electrode is equivalent to an electrochemical oxygen production rate of

<table>
<thead>
<tr>
<th>% H$_2$O$_2$ (w/w)</th>
<th>Current (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DI-1)</td>
<td>-0.011 (0.002)</td>
</tr>
<tr>
<td>5.0</td>
<td>-16.7 (0.2)</td>
</tr>
<tr>
<td>5.0</td>
<td>-16.1 (0.3)</td>
</tr>
<tr>
<td>(DI-2)</td>
<td>-0.164 (0.001)</td>
</tr>
<tr>
<td>3.4</td>
<td>-6.7 (0.1)</td>
</tr>
<tr>
<td>3.4</td>
<td>-7.04 (0.08)</td>
</tr>
</tbody>
</table>

Table 4-1: Current between platinum nanorod array electrode and gold counter electrode, in pure water (DI), 5.0% and 3.4% H$_2$O$_2$. The current for DI-2 is due to residual H$_2$O$_2$ in between the 5.0% and 3.4% H$_2$O$_2$ runs.
Thus the observed current due to the electrochemical decomposition of H₂O₂ comprises ~2% of total oxygen production.

### 4.4.2 Correlation of Axial Velocity and Solution Conductivity

After confirming the electrochemical decomposition of H₂O₂, we tested the hypothesized electrokinetic mechanism described above by measuring the speed of bimetallic rods in H₂O₂ as a function of solution conductivity. Eq. 4.7 predicts that the velocity is inversely proportional to the solution conductivity, provided that increasing the conductivity does not dramatically affect the electrophoretic mobility of the rods.

We prepared PtAu rods by electrodeposition of platinum and gold in aluminum oxide (Al₂O₃) templates as previously described.[19] We released the rods from the template by first oxidizing and dissolving the sacrificial silver metal deposited on the back of the template in 5 M nitric acid, and then dissolving the aluminum oxide template in 5 M sodium hydroxide. After we freed the rods from the templates, the rods were suspended in DI water to give a mixture containing 1.2×10⁸ rods/mL. Next, we measured the average velocity of PtAu rods in 3.7% H₂O₂ in solutions of varying conductivity. In order to distinguish the directed motion of catalytically active rods from ubiquitous Brownian motion, we measured axial velocity rather than center-to-center displacement per unit time. These axial velocities were measured by first capturing video clips of the rods and then analyzing them using MATLAB-based motion analysis programs developed by REU student, Paul Baker (see appendix A). Axial velocities reported represent an ensemble average of between 30 to 60 rods. We varied the conductivity from
8.8 to 410 μS/cm by adding small amounts of either lithium nitrate (LiNO₃) or sodium nitrate (NaNO₃). Solution conductivity was measured using a calibrated microelectrode conductivity sensor and AC impedance methods, described by Hong et al (see appendix B).[20]

As predicted by Eq. 4.7, the axial velocity of bimetallic rods in H₂O₂ drops dramatically by increasing the solution conductivity with the addition of sub-mM concentrations of either LiNO₃ or NaNO₃ (Figure 4-5), which may be due to a number of factors, including decreased electrophoretic mobility, decreased reaction rate, and decreased electric field.
4.4.2.1 Effect of salt on electrophoretic mobility of PtAu rods

To determine the effect of salt on the electrophoretic mobility, zeta potential measurements were made using Brookhaven Instruments ZetaPALS zeta potential analyzer. The zeta potential of PtAu rods was measured in solutions of different concentrations of NaNO₃ (Table 4-2). These results indicated that the electrophoretic mobility...
mobility did in fact decrease, but only approximately 5% over the range of conductivities included in these experiments. Because of the effects of conductivity, the electric field caused by the same current density decreases 98% over the range of conductivities included in these experiments. Therefore, slowing due to a decrease in electric field is the dominant effect caused by changing the conductivity, and the effect of electrophoretic mobility was not considered further.

<table>
<thead>
<tr>
<th>Table 4-2: Effect of conductance on electrophoretic mobility and zeta potential of PtAu nanorods.</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductance (S)</td>
</tr>
<tr>
<td>H₂O</td>
</tr>
<tr>
<td>3 mM NaNO₃</td>
</tr>
</tbody>
</table>

### 4.4.2.2 Effect of salt on overall oxygen production rate

To be certain the reduction in axial velocity was not due instead to a decreased reaction rate, we measured the rate of oxygen evolution (see Chapter 1) in solutions containing PtAu rods, 3.7% H₂O₂, and NaNO₃ concentrations comparable to the highest used in the above experiments (Table 4-3). The rate of oxygen evolution decreased by approximately 33% with the addition of 1 mM NaNO₃ (comparable to values reported previously[21]), which predicts a decrease in velocity of also approximately 33% by the scaling equation put forth previously.[5] However, the observed decrease in reaction rate was not sufficient to account for the >80% observed decrease in axial velocity for NaNO₃ concentrations greater than 1 mM. Furthermore, as discussed in the next chapter, the
current densities measured using the IME set-up indicated that the current density due to H$_2$O$_2$ concentration does not decrease significantly with NaNO$_3$. This suggests that although the overall rate of H$_2$O$_2$ decomposition decreases, the electrochemical H$_2$O$_2$ decomposition is unaffected by the addition of salt.

Table 4-3: Effect of 1 mM NaNO$_3$ on rate of PtAu rod catalyzed decomposition of 3.3% H$_2$O$_2$. Rod solution contains 8.1×10$^8$ PtAu rods/mL.

<table>
<thead>
<tr>
<th>[NaNO$_3$]</th>
<th>Rod solution</th>
<th>O$_2$ evolution (×10$^8$ mol O$_2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>0.09 (0.03)</td>
</tr>
<tr>
<td>-</td>
<td>50 µL</td>
<td>1.8 (0.2)</td>
</tr>
<tr>
<td>1 mM</td>
<td>50 µL</td>
<td>1.21 (0.06)</td>
</tr>
</tbody>
</table>

4.4.3 Correlation of Axial Velocity and Current

We previously reported that adding ethanol to suspensions of PtAu rods in H$_2$O$_2$ resulted in a reduction of oxygen evolution rate, $S$, and interfacial tension, $\gamma$, and we observed a corresponding linear decrease in rod velocity with the product $S\gamma$. However, Eq. 4.7 predicts that the speed of catalytically driven PtAu rods in H$_2$O$_2$ should also scale with current. To test the correlation between current and axial velocity, we compared the speed of PtAu rods in ethanol solutions from reference [5] to the catalytically generated current between a platinum and a gold electrode in contact with reaction mixtures containing hydrogen peroxide and ethanol.
An electrochemical cell, such as the one described above, was filled with 1 mL of reaction solution containing 3.4% H₂O₂ and a known amount of ethanol. We then measured the catalytically generated steady-state short-circuit current between platinum and gold in contact with reaction mixtures containing hydrogen peroxide and ethanol. We observed that the catalytically generated current decreased with the addition of ethanol (Table 4-4), and that the axial velocity for PtAu rods in H₂O₂ reported previously scales with this decrease in current. In fact, a plot of axial velocity for PtAu rods in H₂O₂ (reported previously) versus observed current is nearly identical to the plot of axial velocity versus $S\gamma$, indicating that rod speed correlated with both current and $S\gamma$ (Figure 4-6).

Table 4-4: Effect of ethanol on the catalytically generated current between a platinum and a gold electrode (see Figure 4-6) due to the electrochemical decomposition of 3.4% (v/v) H₂O₂ compared to axial velocity of PtAu rods in H₂O₂/ethanol solutions from reference 2.

<table>
<thead>
<tr>
<th>% Ethanol (v/v)</th>
<th>Current density$^a$ (×10² A/m²)</th>
<th>Axial velocity (μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.61(3)</td>
<td>19</td>
</tr>
<tr>
<td>10</td>
<td>1.67(1)</td>
<td>8.8</td>
</tr>
<tr>
<td>20</td>
<td>1.21(2)</td>
<td>7.2</td>
</tr>
<tr>
<td>33</td>
<td>0.90(1)</td>
<td>5.6</td>
</tr>
<tr>
<td>90</td>
<td>0.278(3)</td>
<td>2.4</td>
</tr>
<tr>
<td>H₂O$^b$</td>
<td>0.0043(8)</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Current density calculated from measured current divided by the area of exposed platinum (2.62×10⁻⁴ m²). $^b$ H₂O is the baseline current density in pure deionized water without added H₂O₂ or ethanol.
4.5 Designing Future Redox Nanomotors

Designing particles with orthogonal but complementary redox properties presents an interesting challenge. One end of the particle would have to be an efficient oxidation catalyst, but an inefficient reduction catalyst. The reverse would be true for the other end (i.e., a good reduction and a poor oxidation catalyst), and the two catalytic ends would

Figure 4-6: Plot of axial velocities of PtAu rods (from reference [5]) vs. current density in ethanol/H₂O₂ solutions.
need to be in electrical contact with one another through the particle to allow current to flow. Finally, the reaction would need to be fast enough to generate field strengths necessary for particle movement. By the Hückel approximation, the electric field required to move a micron-sized colloidal particle with an electrokinetic zeta potential of $-50 \text{ mV}$ in pure water at a speed of $10 \ \mu\text{m s}^{-1}$ is on the order of $400 \ \text{V m}^{-1}$. However, electric fields scale with length, and a $400 \ \text{V m}^{-1}$ field corresponds to a potential difference of only $0.4 \ \text{mV}$ over a $1 \ \mu\text{m}$ long particle.

Reactions which meet the above criteria may be found in the fuel cell literature, such as the electrochemical oxidation of hydrogen or methanol coupled with the reduction of oxygen which proceeds at relatively moderate temperatures and pressures.[22] Although a platinum catalyst can be used as both the anode and the cathode, recent advances have used Pt alloys to optimize either the anode or cathode efficiency. For example, Pt-Co and Pt-Pd alloys are more active for the reduction of oxygen than platinum alone.[23],[24] Conversely, Pt-Ru catalysts exhibit higher activity and longer lifetimes than platinum alone when used as a hydrogen or methanol reducing catalyst.[25] and electrodeposition of these platinum containing alloys has been demonstrated.[26],[27] Approaches to alloy formation may then be applied to template-based methods to fabricate metallic nanorods with alloy segments and tested for motility in fuel solutions via optical microscopy.

In addition to the inorganic fuel cell catalysts, there is a large number of redox enzymes that may be coupled together to power the motion of micro- and nanoscale objects. Heller and Mano have demonstrated the use of glucose oxidase for the oxidation
of glucose coupled to an oxygen reduction enzyme (bilirubin reductase) to drive the motion of millimeter sized carbon fibers at an air-water interface.[28] The authors suggest that this redox mechanism for motion is likely coupled to interfacial tension, but the results demonstrate the use of redox active enzymes to power the motion of synthetic objects. Clever use of nature’s motors may pave the way for more efficient nanomotors that can be engineered to operate under a number of different conditions.

While the speed of Au/Pt nanorods propelled in this manner is comparable to that of flagellar bacteria, the energy conversion efficiency of the former is very small. The product of the rod velocity (~10 μm/s) and drag force (5×10^{-2} pN) gives the mechanical power dissipated by the rod as it moves through the solution, which is on the order of 5×10^{-19} W. The input power (2×10^{-11} W) can be calculated from the oxygen generation rate (~1×10^{-16} mol s^{-1}) at the rod surface and the free energy change of the reaction (−234 kJ mol^{-1}). The resulting efficiency based on these estimate is on the order of 10^{-8}. In contrast, biological energy transduction is quite efficient, often greater than 50%. While biological motors use less exoergic reactions, such as ATP hydrolysis, the main reason for their efficiency is the intimate, atomic-level mechanical coupling of the catalyst with the reactants/products. We believe that energy conversion efficiencies orders of magnitude higher than that of the AuPt nanorod - H\textsubscript{2}O\textsubscript{2} system could be achieved by bearing this principle in mind. This is an exciting prospect because even the very inefficient energy conversion we have so far achieved is capable of generating forces that can turn gears and outrun certain unicellular organisms. Increasing the efficiency by even two orders of magnitude (to 10^{-6}) would give us much faster motion
on the bacterial length scale, and would allow us to make much smaller nanomotors according to the scaling of Eq. 4.7.

4.6 References


Chapter 5

Catalytically Induced Electrokinetics for Switchable Micropumps

5.1 Introduction

The results of the experiments in the previous chapter are consistent with an electrokinetic mechanism for rod motility in which a platinum and gold striped nanorod can catalytically oxidize hydrogen peroxide on the platinum end and reduce it on the gold end (Figure 5-1). The resulting ion flux induces motion of the particle relative to the fluid, propelling the particle towards the platinum end with respect to the stationary fluid. By Galilean invariance, these principles also apply in the case of an immobilized PtAu system, the result in this case being the motion of fluid with respect to a stationary surface. The catalytically induced fluid movement would drive the motion of tracer particles entrained in the fluid, allowing the observation of the fluid motion by monitoring the motion of the tracer particles.
5.2 Catalytically Induced Electrokinetics on AgAu Surfaces

5.2.1 Background

The catalytically induced electrokinetics due to a stationary catalytic object has been demonstrated recently by Kline et al. to in fact drive the motion of tracer particles. The principal reaction driving the fluid motion in this case was the silver (rather than platinum) catalyzed decomposition of hydrogen peroxide, although there may be some contribution due to the oxidation and dissolution of silver metal by H₂O₂. Kline made two interesting observations in these experiments. First, the direction of motion of the tracer particles was a function of the zeta potential of those particles. Positive and very weakly negative particles were observed to move across the gold surface towards the silver...
catalyst, while highly negative particles migrated some distance away from the catalyst. Secondly, when an insulator (SiO₂) was placed between the silver catalyst and the gold substrate, the particle motion was not observed. Thus the catalyst must be in electrical contact with the gold substrate in order to observe the catalytic pumping effect. Both the dependence on tracer zeta potential and the requirement of electrical contact are consistent with an electrokinetic mechanism for fluid pumping. This type of particle transport was previously demonstrated for a non-catalytic reaction involving the corrosion of steel by hydrogen peroxide resulting in the deposition of micron-sized polymer beads on the corroding metal surface.[1] In this chapter, I explore the use of platinum and gold as catalytic surfaces to induce electroosmosis in the region between the two metal surfaces that can be turned on and off by means of an external switch.

5.2.2 Preparation of AgAu Interdigitated Microelectrode (IME)

What is interesting about the experiments described by Kline et al. is that they suggest that the silver is actually catalyzing the reduction of hydrogen peroxide, rather than the oxidation as in the case of the platinum. To test this hypothesis, I prepared a bimetallic interdigitated microelectrode (IME) by electroplating onto one of the two electrodes on a commercially available IME (Abtech Scientific) potentiostatically using a bipotentiostat (Pine model AFRDE5). The electrode being plated onto was the working electrode, while the other was a “passive” electrode. Because of size constraints, a platinum wire (cleaned with concentrated nitric acid prior to use) was used as both a quasi-reference electrode and the counter electrode. Although electroplating was done
potentiostatically, the current at both the working electrode and the passive electrode was carefully monitored. Silver was plated onto a gold IME at a potential of -1.6 V vs. Pt quasi-reference to give a current density of -9 A/m² for 10 minutes. To prevent undesirable processes from taking place on the passive electrode, such as etching or plating, the potential of the passive electrode was biased such that the current was no more than ±1/500 of that on the working electrode for the duration of the plating process.

5.2.3 Amperometry of AgAu IME in the Presence of Hydrogen Peroxide

The platinum electrode was then short-circuited to the gold electrode though a Keithley 2400 Sourcemeter. After the addition of aqueous H₂O₂ solutions to the IME surface, such that all exposed fingers were covered by solution, I observed a positive current from the Ag to the Au electrode in the presence of hydrogen peroxide (Figure 5-2). Furthermore, the direction of current was consistent with the reduction of H₂O₂ on the silver electrode, and the corresponding oxidation of H₂O₂ on gold.
5.3 Electrochemical Decomposition of Hydrogen Peroxide on PtAu IMEs

5.3.1 Preparation of PtAu interdigitated microelectrodes (IMEs)

The possibility of an electrochemical decomposition pathway was confirmed by measuring the steady-state short-circuit current between platinum and gold interdigitated microelectrodes (IMEs) in the presence of H$_2$O$_2$ (Figure 5-3). I prepared bimetallic IMEs
by electroplating onto one of the two electrodes on commercially available IMEs (Abtech Scientific) potentiostatically using a bipotentiostat (Pine model AFRDE5). The electrode being plated onto was the working electrode, while the other was a “passive” electrode. Because of size constraints, a platinum wire (cleaned with concentrated nitric acid prior to use) was used as both a quasi-reference electrode and the counter electrode. Several bimetallic IMEs were prepared by either plating platinum onto as-received gold electrodes (Pt\textsubscript{plated}/Au) or plating gold onto as-received platinum electrodes (Au\textsubscript{plated}/Pt). Electroplating gold onto platinum was preferred because platinum that was electroplated onto gold decomposed hydrogen peroxide with a significant amount of bubble formation, making it difficult to observe tracer motion by optical microscopy, while the as-received evaporated platinum surface in H\textsubscript{2}O\textsubscript{2} solutions generated very few bubbles (one or two bubbles smaller than 2 mm diameter over the course of 1 hour), if at all. Although electroplating was done potentiostatically, the current at both the working electrode and the passive electrode was carefully monitored. Gold was plated on platinum IMEs at a potential of -2.1 V (vs. the Pt quasi-reference) to give a current density of -6.7 A/m\textsuperscript{2} for 10 minutes, resulting in a plated gold thickness of \~0.4 \textmu m, as measured by atomic force microscopy (Figure 5-4). A higher current density of -27 A/m\textsuperscript{2} was needed to plate platinum on gold IMEs, due to its lower plating efficiency. This required a potential of -1.7 V (vs. Pt quasi-reference) for 10 minutes, resulting in a platinum thickness of \~0.4 \textmu m. To prevent undesirable processes from taking place on the passive electrode, such as etching or plating, the potential of the passive electrode was biased such that the current was no more than \pm 1/500 of that on the working electrode for the duration of the plating process.
Figure 5-3: A Pt/Au interdigitated microelectrode (IME) chip used to measure the current between platinum and gold due to the catalytic decomposition of hydrogen peroxide. Two sizes of chips were used, large and small, the difference being the number and length of electrode fingers. For small chips, $L=3$ mm and $N=25$. For large chips, $L=5$ mm and $N=50$, where $L$ is the length of the electrode fingers, and $N$ is the number of fingers per electrodes. For both types of electrodes used, the width of the electrode fingers, $W$, and the spacing between electrodes, $S$, was 10 $\mu$m.
5.3.2 Activation of PtAu IMEs in hydrogen peroxide

Because the catalytic activity of platinum was difficult to control and reproduce, the resulting platinum/gold IMEs were cleaned and activated by soaking the electrode fingers in 6% H₂O₂ for approximately 45 minutes. The electrocatalytic activity of the PtAu was monitored amperometrically for the duration of the activation process (Figure 5-5). This generally resulted in a catalytic activity that was relatively stable, as
demonstrated by a subsequent chronoamperogram of the same PtAu IME in the presence of 6% H₂O₂ (Figure 5-6)

Figure 5-5: Representative activation chronoamperogram demonstrating how the electrocatalytic activity of PtAu interdigitated microelectrodes (IME30) in contact with 6% hydrogen peroxide changes over time.
5.3.3 Amperometry of PtAu IMEs in Hydrogen Peroxide

The platinum electrode was then short-circuited to the gold electrode through an ammeter (Keithley 2487 Picoammeter). After the addition of aqueous H$_2$O$_2$ solutions to the IME surface, such that all exposed fingers were covered by solution, I observed a steady-state current density between the Pt and Au electrodes that varied with H$_2$O$_2$ concentration (Table 5-1). The observed current densities for 0.6 and 6% H$_2$O$_2$, concentrations comparable to those required to move PtAu rods, were 0.12 and 0.68 A/m$^2$ respectively, considerably higher than the short circuit current in deionized (DI) water.

Figure 5-6: Subsequent chronoamperogram of a PtAu interdigitated microelectrode (IME30) in contact with 6% H$_2$O$_2$ demonstrating the steady state current achieved following the activation procedure.
(18.2 MΩ·cm) and 0.18 M sodium nitrate (NaNO₃). Because of the nobility of both platinum and gold, I considered that current due to corrosion of these materials in H₂O₂ is negligible, and attributed the observed current to the spontaneous electrochemical decomposition of H₂O₂ that involved both the platinum and the gold electrode surfaces. Furthermore, the direction of current was consistent with the oxidation of H₂O₂ on the platinum electrode, and the corresponding reduction of H₂O₂ on gold.

Finally, although the measured current density between a platinum and gold electrode had a relative standard deviation of 17% between experiments, this variability did not significantly depend on solution conductivity, which was tuned by changing the electrolyte concentration (Table 5-2).

Table 5-1: Current vs. H₂O₂ concentration on a large Pt plated/Au IME (50 fingers per electrode; each finger is 5 mm long and 10 µm wide).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[H₂O₂] (M)</th>
<th>Current density (A/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6% H₂O₂</td>
<td>1.8</td>
<td>0.68</td>
</tr>
<tr>
<td>0.6% H₂O₂</td>
<td>0.18</td>
<td>0.12</td>
</tr>
<tr>
<td>0.06% H₂O₂</td>
<td>0.018</td>
<td>0.017</td>
</tr>
<tr>
<td>0.006% H₂O₂</td>
<td>0.0018</td>
<td>0.0011</td>
</tr>
<tr>
<td>0.0006% H₂O₂</td>
<td>0.00018</td>
<td>0.000080</td>
</tr>
<tr>
<td>D.I.</td>
<td>-</td>
<td>0.000033</td>
</tr>
<tr>
<td>0.18 M NaNO₃</td>
<td>-</td>
<td>0.000041</td>
</tr>
</tbody>
</table>
5.4 Catalytically Induced Electrokinetics on PtAu IMEs

5.4.1 Experimental Set-up

The electrokinetic mechanism described above requires an electrical connection between oxidation and reduction sites to induce motion of suspended catalytic particles or pump fluid near an immobilized catalyst surface.[2] While the PtAu rods are always connected (always “on”), a switch wired in series with the IME experiment set-up would enable a catalytically powered pump that could be turned on and off externally. In effect, the catalytically induced electrokinetic flows in the gaps between platinum and gold electrode fingers of an IME would be controlled by switching the electrochemical

<table>
<thead>
<tr>
<th>[NaNO₃] (mol/L)</th>
<th>Conductivity (µS/cm)</th>
<th>Current density (A/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>4.9(0.5)</td>
<td>0.52</td>
</tr>
<tr>
<td>3.9 × 10⁻⁵</td>
<td>9.4(0.5)</td>
<td>0.44</td>
</tr>
<tr>
<td>1.5 × 10⁻⁴</td>
<td>20.8(0.5)</td>
<td>0.60</td>
</tr>
<tr>
<td>3.9 × 10⁻⁴</td>
<td>42.9(0.5)</td>
<td>0.45</td>
</tr>
<tr>
<td>7.6 × 10⁻⁴</td>
<td>82.7(0.8)</td>
<td>0.38</td>
</tr>
<tr>
<td>3.8 × 10⁻³</td>
<td>321(3)</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 5-2: Current density due to platinum catalyzed decomposition of 10% H₂O₂ (w/w) vs. electrolyte concentration on a small Au_plate/Pt IME (25 fingers per electrode; each finger is 3 mm long and 10 µm wide).
decomposition off and on. The switch does not affect the rate of non-electrochemical H₂O₂ decomposition occurring at the Pt electrode. This experiment thus allows us to measure the correlation between movement and both chemical and electrochemical H₂O₂ decomposition reactions.

To observe fluid movement, I suspended micron sized tracer particles, such as 2 μm long gold rods (370 nm in diameter; prepared by electrodeposition in templates), 1 μm diameter polystyrene (PS) spheres (Polysciences), or 1 μm diameter carboxylsulfate (CS) polystyrene spheres (Polysciences) in H₂O₂ solutions. These suspensions were deposited onto a platinum/gold IME and the behavior of the tracers was monitored and recorded using a Zeiss Axiovert 200 reflectance/transmission microscope equipped with a digital video camera connected to a PC. A switch was wired in series with the electrochemical set-up such that I could toggle the electrochemical decomposition pathway on and off. Furthermore, the ammeter was attached to a PC so that I could record current as a function of time, which allowed us to synchronize measured currents to observed particle motion and estimate the magnitude of the catalytically generated electric field from the measured current and the solution conductivity.

5.4.2 Observing Catalytically Induced Electrokinetics

I deposited a suspension containing gold tracer particles and a known concentration of H₂O₂ onto a Pt_plated-Au IME surface, and observed the behavior of particles in the center of the IME, where the electric fields are expected to be symmetric and homogeneous in the electrode plane. The particles settled and diffused randomly (i.e.
Brownian motion) in two dimensions across the electrode surface. Initially, the switch was “off” forcing all H₂O₂ decomposition to occur via pathways other than the bimetallic electrochemical mechanism. When the circuit was turned “on”, allowing the electrochemical process between platinum and gold to occur, the gold tracer particles in the plane of the electrodes migrated away from the platinum and towards the gold electrodes (Figure 5-7). Then, the tracer particles moved up and away from the electrode plane, observed experimentally as particles moving out of focus (approximately 2-5 microns), and back towards the platinum electrodes. Finally, tracers settled back to the electrode plane and began migrating again towards the gold electrodes. Considering only the 1-dimensional motion between the platinum and gold electrodes, the tracer particles seem to shuttle back and forth, as illustrated by the trajectory plot for a tracer particle in Figure 5-8 (see also supporting video). This tracer particle motion is reminiscent of the convection type behavior of gold tracer particles observed by Kline et al.[2] Furthermore, PS and CS spheres (diameter = 1 µm in both cases) move similarly (Table 5-3).
Figure 5-7: Schematic illustrating the motion of gold tracer particles due to catalytically induced electroosmosis (A) and fluid continuity (B and C) on a Pt/Au interdigitated microelectrode (IME) surface when the switch in (D) is closed. Closing the switch in (D) results in electron current through the ammeter, A, electroosmotic fluid pumping, $v_{eo}$, and the corresponding return flow above the IME surface due to fluid continuity.
Figure 5-8: One dimensional trajectory plot vs. time for Au rod tracer on a Au_{plated}/Pt IME in a catalytically generated field demonstrating the cyclical migration between the gold electrode (top) and the platinum electrode (bottom). Pt and Au electrodes are short-circuited through the ammeter starting at t = 8.8 seconds. In the electrode plane, the gold tracer migrates towards the Au electrode, then up (not shown in the 1-D plot) and towards the Pt electrode in the convective return flow above the electrode plane. Tracer speed in the electrode plane was 11 μm/s and the electric field is estimated to be 13 V/cm, based on the measured current density of 0.53 A/m² and solution conductivity (5.6 μS/cm).
5.4.3 Tuning Catalytically Induced Electric Fields

As in the case of the rods, the electrokinetic mechanism predicts that this effect should scale with electric field which can be tuned by changing the current density, $J$, and the solution conductivity, $k$ ($E = J/k$). This experiment was therefore repeated on a Au$_\text{electroplated}$/Pt IME using gold tracers suspended in solutions of varying H$_2$O$_2$ concentrations and of varying conductivity (5.0 to 320 $\mu$S/cm) with the addition of NaNO$_3$. These solutions were deposited on the IME surface and the speed of tracers was measured and compared to the electric field estimated from the current density and the solution conductivity. Because the most reproducible tracer migration occurs in the electrode plane, the speed of the particles was measured only in this plane (not out of focus in the

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Current density (A/m$^2$)</th>
<th>Conductivity ($\mu$S/cm)</th>
<th>Electric field (V/cm)</th>
<th>Speed ($\mu$m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gold rods (2 $\mu$m long)</td>
<td>0.53</td>
<td>4.1(0.5)</td>
<td>13.1</td>
<td>10.8</td>
</tr>
<tr>
<td>polystyrene (PS) (D=1 $\mu$m)</td>
<td>0.55</td>
<td>5.9(0.5)</td>
<td>9.3</td>
<td>5.6</td>
</tr>
<tr>
<td>carboxy-sulfate polystyrene (CS) (D=1 $\mu$m)</td>
<td>0.56</td>
<td>5.6(0.5)</td>
<td>10.0</td>
<td>6.07</td>
</tr>
</tbody>
</table>
convection return flow). For each experiment, the speed of several particles (between 4 and 12) was measured and averaged together, and the resulting average speeds were plotted versus electric field, estimated from the ratio of current density and conductivity (Figure 5-9).

Figure 5-9: Plot of tracer speed on four different Pt/Au IMEs vs. catalytically generated electric field estimated from current density and conductivity. Electric field was tuned by changing hydrogen peroxide concentration (3 to 10%) and solution conductivity with the addition of NaNO₃ (4 to 320 µS/cm). Tracers were 2 µm long gold rods (♦). Included in the plot are the speeds of 1 µm diameter polystyrene spheres (▲), and 1 µm diameter carboxysulfate polystyrene spheres (■).
5.4.4 Electrokinetics on IMEs from Externally Applied Electric Fields

I explored how this pumping effect due to catalytically generated electric fields compared to what is expected from classical electrokinetics by measuring the speed of tracers migrating in a field applied from an external current source. The two electrodes of an as-received Au/Au IME (25 fingers each; 10 µm wide; 3 mm long) were connected through a Keithley 2400 sourcemeter and 25 µL of suspension containing tracer particles (gold rods, PS spheres or CS spheres) were deposited such that all exposed electrode surfaces were covered by the solution. Next, I applied steady state current densities of 0.13, 0.67, and 1.3 A/m² and estimated the applied electric field from the imposed current density and the measured conductivity of the suspensions. I then measured the speed of tracer particles migrating in the plane of the electrode surface and plotted them versus the estimated electric field (Figure 5-10).
The observed tracer particle motion is the same as that observed for tracers migrating in the catalytic experiments described above. Particles speeds were also plotted in Figure 5-10 versus the estimated electric field to compare the results obtained for the catalytically induced motion on IMEs. Interestingly, the motion of negatively charged tracer particles (zeta potentials of gold, PS, and CS particles in DI water were all negative, as verified by Brookhaven Instruments ZetaPALS zeta potential analyzer) is
towards the negative electrode, a surprising result unless electroosmotic fluid flow at the fluid/borosilicate glass interface is considered. This experiment shows that tracer movement in this system occurs primarily through electroosmosis, and that the electrophoretic force pushing the tracers in the opposite direction is relatively weak.

5.5 Discussion

I made two key observations during the course of the above IME experiments. First, an electrical connection between the anode (Pt) and the cathode (Au) was necessary to drive the motion of tracer particles. Secondly, the speed of particle migration was essentially a linear function of the effective electric field estimated from the observed current density and the bulk conductivity of the solution.

This first observation is a significant one because if we compare this surface analog to a suspended PtAu particle (which moves in H₂O₂ solution towards its platinum end), the interfacial tension mechanism predicts gold particles would migrate up the oxygen concentration gradient towards the Pt source to minimize their surface free energy. Instead, gold tracer particles on the IME surface seem to be unaffected by any oxygen concentration gradient originating from the platinum electrode if the platinum is not electrically connected to the gold. However, once the platinum and gold electrodes are short-circuited, a current ensues and gold tracer particles begin to move towards the gold electrode.

For both catalytically generated electric fields and externally applied electric fields, the movement of tracers with a negative zeta potential is in the same direction as
the proton flux. This can be explained by considering the electric field caused by the catalytic reaction and the zeta potentials of the tracer particles and the underlying substrate. In the general case, the velocity of a tracer particle undergoing electrophoresis is the sum of an electrophoretic component (the electric field acting on the particle and its double layer) and an electroosmotic component (the electric field acting on the double layer of the wall) according to the following equation (Eq. 5.1):

\[ U_{obs} = U_{ep} + v_{eo} \]  

5.1

In the limit of thin Debye length, the electroosmotic and electrophoretic components can both be described by the Smoluchowski equation respectively, allowing us to express the observed velocity as (Eq. 5.2):

\[ U_{obs} = \frac{\varepsilon (\zeta_w - \zeta_p) E}{\eta} \]  

5.2

where \( \varepsilon \) is the dielectric permittivity of the solution, \( \eta \) is the solution viscosity, and \( \zeta_w \) and \( \zeta_p \) are the zeta potential of the wall and the tracer particle, respectively. From this, we can see that \( \zeta_w \) and \( \zeta_p \) of the same sign compete and drive motion in opposite directions. It is not hard to imagine a situation where the electroosmosis ultimately determines the direction of the tracer (e.g., if \( |\zeta_w| > |\zeta_p| \)).

In the case of an electric field acting on a particle in the absence of electroosmosis \( (v_{eo} = 0) \), the negative particle would move towards the positive electrode. However, with significant electroosmotic flow, a particle in an electric field will still migrate towards the expected electrode, but it would be migrating in a fluid moving due to electroosmosis.
(either upstream or downstream, depending on the sign). If the surface charge on the wall were much greater than the charge on the particle, the motion of the particle would be driven almost entirely by electroosmosis. Considering this, the observation that negative particles migrate towards the negative electrode in the control experiments is not entirely unexpected, as the speed of a particle undergoing electrophoresis in electroosmotic flow goes as Eq. 5.2. Although the zeta potentials of the negative particles were as low as -60 mV, the zeta potential of the glass separating the electrode fingers is known to be < -100 mV at low salt concentrations (<10⁻⁵ M), such as those present in our experiments.

Finally, as predicted by classical electrokinetics and demonstrated in Figure 5-10, the speed of particle movement was essentially a linear function of the effective electric field estimated from the observed current density and the bulk conductivity of the solution. This observation holds true for the movement of gold tracer particles caused by catalytically generated fields as well as externally applied fields. Although the electric field available from the catalytic reaction did not exceed 14 V/cm, the speed of gold tracer particles driven by externally applied fields followed the same trend up to 28 V/cm.

5.6 Conclusions

I found that in addition to the platinum catalyzed decomposition of H₂O₂, a second electrochemical decomposition pathway involving both platinum and gold also occurs. This electrochemical decomposition involving both metals causes a current
between short-circuited platinum and gold electrodes. By stoichiometry and conservation of charge, an ion flux also occurs in the solution connecting the two electrodes, whether Pt/Au IMEs or PtAu nanorods. The electrochemical ion flux in a solution of known conductivity implies an electric field capable of inducing electrokinetic effects at the solid-liquid interface. On an interdigitated electrode with borosilicate glass separating the electrode fingers, the resulting electrokinetic effect is the electroosmotic fluid pumping between the two electrodes. This can be observed by monitoring the motion of tracer particles. The velocity of the electroosmotic fluid pumping is a function of the electric field, whether catalytically generated or externally applied. For the IMEs, the catalytically generated electric field can be turned on and off by means of a switch, allowing catalytic micropumps that can be externally controlled.

5.7 References


Chapter 6

Conclusion

The results of the experiments described in this thesis indicate that the motion of platinum-gold (PtAu) nanorods is more complex than previously thought. Initially, the motion of PtAu nanorods in hydrogen peroxide described in Chapter 1 was attributed to interfacial tension gradients caused by the oxygen concentration gradient emanating from the catalytic platinum end of the nanorod. However, the interfacial tension model described in Chapter 2 was unable to predict the observations by Kline et al.\cite{1} for the complementary catalytic system immobilized on a surface, which could only be explained by an electrokinetic mechanism. Furthermore, my observations in Chapters 4 and 5 are also strongly suggestive of an electrokinetic mechanism, such as that discussed previously.\cite{2,3} This conclusion is strongly reinforced by a more detailed theoretical model described by Velegol et al.\cite{4} These results do not rule out entirely the role of interfacial tension driven flow described in Chapter 3,\cite{5} viscosity gradients,\cite{6} or product-enhanced slip,\cite{7} but do suggest a dominant effect of catalytically induced electrokinetic phenomena that cannot be neglected.

In addition to exploring the role of catalytically induced electrokinetics for the self-propulsion of catalytic particles, I have also demonstrated in Chapter 6 that the catalytically generated electric fields on Pt/Au interdigitated microelectrodes in the presence of H$_2$O$_2$ can result in electroosmotic fluid pumping between platinum and gold electrode fingers. This allowed me to use the IMEs in effect as catalytic micropumps that
could be turned “on” and “off” by means of an external switch. The motion of these tracer particles is dominated by the 1) electroosmotic fluid flow at the electrode/fluid interface and 2) the convective return flow required by fluid continuity. The magnitude of the fluid flow in the plane of the IME was demonstrated to be a function of the electric field, whether externally applied or catalytically generated.

This work has important implications when considering the development of functional nano- and micromachines powered by catalytic redox reactions. For objects propelled by catalytically induced electrokinetics, the speed is a function of both the conductivity of the surrounding solution and the current density, the latter being limited by the rate and efficiency of the catalytic reaction. As conductivity increases, electrophoretic mobility and the electric field driving the motion of PtAu objects described both decrease, which poses a significant challenge for designing self-electrophoretic motors that can operate in more conductive solutions. This challenge may be addressed by using faster and more efficient enzyme-based catalytic redox systems, such as recently described by Heller and Mano,[8] to increase the magnitude of catalytically generated current densities. However, such motors are not likely to operate efficiently in highly conductive solutions found in biological systems, so other approaches may prove more practical for certain applications. Nature is capable of converting chemical to mechanical energy quite efficiently in highly complex biological matrices using other catalytic processes, such as the polymerization of actin [9],[10] (a process different from the actin/myosin system of biomotors) and hydrolysis of ATP and GTP.[11],[12] These processes may be mimicked using non-biological analogs for use in
functional catalytic motors that could be engineered to interact with individual biological
cells, giving rise to new classes of micro/nanomachines.

6.1 References


Appendix A
Motion Analysis

A.1 Introduction

This dissertation discusses the coupling of catalytic chemical events to mechanical forces that induce the motion suspended particles. This required not only measuring reaction velocities, but also mechanical velocities and trajectories as well. This allowed me to relate the rate of chemical reactions to the observed motion of catalytic particles in a fuel solution. Rather than simply measuring the particle speed (center-to-center displacement per unit time), motion analysis of particle behavior involved measuring other parameters that allowed me to quantitatively distinguish between ubiquitous Brownian motion and directed catalytically driven motion. Two methods of extracting motion analysis data from captured real-time video clips were used. The first involved extracting data from real-time video clips manually using PhysVis, a free motion analysis program available on the World Wide Web written by David M. Cowart and Timothy S. Sulliven from Kenyon College (http://physics.kenyon.edu/coolphys/addeyes/addeyes.htm). The second method involved extracting data automatically using computer programs written by this author and Paul T. Baker, a visiting undergraduate physics major from Reed College. In both cases, it is highly advantageous to start with the highest contrast video possible. This greatly simplifies distinguishing particles from the background. This appendix addresses the
procedures and the “tricks” used to extract data for motion analysis using these two methods.

A.2 Method 1: Manual Particle Tracking with Physvis

The first method is very tedious and time consuming, but is also quite straightforward and allows for efficiently checking the reasonableness of extracted data. In this first approach, a real-time video clip is opened using PhysVis v.1.4.1 (available at the time of publication from http://physics.kenyon.edu/coolphys/addeyes/addeyes.htm):

1. Open PhysVis

2. Click “File”, then “Open”, then select the path and filename for the video you want to analyze.

3. Calibrate the video frame by clicking on two ends of an object of known dimensions. For video microscopy, the best reference distances are the dimensions of a video frame which can be measured using a calibrated microscope.

4. Click “Take Data” button

5. Click on a point of interest and PhysVis records:
   - time
   - world x value (according to calibration)
   - world y value (according to calibration)
   - world radius (distance from origin according to calibration)
   - theta (angle from calibrated y-axis direction)
   - frame number
- pixel intensity
- x pixel value (uncalibrated)
- y pixel value (uncalibrated)
- pixel radius (pixel distance from origin; uncalibrated)

6. When data collection is complete, click “Store”. PhysVis will only allow collecting 2 pieces of data per “Store” function. However, you may “Store” as many times as you like with the same data set (i.e., if you need to record world x value, world y value, and time, then you will need to “Store” twice. Once to store x and y values, and once to store time).

For the motion analysis of suspended rods, I recorded the Cartesian coordinates of the head \((x_h, y_h)\) and tail \((x_t, y_t)\) of a particle over a given time interval, \(\tau\) (typically every 0.1 seconds for 5 seconds). This data was exported manually by cutting and pasting the data from data files saved from PhysVis into an Excel spreadsheet I developed to calculate a number of useful parameters. The following is a list of these parameters, and the Excel spreadsheet formulas used to calculate them:

1. particle center of volume \((X, Y)\):
   \[
   (X, Y) = (\text{AVERAGE}(x_h, x_t), \text{AVERAGE}(y_h, y_t))
   \]

2. particle length \((L)\):
   \[
   L = \text{SQRT}((A3-E3)^2+(B3-F3)^2)
   \]

3. particle orientation \((\theta)\):
   \[
   \theta = \text{ATAN2}((x_h-x_t)/L)
   \]

4. center-to-center displacement \((d)\):
   \[
   d = \text{SQRT}((J4-J3)^2+(K4-K3)^2)
   \]
4. instantaneous particle speed (speed):

\[ \text{speed} = \frac{d}{\tau} \]

5. instantaneous direction of motion (\( \phi \)):

\[ \phi = \text{ATAN2}((X_{\text{frame,b}} - X_{\text{frame,b-1}})/d) \]

6. instantaneous directionality (directionality, correlation between \( \theta \) and \( \phi \)):

\[ \text{directionality} = \text{COS}(\theta - \phi) \]

7. instantaneous axial velocity (\( v_z \)):

\[ v_z = \text{speed} \times \text{directionality} \]

8. 2-D translational diffusion coefficient (\( D_{\text{trans}} \), \( d^2 \) per unit time):

\[ D_{\text{trans}} = \frac{d^2}{\tau} \]

9. 2-D rotational diffusion coefficient (\( D_{\text{rot}} \), \( \theta^2 \) per unit time):

\[ D_{\text{rot}} = \frac{\theta^2}{\tau} \]

Each of the above parameters measured manually using Physvis can also be averaged over time. This is extremely useful for obtaining reliable data and statistics. One of the great advantages of this method is that individual particles can be analyzed and the reasonableness of the measured parameters can be assessed by comparing the quantitative data extracted into the Excel spreadsheet. However, this method is also extremely tedious, taking as long as 1 hour to obtain reliable data for a single particle. Because reliable statistics depend heavily on the amount of data used to obtain those statistics, several particles would need to be tracked, and it would take as long as a week to analyze a single video.
A.3 Method 2: Automatic Particle Tracking with MATLAB

To aid in extracting the necessary motion analysis parameters from captured video clips, I wrote two major programs using MATLAB (MathWorks), a commercial software package that is extremely useful for creating, manipulating, and analyzing matrices. In addition to the base program, there are a number of commercially available toolboxes that facilitate the use of MATLAB with digital images and videos. Furthermore, MATLAB can be used as a very versatile programming language that can greatly simplify performing complex and routine operations to extract measurable motion parameters from captured video clips.

Both of the programs written use the same principles described above, and some of the same equations to calculate the measurable motion analysis parameters. These programs depend on the ability of MATLAB to distinguish between objects of interest and the video frame background, so high contrast videos are required to obtain reliable data. High contrast videos of colloidal particles, such as the PtAu rods discussed in this thesis, are most easily obtained by transmission (rather than reflectance) optical microscopy. These programs also depend on the ability to identify objects in one captured video frame and a subsequent frame as the same objects. The first of these programs follows individual particles according to some user defined variables, and then reports the particle speed and standard deviation.
A.3.1 Importing Videos for Analysis

Before videos can be analyzed with MATLAB, they must first be imported. This is the program I wrote, building on a program previously written by Brent Mantooth, to import AVI files into MATLAB so that they can be prepared for analysis by MATLAB. Only AVI files can be used with this program. Commented program code follows:

```matlab
% usage: mov = wloadtiffs2()

% this m file will load a sequence of image files and concatenate them into a movie matrix.

% configured to read non square images

% see function jgetframe for square images

% see function jgetimage for non square images

% auth: Brent Mantooth

% P. Weiss Lab, Penn State Univ. Dept. of Chemistry

% Sep 5, 2003

% Modified by Wally Paxton

% Jan 21, 2003

function mov = wloadtiffs()

prefix=input('Filename prefix (ex Comp1): ','s');
```
start=input('First File Number: ');
last=input('Last File Number: ');
interval=input('Frame interval: ');
extension=input('Extension: ', 's');

for i = start:interval:last
    filename = sprintf('%s%d.%s', prefix, i, extension); % the number d can either be padded with zeros (%03d to pad with 3 zeros) or not (as in this case).
    a = imread(filename);
    a = rgb2gray(a);
    %a = a(1:1024,1:1024);
    a = uint8(a);
    %a = imresize(a,.5,'bicubic');
    if(mod(i,5)==0)
        disp(sprintf('Reading image %d of %d', i-start+1, last-start+1));
    end
    if(i == start);
        mov = a;
    else
        mov = cat(1,mov,a);
    end
end
A.3.2 Preparing Videos for Analysis

After importing the video frames from an AVI file, the video must be prepared for analysis. This means that the color or gray scale video must be converted into a binary video, where objects are easily distinguished from background. This involves setting a pixel intensity threshold. All pixels with an intensity higher than the threshold becomes a 1 (object), and anything below that threshold becomes a 0 (background). Ideally, the video starts with a high contrast between objects and background before analysis with MATLAB, so it is to the user’s advantage to spend time optimizing video contrast when the videos are captured.

The following short program prepares a video imported into MATLAB with wloadtiffs2 for analysis by converting it into a binary video. Commented program code follows:

```matlab
function mov_bw_clean_dilate = wmovprep(mov,threshold);

% This m-file will convert a catenated movie matrix (imported with
% wloadtiffs) to a movie matrix ready for motion analysis with
% wtrackobjects. It will turn grayscale image to bw with a user defined
% threshold. Then it cleans isolated pixels. Finally, it dilates individual
% objects to simplify analysis with 'wtrackobjects'.

% mov is the catenated movie matrix file
```
% 'threshold' is the pixel threshold from 0 to 255

mov_bw = im2bw(mov,(threshold/255));

mov_bw_clean = bwmorph(mov_bw,'clean');

% mov_bw_clean_dilate = imdilate(mov_bw_clean,strel('disk',1)); % This line will
dilate objects 1 pixel all the way around. For %small objects.

A.3.3 Automatic Tracking of Individual Particles

After importing and preparing the video for analysis, the binary video can then be
analyzed using either wtrackobj2 (below) or ptrackobj2 (A.3.4). Commented program
code follows:

% Tracking one object for several frames
% Wally Paxton, Nov 11, 2003
%
% [traj dist]=wtrackobj2(mov,szy,num_frames,frame_advance)
% 'mov' is binary movie file which has been cleaned and dilated
% 'szy' is image height per image in pixels (usually 240)
% 'num_frames' is the number of frames you want to analyze
% 'frame_advance' specifies how often data is sampled

function [traj,dist]= wtrackobj2(mov,szy,num_frames,frame_advance)

[I1_label num_1]=bwlabel((jgetimage(mov,szy,1)),4);                     %identifies objects in
first frame with X x X resolution
imview(I1_label);
o=input('Which object would you like to track? ');

I1_label(I1_label==o)=o+100;
o=o+100;

for i=1:frame_advance:num_frames-1;       % Will track object 'o' skipping 'frame_advance' frames for n-1 frames
  if(i==1)                                % If 'i' is one, then the current image is the first frame
    current=jgetimage(mov,szy,1);       % and the 'current_label' frame is also I1_label
    current_label=I1_label;
    F2_o_max=1;
  else                                    % Otherwise, the current frame is the 'next' from the previous run
    current=next;                       % and the current_label is the 'next_label' from the previous run
    current_label=next_label;
  end

if F2_o_max>0;
  next=jgetimage(mov,szy,i+1);
  [next_label num_2]=bwlabel((next), 4); % labels next frame

  % This sub-routine will correlate labels from current frame to next frame
current_data=regionprops(current_label, 'basic');

current_o_box=round(current_data(o).BoundingBox);

F1_o_box_y=current_o_box(2);
F1_o_box_x=current_o_box(1);
F1_o_box_cy=current_o_box(4);
F1_o_box_cx=current_o_box(3);
F1_o_num=(current_label(F1_o_box_y:(F1_o_box_cy+F1_o_box_y-1),...  
    F1_o_box_x:(F1_o_box_cx+F1_o_box_x-1)));  % F1_o_num is the label  
    of the object in the bounded box, frame 1

F2_o_num=(next_label(F1_o_box_y:(F1_o_box_cy+F1_o_box_y-1),...  
    F1_o_box_x:(F1_o_box_cx+F1_o_box_x-1)));  % F2_o_num is the  
    label of the object in the bounded box, frame 2

F1_o_max=max(F1_o_num);  % Finds column max for each column in  
F1(2) o_num
F1_o_max=max(F1_o_max');  % Finds max of column max in F1(2) o_max
F2_o_max=max(F2_o_num);
F2_o_max=max(F2_o_max');

if F2_o_max>0;

    next_label(next_label==(F2_o_max))=o;

current_label(current_label==(o))=o;

current_label_track=zeros(size(current_label));

current_label_track(current_label<100)=1; % This makes a color-coded frame based on label

figure(1),imshow(current_label_track); % This displays the labeled frame in figure(1)

title(i);

current_props=regionprops(current_label, 'basic');

next_props=regionprops(next_label, 'basic');

centroid1=current_props(o).Centroid;

centroid2=next_props(o).Centroid;

distance=((centroid1(1)-centroid2(1))^2+(centroid1(2)-centroid2(2))^2)^.5;

if (i==1)
    traj=[(current_props(o).Centroid); (next_props(o).Centroid)];
    dist=distance;
    count=1
else
    traj=cat(1,traj,(next_props(o).Centroid));
    dist=cat(1,dist,distance);
end

% disp(sprintf('Processing frame %d ...',i));

count=count+1;
else
    continue
end

else
    continue
end

end

if count<num_frames-1
    disp(sprintf('Lost object at frame %d.',(count-1)*frame_advance));
else
end

disp(sprintf('Processed %d of %d frames.',(count-1),round(num_frames/frame_advance)));

speed_ave=((mean(dist))/(frame_advance/30))*0.39; % returns average particle speed in microns per second

speed_stdev=((std(dist))/(frame_advance/30))*0.39;

disp(sprintf('Average Speed: %4.2f(%.2f)',speed_ave,speed_stdev));
A.3.4 Automatic Tracking of Particle Ensembles

The second of these MATLAB based programs incorporated the code used to track individual particles, but tracked any number of particles chosen by the user. Comented program code follows:

```
function [infoOut,varargout] = ptrackobj2(mov,numFrames,frameInterval,varargin);

% tracks several user specified objects simultaneously for several frames
% accounts for directionality of rods in addition to finding velocities
%
% Usages: infoOut = ptrackobj2(mov,numFrames,frameInterval)
% [infoOut rawData] = ptrackobj2(mov,numFrames,frameInterval)
% [...] = ptrackobj2(mov,numFrames,frameInterval,pixelSize)
%
% where 'mov' is a movie file loaded and prepared with WLOADTIFFS and
% WMOVPREP respectivley, 'numFrames' is the number of frames to be analyzed,
% 'frameInterval' is the frame interval of the analyzed movie. Optional
% fourth input, 'pixelSize', is the width of one pixel in microns in the video.
% Defaults to 0.39.
%
% 'infoOut' is a 8xn matrix, the columns hold the average speeds,
% the standard deviations in the speeds, the average directionality, the
% standard deviations in the directionality, the average axial velocity the diffusion
```
% coefficients, the rotational diffusion coefficients and the frame in which the
% object was lost to the tracker. The rows designate each individual object.
% All distances are in microns and times in seconds.
% 'rawData' is a cell array containing the frame by frame distances,
% directionalities, orientations, directions of motion, rotations, distance
% factors, areas, and lengths for each particle.
%
% the one output version uses considerably less memory to run
%
% see PINFOAVE and PEXTRACT for data analysis
%
% authors: Paul Baker & Walter Paxton
% last update: 3 August 2004

warning off MATLAB:divideByZero

if nargout>2
    error('too many outputs');
elseif nargout==0
    error('no output argument specified');
end

% declare variables
% global
global dist
global PIXELSIZE

% constant
FRAMEHEIGHT=240; % frame height in pixels
INTERVAL=(1/30)*frameInterval; % time interval in seconds between two frames
if nargin==4 % pixel width in microns
  PIXELSIZE=varargin{1,1};
else
  PIXELSIZE=.39;
end

% other
[currentLabel numObj]=bwlabel(jgetimage(mov,FRAMEHEIGHT,1));
lost=zeros(numObj,1)+numFrames; % frame object was lost to tracker
speedAve=zeros(numObj,1);
speedStDev=zeros(numObj,1);
directAve=zeros(numObj,1);
directStDev=zeros(numObj,1);
axialAve=zeros(numObj,1);
D=zeros(numObj,1);
Drot=zeros(numObj,1);

dist=zeros(numObj,numFrames-1)-1; % centroid to centroid distance between frames

direct=zeros(numObj,numFrames-1)-2; % directionality

rot=zeros(numObj,numFrames-1); % rotation between frames

distFact=zeros(numObj,numFrames-1); % distance factor

if nargout==2

dir=zeros(numObj,numFrames-1); % direction of centroid motion

orient=zeros(numObj,numFrames-1); % object orientation

area=zeros(numObj,numFrames-1);

oldOrient=0;

else

oldOrient=zeros(numObj,1);

end

nextProps=struct([]);

check=input('Would you like to check for major area and speed changes (y/n): ','s');

imview(currentLabel); % get user specifications for which objects to track

objects = input('list objects to track in vector form ([a b c ...], a:b, etc.) or input "0" for all: ');

if (objects==0)

obj=1:numObj;


else
    obj=objects;
end

for a=1:numFrames-1;    % loops tracking process across all frames

    % establishes labels and region properties for frames in use
    if a==1
        currentProps=regionprops(currentLabel, ... 
          'Area','BoundingBox','Centroid','Orientation','MajorAxisLength');
    else
        currentLabel=nextLabel;
        currentProps=nextProps;
    end

nextLabel=bwlabel(jgetimage(mov,FRAMEHEIGHT,a+1));

    for b=obj;    % tracks all objects between 2 frames
        if a<lost(b)

            if currentProps(b).Area<3    % checks size
                lost(b)=a;
            end

        end
    end
continue

elseif currentProps(b).Area>180

    lost(b)=a;

    continue

end

nextObj=findnext(b,currentProps,nextLabel);

if ~(nextObj==0)

    % labels object in next frame the same as in current frame and ensures no
duplicate labels

    if ~(nextLabel(nextLabel==nextObj)==b)

        if isempty(find(nextLabel(nextLabel==b)))==0

            nextLabel(nextLabel==b)=-1;
        end

        nextLabel(nextLabel==nextObj)=b;
        nextLabel(nextLabel==-1)=nextObj;

    end

% establishes region properties for next frame using the new label numbers
nextProps=regionprops(nextLabel, ...

   'Area','BoundingBox','Centroid','Orientation','MajorAxisLength');

% calculates the distance the particle travels between frames

dist(b,a)=((currentProps(b).Centroid(1)-nextProps(b).Centroid(1))^2+ ... 
   (currentProps(b).Centroid(2)-nextProps(b).Centroid(2))^2)^.5*PIXELSIZE;

% checks for major area and speed changes if user specifies

if check=='y'

   bool=checker(a,b,currentProps,nextProps);

   if bool==1

      lost(b)=a;

      dist(b,a)=-1;

      continue

   end

end

% calls directanalysis and assigns rawData values if applicable

if nargout==2

   area(b,a)=currentProps(b).Area;

   length(b,a)=currentProps(b).MajorAxisLength;

   if a>1
oldOrient=orient(b,a-1);
end

[direct(b,a) rot(b,a) orient(b,a)
dir(b,a)]=directanalysis(a,b,currentProps,nextProps,oldOrient);

% influence factor
distFact(b,a)=influence(b,currentLabel,currentProps);
else

[direct(b,a) rot(b,a)
oldOrient(b)]=directanalysis(a,b,currentProps,nextProps,oldOrient(b));
end
else % i.e. if nextObj==0
lost(b)=a;
end
end

% make sure nextProps is nonempty before continuing "for a" loop
if and(b==max(obj),isempty(nextProps)==1)
nextProps=regionprops(nextLabel, ...
'Area','BoundingBox','Centroid','Orientation','MajorAxisLength');
end
end % for b
if lost(obj)<a
    break
end

end  % for a

for b=obj           % calculates particle specific averages for output

if dist(b,:)==-1  % i.e. no data
    speedAve(b)=0;
    speedStDev(b)=0;
    D(b)=0;
    Drot(b)=0;
    dist(b,:)=0;
    direct(b,:)=0;
else
    speedAve(b)=mean(dist(b,find(~(dist(b,:)==-1))))/INTERVAL;
    speedStDev(b)=std(dist(b,find(~(dist(b,:)==-1))))/INTERVAL;
    directAve(b)=mean(direct(b,find(~(direct(b,:)==-2))));
    directStDev(b)=std(direct(b,find(~(direct(b,:)==-2))));
    dist(b,find(dist(b,:)==-1))=0;
end
direct(b,find(direct(b,:)==-2))=0;
axialAve(b)=sum(direct(b,:).*((dist(b,:)/INTERVAL)))/(lost(b)-1);
D(b)=sum(dist(b,:).*dist(b,:))/(lost(b)-1)/(4*INTERVAL);
Drot(b)=sum(rot(b,:).*rot(b,:))/(lost(b)-1)/(4*INTERVAL);
end

infoOut=cat(2,speedAve,speedStDev,directAve,directStDev,axialAve,D,Drot,lost);

if nargout==2
    varargout={ {dist,direct,orient,dir,rot,distFact,area} };
end

warning on MATLAB:divideByZero

function nextObj=findnext(b,currentProps,nextLabel)

% find object in next frame
nextObj=0;
bound=round(currentProps(b).BoundingBox);

% double box size or expand to limits of frame
if bound(2)-round(.5*bound(4))>0;
    startbox(1)=bound(2)-round(.5*bound(4));
else
    startbox(1)=1;
end

if bound(1)-round(.5*bound(3))>0;
    startbox(2)=bound(1)-round(.5*bound(3));
else
    startbox(2)=1;
end

if (bound(4)*2+startbox(1))-1<size(nextLabel,1);
    endbox(1)=(bound(4)*2+startbox(1))-1;
else
    endbox(1)=size(nextLabel,1);
end

if(bound(3)*2+startbox(2))-1<size(nextLabel,2)
    endbox(2)=(bound(3)*2+startbox(2))-1;
else
    endbox(2)=size(nextLabel,2);
end
else

    endbox(2)=size(nextLabel,2);

end

% tags the region in BoundingBox of next frame

    box=nextLabel(startbox(1):endbox(1),startbox(2):endbox(2));

boxedObj=box(find(~box==0)); % find nonzero elements of box

if isempty(boxedObj)==1

    nextObj=0;

elseif isconst(boxedObj)==1

    nextObj=boxedObj(1);

else % i.e. more than one object in new BoundingBox

    % area comparison

    props=regionprops(nextLabel,'Area');
    cont=getcontents(boxedObj);
    areas=cat(2,props(cont).Area);
    diff=abs(areas-currentProps(b).Area); % compute area differences
    minDiff=cont(find(diff==min(diff))); % identify particles that minimize area difference

    if length(minDiff)==1

        nextObj=minDiff;

    else

        endbox(2)=size(nextLabel,2);

    end
else

    while ~any(nextObj==minDiff)

        [A L]=bwdist(nextLabel);

        nextObj=nextLabel(L(round(currentProps(b).Centroid(1)-
        1)*size(nextLabel,1)+round(currentProps(b).Centroid(2))));

        nextLabel(find(nextLabel==nextObj))=0;

    end

end

end

function [direct, rot, varargout]=directanalysis(a,b,currentProps,nextProps,oldOr)

% computes directional analysis calculations

% convert to radians

or=currentProps(b).Orientation*pi/180;

% assigns -pi<or<pi, assumes that no rotations >pi/2 occur

    if a>1 && abs(or-oldOr)>pi/2 && or>0

        or=or-pi;

    elseif a>1 && abs(or-oldOr)>pi/2 && or<0
or=or+pi;
end

% calculates direction of motion, if no movement assigns default
if currentProps(b).Centroid==nextProps(b).Centroid
dir=or;
else
dir=atan2(currentProps(b).Centroid(2)-nextProps(b).Centroid(2), nextProps(b).Centroid(1)-currentProps(b).Centroid(1));
end

% defaults initial orientation (or) to be in vague direction of motion (dir)
if a==1 && abs(dir-or)>pi/2 && or>0
or=or-pi;
elseif a==1 && abs(dir-or)>pi/2 && or<0
or=or+pi;
end

% maintains continuity across -x axis in dir
if abs(or-dir)>pi && abs(or)>pi/2 && abs(dir)>pi/2 && dir>0
dir=dir-2*pi;
elseif abs(or-dir)>pi && abs(or)>pi/2 && abs(dir)>pi/2 && dir<0
dir=dir+2*pi;
end
% outputs

rot=(currentProps(b).Orientation-nextProps(b).Orientation)*pi/180; % rotation in radians between frames

direct=cos(dir-or); % directionality

if nargout==4
    varargout={or, dir};
else
    varargout={or};
end

function distFact=influence(obj,label,props)

% determines the distance factor for a particular object

global PIXELSIZE

cent=round(props(obj).Centroid);

distFact=0;

distTo=1;

while(distTo*PIXELSIZE<=10)
    label(find(label==obj))=0; % set obj to 0
[D L]=bwdist(label);

distTo=D(size(D,1)*(cent(1)-1)+cent(2)); % identify nearest obj to cent

if distTo*PIXELSIZE<=10

obj=label(L(size(D,1)*(cent(1)-1)+cent(2))); % reassign obj

distFact=distFact+1/(distTo*PIXELSIZE)^3; % calculate distance factor

end

end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%

function bool=checker(a,b,currentProps,nextProps)

% check for major changes in object being tracked

global dist

bool=false;

if nextProps(b).Area>currentProps(b).Area &&
nextProps(b).Area>(currentProps(b).Area*2) % collision

bool=true;

elseif nextProps(b).Area<currentProps(b).Area &&
nextProps(b).Area<(currentProps(b).Area*.5) % breakup

bool=true;

elseif a>1 && abs(dist(b,a)-dist(b,a-1))>1.2 % speed change

bool=true;

end
function output=breakup(input)

    % checks if broken particles are really the same (i.e. just a video problem)
    % not yet implemented
    breakupTolerance=.1;
    inBox=getcontents(boxedObj);    % identify which particles are in 'box'
    area=0;

    for c=inBox             % sums area of all particles in 'box'
        area=area+nextProps(c).Area;
    end

    if and(area*(1+breakupTolerance)>currentProps(b).Area,area*(1-
        breakupTolerance)<currentProps(b).Area)
        for c=inBox    % give separated particles same label
            nextLabel(nextLabel==c)=inBox(1);
        end
        nextObj=inBox(1);
    else    % use BWDIST to choose closest particle to current Centroid
        [A L]=bwdist(nextLabel);
    end
A.4 Conclusions

The manual particle tracking procedure using PhysVis is both good and bad. While it is a very tedious method of obtaining data from captured videos, it is also very straightforward and can be checked quickly and easily for reasonableness. On the other hand, the automatic particle tracking methods made possible with MATLAB generate a lot of data very quickly, but it is more difficult to check the reasonableness of the large volume of data. It is therefore very useful to use both methods in conjunction with one another. The manual particle method can be used to test the reliability of the automatic methods, and both methods can be used together to extract valuable motion analysis data from captured video clips.
Appendix B

AC Impedance Spectroscopy for Conductivity Measurements

B.1 Introduction

One important part of the electrokinetic mechanism is that the velocities of catalytically induced electroosmosis or self-electrophoresis is proportional to the magnitude of the catalytically generated electric field. By Ohm’s law, this electric field is inversely proportional to the solution conductivity. Therefore, in order to correctly estimate the electric fields responsible for the observed catalytically induced electrokinetic effects, I needed to measure solution conductivities in addition to current densities. Because bulk electrodes that are reused can contaminate reaction solutions prepared freshly for each experiment, and because of the small volumes of these reaction solutions, I developed a method of measuring the conductivity of small volumes (less than 25 mL) that would not contaminate reaction solutions. This method was based on the AC impedance spectroscopy of aqueous solutions,[1],[2],[3] and has been used as the basis for conductometric microsensors, such as those used to detect *e. coli* and other bacteria[4] and for measuring the conductivity of conducting polymers.

B.2 AC Impedance Background

The impedance of a circuit with both resistive and capacitive components (RC circuit), such as those found in electrochemical cells, can be probed using a low
oscillating voltage that typically varies from $10^6$ to 1 Hz. The current in the circuit is monitored and compared to the driving alternating voltage. For an RC circuit, the frequency of the observed current and the driving voltage are the same, but the current maximum in each period lags behind the voltage maximum by a phase angle, $\phi$.

The impedance response of the electrical circuit is measured as a function of frequency, and the total impedance, $Z$, for an electrical circuit at any given frequency is related to the circuit resistance, $R$, and the capacitative reactance, $X_c$, (equivalent resistance due to capacitance) of the equivalent circuit through Eq. B.1:

$$|Z|^2 = R^2 + X_c^2$$ \hspace{1cm} B.1

Furthermore, the phase angle between the current and voltage maximums is related to the capacitative reactance and the resistance of the equivalent circuit though Eq. B.2:

$$\tan \phi = \frac{X_c}{R}$$ \hspace{1cm} B.2

The impedance of an ideal resistor is frequency independent, but the capacitative reactance of an ideal capacitor is a function of frequency according to Eq. B.3:

$$X_c = \frac{1}{2\pi f C}$$ \hspace{1cm} B.3

where $f$ is the frequency of the AC signal and $C$ is the capacitance of the equivalent circuit.

For the conductivity sensors described in this appendix, the equivalent circuit is given in Figure B-1. A Bode plot (named for mathematician Hendrik Wade Bode) of the impedance for this equivalent circuit versus frequency is given in Figure B-2, using $C_{DL-1,2} = 5 \times 10^{-9}$ F, $R_{solution} = 3500$ $\Omega$, and $C_{cell} = 3 \times 10^{-11}$ F and demonstrating three different
regions of impedance. Below $10^4$ Hz, impedance is primarily capacitive due to the charging/discharging of the electrical double at the electrode surface. Between $10^4$ and $10^5$ Hz, the impedance levels off indicating the observed impedance is primarily due to the frequency-independent solution resistance. At frequencies higher than $10^5$ Hz, the impedance of the cell is affected by the cell capacitance in parallel with the series consisting of the double layer capacitances and the solution resistance, resulting in a decrease in impedance at the highest frequencies.

Figure B-1: Equivalent circuit for an interdigitated microelectrode conductivity sensor based on AC impedance spectroscopy. $R_{\text{solution}}$ is the solution resistance and $C_{\text{cell}}$ is the capacitance of the cell. $C_{DL-1}$ and $C_{DL-2}$ are the capacitances of the electric double layer for the electrodes in contact with the solution. (~) is the signal generator and $i$ is the current sensor, both part of the AC impedance instrumentation (CHI660A, CH Instruments).
B.3 Conductivity Sensors Based on AC Impedance

A conductivity sensor based on AC impedance methods was devised to measure the conductivity of very small samples of reaction mixtures. The purpose of this sensor was to minimize the amount of reaction mixture that would need to be prepared and to allow a way of measuring conductivity that did not require putting conductivity probes into the small volumes of reaction mixture, a procedure that could contaminate the sample with residual ions on the probes and dramatically affect the conductivity of very low electrolyte solutions. The conductivity sensor consisted of a gold interdigitated microelectrode (IME) with two electrodes each consisting of 50 electrode fingers that
were 5 mm long and 20 µm wide with a 20 µm gap between electrode fingers. The two
electrodes of the IME were connected to an electrochemical workstation (CHI660A, CH
Instruments). The reference and counter electrode leads from the instrument were both
connected to one of the electrodes on the gold IME. The working electrode lead was
connected to the second electrode of the IME. A 25 mL sample of aqueous solution was
deposited onto the IME such that all of the electrode fingers were covered. The solution
impedance was scanned by applying an alternating current with peak voltages of 0.5 volts
at a frequency starting at 10^6 Hz and decreasing to 1 Hz. A representative Bode plot is
given in Figure B-3, indicating the minimum phase angle and the corresponding
frequency. This frequency was used to determine the impedance that was due primarily to
the solution resistance, \( R_{\text{solution}} \). Because some of the impedance at this frequency is due
in part to a small capacitive component, the exact impedance due to solution resistance
and capacitance of the electrical double layer was calculated from the measured
impedance and the phase angle using Eq. B.4, obtained by combining Eq. B.1 and
Eq. B.2.

\[
R_{\text{solution}} = \frac{Z^2}{\sqrt{1 + (\tan \phi)^2}}. \tag{B.4}
\]
Figure B-3: Bode plot of deionized water on the interdigitated array microelectrode conductivity sensor. From this plot, the minimum phase angle indicates the frequency where the impedance is dominated by the solution resistance, $R_{solution}$, (lower plot) and the impedance at that frequency (upper plot).
B.4 Calibration Curve

A calibration curve for the conductivity sensor was generated by observing the frequency response of the impedance for standard solutions of varying known conductivity. From the resulting Bode plots, I noted the minimum phase angle, the frequency where the minimum phase angle was observed, and the impedance measured at this frequency. This was repeated for five conductivity standards: 1.30, 5.00, 10.00, 20.00, and 50.00 µS/cm. I measured the solution resistance for each solution twice, and then I compared the measured conductance \(1/R_{solution}\) to the standard conductivity value for each solution (Table B-1). The resulting calibration curve is shown in Figure B-4, and linear regression analysis indicated that the bulk conductivity, \(k\) in µS/cm, scaled with the observed conductance, \(y\) in µS, according to Eq. B.5:

\[
    k = \frac{y - 2.993}{7.33}.
\]
Table B-1: Measured solution conductance and conductivity for the conductivity standard solutions at 23 °C. Because the conductivity varies with temperature, the bulk conductivities were calculated from the standard conductivities and the temperature coefficient listed on the bottles of the conductivity standards.

<table>
<thead>
<tr>
<th>Conductivity standard</th>
<th>Bulk conductivity (µS/cm)</th>
<th>Conductance (µS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.30 µS/cm</td>
<td>1.24</td>
<td>11.13</td>
</tr>
<tr>
<td></td>
<td>1.24</td>
<td>11.16</td>
</tr>
<tr>
<td>5.00 µS/cm</td>
<td>4.79</td>
<td>39.03</td>
</tr>
<tr>
<td></td>
<td>4.79</td>
<td>39.68</td>
</tr>
<tr>
<td>10 µS/cm</td>
<td>9.59</td>
<td>76.46</td>
</tr>
<tr>
<td></td>
<td>9.59</td>
<td>75.95</td>
</tr>
<tr>
<td>20 µS/cm</td>
<td>19.22</td>
<td>138.8</td>
</tr>
<tr>
<td></td>
<td>19.22</td>
<td>140.3</td>
</tr>
<tr>
<td>50 µS/cm</td>
<td>48.05</td>
<td>356.9</td>
</tr>
<tr>
<td></td>
<td>48.05</td>
<td>355.4</td>
</tr>
</tbody>
</table>

Figure B-4: Calibration curve for conductivity standards at 23 °C.
In addition to measuring solution conductivity by AC impedance, I was also able to use Eq. B.1 and the value of \( R_{\text{solution}} \) obtained from Eq. B.4 to determine the capacitance of the electrical double layer, and found it to be on the order of \( 10^{-6} \text{ F/cm}^2 \), which is comparable to what is expected for electrical double layer capacity.[5]

**B.5 References**


VITA

Walter F. Paxton

In 1998, Walter F. Paxton received an AAS degree from Ricks College in Rexburg, ID (now BYU-Idaho) and graduated from Brigham Young University with a B.S. in Chemistry in 2001. He began his research exploring the copper-based polymerization of acrylates, and later became interested in catalytic motors and electrokinetic phenomena. In 2005, he received the American Chemical Society Inorganic Chemistry Young Investigator Award in Nanoscience for his work on catalytic nanomotors.