## CATALYTIC NANOMOTORS: FABRICATION BY DYNAMIC SHADOWING GROWTH, PROPULSION MECHANISM, AND MOTION CHARACTERIZATION

by

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(Under the Direction of Yiping Zhao)

## ABSTRACT

Autonomous catalytic nanomotors with nanometer-to-micrometer dimensions convert chemical energy into mechanical energy via a catalyzed chemical reaction. They represent an emerging nanotechnology field and promise important technological advances in drug delivery, disease treatment, transport, assembly, and other applications at the nano-scale. This dissertation focuses upon the fabrication of catalytic nanomotors using dynamic shadowing growth, motion characterization, motion engineering, and understanding the propulsion mechanism. Unique nanomotor structures were fabricated using dynamic shadowing growth, and novel swimming behaviors are presented and analyzed.

Two different major propulsion mechanisms are responsible for catalytic nanomotor movement: bubble propulsion and self-electrophoresis. For catalyst-coated insulator backbone nanomotors, a bubble propulsion model is proposed. The driving force depends upon the fluid surface tension and the concentration of H<sub>2</sub>O<sub>2</sub>, and the model predictions are supported by the data. A torsion balance directly measures the driving force. The force is  $10^{-14} - 10^{-13}N$  per nanomotor and has a linear H<sub>2</sub>O<sub>2</sub> concentration dependence with a slope of  $4.82 \times 10^{-14}$  N per percentage of H<sub>2</sub>O<sub>2</sub>. Asymmetric Pt/Au catalytic micromotors were fabricated also, and the exposed Au surface area *A* is changed systematically to alter the speed given by  $u \propto A^{3/2}$ .

Swimming behaviors are altered by designing various geometrical shapes; dynamic shadowing growth allows for a wide range of shapes and sizes. Various swimming behaviors are exhibited by altering the geometry, and/or changing the location of the Pt catalyst. Multi-component rotational nanomotors consisting of Pt coated TiO<sub>2</sub> nanoarms grown upon ~ 2.01  $\mu$ m diameter silica microbeads are fabricated. The structures rotate at a rate of 0.15 Hz per % H<sub>2</sub>O<sub>2</sub> concentration. Tadpole-shaped nanomotors with Pt coated on the microbeads swim in circular trajectories. The swimming trajectories are fine-tuned by altering the arm length, and simulations based on the method of regularized Stokeslets, provided by the University of Illinois Urbana-Champaign, correctly capture the experimental trends.

The formation of nanomotor systems by the self-assembly of two or three nanomotors together is presented. These systems are more complex than previously studied ones, and we show examples of 2-nanomotor spinning clusters, helicopter nanomotors with multiple parts, and V-shaped spinning nanomotors that are assembled using ferromagnetic materials to couple the spinners to microbeads.

INDEX WORDS: Nanomotor, Catalysis, Dynamic Shadowing Growth, Nanorod, Microhydrodynamics, Self-Electrophoresis, Bubble Propulsion, Self-Assembly

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B.S., University of Georgia, Athens, GA 2005

A Dissertation Submitted to the Graduate Faculty of the University of Georgia in Partial Fulfillment of the Requirements for the Degree

## DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2011

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## ACKNOWLEDGEMENTS

First and foremost, I would like to thank my adviser Dr. Yiping Zhao without whom this work would not have been possible.

I would also like to thank Dr. Jason Locklin, Dr. Steven Lewis, Dr. K. K. Mon, and Dr. Leidong Mao for serving on my advisory committee.

I am greatly obliged to my colleagues in the lab for their invaluable support and assistance in my pursuit of my doctorate: Dr. Yongjun Liu, Dr. Wilson Smith, Dr. Yuping He, Mr. Justin Abell, Mr. Manoj Manjare, Mr. George Larsen, and Mr. Nick Fragnito.

ACKNOWL	EDGEMENTS iv
LIST OF TA	BLES
LIST OF FIC	GURES viii
CHAPTER	
1	INTRODUCTION1
	1.1 Natural Biological Motors
	1.2 Hybrid Nanomotors4
	1.3 Artificial Catalytic Nanomotors
	1.4 Artificial Nanomotor Swimming Behaviors10
	1.5 Low Reynolds Number Hydrodynamics16
	1.6 Propulsion Mechanisms
	1.7 Contents of Dissertation
2	FABRICATION OF CATALYTIC NANOMOTORS
	2.1 Template-Mediated Nanomotor Growth28
	2.2 Physical Vapor Deposition
	2.3 Advanced Assemblages
	2.4 Conclusions
3	CATALYTIC NANOMOTOR PROPULSION MECHANISM40
	3.1 Bubble Propulsion Model41
	3.2 Driving Force for a Single Nanomotor48
	3.3 Comparing the Self-Electrophoresis and Bubble Propulsion Models .53
	3.4 Conclusions
4	TUNING NANOMOTOR MOTION BY GEOMETRIC ENGINEERING61
	4.1 Rotary Multi-Component Nanomotors61
	4.2 Tadpole-Shaped Nanomotors70
	4.3 Conclusions
5	SELF-ASSEMBLED NANOMOTOR SYSTEMS
	5.1 Spinning Clusters

# TABLE OF CONTENTS

5.2 Randomly Self-Organized "Helicopter" Nanomotor Systems	95
5.3 Magnetic Self-Organized "Helicopter" Nanomotor Systems	97
5.4 Flexible Joint Swimmer1	00
5.6 Conclusions1	03
6 CONCLUSIONS AND FUTURE WORK1	04
REFERENCES1	06

# LIST OF TABLES

	Page
Table 1.1 Current density reading for various H <sub>2</sub> O <sub>2</sub> concentrations	

## LIST OF FIGURES

Page
Figure 1.1 Schematic of the constituent parts of a bacterial flagellum: an example of a naturally
occurring biological nanomotor
Figure 1.2 (a) Over a 38 s. interval, actin filaments migrate across the myosin-immobilized
surface; (b) filament velocity vs. ATP concentration; speed initially increases with
ATP concentration and eventually plateaus around 200 µM5
Figure 1.3 Left column: fluorescent rotamine-actin comet tail for a directional bead and a
stationary bead; middle column: micrograph of the two beads; right column: bead
positions superimposed on fluorescent images (bar = $5 \mu m$ )
Figure 1.4 (a) & (c) Ni nanorod rotors; (b) $F_1$ -ATPase biomolecular motor; (d) schematic of the
combined architecture
Figure 1.5 Number of publications for nanomotor research during the years of 1995-2009. The
inset graph shows chemically powered catalytic nanomotor research
Figure 1.6 Oxidation of hydrogen peroxide leading to propulsion of the Au/Pt nanorod
nanomotor toward the Pt catalyst, an effect of self-electrophoresis
Figure 1.7 (a) Fast rotary tri-metallic nanomotor; (b) TiO2 rotary nanomotor 10
Figure 1.8 (a) trajectories for Janus sphere particles in $H_2O_2$ solutions; (b) 10% w/v Janus sphere
trajectory and mean square displacement vs. time
Figure 1.9 (a) and (b) Swimming trajectories of Pt and CNT/Pt anode nanomotor respectively;
(c) speed distribution for the two nanomotors
Figure 1.10 (a) SEM of striped Pt/Au/Ni nanorod nanomotor; (b) "PSU" spelled out with
nanomotor trajectories controlled by magnetic field

Figure 1.11 Speed vs. time for nanomotors at temperatures (a), (b), and (c) of $40^{\circ}$ C, $48^{\circ}$ C, and					
58° C, respectively. The inset shows the speed averages vs. temperature					
Figure 1.12 SEM of an artificial bacterial flagellum propelled by an external magnetic field 18					
Figure 1.13 A schematic of the diffusiophoresis model in which a sphere with a single point					
catalyst site generates a concentration gradient of reaction products, driving the					
sphere away from this location					
Figure 1.14 Autonomous swimming plates that have alternating hydrophilic-hydrophobic sides					
which induce self-assembly. The Pt coated on one side drives the plates across the					
aqueous solution of $H_2O_2$ by bubble impulse					
Figure 1.15 Micrograph images of a jet of nanobubbles coming from a spinning Au/Ni nanorod					
nanomotor					
Figure 1.16 Oxygen evolution vs. time for Au/Pt nanomotors in 3.7% H <sub>2</sub> O <sub>2</sub>					
Figure 1.17 Product of surface tension and oxygen evolution vs. speed					
Figure 1.18 Microelectrode current measurement device					
Figure 2.1 Fabrication process of template directed electroplating. First Ag is evaporated onto					
the Al <sub>2</sub> O <sub>3</sub> porous membrane and a Ag is electroplated onto this film; Au and Ag are					
deposited into the pores, then the Ag film and the membrane are dissolved releasing					
the nanorods					
Figure 2.2 Examples of template directed electrodeposition-grown nanomotors: (a) Schematic of					
a Pt/Au striped nanorod nanomotor; (b) Ni/Au nanorotor; micrograph of tubular					
microengines; lithography template rotary gear					
Figure 2.3 SEM image showing a Pt-coated silica microsphere					

- Figure 2.6 (a) Optical micrograph of a partial monolayer of silica microbeads: (b) SEM top view of a similar monolayer after the thick layer of TiO<sub>2</sub> is deposited at an angle of  $\theta \sim 86^{\circ}$

- Figure 2.9 Fabrication of Pt-SiO<sub>2</sub> self-propelled dimers. First a monolayer of SiO<sub>2</sub> microbeads is placed onto a substrate; then a Cr adhesion layer is deposited followed by Pt; lastly, the structures are annealed at 900 °C and then suspended into water by sonication .. 38

Figure 3.4 SEM top view (a), cross-sectional view (b), and TEM (c) images of Si/Pt nanorods. 51

- Figure 4.1 (a) 2.01  $\mu$ m diameter silica microbeads forming a closely-packed monolayer; (b) TiO<sub>2</sub> (~6  $\mu$ m) is first deposited onto the microbeads at an angle  $\theta = 86^{\circ}$ ; (c) the substrate

is rotated to	$\theta = 0^{\circ}$	and a thin	layer (~1	50 nm)	of Pt is	deposited	l in an	asymme	etrical
manner; (d)	SEM in	nage of the	resulting	structu	re				62

- Figure 4.3 (a) Center of mass trajectories for single multi-component nanomotors in various
   H<sub>2</sub>O<sub>2</sub> concentrations; (b) orbital speed for the same structures. The curve is a best-fit for a Langmuir Isotherm.

Figure 4.4 Free body diagram showing directions of the driving force and viscous drag force. . 67

- Figure 4.7 Scanning electron micrographs with arms of various lengths: (a) 0 μm; (b) 1.25 μm;
  (c) 2.5 μm; (d) 3.75 μm; (e) 5 μm; (f) 6.25 μm; (g) arm length vs. QCM reading.....72
- Figure 4.8 Typical nanomotor geometry used in the simulations, corresponding to an arm length of 3.5 μm (axes labels are in microns). A nanomotor is modeled as a sphere connected to a section of an ellipsoid representing the arm. Sections of different lengths are removed from the free end of the ellipsoid to match experimental conditions. The

- Figure 4.12 Experimental (black symbol  $\Box$ ) vs. simulational (red symbol  $\Delta$ ) data for speed vs. curvature  $\kappa$ . For the experiment, there exists a roughly linear increase of curvature with respect to speed (the speed is increased by increasing the concentration of H<sub>2</sub>O<sub>2</sub>).

- Figure 5.3 (a) A schematic of the helicopter-shaped multi-structured nanomotor showing the axis and direction of rotation of the top component; (b) a schematic of the top component pivots along with rotation as well; (c) the movie frames in ~ 1/5 sec. interval, from

left to right, showing the rotation of the top nanomotor in the clockwise manner if viewed from the top. The whole structure only drifts slightly while the rotor spins. 96

- Figure 5.5 (a) The illustration of a three-component structure pivoting about the point of contact between the tail of the leader and the middle of the two heads of the trailer allowing the bending of  $\pm \alpha$ ; (b) The movie frames, ~ 1/8 sec. interval, from left to right showing the structure colliding with a stationary particle (a structure similar to the trailer) then turning to maneuver around the object; the position of the images are taken at different locations to follow the trajectory of the particle; (c) a representative SEM image of the trailer consisting of two tadpole swimmers likely fussed by the deposition process; (d) a representative SEM image of a structure similar to the threecomponent structure described with both the leader and trailer; (e) the flex angle  $\alpha$ defined by the difference in angle between the trailer and the leader; (f) a plot of the flex angle  $\alpha$  vs. time during the maneuver showing the flexibility of the structure.101

#### CHAPTER 1

#### INTRODUCTION

Richard Feynman's 1959 talk titled "There's Plenty of Room at the Bottom" was concluded by a challenge to build a microscopic motor with a prize of \$1,000. Shortly afterward, William McLellan engineered by hand a motor that was smaller than one sixty-fourth of an inch and was awarded the prize [1]. Since that time, the practical fabrication of micrometer-sized mechanical structures was made possible by borrowing techniques from widely used and developed semiconductor device fabrication techniques of photolithography and chemical wetetching fabrication. This new branch of engineering microscopic devices became known as microelectromechanical systems or MEMS. As technology progressed, the dimensions of these systems became smaller leading to nanoelectromechanical systems, NEMS, and new techniques emerged allowing for simple large-scale fabrication of micro- and nanomotors. MEMS devices are electrical by nature, but towards the turn of the century, the use of on-board catalysts combined with chemical fuel to create autonomous nanomotors became prevalent, and ever since then, the field is expanding at an accelerating rate. These devices are called catalytic nanomotors, and they move without the presence of an external field; this is a desirable characteristic because operation is possible in any environment as long as a chemical fuel is present.

The investigation of autonomous, self-propelled nano- and microscale motors and actuators is an important endeavor for the future of drug delivery, transportation of nano-cargo, moving sensors, noninvasive surgery, and the engineering of functional nanomachines [1-6]. However, many difficulties exist in the logistics of manufacturing and controlling such small devices. The term catalytic nanomotor refers generally to microscopic autonomous structures which swim in a solution that contains some type of fuel which reacts with a catalyst, and the prefix nano refers to usually at least one dimension that is measured in nanometers. The term micromotor would perhaps be more appropriate since they have to be observed through an optical microscope while swimming which means the largest dimensions are usually measured in microns. To fabricate machinery at these dimensions, engineers cannot simply scale-down macroscopic analogues due to energy conversion considerations, the hydrodynamics at low Reynolds number, and difficulty manipulating tiny structures. Macroscopic machinery carries onboard energy generally in the form of chemical fuel and consumes this fuel until exhaustion which is impractical for a nanomachine. Also, macroscopic machinery usually is a complex system of moving parts that operate in coordination, and these parts are directly assembled together to form the system. For a nanomachine, energy must be derived from the environment through external fields or by converting chemical energy stored in the swimming environment into mechanical work since it cannot carry the fuel that will be consumed. Nanomachines also cannot be directly manipulated and therefore must consist of a very small number of independent parts (most are single particles) until more sophisticated design techniques are developed. The combination of chemically powered nanomotors with external fields is also used for direct manipulation. Nature has been using this concept of converting chemical energy into mechanical work since the earliest life forms began appearing on Earth and exists in practically every proactive process in biology; therefore, researchers in this field have been taking cues from a wide variety of naturally occurring biological nanomotors which are ubiquitous in living organisms. Future advanced applications may be able to carry out similar cellular processes seen in nature.

## **1.1 Natural Biological Nanomotors**

Investigations into the manufacturing of artificial nanoscale robots and actuators was spawned by the discovery and the desire to emulate naturally occurring biological nanomotors [7] that are necessary for the most essential and primitive biological functions [8-11]. Examples of these functions are the transportation of biochemicals through the cell and cell mobility. Recent advances in molecular biology have illuminated the properties of moving proteins with the most rigorously studied being myosins, kinesins, and dyneins [8]. These cytoplasmic proteins



Figure 1.1 Schematic of the constituent parts of a bacterial flagellum: an example of a naturally occurring biological nanomotor (from Ref. [12]).

are responsible for various activities in the cell such as the transportation of substrates from one location to another, mitosis, meiosis, and muscle contraction to name a few. Each one derives

energy from the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP); ATP exists in a higher energy configuration than ADP so the free energy released from the hydrolysis can be used for mechanical work [8]. Through ATP, the vital energy exchange is made possible.

One of the most famous and well-studied examples of an (indirectly) ATP-driven molecular motor is the bacterial flagellum [12]. This helical-shaped motor exists in mobile bacteria such as *Escherichia coli* and allows the organism to move toward food or away from toxins [12]. Figure 1.1 shows how the filament section of the flagellum, which propels the organism, is attached to a molecular rotor (shown as *C ring*) which is driven by a proton gradient maintained by the hydrolysis of ATP [12]. As the rotor spins, the torque is converted by the filament into linear motion allowing for active swimming. Although current nanoengineering cannot construct such an intricate and beautiful machine yet, some simple artificial motors can now be fabricated that are similar to swimming bacteria in that they are autonomous swimmers, are the same size as a bacterium or smaller, swim with similar velocities or faster, and convert local energy sources into movement. The difficulty in manufacturing a system like the flagellum is in the intricacy and complexity of the assembly of proteins of which this system consists. This example from nature is the epitome of what researchers are trying to recapture, and it poses a great design challenge to researchers.

## **1.2 Hybrid Nanomotors**

Billions of years of evolution have allowed for the design perfection of naturally occurring motors and therefore they perform well defined and controlled behaviors. The most



Figure 1.2 (a) Over a 38 s. interval, actin filaments migrate across the myosin-immobilized surface; (b) filament velocity vs. ATP concentration; speed initially increases with ATP concentration and eventually plateaus around 200 μM (from Ref. [13]).

practical method researchers use to design functional artificial motors is to make use of readily available motor structures from nature [8-10]. By combining naturally occurring components to artificially fabricated structures, hybrid nanomotors were made possible. Figure 1.2 (a) shows a 2D plot of the migration of actin filaments over a myosin-immobilized surface for a 38 s. interval, and Fig. 1.2 (b) shows the dependence of ATP concentration on the speed of the actin filaments across the surface [13]. Figure 1.2 (b) shows that as the concentration of ATP increases, the speed of the actin filament increases until a limiting concentration is reached. The



Figure 1.3 Left column: fluorescent rotamine-actin comet tail for a directional bead and a stationary bead; middle column: micrograph of the two beads; right column: bead positions superimposed on fluorescent images (bar = 5  $\mu$ m) (from Ref. [14]).

active myosin responds to the presence of a chemical fuel converting the chemical energy into kinetic energy. This example shows the importance of chemically-powered molecular motors in the field of biology and how the actuation of nanomotors with locally available fuel is possible. As another example, the transportation of inorganic cargo was shown to be possible through the catalysis of actin filament polymerization [14]. In this study, 0.5  $\mu$ m ActA-coated polystyrene beads were propelled in an actin environment with an average velocity of 0.1 – 0.15  $\mu$ m/s. Figure 1.3 shows an active and a stationary microbead in 4 movie frames separated by 30 s. The "comet tail" arises from fluorescence imaging and shows the location of the rotamine-actin illuminating the trajectory of the bead.

Another interesting example is a rotary structure that combines a metal nanorod that is the "propeller" attached to the biomolecular motor ATP synthase that spins the propeller. The Ni nanorod and the biomotor are attached via a biotin-streptavidin linkage. Figure 1.4 shows how the Ni propeller and the F<sub>1</sub>-ATPase biomolecular motor are combined; as ATP is applied to the system, the propeller begins to rotate [15]. These two examples show the practical fabrication of combined artificial and natural parts; the next natural step was to design purely artificial catalytic nanomotors.



Figure 1.4 (a) & (c) Ni nanorod rotors; (b) F<sub>1</sub>-ATPase biomolecular motor; (d) schematic of the combined architecture (from Ref. [15]).

## **1.3 Artificial Catalytic Nanomotors**

In the literature, the term catalytic nanomotor generally refers to artificial, inorganic structures that use a chemical to gain mobility via an onboard catalyst. In this manner, they are analogues of naturally occurring bionanomotors which utilize energy obtained from the environment to do work and are ubiquitous in nature. In the years of 1995-2009, there was a marked increase in the effort to manufacture and understand nanomotors [16]. Figure 1.5 shows a chart of the number of publications during this period by year; the inset shows the quantity of publications regarding chemically powered nanomotors, upon which this thesis focuses.



Figure 1.5 Number of publications for nanomotor research during the years of 1995-2009. The inset graph shows chemically powered catalytic nanomotor research (from Ref. [16]).

The most commonly used chemical fuel is hydrogen peroxide H<sub>2</sub>O<sub>2</sub>. Under usual conditions, hydrogen peroxide spontaneously decomposes into water and oxygen, H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  2 H<sub>2</sub>O + O<sub>2</sub>, but at a very slow rate. This decomposition is an exothermic reaction with a Gibbs Free Energy of  $\Delta G = -119.2$  kJ/mol [17]. A catalyst can greatly increase the reaction rate, and

most of the transition metals catalyze this reaction, but the most effective catalyst is Pt. Since a large amount of energy is available as the  $H_2O_2$  decomposes, catalytic nanomotors are able to gain mobility by carrying an onboard catalyst. Figure 1.6 is an example Au/Pt nanorod nanomotor which moves translationally toward the Pt catalyst in a solution of hydrogen peroxide as shown by the arrow on the left side [3].



Figure 1.6 Oxidation of hydrogen peroxide leading to propulsion of the Au/Pt nanorod nanomotor toward the Pt catalyst, an effect of self-electrophoresis (from Ref [3]).

For the nanorod nanomotor in Fig. 1.6, the motion is a result of an oxidation/reduction reaction. Although  $H_2O_2$  is generally the most commonly used source of energy, other chemical fuels that are more bio-compatible such as glucose have been used as well [18-20], which for future biological applications may be a more appropriate fuel. Along with translational motion such as the structure shown in Fig. 1.6, rotational motion has been shown to be possible through systematic design as well. Figure 1.7 (a) shows a fast-spinning Au/Ru/Pt nanowire fabricated by both electrochemical deposition as well as physical vapor deposition [21], and Fig. 1.7 (b) shows a Pt-coated TiO<sub>2</sub> rotary nanomotor [22]. Recently, researchers have focused upon the specific design techniques to engineer the types of motions desired, and this can be accomplished by using specific types of materials, combining fabrication techniques, and focusing upon geometry.



Figure 1.7 (a) Fast rotary tri-metallic nanomotor (from Ref. [21]); (b) TiO<sub>2</sub> rotary nanomotor (from Ref. [22]).

## **1.4 Artificial Nanomotor Swimming Behaviors**

Catalytic nanomotors behave differently than macroscopic objects due to the particles' Reynolds number as discussed in section 1.5. The solution in which nanomotors move has a large impact upon the types of motion observed: viscosity is a dominating force and random thermal fluctuations must be considered as well. Catalytic nanomotors are small enough that the collisions of the surrounding molecules have a large impact on their momentum. Microscopic particles in a solution move with random fluctuations due to thermal motion of surrounding molecules. As the molecules collide with the particle, momentum is transferred, and movement ensues. Because of the randomness of these collisions, this so-called Brownian motion can only be described statistically. The trajectory of a particle moving under the influence of the random bombardment of molecules is known as a random walk which is a term for a trajectory of successive steps in random directions. The diffusion of a particle in 1D is given by  $\langle x^2 \rangle = 2Dt$ where *D* is the diffusion coefficient and *t* is time [23]. The diffusion coefficient is expressed as D = kT/f in which k, T, and f are Boltzmann's constant, temperature, and frictional coefficient respectively. For a spherical particle of radius a moving in 2D undergoing Brownian motion, the average squared distance is given by,

$$\left\langle r^2 \right\rangle = \frac{2kT}{3\pi\eta a}t,\tag{1.1}$$

in which  $\eta$  is the viscosity of the fluid [24]. Eq. (1.1) shows that there is a linear relationship between the average squared distance and time. If *T* and  $\eta$  are held constant, then the radius of the sphere dictates how much influence the surrounding molecules have. Since  $\langle r^2 \rangle$  is inversely proportional to this radius, the smaller the particle is, the greater the influence of the surrounding molecules, and therefore, catalytic nanomotors experience significant agitation. Equation (1.1) allows for experimental verification of Brownian motion. If the particle has a nonlinear slope, then other forces are at work. Actively propelled catalytic nanomotors move similarly to Lévy walk supperdiffusive action [25]. This type of active motion is characterized by the relationship,

$$\langle r^2 \rangle \propto t^{\alpha},$$
 (1.2)

in which  $1 < \alpha < 2$ .

Howse et al. fabricated polystyrene microspheres half-coated with Pt for a self-propulsion study. Figure 1.8 (a) shows the trajectories for spherical Janus particles moving in various concentrations of  $H_2O_2$  [26]. Figure 1.8 (b) shows the nonlinearity of the propelled Janus particle which is indicative of active propulsion; the graph shows the distance squared vs. time for the 10% w/v  $H_2O_2$  with trajectory. A typical way to determine if active motion is present is to determine whether  $\alpha > 1$ .



Figure 1.8 (a) trajectories for Janus sphere particles in H<sub>2</sub>O<sub>2</sub> solutions; (b) 10% w/v Janus sphere trajectory and mean square displacement vs. time (from Ref. [26]).

Equation (1.1) describes the movement of a spherical particle undergoing Brownian motion, and this shaped nanomotor has been studied extensively due to symmetry [27-30]. Several geometrical structures have been studied besides the sphere. The cylinder can be approximated as a distorted sphere or a prolate spheroid. The most common are the cylindrically-shaped bi-metallic nanomotors which consist of a catalyst and another metal [1, 31, 32]. These



Figure 1.9 (a) and (b) Swimming trajectories of Pt and CNT/Pt anode nanomotor respectively; (c) speed distribution for the two nanomotors (from Ref. [33]).

nanomotors typically move toward the catalyst in a translational manner. Since the drag force plays such a significant role, the geometry dictates the types of movement exhibited by a nanomotor. Because the geometry plays such a vital role, motion can be engineered by designing the geometrical shape using a dynamic growth technique. The most challenging aspect of catalytic nanomotor research is arguably how to control the movement and this problem is addressed in this dissertation.

The direct manipulation of catalytic nanomotors in order to modify and control motion is a difficult task; however, some advances have been made that allow for either indirect or direct manipulation or motion control. Figure 1.9 shows the various trajectories of two Au/Pt nanorod nanomotors: (a) Au/Pt without carbon nanotube (CNT) doped into the Pt; (b) with CNT [33]. Figure 1.9 (c) clearly indicates that the CNT-doped Pt anode for the Pt/Au nanorod nanomotor is faster than the traditional Pt/Au nanomotor. Another common control tactic is to incorporate a ferromagnetic material into the nanomotor, and then it is controllable by an external magnetic field. Figure 1.10 (a) shows an SEM image of a Pt/Au nanorod nanomotor with alternating sections of Ni. Figure 1.10 (b) shows controlled trajectories of these structures using an external magnetic field to write the letters "PSU" for Pennsylvania State University [34].



Figure 1.10 (a) SEM of striped Pt/Au/Ni nanorod nanomotor; (b) "PSU" spelled out with nanomotor trajectories controlled by magnetic field (from Ref.[34]).

Pt/Au nanorod nanomotors can also be controlled by adjusting the temperature of the solution; a result arising from the increase break-down of  $H_2O_2$  at higher temperatures [35]. Figure 1.11 shows the speeds for three different temperatures and the higher temperatures lead to



Figure 1.11 Speed vs. time for nanomotors at temperatures (a), (b), and (c) of 40° C, 48° C, and 58° C, respectively. The inset shows the speed averages vs. temperature (from Ref. [35]).

higher speeds. The arrow on the bottom of the graph shows the point in time at which the temperature pulse begins. The speed increases for each case during the pulse and the three arrows for the three cases at the point peaks show when the pulse ends and the temperature returns to the initial value.

Just as natural biomotors have specific functions based upon their physical and chemical specifications, catalytic nanomotors exhibit various behaviors based upon their compositions and physical dimensions. A commonality between fabrication methods is the asymmetric distribution of the catalyst as the asymmetry allows for directional movement. Several design techniques and explanations of the underlying physics exist in the literature, and at present, both contradictions and agreements exist about how these motors operate [36]. Recent research suggests that the

discrepancies over the propulsion mechanisms may be due to the types of materials used for fabrication, and although researchers are getting ever closer to understanding this mechanism, there are still some unexplained phenomena. To understand how nanomotors behave in a viscous fluid, the equations of low Reynolds number must be studied.

## 1.5 Low Reynolds Number Hydrodynamics

Propulsion of particles at low Reynolds number is an interesting fluid dynamics problem since without any applied forces, the particle remains at rest. The Reynolds number in fluid mechanics is a measurement of how the various forces acting on a fluid will affect the flow of that fluid. The movement of a propelled particle through stationary fluid is physically indistinguishable from fluid flowing around the particle. Fluid motion in general is described by the Navier-Stokes equation,

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{f}, \qquad (1.3)$$

where  $\rho$ , **v**, p,  $\mu$ , and **f** are the fluid density, flow velocity, pressure, viscosity, and the body force per unit volume respectively [37]. The dimensionless Reynolds number, the ratio between inertial forces and viscous forces, is given by Re =  $\rho v L / \mu$ , where *L* is the length dimension of the particle [37, 38]. The Reynolds number determines whether the flow is laminar or turbulent dictated by low or high Reynolds number respectively. Nanomotor dimensions fall in the range of a few hundred nanometers to several microns placing them in the low Reynolds number domain; therefore nanomotor motion is dominated by viscous drag forces and the flow is laminar. For example: a nanomotor of dimension *L* = 5 µm moving at *v* = 10 µms<sup>-1</sup> in water, Re  $= 5 \times 10^{-5} \ll 1$ . In this way, the shape of the swimmer completely determines the behaviors of the propelled object. Flow near a particle at low Reynolds number can be approximated by the Stokes solutions in which the nonlinearity is removed. Creeping flow is applicable when the fluid flow is very slow. When these criteria are met, two equations known as the Stokes solutions describe the motion,

$$\nabla p = \mu \nabla^2 \mathbf{v} + \mathbf{f}$$

$$\nabla \cdot \mathbf{v} = 0$$
(1.4)

Because Re << 1, it is reasonable to assume that the inertial terms in the Navier-Stokes equation may be ignored reducing it to the linearized steady-state Stokes solutions in Eq. (1.4). For a catalytic nanomotor, viscous drag dominates which implies that nanomotor's shape governs movement. As an example, the well-known Stokes' Law for drag on a spherical particle at low Reynolds number is given by  $\mathbf{F}_{s}^{\mathbf{D}} = -6\pi\mu a\mathbf{v}$ , where *a* is the radius of the sphere; the sphere is symmetrical and isotropic, so no torque is induced. As the shape of the particle becomes more complex, then the equations of motion must be adjusted accordingly. Most approximations are conducted by modifying spheres and ellipsoids, and approximations can be generalized for particles without any symmetry as well. The catalytic nanomotors considered in this thesis are non-deformable, but analysis for flexible structures does exist. The general analysis assumes that rigid-body motion results from external forces and torques which exactly balance the forces and torques resulting from the fluid drag.

The equations of micro-hydrodynamics and the coupling between force and torque have to be considered. The governing equations for particles moving in a viscosity-dominated environment are given by the Stokes equations in Eq. (1.4) which are relations for a particle moving with constant velocity and constant rotation,

$$\begin{bmatrix} \mathbf{F} \\ \mathbf{\tau} \end{bmatrix} = \begin{bmatrix} \mathbf{A} & \widetilde{\mathbf{B}} \\ \mathbf{B} & \mathbf{C} \end{bmatrix} \begin{bmatrix} \mathbf{v} \\ \boldsymbol{\omega} \end{bmatrix}, \tag{1.5}$$

where **F** is the hydrodynamic force,  $\tau$  is the hydrodynamic torque, **v** is the translational velocity, **\omega** is the angular velocity, and **A**, **B**, and **C** are second-order tensors dependent upon geometry [37]. Eq. (1.5) is known as the resistance matrix as is determined by the shape of the structure. By solving for this matrix, the particle dynamics can be understood.



Figure 1.12 SEM of an artificial bacterial flagellum propelled by an external magnetic field (from Ref. [39]).

As an example, the resistance matrix for the helical structure with a magnetic head is shown in Fig. 1.12 is estimated [39]. Since the structure is propelled by an applied magnetic field, the driving force is determined by suspending the helix in the solution by exactly countering the gravitational force. The first equation in Eq. (1.5) is used to determine the value of the coefficient **B** by knowing the value of  $\boldsymbol{\omega}$ . The other various parameters are solved in a similar ways. The values obtained were  $a = 1.5 \times 10^{-7}$ ,  $b = -1.6 \times 10^{-14}$ , and  $c = 2.3 \times 10^{-19}$ .
## **1.6 Propulsion Mechanisms**

The various reports in the literature lead to the conclusion that several different underlying propulsion mechanisms may exist to describe nanomotor motion. A review of the various examples can be found in Ref. [36]. The major discrepancy involves the direction of motion for a catalytic nanomotor. Both conclusive evidence for the movement toward the catalyst [32] as well as away from the catalyst has been observed [22, 40]. Two possible mechanisms have been proposed to describe motion away from the catalyst site: diffusiophoresis and bubble propulsion, and two have been proposed for motion toward the catalyst: interfacial tension gradients and self-electrophoresis.

## 1.6.1 Diffusiophoresis

The asymmetry of a catalytic nanomotor plays an important role in nanomotor motion. When the catalyst is distributed in a manner such that the reaction products accumulate on one side of the structure, then diffusiophoresis may be responsible for propulsion. Golestanian et al.



Figure 1.13 A schematic of the diffusiophoresis model in which a sphere with a single point catalyst site generates a concentration gradient of reaction products, driving the sphere away from this location (from Ref. [29]).

developed a model [29] which consists of a spherical structure with a point catalyst as shown in Fig. 1.13 marked "enzymatic site." In this model, the reaction products that have accumulated at the catalyst site begin to diffuse away from the location of higher reaction product concentration driving the sphere away from this location as well. Since the sphere is constantly generating this concentration gradient, it is continually being propelled away from its catalyst site. If the excess reaction particles are being released from the active site at a rate  $\frac{dN_p(t)}{dt}$  the diffusion equation can be written as,

$$\partial_t \rho(\mathbf{r},t) - D\nabla^2 \rho(\mathbf{r},t) = \frac{dN_p(t)}{dt} \delta^3 (\mathbf{r} - \mathbf{r}_s), \qquad (1.6)$$

where  $\rho$ , D,  $\mathbf{r}_s$  are the density and diffusion coefficient for the reaction particles and location of the catalyst site respectively [29]. The movement away from the catalyst has been verified [22, 40]. This mechanism explains how a catalytic nanomotor is propelled away from the catalyst site as well, but another mechanism has been proposed to explain the same phenomenon.

### 1.6.2 Bubble propulsion

Autonomous movement of macroscopic plates was proposed to arise by the impulse of bubbles generated at the Pt catalysts site shown in Fig. 1.14 [41]. Plate movement as the result of bubble formation and eruption were clearly observed because the plates were large and floated along an aqueous  $H_2O_2$  solution. The plates also have alternating hydrophilic and hydrophobic surfaces which allow for self-assembly. One of the results of this experiment indicated that the activity of the plates increased the incidence of interaction and therefore, self-assembly. The active motion acts as a means of enhancing and increasing the rate at which the plates aggregate.



Figure 1.14 Autonomous swimming plates that have alternating hydrophilic-hydrophobic sides which induce self-assembly. The Pt coated on one side drives the plates across the aqueous solution of  $H_2O_2$  by bubble impulse (from Ref. [41]).

Ni/Au nanorods grown by TDEP were shown to be propelled by bubble propulsion as well [1]. Figure 1.15 shows a sequence of microscope images illuminating the jet of nanobubbles emanating from the Ni catalyst [1]. Bubble jets are clearly shown to propel rolled-up nanojet engines as bubbles are ejected from one side of the tube while  $H_2O_2$  fuel enters into the other side [42]. Physical models relating bubble propulsion to autonomous motion have been presented



Figure 1.15 Micrograph images of a jet of nanobubbles coming from a spinning Au/Ni nanorod nanomotor (from Ref. [1]).

in the literature as well. A model we derived explains how the mass change of  $O_2$  bubbles detaching from the surface of a Pt-coated SiO<sub>2</sub> Janus sphere drives the particle and relates the speed of the nanomotor to the surface tension and  $H_2O_2$  concentration,

$$v \propto \gamma^2 \frac{k\alpha c}{1+\alpha c},$$
 (1.7)

where  $\gamma, \alpha, c$  are surface tension, the Langmuir adsorption constant, and concentration respectively [28]. Details are described in section 3.1. Direct observations of bubbles coming from the surface, observations of nanomotors moving away from the stream of bubbles, and movement away from the catalyst makes a convincing argument that this model is correct for the particular nanomotor studied; however, there are other examples of nanomotors moving toward the catalyst which implies other forces are working on these structures.

#### 1.6.3 Interfacial Tension Induced Motion

An interfacial tension model is proposed to explain the movement of Au/Pt nanorod nanomotors fabricated by TDEP, and explains how this structure moves towards the Pt catalyst [31]. Details of which are described in section 2.1. The Pt catalyst creates an interfacial tension gradient due to the larger quantity of O<sub>2</sub> near the Pt side of the nanomotor. Figure 1.16 shows the oxygen evolution vs. time for a suspension of Au/Pt nanorod nanomotors in 3.7% H<sub>2</sub>O<sub>2</sub>. This difference in surface tension is a function of the amount of O<sub>2</sub> generated which is proportional to the concentration of H<sub>2</sub>O<sub>2</sub> of the solution. The model suggest the speed, v, is linearly proportional to the surface tension of the solution and this corresponds well to the experimental data, where  $S, R, \gamma, \mu, D, L$  are oxygen evolution rate, nanorod radius, surface tension, viscosity, diffusion coefficient and nanorod length respectively. The model not only correctly describes the



Figure 1.16 Oxygen evolution vs. time for Au/Pt nanomotors in 3.7% H<sub>2</sub>O<sub>2</sub> (from Ref. [31]).

$$v \propto \frac{SR^2\gamma}{\mu DL},$$
 (1.8)

direction of motion, but also predicts the correct magnitude of force. Figure 1.17 shows the relationship between the surface tension and speed which is predicted by Eq. (1.8) to be linear. Although successful, this model has a strong competitor which also accurately depicts the movement of bimetallic structures toward the catalyst, and this model is electrochemical by nature and is known as self-electrophoresis.

# 1.6.4 Self-Electrophoresis

When a catalytic nanomotor consists of two contacting metals, each metal acts as an electrode with one acting as a cathode and the other as an anode in the catalytic break-down of  $H_2O_2$ . The driving force for this particular catalytic nanomotor is electrochemical by nature and a



Figure 1.17 Product of surface tension and oxygen evolution vs. speed (from Ref. [31]).

by bipolar electrochemical model for nanorod nanomotors consisting of Au and Pt ends was first proposed by Paxton and Sen [2, 32]. Figure 1.6 shows the model of an Au/Pt nanorod nanomotor in which oxidation occurs at the Pt anode and reduction at the Au cathode for the overall reaction of  $H_2O_2 \rightarrow H_2O + O_2$  [32].

Pt: 
$$H_2O_2 \rightarrow O_2 + 2H^+ + e^-$$
  
Au:  $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$  (1.9)

As shown in Fig. 1.6 the protons migrate from the Pt end to the Au end to recombine with the electrons, and in this process, the nanorod moves in the opposite direction, i.e. toward the Pt end.

A scaling analysis for bimetallic nanorod structures gives an expression for nanomotor velocity with the form

$$u \propto \frac{\zeta Fh\lambda_D}{\eta D_+} j, \tag{1.10}$$

in which  $\zeta$ , *F*, *h*,  $\lambda_D$ ,  $\eta$ ,  $D_+$ , *j* are surface charge, Faraday constant, nanomotor length, Debye thickness, viscosity, diffusion coefficient of protons, and the reaction flux, respectively [43]. Figure 1.18 shows a Pt/Au microelectrode chip which measures the current between the anode and cathode to show the electrochemical nature of hydrogen peroxide catalyzed breakdown [44].



Figure 1.18 Microelectrode current measurement device (from Ref. [44]).

Table 1.1 gives the results of the current measurements showing a higher current density for higher concentrations of  $H_2O_2$  as expected. This model has been used to predict convective flow

experiment	[H <sub>2</sub> O <sub>2</sub> ] (M)	current density (A/m <sup>2</sup> )
6% H <sub>2</sub> O <sub>2</sub>	1.8	0.684(4)
0.6% H <sub>2</sub> O <sub>2</sub>	0.18	0.116(1)
0.06% H <sub>2</sub> O <sub>2</sub>	0.018	0.0162(4)
0.006% H <sub>2</sub> O <sub>2</sub>	0.0018	0.00099(4)
0.0006% H <sub>2</sub> O <sub>2</sub>	0.00018	0.000095(2)
D.I.		0.000033
0.18 M NaNO3		0.000041

Table 1.1 Current density reading for various H<sub>2</sub>O<sub>2</sub> concentrations (from Ref. [44]).

induced by propelled micro tracer particles in a catalytic micropump [45]. In this system, an Ag island is placed in the middle of an Au substrate. The electroosmotic flow causes the particles to be pumped in a tight convection roll close to the Ag electrode.

## **1.7 Contents of Dissertation**

This dissertation consists of 6 chapters. Chapter 1 focuses on the state of catalytic nanomotor research to date. Researchers and engineers have utilized the secrets of naturally occurring nanomotors as a design guideline for manufacturing artificial catalytic nanomotors. The research has also focused upon the propulsion mechanisms and the swimming behaviors that are associated with active movement at low Reynolds number. Chapter 2 describes the nanomotor design techniques of dynamic shadowing growth as well as template-directed electroplating. The technique utilized in our lab, dynamic shadowing growth, combines physical vapor deposition and dynamic substrate manipulation. Dynamic shadowing growth has two subcategories: oblique angle deposition and glancing angle deposition which allow for different nanomotor

design and fabrication. Chapter 3 presents the propulsion mechanisms studied including bubble propulsion and self-electrophoresis as well as the measurement of the driving force for a single nanomotor. Chapter 4 discusses motion engineering based upon geometrical design. The movement of a nanomotor is highly dependent upon shape, and by using dynamic shadowing growth, swimming behaviors can be engineered. The chapter covers rotary V-shaped and, tadpole-shaped structures that swim in large circular orbits. Chapter 5 is dedicated to the manufacturing of complex nanomotor systems in which nanomotors consist of multiple independent parts. Lastly, Chapter 6 is devoted to conclusions drawn from this work as well as the possible future experiments and applications.

### CHAPTER 2

## FABRICATION OF CATALYTIC NANOMOTORS

A major challenge in catalytic nanomotor research is the fabrication of such small devices. Researchers generally agree that a necessary feature of a catalytic nanomotor is the distribution of an onboard catalyst asymmetrically on a nanostructured backbone since it is agreed that reaction product gradients are necessary for propulsion. Two main methods exist for catalytic nanomotor fabrication: template directed electroplating (TDEP) and physical vapor deposition (PVD); both methods are affective for fabricating catalytic nanomotors with different structural materials and both allow for the asymmetrical distribution of the catalyst necessary for propulsion. The PVD technique called dynamic shadowing growth (DSG) has several advantages over the TDEP method such as a wider range of geometries are possible, the fabrication is less complex, and uniformity among structures is easily achieved. Some less common techniques exist as well, but this chapter will present the TDEP method for completeness but will focus on DSG as the technique for nanomotor fabrication in this thesis.

### 2.1 Template-Mediated Nanomotor Growth

Nanorod nanomotors with sections of various metals can be fabricated using electrochemistry combined with template growth. The fabrication of metallic barcode nanorods by template directed electroplating (TDEP) was first shown by Natan et al [46]. In this study, a porous Al<sub>2</sub>O<sub>3</sub> membrane with uniformly sized pores is used as a template for the electrochemical



Figure 2.1 Fabrication process of template directed electroplating. First Ag is evaporated onto the  $Al_2O_3$  porous membrane and a Ag is electroplated onto this film; Au and Ag are deposited into the pores, then the Ag film and the membrane are dissolved releasing the nanorods (from Ref. [46]).

deposition of an array of metallic nanorods which can be released from the template by dissolving the membrane and the sacrificial metal layer. As shown in Fig. 2.1, the fabrication process of multi-metal nanorods consists of Ag evaporation onto the membrane, followed by an electrochemical deposition of an Ag film, Au and Ag are then electrodeposited into the pores of the membrane, and finally the Ag film and Al<sub>2</sub>O<sub>3</sub> membrane are dissolved to release the nanorods. Since it is necessary to have multiple materials for the fabrication of catalytic nanomotors, TDEP is an appropriate method since it allows a single structure to consist of

multiple metals but is limited to the types of materials that can be deposited electrochemically. Clearly the shape of the resulting nanorod is dependent upon the shape of the template from which it is cast which is another limitation of the method.



Figure 2.2 Examples of template directed electrodeposition-grown nanomotors: (a) Schematic of a Pt-Au striped nanorod nanomotor (from Ref. [31]); (b) Ni-Au nanorotor (from Ref. [1]); (c) micrograph of tubular microengines (from Ref. [47]); (d) lithography template rotary gear (from Ref. [48]).

For catalytic nanomotors, the asymmetric distribution of the catalyst is necessary for directed movement as will be discussed. The catalyst layer is easily placed on one end of the nanorod by adding multiple layers to the nanorod structure so that this asymmetry exists. Mallouk and Sen fabricated autonomous Au/Pt striped nanorods using the TDEP method, shown in Fig. 2.2 (a), in which the Pt catalyzes the decomposition of  $H_2O_2$ . They hypothesized that the interfacial tension created by the oxygen reaction product was the cause of the movement as discussed in the propulsion mechanism section 1.6.3 [31]. Ozin et al. fabricated Au/Ni nanorotors using TDEP as well; in this study, the Ni acts as the catalyst for the decomposition of

 $H_2O_2$ , and when the Au end of the nanorod becomes tethered to the surface of the microscope slide, the nanorotors spin about the tether point with the Ni end propelling the rotor shown in Fig. 2.2 (b) [1]. This method was also used for fabricating alloys for increasing nanomotor speed [33] and electroplating not only along the axis of the rod, but along one face as well [49]. Template electroplating has been used without Al<sub>2</sub>O<sub>3</sub> membranes to fabricate tubular microengines as seen in Fig. 2.2 (c) [47], and another example shown in Fig. 2.2 (d) uses a template made with lithography to fabricate a rotating gear structure [48]. TDEP also allows for the addition of multiple layers to increase control such as by adding a ferromagnetic material into the rod to control the direction of swimming magnetically [34]. Mirkin et al. combined both TDEP and physical vapor deposition to design catalytically driven nanorotors as well [49]. TDEP is an effective and popular way to produce a large number of nanorod nanomotors with multiple metals that are roughly uniform in shape. The major limiting factor for this process, as stated previously, is the shape of the template. The physical vapor deposition method known as dynamic shadowing growth is a more versatile method which overcomes some of the limitations of TDEP.

# 2.2 Physical Vapor Deposition

Physical vapor deposition (PVD) has been shown to be an effective and useful catalytic nanomotor fabrication method, and is becoming increasingly more prevalent in this field. PVD is an easy and cost-effective method that consists of coating substrates by the heating and evaporation of metals and metal-oxides in a vacuum environment. Some advantages over TDEP exist such as the ability to deposit a wider range of materials, the process takes far fewer steps,

and by combining PVD with substrate manipulation, a greater spectrum of geometries with asymmetric catalyst distributions is possible.

The simplest form of PVD is the deposition of a thin film onto a substrate. In this case, the substrate is placed directly above the source material at a 0° vapor incidence angle (the vapor direction is parallel to the substrate surface normal) and is coated with a film of the evaporated material. Using PVD in this case, a very simple catalytic nanomotor can be fabricated by coating a catalyst layer onto a structure that is first deposited onto the substrate which satisfies the condition of asymmetry. The half-coating of submicron silica spheres with a metal was demonstrated by Whitesides et al [50]. The so-called Janus sphere consists of two hemispheres with differing materials. If one of these two materials was a catalyst, then directed propulsion was hypothesized to ensue in the presence of fuel [30]. Experimental verification of active motion was demonstrated first by using Pt-coated polystyrene microspheres [26] and later using Pt-coated silica microspheres shown in the SEM in Fig. 2.3 [28].



Figure 2.3 SEM image showing Pt-coated silica microsphere.

A Janus sphere with one side Au and the other Pt was fabricated as well [51], and another example consists of a microsphere with various overlapping sections of Au and Pt in which the exposed Au area determines the nanomotor motion behaviors [27], as will be discussed below. Clearly, other structures besides spheres can be coated in a similar manner; Au/Ru bimetallic nanorods fabricated by TDEP were distributed onto a substrate and modified by PVD thin film depositions of Cr, SiO<sub>2</sub>, Pt, and Au to make fast micro-rotors [21]. Thin film PVD combined with circular or square patterned photoresists resulted in catalytic microtube jet engines capable of reaching speeds of ~ 2 mm/s [42].

PVD truly becomes advantageous for catalytic nanomotor fabrication when substrate manipulation is included. Dynamic shadowing growth (DSG) is a physical vapor deposition technique that uses substrate manipulation and the shadowing effect. By tilting the substrate to a large angle (>80°) during vapor deposition, an array of nanostructures grows on the surface of the substrate, and because of the large angle, this is known as oblique angle deposition (OAD) shown in Fig. 2.4 [52-55]. Glancing angle deposition (GLAD) is OAD plus substrate rotation.



Figure 2.4 Schematic of OAD/GLAD: the angle between the surface normal,  $\overline{N}$ , and the evaporation direction,  $\theta$ , is large (>80) controlled by motor 2 (OAD). Motor 1 controls the substrate rotation (GLAD).

When the vapor flux approaches the substrate at a large angle, the random nucleation islands that form on the surface serve as seeds of growth. Further accumulation of the vapor on the surface after the formation of the islands is restricted to these sites leading to an array of nanorods. This phenomenon is called the shadowing effect, and the process is shown in Fig. 2.5. Also, further control over nanostructure geometry is possible by the rotation of the substrate which is a process known as glancing angle deposition (GLAD). Since the asymmetric distribution of the catalyst is easily accomplished with DSG, and also since nanomotor geometry is important in the types of swimming behaviors exhibited, these techniques are effective for growing complex nanomotor geometries.



Figure 2.5 Vapor begins to deposit on a flat substrate to form nucleation points. As more accumulation occurs, it is restricted to the points of nucleation due to the shadowing effect, and an array of nanorods forms.

Regular nanorod arrays are possible as well by depositing on a substrate that has been seeded. If a monolayer of nano or microbeads is distributed onto a surface, then the growth will be restricted to the beads themselves taking the place of the random nucleation islands that would be present on a flat substrate. Using this simple process, very uniform structures can be fabricated [22]. Figure 2.6 (a) shows an optical micrograph of a partial monolayer of ~2.01  $\mu$ m SiO<sub>2</sub> microbeads. By tilting this substrate to a large angle as shown in Fig. 2.4, the shadowing effect limits the growth to the beads. Figure 2.6 (b) shows an example SEM top view of an array of microbeads with an oxide layer deposited at a large angle. By manipulating the substrate during the deposition, a variety of structures can be achieved. After nanostructure growth, the individual micro or nanostructures can be removed from the surface and suspended. He et al. demonstrated the fabrication of rotary nanorods, rotary L-shaped structures, and rolling spiral nanomotors [40]. Figure 2.7 illustrates the step-by-step fabrication of an L-shaped Si nanomotor.



Figure 2.6 (a) Optical micrograph of a partial monolayer of silica microbeads; (b) SEM top view of similar monolayer after a thick layer of TiO<sub>2</sub> is deposited at an angle of  $\theta \sim 86$ .

In the first step (top of Fig. 2.7), the Si source material is deposited at a large angle  $\theta$ ; next the substrate is rotated 180° azimuthally and another deposition of Si follows so that the angle of growth is in the opposite direction; and lastly, to deposit the Pt catalyst, a thin film of Pt is deposited at a small angle. The resulting structure is L-shaped with asymmetrically deposited Pt.



Figure 2.7 Fabrication process of an L-shaped nanorod nanomotor (from Ref. [40])

The advantages of using DSG as opposed to TDEP for the fabrication of catalytic nanomotors are many. First, practically any material can be used. With TDEP, only materials that can be deposited electrochemically can be used while any material that can be evaporated can be deposited in a PVD system. Secondly, the shapes of the structure can be programmed by manipulating the rotation of the substrate holder and angle of incidence of the vapor. Third, making multilayered structures is simple, and the catalyst placement can easily be modified having a major impact on the swimming behaviors achieved. Also, fabricating large quantities of practically identical structures is possible.

## 2.3 Advanced Assemblages

The template-directed electroplating and physical vapor deposition techniques described above are effective methods for producing individual nanomotors, but to manufacture more complex geometries, self-assembly techniques must be utilized. The engineering of structures with multiple individual parts is a particularly difficult challenge. Initial attempts have been made to assemble multiple parts to fabricate complex nanomotor structures, and this challenge represents the next step in nanomotor research and engineering. Assemblages of macroscopic catalytically driven PDMS plates were shown to organize themselves more rapidly due to the active motion resulting from the catalyzed reaction of the Pt section [41]. These aggregates are described to organize themselves based on altering hydrophobic and hydrophilic sections of the plates. Another example consists of flexible hinged nanorods which were achieved by electrodepositing a nanorod consisting of 3 sections: Pt/Au/Pt [56]. The rods were then encapsulated by a polymer and the Au section was then etched leaving the two Pt sections attached but separated by flexible material. Using magnetic navigation and oppositely charged polymers, Sen et al. was able to direct a nanorod nanomotor to a spherical cargo, pick up the cargo, and move it [57]. Figure 2.8 shows a nanomotor picking up cargo and moving it through a microchannel [58].



Figure 2.8 Loading of a magnetic nanoparticle with a Au/Ni/Au/Pt-CNT nanomotor (from Ref. [58]).

Sphere dimers consisting of Pt and SiO<sub>2</sub> microspheres were also fabricated by depositing a half sphere of Pt onto the microbeads and annealing them at 900 °C [59]. The annealing process causes the Pt to become approximately spherical but remain attached to the microbead. A schematic of the fabrication process can be seen in Fig. 2.9. Other examples include doublets of self-propelled Janus spheres [60] as well as interacting spinning nanorods [21]. By magnetizing



Figure 2.9 Fabrication of Pt-SiO<sub>2</sub> self-propelled dimers. First a monolayer of SiO<sub>2</sub> microbeads is placed onto a substrate; then a Cr adhesion layer is deposited followed by Pt; lastly, the structures are annealed at 900 °C and then suspended into water by sonication (from Ref. [59]).

structures with ferromagnetic materials grown by DSG, assemblages of various structures were also achieved [61].

# **2.4 Conclusions**

Fabricating structures that have the ability to derive energy for use as a driving mechanism at the micro and nanoscale is a major challenge for this field. The ultimate goal of this research is to develop functional nanomachinery. To accomplish this goal, nanomotors must first be controllable before they can be incorporated into a larger system. Since motion at low Reynolds number is so dependent upon the viscosity, there needs to be an emphasis on nanomotor shape in order to program the particles' trajectories. Dynamic shadowing growth

allows for the controlled and programmable fabrication of catalytic nanomotors giving it an advantage to TDEP, although this technique is useful for some applications as well. A thorough optimization of nanomotor fabrication will allow for the perfection of the engineering of autonomous structures.

### CHAPTER 3

### CATALYTIC NANOMOTOR PROPULSION MECHANISM

Catalytic nanomotors move under different propulsion mechanisms depending upon the materials of which the structures consist. All catalytic nanomotors consist of an onboard catalyst which allows for the conversion of energy from the environment. The type of catalyst, the location and the distribution dictate the types of swimming behaviors exhibited. Also, depending upon what is in contact with this catalyst, differing motions arise: if the structure consists of an electrically insulating backbone, then the propulsion generated arises from the excess reaction products and a resulting motion away from the higher concentration of products near the catalyst occurs, or in the case in which the catalyst is in electrical contact with another conductor, effects of electrochemistry cause the nanomotor to move in the direction of the catalyst. Experiments conducted in this thesis support the claim that spherical catalytic nanomotors coated with a Pt catalyst only move due to the mass of the  $O_2$  bubble being ejected analogous to a rocket's payload propulsion. The magnitude of this force is estimated by directly measuring the torque applied to a torsion balance of an array of nanorod nanomotors allowing for the calculation of the force for a single nanomotor. The effect of the various propelling mechanisms is also studied by comparing the two competing forces: bubble propulsion and self-electrophoresis. By adding an overlapping surface of Au to the same silica microbead, the movement can be modulated which is an effect of the competing forces. By understanding the propelling mechanism for catalytic nanomotors, another tool for motion engineering is available.

## **3.1 Bubble Propulsion Model**

Since we observed a surface tension dependence on the movement of Pt-coated silica microspheres, we hypothesized that the movement was indeed caused by bubble ejection. Since gas bubble growth rates in solution are dependent upon the surface tension between the fluid and gas, correlating these data to a bubble propulsion model was the most natural route. The model presented is based upon a sphere moving at low Reynolds number in which movement is away from the catalyst and the nanomotor speed is a function of  $H_2O_2$  concentration as well as surface tension. Supporting experiments were performed with Pt-coated silica microspheres and the results matched very well with the model.



Figure 3.1 (a) Schematic of the Pt-coated silica microsphere; (b) a SEM image showing same structure (from Ref. [28]).

The starting point of the model can be summarized in Fig. 3.1 (a). The spherical nanomotor is propelled away from the Pt coating, and a drag force induced by the viscosity of the solution opposes this motion resulting in a steady state. On the right of Fig. 3.1 (a), bubbles are shown being ejected which propels the motor although  $O_2$  bubbles were not directly observed during experiments due to the limitations of optical microscopy. Considering a non-conducting spherical colloid with one hemisphere consisting of a catalyst as shown in Fig. 3.1, the reaction

 $H_2O_2 \xrightarrow{catalyst} H_2O + O_2(g)$  creates a higher concentration of oxygen gas on the catalyst surface in comparison to the non-catalyst surface. The concentrated oxygen coalesces to form bubbles with a critical nucleation radius  $R_0$  on the catalyst surface. The dissolved oxygen surrounding a bubble continues to diffuse into the bubble causing it to grow while the buoyancy force and surface adhesion compete against one another. The bubble continues to grow until it reaches the detachment radius  $R_D$  and is released from the surface; the detachment results in a momentum change which induces a driving force,  $\vec{F}_{drive}$ , away from the catalyst surface. During the bubble detachment, the shape of the bubble is distorted, and the initial detachment velocity is non-zero and has a horizontal component as shown in Fig. 3.1 (a) (the vertical component will be balanced by the gravitational force [62]). Since the catalyst is not consumed in the reaction, as a bubble detaches from the surface, a new bubble will be generated and released as long as hydrogen peroxide is present, and so the nanomotor is continuously propelled in the solution through continuous momentum change caused by a jet of oxygen bubbles. The direct observation for nanobubbles forming and being released from the surface has not occurred to our knowledge; however evidence exists for the presence of nanobubbles on rough surfaces in saturated solutions of air [31]. These nanobubbles likely act as nucleation points for bubble growth for a locally saturated solution, and at a certain radius,  $R_D$ , the bubble will detach which is dependent upon the competition between the contact angle of a rough Pt surface and gravitational interaction. For simplicity, we assume that the bulk hydrogen peroxide concentration remains constant during the reaction and that the bubble retains its shape and volume as it detaches. Also, we only consider the speed of the bubble in the horizontal direction as shown in Fig. 3.1 (a). Under the steady

state,  $\frac{dv}{dt} = 0$  and  $\frac{dM}{dt} = 0$  (the mass *M* of the colloid-bubble system does not change due to the

balance of the catalytic reaction and bubble detachment).  $F_{drive}$  is due to the reaction force caused by the detachment of the bubbles, which will be balanced by the viscous drag force,  $\vec{F}_{drag}$  to reach a constant horizontal speed v,

$$F_{drive} = N \frac{\Delta m}{\Delta t} (v_0 - v), \qquad (3.1)$$

where *N* is the number of bubbles detached from the surface,  $\Delta m$  is the mass change induced by a single bubble,  $\Delta t$  is the average bubble growth time until detachment, and  $v_0$  is the initial horizontal speed of a detached bubble which may depend on the density of the surrounding fluid and acceleration of gravity. The term on the right in Eq. (3.1) is caused by the momentum change of the bubbles. Considering a spherical particle,  $F_{drag} = -6\pi\mu av$ , where *a* is the radius of the colloid and  $\mu$  is the viscosity of the liquid [38]. The speed of the colloid can be rewritten as  $v = \frac{\Delta m}{\Delta t} v_0 / (6\pi\mu a + \frac{\Delta m}{\Delta t})$ . In general,  $6\pi\mu a >> \frac{\Delta m}{\Delta t}$  (for a sphere with a diameter of 2.0 µm,  $6\pi\mu a \sim 10^{-9}$  Kg/s for water and  $\frac{\Delta m}{\Delta t} \sim 10^{-22}$  Kg/s according to Paxton *et al.* who measured the oxygen generation rate per area Pt catalyst in 3.7% hydrogen peroxide as  $8.4 \times 10^{-8}$  mol/cm<sup>2</sup>s) thus,

$$v \approx N \frac{\Delta m}{\Delta t} \frac{v_0}{6\pi\mu a}.$$
(3.2)

Since the Reynolds number of the bubble system is very small, we neglect the effect of the fluid flow resulting from the displacement of the bubble

To estimate the bubble average detachment rate we use a simple bubble growth model. We assume that the  $O_2$  inside a bubble is an ideal gas with a constant pressure *P* and changing volume V during the bubble growth, as presented by Favelukis *et al.* [63], i.e.,  $PV = nR_gT$ where  $R_g$  is the universal gas constant, T is temperature, and n is the molar number of O<sub>2</sub>. (This is a very simple assumption on bubble growth, and can be changed to other bubble growth treatments). The bubble radius R obeys the following rate equation,

$$\frac{dR(t)}{dt} = \frac{R_g T}{P} \frac{1}{4\pi R^2} \frac{dn}{dt} = \frac{R_g T}{P} r, \qquad (3.3)$$

where *r* is the catalytic reaction rate that represents the molar flux of  $O_2$  diffusing into the bubble. Since we assume a steady-state system, the reaction rate *r* is constant, and is determined by the rate of  $H_2O_2$  being adsorbed onto the catalyst surface as well as the catalytic reaction rate constant *k*. Assuming the adsorption of the  $H_2O_2$  follows the Langmuir isotherm, the catalytic reaction rate can be written as,

$$r = \frac{k\alpha c}{1 + \alpha c},\tag{3.4}$$

where *c* is the bulk concentration of H<sub>2</sub>O<sub>2</sub>, and  $\alpha$  is the Langmuir adsorption constant. Combining Eq. (3.3) and (3.4),

$$R(t) - R_0 = \frac{R_g T}{P} \frac{k\alpha c}{1 + \alpha c} \Delta t$$
(3.5)

From Eq. (3.5), the average time for a bubble to grow from  $R_0$  to  $R_d$  can be determined and the average rate of mass change is,

$$\frac{\Delta m}{\Delta t} = \frac{4\pi \rho_{O_2} (R_d^3 - R_0^3) R_g T}{3P[R(t) - R_0]} \frac{k\alpha c}{1 + \alpha c},$$
(3.6)

where  $\rho_{0_2}$  is the density of oxygen. In Eq. (3.6),  $R_0$  is determined by the saturation concentration of oxygen and the surface tension,  $\gamma$ , of the liquid,  $R_0 = 2\gamma \kappa / (c_s - c_{eq})$ , where  $\kappa$  is Henry's constant,  $c_s$  is the saturation oxygen concentration for bubble nucleation and  $c_{eq}$  is the oxygen solubility [64]. Considering the bubble detachment radius,  $R_d \propto \gamma$ , which has been verified numerically due to an effect of surface tension near the location of bubble detachment as the bubble deforms [65], and combining Eq. (3.2) and Eq. (3.6), we obtain an expression for motor speed v in terms of H<sub>2</sub>O<sub>2</sub> concentration and surface tension,

$$v \propto \frac{R_s T \rho_{O_2} v_0}{\mu a P} \gamma^2 \frac{k \alpha c}{1 + \alpha c}.$$
(3.7)

Equation (3.7) predicts that the motor speed v is proportional to  $\gamma^2$ , and depends upon hydrogen peroxide concentration c in a complex manner. Previously, a linear dependence upon surface tension was proposed by the surface tension model [31], and a non-linear dependence upon concentration c has been previously reported as well [66]. To test the validity of Eq. (3.7), we have investigated the autonomous motions of Pt-coated spherical silica colloids micromotors under different hydrogen peroxide concentrations c and various values of surface tension  $\gamma$ .

The Pt coated silica microspheres were fabricated following the protocol by Whitesides [50] and Howse [66]. The silica colloid has a diameter of ~ 2.01  $\mu$ m and the Pt coating was 50 nm, as shown in the SEM image in Fig. 3.1 (b). The detached colloid spheres were then dispensed into H<sub>2</sub>O<sub>2</sub> solutions with different values of concentration and surface tension, and the motions were recorded via a 1491 INi VanGuard microscope and a CCD camera. We observed the beads in the steady state, i.e. constant velocity. The surface tension of the 2% H<sub>2</sub>O<sub>2</sub> solutions was altered by adding various concentrations of sodium dodecylsulfate (SDS) and was measured

by a pendant-drop method. Figures 3.2 (a) and 3.2 (b) show the average speed of the colloid motors for different H<sub>2</sub>O<sub>2</sub> concentration *c* at fixed surface tension  $\gamma = 72 \text{ mN/m}$  (the surface tension of water) and different surface tension  $\gamma$  for fixed *c* = 2% respectively. Each data point on both graphs represents the average of the average velocity for 10 microbeads taken over 10 second time intervals. The corresponding Brownian motion speeds have been subtracted and are also given in the two plots. The *v*-*c* plot shows a strong nonlinear relationship while the *v*- $\gamma$  data appears slightly exponential.



Figure 3.2 Active motion of Pt-coated silica microbeads in dilute hydrogen peroxide bath: (a) the average colloid motion speed v versus the hydrogen peroxide concentration c for fixed surface tension 72 mN/m. The dashed line represents the speed of the Brownian motion; (b) the average colloid motion speed v versus surface tension  $\gamma$  in 2% H<sub>2</sub>O<sub>2</sub>. The dashed lines with symbols show Brownian motion speed for various surface tension values of which were subtracted from the data. The solid curves in both figures are the fitting results using Eq. (3.7) (from Ref. [28]).

Those data can be fitted quite well by Eq. (3.7): for the concentration dependence data, Eq. (3.7) can be simplified as  $v = P_1 c/(P_2 + c)$ , where  $P_1$  and  $P_2$  are two fitting parameters. The fitting curve in Fig. 3.2 (a) gives  $P_1 = 6.2$  and  $P_2 = 0.5$ . For low concentrations *c*, a roughly linear dependence exists, and linear relationship between force and concentration for low concentrations has been shown [67], but for higher concentrations a limiting value is eventually reached. From Fig. 3.2 (a) one can see that the motor velocity starts to level off at 2% H<sub>2</sub>O<sub>2</sub> concentration. Howse et al. has suggested this phenomenon is a result of a two-stage decomposition of hydrogen peroxide by the catalyst which results in a typical Michaelis-Menten kinetics for enzymes, while in our model, the reaction is naturally limited by the Langmuir isothermal (H<sub>2</sub>O<sub>2</sub> adsorption). For the surface tension dependence, Eq. (3.7) can be reduced to  $v = P_3\gamma^2$ , and the best fit in Fig. 3.2 (b) gives  $P_3 = 0.00084$ , which demonstrates a very good agreement between the model and the experimental data. Since Eq. (3.7) links the concentration *c* and surface tension  $\gamma$  together, the fitting parameters  $P_1$ ,  $P_2$ , and  $P_3$  are inherently linked by the

equation,  $P_3 / P_1 = \frac{c}{\gamma^2 (c + P_2)} \Big|_{\gamma = 72mN/m, c = 2\%}$ . For the data shown in Figs. 3.2 (a) and 3.2 (b),

 $\gamma = 72$  mN/m and c = 2%, and the value  $\frac{c}{\gamma^2(c+P_2)}$  is estimated to be  $1.5 \times 10^{-4}$ . From the fitting parameters we estimate the value  $P_3/P_1 \approx 1.4 \times 10^{-4}$ . This further suggests a solid agreement between theory and experiment.

In conclusion, we have presented a simple model based upon oxygen bubble detachment to explain the driving force for catalytic nanomotors. We show that the propulsion is dependent upon the surface tension of the solution and on the concentration of hydrogen peroxide along with the velocity of the detached bubbles. We describe this motion through the generation of oxygen gas from the catalytic break-down of hydrogen peroxide and the formation and release of oxygen bubbles from the surface of the catalyst resulting in a change of momentum. The motion behaviors of spherical colloids have been used to test the validity of the model due to their symmetry and relatively simple and inexpensive production. The model can be applied to nanomotors of any shape by adjusting the geometric parameters. However, for systems with two metal junctions such as Au/Pt system, other propelling mechanisms may dominate the motion due to a larger propelling force. Even under such a situation, the bubble induced propelling could be considered as a useful modification.

### **3.2 Driving Force for a Single Nanomotor**

The driving force of an individual nanomotor is difficult to measure directly at the nanometer length scale. Indirect methods are possible by linking the drag force and nanomotor speeds to determine the magnitude of force to propel a nanomotor at that velocity. Researchers have estimated the driving force using this method; for example, the members of the Penn State group calculated the drag force of a cylindrical bi-metallic Au/Pt nanorod in hydrogen peroxide [31]; He et al. calculated the value of a Si/Pt nanorod nanomotor as  $F_{drive} \approx 1.8 \times 10^{-13} N$  using the same method [40]. This method does not however account for such forces as friction, and it is an estimation based upon the dimensions of the nanomotor. Hence, it is an indirect method for measuring the force. Potential methods to directly measure the force exerted on individual nanomotors are possible: an atomic force microscope (AFM) or a torsion balance. To measure the force with AFM, nanomotors must be attached to the AFM tip, and the force may be measured by knowing the force constant of a commercially available cantilever of which is typically around 0.1 N/m. For a force of  $F \sim 10^{-13}$  N, the cantilever would experience a displacement of ~ 1/100th of an Angstrom which is beyond the AFM detection limit. The torsion balance is a simpler set-up since billions of nanomotors can be measured simultaneously. It cannot give the exact force for each individual nanomotor, but it can give a statistical estimation. Here, we directly measure this driving force with the use of a simple torsion balance; we

measure the force of a large group of nanorod nanomotors in  $H_2O_2$  that are attached to a silicon substrate, and we estimate the force due to each individual nanorod [67]. We show that a linear relationship exists between hydrogen peroxide concentration and force.



Figure 3.3 (a) Schematic of the torsion balance to measure propelling force; the right balance weight has a silicon substrate with nanorod nanomotors attached. The laser light reflects off the mirror and lands upon a ruler where the displacement may be measured. (The angle is exaggerated for clarity); (b) A magnified side-view of the substrate containing nanomotors deposited at an angle *φ*. The driving force is perpendicular to the lined defined by the rods axis (from Ref. [67]).

Our torsion balance consists of metal wire suspending a solid metal piece between the top support and the base as shown in the center of Figure 3.3 (a). The center piece contains a thin metal rod of length l=15.88 cm placed through the middle of the object. Two cylindrically shaped weights that balance the system hang on both sides of the thin rod. On the side of each weight, a flat surface was cut away in order to easily attach the nanomotor substrate (Fig. 3.3

(b)). A  $1 \times 1$  cm<sup>2</sup> silicon substrate coated with ~ 4 µm Si nanorods (quartz crystal microbalance reading) and a 150 nm Ag thin film is attached to the flat surface as shown in Fig. 3.3 (b). The nanomotors were only attached on the right side of the torsion balance. A laser pointer was secured to a desk that was aimed toward a small silicon reflecting surface fixed upon the center bar, and the laser light was reflected onto a ruler at a distance y = 219.7 cm. Since the nanomotors are coated at an angle on the Si surface as shown in the enlarged object in Fig. 3.3 (b), when this surface is submerged into the H<sub>2</sub>O<sub>2</sub> solution, the direction of the driving force is perpendicular to the nanorods which will provide a horizontal force that rotates the tension wire also shown in Fig. 3.3 (b). This rotation causes a deflection  $\Delta x$  of the laser beam in the horizontal direction. The distance  $\Delta x$  corresponds to the displacement on the ruler caused by the catalytic reaction. We carefully submerged the weight into a 250 ml beaker of DI water, and then 30% hydrogen peroxide was drop-added according to the desired concentration. The control experiment consisted of adding water instead of the concentrated hydrogen peroxide.

The torsion constant for the apparatus was determined through the periodic rotation of the tension wire. The torque is given by  $\tau = Fd \approx k\theta$ , where *F* is force, *d* is the length of the lever arm,  $\theta$  is the angle of rotation, and *k* is the torsion constant of the balance. Since only small angles are observed, we make the approximation:  $\tan \theta \approx \theta$ . By measuring the period of oscillation, we may determine the torsion constant,

$$k = \frac{4\pi^2 I}{T^2} \tag{3.8}$$

where *I* is the moment of inertia. Since calculating the moment of inertia for our asymmetric center piece is impractical, we added the thin rod alone symmetrically through the middle of the center piece which increased the total moment of inertia to  $I + \Delta I$ , giving a longer period of

$$T' = 2\pi \sqrt{\frac{I + \Delta I}{k}} \,. \tag{3.9}$$

This leads to

$$k = \frac{4\pi^2 \Delta I}{T'^2 - T^2}.$$
 (3.10)

The thin rod has a moment of inertia  $\Delta I = \frac{1}{3}ml^2$ , where m = 19.52 g is the mass and l = 15.83 cm is the length of the rod, and we measured the two oscillation periods: one for the center piece alone,  $T = 0.46 \pm 0.06$  sec., and one for the center piece and the thin rod combined,  $T' = 3.47 \pm 0.04$  sec. With these values, we determined the torsion constant for our apparatus to be  $k = (3.70 \pm 0.07) \times 10^{-4} Nm$ .



Figure 3.4 SEM top view (a), cross-sectional view (b), and TEM (c) images of Si/Pt nanorods (from Ref. [67]).

Previous research has shown a roughly linear hydrogen peroxide concentration dependence on velocity of Au/Pt striped nanorods [31]. Here we show the force applied by our nanorod catalytic nanomotors is also concentration dependent which is expected since the driving force is a result of the catalyzed reaction, and higher concentrations of  $H_2O_2$  lead to more



Figure 3.5 Relationship between concentration of hydrogen peroxide and force for individual nanomotors. The solid line is from linear fitting (from Ref. [67]).

reaction products. The driving force gives the measurable value  $\Delta x$ . Using the small-angle approximation, we have  $2\theta \approx \Delta x/y$ , and the force is now,

$$F \approx \frac{k\Delta x}{2dy}.$$
(3.11)

Equation 3.11 allows us to measure the force in the horizontal direction. The total number and the arrangement of the nanorod array on the surface can be estimated from the scanning electron microscope image as shown in Figure 3.4 [40]. The density of the nanorods on the surface is 2.0  $\times 10^9/\text{in}^2$  which gives  $3.1 \times 10^8$  nanorods on a  $1 \times 1$  cm<sup>2</sup> area sample. Figure 3.4 also shows that the nanomotors are tilted at an angle of  $\phi \approx 55^\circ$  with respect to the surface normal, so the driving force has two components. The total driving force can be estimated as,

$$F_{drive} = \frac{F_x}{\sin(\phi)}.$$
(3.12)

Figure 3.5 summarizes the results that show an approximately linear relationship between concentration and force with a slope of  $4.82 \times 10^{-14}$  N per percentage of hydrogen peroxide. The force applied by the nanomotors depends upon the concentration of hydrogen peroxide, and the force measurements via torsion balance for catalytic nanomotors are in good agreement with previous results in the literature.

#### 3.3 Comparing the Self-Electrophoresis and Bubble Propulsion Models

Nanomotor structures with electrically insulating underpinnings such as  $Pt/SiO_2$  [28] or  $Pt/TiO_2$  [22] are propelled by a mechanism other than self-electrophoresis. For bimetallic nanomotors such as Au/Pt nanorods [21, 32, 35, 49] or spherical microbeads [51], the two metals can act as anode and cathode, and an electrochemical decomposition of  $H_2O_2$  leads to a flux of charges inside and outside the nanomotor [32] explaining why movement is toward the catalyst. Most bimetallic nanomotors have been constructed symmetrically, especially the hetero-rod structures, and the self-electrophoresis mechanism has only been studied as a function of the type of metal used, the  $H_2O_2$  concentration, and applied electric potential [68]. The direct comparison between mechanisms has yet to be studied since the design of similar motors operating under differing mechanisms has not been demonstrated. In this letter, we use a dynamic shadowing growth method to fabricate asymmetric bimetal-coated catalytic micromotors by systematically changing the area of the exposed Au section. Similar micromotors governed by the non-self-electrophoresis mechanism are compared with the bimetallic motors.

Five spherical Pt/Au micromotors with various Au exposure surface areas were fabricated by depositing metals in a custom-built electron beam evaporation system (Torr International) using the dynamic shadowing growth method as shown in Fig. 3.6. The 2.01  $\mu$ m silica microbead suspensions (Cat. # SS04N/7829, Bangs Laboratories) were first diluted with a 1:45 volume ratio in methanol, and a droplet of the diluted solution with a volume of 1  $\mu$ L was spread onto a 2 cm × 0.8 cm cleaned silicon surface as shown in Fig. 3.6 (c). The substrates were placed inside a chamber at  $\approx 10^{-6}$  Torr. Next, as shown in Fig. 3.6 (a), a 10 nm Ti adhesion layer was deposited onto the substrates (surfaces of the beads) followed 50 nm Au measured by quartz



Figure 3.6 (a) Ti and Au are deposited onto the substrate at  $\theta = 0^{\circ}$ ; (b) Pt is deposited onto the substrate after the substrate holder is rotated a polar angle of  $\theta$ , (c) the spread individual 2.01 µm beads on Si surface; (d) a SEM image of a asymmetric Pt/Au micromotor with  $\theta = 40^{\circ}$  (from Ref. [27]).

crystal microbalance (QCM). The substrate then was rotated to a polar angle  $\theta$ , i.e., the vapor incident angle formed the angle  $\theta$  with respect to substrate normal as shown in Fig. 3.6 (b). Then a 50 nm layer of Pt was deposited. Depending on the rotating angle  $\theta$ , the last Pt deposition
leaves only part of the Au layer exposed as shown in Fig. 3.6 (b), and the Pt coverage on the individual beads will be the same regardless of  $\theta$ . The five motors fabricated had Pt deposited at angle  $\theta$  set to 0°, 20°, 40°, 60°, and 80°. The deposition rate was monitored by QCM  $\approx$  0.5 nm/s. An SEM image is shown in Fig. 3.6 (d). For this sample,  $\theta = 40^{\circ}$ , the exposed Au surface is in the upper right corner. As a control, micromotors of the same beads (2.01 µm SiO<sub>2</sub>) with only Ti and Pt depositions were fabricated.

The as-deposited micromotors were re-suspended by sonication < 1 min. The beads were pipetted by 2.0 µL droplets onto a clean Si wafer followed by the addition of 2.0 µL of 10% H<sub>2</sub>O<sub>2</sub> so the effective concentration was 5%. Videos were captured with an Imperx CCD camera under 10× magnification light microscope (Mitutoyo FS110) in reflection mode. 20 second movies were made at a frame rate of 20 frames/s. Videos were analyzed with tracking software; the micromotors settle to the surface of the Si wafer and thus move in 2D. The output files were analyzed by software that calculates the speed and mean squared displacement; all analysis software was developed in our lab.

For a microsphere, significant thermal fluctuations, i.e., Brownian motion, are always present that influence the particles' motion behaviors. The mean squared displacement  $\langle r^2 \rangle$  and the average speed *u* were calculated from the video data. For a sphere of radius *a* undergoing Brownian motion,  $\langle r^2 \rangle$  is given by Eq. (1.9) in section 1.4. For a propelled sphere moving at speed *u* in 2D, the  $\langle r^2 \rangle$  is given by [66]

$$\langle r^2 \rangle = 4Dt + \frac{u^2 \tau_R^2}{2} \left[ \frac{2t}{\tau_R} + e^{-2t/\tau_R} - 1 \right]$$
 (3.13)

where  $\tau_{R} = kT/8\pi\eta a^{3}$  is the rotational diffusion coefficient. For  $t \ll \tau_{R}$ , the characteristic diffusion coefficient is given by  $\sqrt{4Dt} = \langle r^{2} \rangle$ . For the case of the sphere being propelled at speed

*u* and  $t >> \tau_R$ , the effective diffusion coefficient is given by  $D' = D + \frac{1}{4}u^2\tau_R$  showing an augmentation of *D* characteristic of a random walk [66].



Figure 3.7 Mean squared displacement  $\langle r^2 \rangle$  as functions of time *t* for asymmetric Pt/Au micromotors with vapor incident angle  $\theta$ ; the curves for two control samples are also shown: one for the Pt-only micromotor in 5% H<sub>2</sub>O<sub>2</sub> (symbol  $\circ$ ) and the other is Brownian motion in H<sub>2</sub>O (symbol  $\Box$ ) (from Ref. [27]).

Figure 3.7 shows the  $\langle r^2 \rangle$ - *t* relationships obtained experimentally for both the asymmetric Pt/Au and the Pt-only micromotors. These data were obtained by calculating  $\langle r^2 \rangle$  for 10 trajectories for each sample and averaging the data. The curve with symbol  $\Box$  in Fig. 3.7 shows Brownian motion in DI water. A linear fit gives a value of 0.43  $\mu$ m<sup>2</sup>/s while using Eq. (1.1) for a microbead of radius  $a = 10^{-6}$  m, the value calculated is 0.88  $\mu$ m<sup>2</sup>/s. The other curves in Fig. 3.7 show the active motion of various micromotors in H<sub>2</sub>O<sub>2</sub>. An increase in the exponents

for the  $\langle r^2 \rangle$ - *t* relationships is clearly seen. The graph shows that the most pronounced activity was observed for the asymmetric Pt/Au micromotors with  $\theta = 60^\circ$  and  $80^\circ$ , and there is a clear correlation between the increase of  $\theta$  and the amount of active swimming taking place for the asymmetric Pt/Au micromotors. The  $\langle r^2 \rangle$ - *t* curve for the Pt-only micromotors, shown with symbol  $\circ$ , rests between the curves for the asymmetric Pt/Au micromotors with  $\theta = 40^\circ$  and  $60^\circ$ .



Figure 3.8 The average speed *u* of the asymmetric Pt/Au micromotor vs. Au exposed surface area *A*. The blue curve shows the fitting of  $u \propto A^{\frac{3}{2}}$ . The speed of the Pt-only micromotor is shown as the dashed line (from Ref. [27]).

Each structure has the same Pt surface area exposed to the solution of  $H_2O_2$ . The two major differences between each asymmetric Pt/Au micromotor is the overlap location or the electrical contact location of the two metals and the exposure area of the Au to the solution. For the electrochemical mechanism to be taking place both the Pt and Au must be exposed to the solution and the two metals must be in contact. Figure 3.8 plots the experimentally obtained

average speed u of the asymmetric Pt/Au micromotors as a function of the Au exposure area, A. With the increase of the Au exposure area A, the speed u increases monotonically. A relationship is estimated from the known theory. According to the self-electrophoresis mechanism, the speed of a cylindrical bimetallic nanomotor at low Reynolds number arising from electrokinetics is given by Eq. (1.10) in section 1.5.4. This model was presented by Posner et al. and arises from self-electrophoresis in viscosity-dominated length scales [43]. Increasing A alters two parameters in Eq. (3.15): the reaction flux i and the length of the catalytic motor h. The Au surface area is the limiting factor since the Pt surface area is larger. Thus, the reaction flux,  $j \propto A$ . Also the Au surface area is effectively linked to the length, and by dimensional analysis  $h \propto \sqrt{A}$ . Thus, from Eq. (3.15) the average speed u of the scales as  $u \propto A^{\frac{3}{2}}$ . When the exposed Au surface area A is zero, there should be no deterministic motion for the micromotor; however, as stated above, other mechanisms may be present. The only difference between the asymmetric Pt/Au bimetallic micromotor with  $\theta = 0^{\circ}$  case and the Pt-only micromotor is that for the former, there is a layer of Au that is completely covered by the Pt, and for the latter, no Au is present at all. In both cases, the exposed Au surface area is A = 0. Therefore, the two cases should appear to be identical; however the speed for the  $\theta = 0^{\circ}$  Pt/Au bimetallic micromotor is  $u_{0^{\circ}} = 1.2 \pm 0.2 \,\mu\text{m/s}$ whereas the speed for the Pt-only micromotor is  $u_{\rm Pt} = 1.6 \pm 0.5 \,\mu\text{m/s}$ , which is significantly higher. As shown in Fig. 3.8, the case for  $A = 0 \ \mu m^2$  corresponds to  $u_{0^\circ}$  which is very close to the Brownian motion value,  $u = 1.1 \pm 0.2 \,\mu\text{m/s}$ . The presence of the Au seems to have an influence even when it is not exposed to the solution. The curve in Fig. 3.8 shows a fitting using the equation  $b + cA^{\frac{3}{2}}$ , with a goodness-of-fit of 0.91, where  $b = 1.1 \pm 0.1 \,\mu\text{m/s}$ , which corresponds to the Brownian motion. In addition, Fig. 3.8 also plots the *u* of the Pt-only micromotor (the dashed line). The non-self-electrophoresis micromotors have an average speed of  $1.6 \pm 0.5 \mu$ m/s, which is smaller than that of the Pt/Au micromotors with  $\theta = 60^{\circ}$  and  $80^{\circ}$  ( $1.8 \pm 0.3 \mu$ m/s and  $2.7 \pm 0.5 \mu$ m/s). Since both the asymmetric micromotors and the Pt-only micromotors have the same Ptcoating area, our results demonstrate that the self-electrophoresis mechanism generates greater active motion.

In summary, we have designed asymmetric Pt/Au coated catalytic micromotors using a dynamic shadowing growth method, and explored their motion behavior by systematically increasing the exposed Au surface area. We also compare the self-electrophoresis mechanism with the other non-electrochemical mechanism for motors with similar size and morphology. The motion behaviors of asymmetric Pt/Au spherical micromotors can be modulated by varying the overlapping of the two metals through a dynamic shadowing growth method. This provides an alternative way to systematically design nanomotors and fine-tune swimming behaviors.

### **3.4 Conclusions**

A bubble propulsion model based on a half-coated microbead with a Pt catalyst is presented and explains the relationship of nanomotor speed vs.  $H_2O_2$  concentration as well as surface tension which is altered with the addition of a surfactant. The driving force of this bubble propulsion mechanism that is in effect when the nanomotor consists of an electrically insulating backbone can be measured directly using a torsion balance. To compare the difference between the self-electrophoresis model and the bubble propulsion model, an Au/Pt microbead with various overlapping surface areas is fabricated and compared with the Pt-only coated microbead. The results of this experiment show that the self-electrophoresis mechanism produces higher activity than the bubble propulsion or diffusiophoresis mechanisms alone. By adjusting the types of materials deposited onto the nanomotor backbone, behaviors can be altered and even tuned to perform specific swimming behaviors.

### **CHAPTER 4**

## TUNING NANOMOTOR MOTION BY GEOMETRIC ENGINEERING

As a particle moves in a low Reynolds number regime, the inertial terms in the Navier-Stokes equation (Eq. 1.3) can be ignored because the viscosity dominates. Since the viscosity causes drag on a particle, the size of a catalytic nanomotor and the physical shape contributes tremendously to how much drag force and/or torque is applied while moving through the viscous liquid. Also, as stated before, the location of the catalyst is a major factor of how a nanomotor is going to swim. In a DSG system, adjusting the location of the catalyst is simple, and by altering the location and distribution, drastically different motion behaviors emerge. Also with DSG, the ability to fine-tune the geometry by programming substrate rotation allows for the engineering of swimming behaviors. This chapter is devoted to the study of geometry-dependent nanomotor motion behaviors.

### 4.1 Rotary Multi-Component Nanomotors

This study outlines the fabrication and dynamics of a rotational catalytic nanomotor. Multi-component rotary catalytic nanomotors consisting of a spherical silica microbeads with  $TiO_2$  nanoarms coated asymmetrically with Pt are fabricated by DSG [22], which allows for the simultaneous fabrication of a large number of uniform structures. In H<sub>2</sub>O<sub>2</sub>, these nanomotors anchor to the surface with the colloid beads, and the long arms rotate about an axis through the center of the silica microbead. The rotational frequency of the rotors strongly depends upon the H<sub>2</sub>O<sub>2</sub> concentration and surface tension of the solution similar to the results presented in section 3.1. As described in section 2.2.1, DSG combines the shadowing effect with substrate manipulation in a physical vapor deposition system. The shadowing effect occurs during oblique angle deposition (OAD) in which the substrate's normal is placed at an angle  $\theta > 80^\circ$  with respect to the incident vapor direction. On a flat substrate, random nucleation resulting from vapor accumulating on the surface serves as growth centers for aligned nanorods. Patterned substrates substitute for the nucleation centers and become templates for growing uniform aligned nanostructures. Our structures begin with a monolayer of silica microbeads (Fig. 4.1 (a)), and then we evaporate TiO<sub>2</sub> (Fig. 4.1 (b)) and Pt (Fig. 4.1 (c)) onto the monolayer. Figure 4.1 (d)



Figure 4.1 (a) 2.01 µm diameter silica microbeads forming a closely-packed monolayer; (b) TiO<sub>2</sub> (~6 µm) is first deposited onto the microbeads at an angle  $\theta = 86^{\circ}$ ; (c) the substrate is rotated to  $\theta = 0^{\circ}$  and a thin layer (~150 nm) of Pt is deposited in an asymmetrical manner; (d) SEM image of the resulting structure.

shows an SEM image of a typical multi-component nanomotor as a result of the growth process; the silica microbead has a radius of  $a \sim 1 \mu m$ , and the arm length and radius of the TiO<sub>2</sub> nanorods are  $l \sim 3.5 \mu m$  and  $r \sim 500 nm$ , respectively. The TiO<sub>2</sub> arm appears asymmetric at the base and the tip slightly resembling a human index finger, and this asymmetric shape can help us to judge the direction of the propulsion force. The as-deposited TiO<sub>2</sub> has an amorphous phase.

The fabrication process takes advantage of DSG. We start with patterned substrates consisting of closely-packed two-dimensional arrays of silica microbeads spread upon silicon wafers. 2.01 µm silica microbeads (Bangs Laboratories) are drop-cast onto clean 2 cm<sup>2</sup> silicon substrates as shown in a  $40 \times$  micrograph (Fig. 4.1 (a)). We mount the substrates onto a substrate holder and place them into a vacuum chamber, and then we evacuate the chamber to a background pressure of ~  $10^{-6}$  Torr. The colloid-covered substrate surface normal is rotated to  $\theta = 86^{\circ}$ , with respect to incident vapor (Fig. 4.1 (b)). We evaporate TiO<sub>2</sub> in the chamber, and it accumulates on the substrates at a deposition rate of ~ 0.5 nm/s read by a quartz crystal microbalance (QCM) facing the vapor direction. Where colloids are present on the substrate, OAD causes uniformly aligned arms to form upon each colloid. The arms are grown until the QCM reads  $\sim 6 \,\mu\text{m}$ . The actual length of the arms is shorter than the reading of the QCM due to the large angle of incidence. We then rotate the substrates back to  $\theta = 0^{\circ}$  followed by a deposition of a 150 nm layer of Pt (Fig. 4.1 (c)). Since we grow the arms at an angle, the Pt coats only one side of the arms making the structures asymmetric; the asymmetric placement of the catalyst is essential for nanomotor movement.

The structure of the resulting catalytic nanomotor is characterized by scanning electron microscopy (Fig. 4.1 (d)). For nanomotor characterization, we remove the structures from the substrate and suspend into solutions with various concentrations of sodium dodecyl-sulphate (SDS) via sonication. We drop the solution onto a clean glass microscope slide with a pipette, and the  $H_2O_2$  is added to the solution in the same manner. We observe and record the motion with a VanGuard 1400INi optical microscope combined with a CCD camera (Imperx).

The multi-component catalytic nanomotors rotate autonomously in solutions of  $H_2O_2$ . The autonomous motion is made possible by the asymmetric distribution of Pt onto the structures

![](_page_81_Figure_0.jpeg)

Figure 4.2 Typical nanomotor behavior: moving from left to right, each frame selected from a video of a single rotation of the nanomotor in 1% H<sub>2</sub>O<sub>2</sub> shows the progression of rotation after 1 sec. (from Ref. [22]).

When the nanomotors are placed into solutions of H<sub>2</sub>O<sub>2</sub>, the structures rotate at various frequencies on the surface of the glass slide depending upon the concentration of H<sub>2</sub>O<sub>2</sub> and the surface tension of the solution. An example of our structure rotating in 1% H<sub>2</sub>O<sub>2</sub> is shown in stills from a movie in Figure 4.2. Each frame in the image viewed from left to right portrays the advancement of 1 s. In this case, the rotational frequency is roughly 0.15 Hz, and similar values were reported for Au/Ni bimetallic nanorods [69] and Au/Pt/Au nanorods [49]; slightly higher values of ~ 1 Hz were observed for Si/Pt L-shaped nanorod nanomotors [40]. The multicomponent nanomotors rotate about an axis through the center of the microbead and perpendicular to the TiO<sub>2</sub> arm that rotates on the plane of the glass slide. The continuous disproportionate concentrations of H<sub>2</sub>O<sub>2</sub> on the Pt-coated side of the structure leads to a propelling force away from the Pt-coat verifiable by the asymmetry of the structures (Fig. 4.1 (d)); the structures' shape allows us to determine that the propulsion is directed away from the catalyst. A large number of structures are observed simultaneously, and all of the structures rotate at the same approximately constant frequency. When the H<sub>2</sub>O<sub>2</sub> fuel is injected into a solution of these structures, they immediately begin rotating, and steady rotation is quickly reached; the acceleration is difficult to measure due to mixing and turbulence from eddy currents. We observe small translational displacements as well, in which the microbead portion

![](_page_82_Figure_0.jpeg)

Figure 4.3 (a) Center of mass trajectories for single multi-component nanomotors in various  $H_2O_2$  concentrations; (b) orbital speed for the same structures. The curve is a best-fit for a Langmuir Isotherm (from Ref. [22]).

of the nanomotor slips along the surface of the glass microscope slide; the trajectory depends upon the concentration of H<sub>2</sub>O<sub>2</sub>. Figure 4.3 (a) presents some characteristic trajectories of nanomotors at several H<sub>2</sub>O<sub>2</sub> concentrations. The particles' geometrical centers tend to move in a circular fashion while simultaneously rotating comparable to previous reports [69]. For low concentrations, the radii become larger as the H<sub>2</sub>O<sub>2</sub> concentration increases; as we continue to increase the H<sub>2</sub>O<sub>2</sub> concentration, the radii begin to decrease. The orbital speeds of the nanomotors' centers are plotted as a function of H<sub>2</sub>O<sub>2</sub> concentration; the speed increases roughly linearly with low concentrations and then gradually reaches a limit (Figure 4.3 (b)). The relationship follows the well-known Langmuir isotherm type of function  $v = P_1c/(c + P_2)$  as shown by the curve that fits the data where  $P_1$  and  $P_2$  are parameters referring to the specific system in question and *c* is the concentration of H<sub>2</sub>O<sub>2</sub>; the detailed relationship between the velocity and the Langmuir isotherm is presented in Ref. [28]. We explain the observed constant rotational frequency by the opposing torques applied to the arm of each nanomotor supplied by the catalytic driving forces and fluid drag forces (Figure 4.4). Previous studies have shown that catalytic nanomotors are propelled away from their catalyst site for structures consisting of insulating materials [40] (nanomotors with conducting metals move under the influence of self-electrophoresis and move toward the catalyst) [32]; our structure consists of an insulating backbone and we observe that the driving force is directed away from the Pt. Assuming that the force acting on the catalytic surface is uniformly distributed, the driving torque may be calculated by integrating  $d\tau = F'zdA$ , the torque applied by the catalyst onto an area dA at a distance z from the axis of rotation through the center of the spherical colloid; F' is the force per unit area, and our previous studies show a linear relationship exists between force and H<sub>2</sub>O<sub>2</sub> concentration, c, as  $F' = \chi c$  with slope  $\chi \sim 0.001$ N/m<sup>2</sup> per percentage H<sub>2</sub>O<sub>2</sub> concentration [67]. Assuming that the arm is roughly a cylinder of length l and radius r and that the catalyst covers half of the cylinder so that  $dA = \pi r dz$ , we have,

$$\tau_{drive} = \pi r F \int_{a}^{l+a} z dz = \pi r \left[ \frac{1}{2} l^2 + la \right] F'.$$
(4.1)

Considering fluid resistance acts on the arm in a non-uniform manner due to the speed difference on the arm (Figure 4.4), the drag force acting onto different locations *z* along the nanorod is different,  $F_{drag} = \frac{8\pi^2 \mu z}{\ln(\frac{2z}{r}) + \frac{1}{2}}v$ , where  $\mu$  is the viscosity of the fluid. For a given rotational frequency *f*, the velocity at a point *z* along the axis of the cylinder is  $v = 2\pi f z$ ; therefore, the torque corresponding to the drag force applied to the arm is,

$$\tau_{drag} = 8\pi^2 f \mu \int_{a}^{l+a} \frac{z^2 dz}{\ln\left(\frac{2z}{r}\right) + \frac{1}{2}} = 8\pi^2 f \mu \left(\frac{r^3}{8}\right) e^{-\frac{3}{2}} \left[G\left((l+a)^3\right) - G\left(a^3\right)\right], \tag{4.2}$$

where  $G(x) = \text{Ei}\left(\ln\left(\frac{8x^3}{r^3}\right) - \frac{3}{2}\right)$  and Ei(x) is the exponential integral with series representation

![](_page_84_Figure_2.jpeg)

Figure 4.4 Free body diagram showing directions of the driving force and viscous drag force.

 $\operatorname{Ei}(x) = \gamma + \ln x + \sum_{k=1}^{\infty} \frac{x^k}{kk!}$  where  $\gamma$  is the Euler-Mascheroni constant. For the steady state rotation

observed, we have  $\tau_{drive} = -\tau_{drag}$ ; thus the rotational frequency f is,

$$f = \frac{e^{\frac{3}{2}}}{\pi\mu r^2} \frac{\left[\frac{1}{2}l^2 + la\right]}{\left[G((l+a)^3) - G(a^3)\right]} \chi c.$$
(4.3)

Equation (4.3) shows a linear relationship between  $H_2O_2$  concentration, *c*, and rotational frequency, *f*.

Combining Eq. (4.3) and the parameters stated above, we expect that  $df/dc \sim 0.2$  Hz per percentage H<sub>2</sub>O<sub>2</sub>. We also observe the change of rotation frequency *f* as a function of H<sub>2</sub>O<sub>2</sub>

concentration, *c*, for nanomotors without slipping (Figure 4.5 (a)). The graph shows a linear relationship which qualitatively agrees with Eq. (4.3). The fitting gives the slope =  $0.15 \pm 0.01$  Hz per percentage H<sub>2</sub>O<sub>2</sub>. This value is close to the value predicted by Eq. (4.3) of 0.2 Hz per percentage H<sub>2</sub>O<sub>2</sub>. The expected rotational frequency is slightly higher than the experimental data

![](_page_85_Figure_1.jpeg)

Figure 4.5 (a) The plot of rotation frequency *f* versus  $H_2O_2$  concentration. Each point is the average of 5 measurements; the line is the best linear fit; (b) the plot of rotation frequency versus surface tension  $\gamma$  at constant 5% hydrogen peroxide; the curve is a best-fit for  $f = D\gamma^2$  (from Ref. [22])

which may be explained by interactions of the nanomotor with the glass slide since we observe the particles on the surface of the slide, or the assumptions for Eq. (4.1) and Eq. (4.2) do not hold perfectly since the experimental nanomotors are not perfectly covered with Pt on one side; we assume that the Pt is coated on exactly half of a cylindrical nanorod which is an unrealistic assumption. With a partially covered half-rod surface, the numerator in Eq. (4.3) decreases which can make Eq. (4.3) match with the experimental value. For lower concentrations of  $H_2O_2$ , altering the concentration has a significant effect on the observed rotational frequency; however, as the concentration increases, the rotational frequency reaches a limit and the linear relationship no longer holds for higher concentrations. The Pt catalyst is limited in its ability to catalyze  $H_2O_2$  according to concentration and surface area, etc. This effect is likely caused by catalyst saturation which has been suggested in the literature in which the concentration dependence upon velocity follows the non-linear Langmuir isotherm [28, 66].

Altering the rotational frequency is also easily accomplished via lowering the surface tension of the solution which is consistent with previous studies [28, 31]. We observed that lowering the surface tension  $\gamma$  monotonically lowers the rotation rate as well (Figure 4.5 (b)). The surface tension was changed by adding various concentrations of sodium dodecly-sulphate (SDS), into water and hydrogen peroxide, and was measured through a pendant-drop method (Future Digital Scientific, Co., OCA15). SDS decreases the rate of rotation implicating that the driving mechanism is coupled to the surface tension of the liquid. In section 3.1, a theoretical model explaining nanomotor propulsion via the ejection of oxygen nanobubbles is presented which predicts a strong surface tension dependence upon force and therefore speed:  $F \propto c \propto v \propto \gamma^2$ ; soundly supported by experimental evidence. From Eq. (4.3), we also expect that  $f \propto \gamma^2$ . The parabolic curve is fitted with  $f = D\gamma^2$ , where D is a fitting parameter (Figure 4.5 (b)). The curve reveals that the  $f \propto \gamma^2$ -trend holds also in this study. This further implies that the nanobubble injection model works well for these multi-component catalytic nanomotors.

In conclusion, we have designed a simple nanomotor that can be very easily and inexpensively fabricated using dynamic shadowing growth, and a very large number of these structures can be fabricated simultaneously. The nanomotors are multi-component structures consisting of silica microbeads defining the rotation axis and  $TiO_2$  nanoarms; they exhibit regular predictable motion with a strong dependence upon hydrogen peroxide concentration and

surface tension. The constant rotational frequency may be understood by the balance of the propelling driving torque and the viscous drag torque.

### 4.2 Tadpole-Shaped Nanomotors

Catalytic nanomotors with silica microbead heads and  $TiO_2$  arms are systematically designed by DSG. The swimming trajectories are fine-tuned by altering the arm length and orientation exploiting geometry-dependent hydrodynamic interactions at low Reynolds number. The curvature, angular frequency, and radius of curvature of the trajectories change as a function of arm length. Simulations based on the method of regularized Stokeslets are also described and correctly capture the trends observed in the experiments; the simulational results were provided by Prof. David Saintillan at the University of Illinois Urbana Champaign (UIUC).

DSG is effective for controlling particle geometry; therefore, it is an appropriate method to perform a detailed study about the effects of geometry on the swimming characteristics. Here we devote our study to fine-tuning geometries of similarly shaped structures to gain a broader understanding of the importance of morphology in nanomotor engineering. By utilizing DSG to break the symmetry of a spherical microbead by adding an oxide arm of different lengths and relative angels, the relationship between the motion observed and the length and orientation of the arm can be studied. The trajectories also change as a function of the speed of the structures which we adjust by changing the concentration of the propelling fuel H<sub>2</sub>O<sub>2</sub>. A physical interpretation explaining the behaviors observed is constructed by analyzing the equations of low Reynolds number flow, constructing a simulational model, and comparing simulational and experimental results. An asymmetrical nanomotor consisting of a spherical microbead with an arm extending to different lengths and angles was fabricated to alter their swimming behavior as

shown in Fig. 4.6 (a). A self-assembled monolayer of silica microbeads of 2.01  $\mu$ m in diameter (Bangs Laboratories) is dispersed on a clean 2 cm × 2 cm Si substrate by diluting the microbeads in methanol (1:5 ratio) and dropping 3  $\mu$ L by pipette onto the Si. A cross-section depiction of the fabrication process is shown in Fig. 4.6 (b). A 40X optical micrograph of the resultant monolayer is shown Fig. 4.6 (c); many of the microbeads are arranged in a close-packed monolayer. A 10 nm thin film of Ti is first evaporated onto the beads by electron beam evaporation as an adhesion layer followed by a 50 nm Pt deposition.

![](_page_88_Figure_1.jpeg)

Figure 4.6 (a) Schematic of a silica microbead monolayer; (b) optical micrograph of the monolayer under 40X magnification; (c) Ti and Pt are evaporated onto the monolayer; (d) SEM top-view of the monolayer with  $TiO_2$  arms; (e) and schematic of the deposition of the  $TiO_2$  arms at a large angle.

For these two thin-film depositions, the vapor incidence direction is parallel to the substrate surface normal. The substrate is then tilted to an angle of  $86^{\circ}$  with respect the vapor incidence direction, and a thick layer of TiO<sub>2</sub> is then evaporated onto the monolayer to grow the

![](_page_89_Figure_0.jpeg)

Figure 4.7 Scanning electron micrographs with arms of various lengths: (a) 0 μm; (b) 1.25 μm;
(c) 2.5 μm; (d) 3.75 μm; (e) 5 μm; (f) and 6.25 μm; (g) arm length vs. QCM reading.

arm section of the structure. This large-angle deposition method is known as oblique angle deposition (OAD) which is a subclass of DSG. An example of the result may be seen in a topview SEM micrograph shown in Fig. 4.6 (d). During the deposition, the thickness of the deposited films is monitored in-situ by a quartz crystal microbalance (QCM) which directly faces the vapor. The TiO<sub>2</sub> was evaporated to 5 different QCM-reading lengths: 1.25  $\mu$ m, 2.5  $\mu$ m, 3.75  $\mu$ m, 5  $\mu$ m, and 6.25  $\mu$ m shown in Fig. 4.7. Another structure was fabricated using glancing angle deposition (GLAD) which combines OAD and substrate rotation. GLAD is accomplished by rotating the substrate azimuthally at a constant speed during OAD deposition of the TiO<sub>2</sub>. Because the substrate rotates continually, the microbeads receive vapor from all directions often

![](_page_90_Figure_0.jpeg)

Figure 4.8 Typical nanomotor geometry used in the simulations, corresponding to an arm length of  $3.5 \ \mu m$  (axes labels are in microns). A nanomotor is modeled as a sphere connected to a section of an ellipsoid representing the arm. Sections of different lengths are removed from the free end of the ellipsoid to match experimental conditions. The figure also shows the mesh used in the regularized Stokeslet algorithm, which was obtained by parameterization of the sphere and ellipsoid surfaces (with permission from D. Saintillan).

resulting in an arm which is perpendicular to the substrate surface. For the GLAD TiO<sub>2</sub> structure, the QCM reading reached 7  $\mu$ m while the substrate rotation speed remained at ~22.5°/sec.

With the help of UIUC, we also perform simulations that include an accurate representation of the nanomotor geometry with full hydrodynamic interactions between components of the nanomotor and with the supporting wall, Brownian motion as a result of thermal fluctuations, as well as frictional forces with the wall. A sample geometry is illustrated in Fig. 4.8, and is composed of a rigid sphere connected to a section of an ellipsoid to model the

fan-like shape of the arm in the experiments. By removing sections of different lengths on the free end of the ellipsoid, different arm lengths can be modeled for direct comparison with the experimental results. Particle dynamics are captured using the method of regularized Stokeslets [70] which is a variant of the classic boundary integral method for linearized viscous flow [71] and allows for the direct numerical calculation of the resistance matrix. Hydrodynamic interactions with the walls are accounted for using the method of images for regularized Stokeslets [72, 73] which makes use of a regularized version of the classic Green's function for Stokes flow in the vicinity of a no-slip wall [74]. The method was tested extensively for simple particle shapes (spheres, spheroids) and showed very good agreement with previously published results down to short separation distances [38]. Once the resistance matrix is known, it can be inverted to yield the mobility matrix, which is then used to calculate particle velocities and trajectories using a time-marching method. To qualitatively reproduce the trends seen in experiments, we find that including a frictional force and torque with the wall (in addition to the driving force due to the catalytic reaction) is required. Several models for friction were investigated, and the best agreement with the experimental data was obtained using the model of Liu and Bhushan [75, 76] for velocity-dependent friction at the micro/nanoscale which expresses the frictional force and torque on the particle in terms of its linear and angular velocities using an affine relationship. Because the velocities themselves depend linearly on the catalytic propulsion force *f*, the frictional force and torque may be expressed as,

$$F = F_0 + [(F_1 - F_0)/(f_1 - f_0) \cdot (f - f_0)], \qquad (4.4)$$

$$T = T_0 + [(T_1 - T_0)/(f_1 - f_0) \cdot (f - f_0)],$$
(4.5)

where  $F_0$ ,  $T_0$  and  $F_1$ ,  $T_1$  are the maximum and minimum possible values of the values of frictional force and torque, respectively. The remaining constants were selected to match experimental data for the trajectory curvatures, and in our simulation, the following values were used:  $F_0= 0.001$  pN,  $F_1= 0.0018$  pN,  $f_1= 1.2$  pN,  $f_0=0.4$  pN,  $T_0= 0.0000107$  fN.m,  $T_1= 0.000025$  fN · m. Finally, Brownian fluctuations were included using the Langevin equation in which the magnitude of the random displacements was calculated from the mobility matrix to satisfy the fluctuation-dissipation theorem [77]. A more detailed description of the numerical methods is deferred to a future publication.

Figure 4.6 (a) shows the nanomotor structure which is comprised of a spherical microbead half-coated with Pt and a  $TiO_2$  arm extending from the top of the Pt section. Since the Pt is evaporated at 0°, the microbead has two hemispheres: one silica and one Pt. As a result of the deposition process in which the  $TiO_2$  is deposited at a large angle described in the fabrication section, the arm is tilted at an angle with respect to the line defining the separation of the two hemispheres between the Pt coating and the bare silica as seen in Fig. 4.6 (a) and (b). The original monolayer onto which we evaporate Pt and  $TiO_2$  is not a complete monolayer; there are domains on the substrate that do not have any microbeads present as can be seen in Fig. 4.6 (c). Since the monolayer is not complete, not all of the structures are the same after the deposition. Due to the shadowing effect, the microbeads that are completely surrounded in the closely packed crystal have a different morphology than the microbeads on the edge of the domain. The former make up the vast majority of the structures, and the structures that result from shadowing on the edge of the domain are relatively rare so we do not consider these for the analysis. For the nanomotors resulting from within the domain, the arms grow from the tops of microbead only

due to the shadowing of the adjacent microbeads forming fan blade-like arms. The SEM image in Fig. 4.6 (d) shows the final structure still in a closely-packed monolayer.

![](_page_93_Figure_1.jpeg)

Figure 4.9 (a) SEM showing the increasing arm diameter with increased length; (b) and schematic of OAD-grown nanomotor with the  $TiO_2$  arm situated at an angle to the line separating the half-coated microbead.

Figure 4.7 shows representative SEM images of individual nanomotors of various arm lengths. Figure 4.7 (a) shows a Pt-coated sphere with no TiO<sub>2</sub>; Fig. 4.7 (b) has a short TiO<sub>2</sub> arm, and in this image, the arm is facing downwards toward the Si wafer; Figs. 4.7 (c), (d), and (e) show side-views of the nanomotors and the TiO<sub>2</sub> arms are flat; Fig 4.7 (f) shows the longest structure that is oriented in such a manner as to show the side and top of the structure simultaneously. The structures shown in Fig. 4.7 are examples of each nanomotor studied with QCM thickness reading:  $t = 1.25 \,\mu\text{m}$ , 2.5  $\mu\text{m}$ , 3.75  $\mu\text{m}$ , 5  $\mu\text{m}$ , and 6.25  $\mu\text{m}$  shown in Figs. 4.7 (a) – (f) respectively. For OAD, the actual length of the oxide arm does not correspond to the QCM reading since the substrate has an angle of 86° with respect to the vapor incidence

direction while the QCM itself is faced directly toward the vapor; due to the large angle, a smaller amount of material accumulates on the substrate than on the QCM. The graph in Fig. 4.7 (g) shows the QCM reading thickness, *t*, vs. actual measured arm lengths, *l*, which is an OAD-grown structure. The actual length *l* is significantly shorter than the QCM reading, *t*; the actual lengths measured using SEM are as follows:  $t = 1.25 \,\mu\text{m}$ :  $l = 0.86 \pm 0.06 \,\mu\text{m}$ ;  $t = 2.5 \,\mu\text{m}$ :  $l = 1.7 \pm 0.1 \,\mu\text{m}$ ;  $t = 3.75 \,\mu\text{m}$ :  $l = 2.5 \pm 0.1 \,\mu\text{m}$ ;  $t = 5 \,\mu\text{m}$ :  $l = 3.0 \pm 0.2 \,\mu\text{m}$ ; and  $t = 6.25 \,\mu\text{m}$ :  $l = 3.47 \pm 0.08 \,\mu\text{m}$ . As the oxide layer accumulates, the width of the TiO<sub>2</sub> arm tends to increase as the length of the arm increases as shown in Fig. 4.9 (a).

The width of the arm is slightly smaller than the diameter of microbead at the base of the arm, and the arm tends to "fan out" at the ends. As an example, in Fig. 4.9 (a), the width of the arm increases from  $d = 1.6 \mu \text{m}$  to 1.8  $\mu \text{m}$  using the ruler function on the SEM. Figure 4.9 (b) illustrates the fanning phenomenon and defines the value of the width of the arm, *d*. The fan shape can also be seen in Fig. 4.7 (b) and Fig. 4.7 (e) as well. Side-view images show that the arms are rather thin as can be seen in Fig. 4.7 (c) and Fig. 4.7 (d), so the structures do quite resemble fan blades. The microbeads on the edge of the crystal lattice closest to the vapor direction have a different morphology and are not considered in the analysis.

After fabrication, each substrate was placed into a small glass vial with DI water, and the vial was then sonicated in a sonication bath for < 1 minute to remove the nanomotors from the substrate and to suspend them in the water. Samples of 2  $\mu$ L nanomotor suspensions were dropped by pipette onto clean silicon slides for observation. 2  $\mu$ L droplets of hydrogen peroxide of various concentrations were added to the nanomotor suspensions to activate the motion. The nanomotors were tracked using a CCD (Imperx IPX-VGA210) with a temporal resolution of 20 frames per second coupled with reflected light microscopy (Mitotoya FS-110) and custom-

developed tracking software. Once the droplet is placed on the silicon wafer, the nanomotors quickly settle to the surface of the silicon substrate; we observe the swimming at the substrate surface so that they remain in the focal plane. The video files were analyzed using the tracking software to determine various parameters of interest such as speed, curvature, etc. SEM images were taken of each sample in order to analyze the morphology of the structures, and these images were obtained by dropping nanomotor suspensions onto clean Si wafers and allowing the droplets to dry. As the droplets dry, the orientation of the nanomotors as they adhere to the wafers is random; this allows us to closely observe the structures' morphologies by looking at a large number of structures oriented in different directions.

During observation, the optical microscope is focused on the observation slide, and since most of the particles settle to the surface, the particles move on the plane of the surface and so the trajectories were observed in 2D. Due to the geometry of the structures shown in Fig. 1 (a), the trajectories should be either linear or curved with perturbations arising from system fluctuations. To analyze the effect of changing the geometry of the particles, the extent to which the trajectories are altered needs to be determined. A natural value to calculate in order to characterize the trajectory of the curves, is the curvature,  $\kappa(t)$ , which gives a quantitative value for how much the trajectory is changing direction. Our experiments return a list of the *x* and *y* coordinates of the particle which describes its motion over a certain time interval in accordance to its **v** and  $\omega$ , determined as illustrated above. This discrete set of x-y coordinates is fit with a circular path whose radius gives an estimate of the average curvature of the actual irregular orbital trajectories. Kása proposed a method to find a circle-fit which best represents a collection of data points [10]. We employed this method to obtain the average curvature value. It is based on the fact that a reasonable measure of the fit of the circle  $(x-a)^2 + (y-b)^2 = r^2$  to the points

![](_page_96_Figure_0.jpeg)

Figure 4.10 (a) The plot shows the trajectories of nanomotors with 4 different arm lengths  $l = 0.86 \mu m$ , 1.7  $\mu m$ , 2.5  $\mu m$ , and 3.0  $\mu m$ . As the arm length increases, the radius of curvature decreases until some unknown minimum is reached. Each plot is a 10 s. interval, and the centers of each trajectory have been deliberately moved to a mutual middle; (b) simulated nanomotor trajectories, for same arm lengths as in (a) showing similar trends as the experimental data. Axes labels are in microns.

 $(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$  is given, in essence, by minimizing the sum of the squares of the distances from the points to the circle, over the parameters a, b and r. The minimizing function in Kása's method is, in fact, the sum of squares of the square of the distances and is given by

$$SSK(a,b,r) = \sum_{i=1}^{n} \left( r^2 - (x_i - a)^2 - (y_i - b)^2 \right)^2$$
(4.6)

Kása further points out that solutions for a and b can be obtained by solving linear equations, and the radius of curvature is found to be:

![](_page_97_Figure_0.jpeg)

Figure 4.11 (a) Experimental (black symbol  $\Box$ ) vs. simulational values (red symbol  $\Delta$ ) for curvature  $\kappa$  vs. TiO<sub>2</sub> arm length. For  $\kappa$ , both the simulational values and the experimental values follow the same trend of a roughly linear increase with the exception of the  $l = 3.5 \mu m$  arm length; (b) experimental (black symbol  $\Box$ ) vs. simulational values (red symbol  $\Delta$ ) for angular frequency  $\omega$  vs. TiO<sub>2</sub> arm length. The simulational results show a similar relationship with experimental  $\omega$ , and appear to be reaching a limiting value as the arm length increases. The outlier as in Fig. 5 (a) appears to be  $l = 3.5 \mu m$ .

$$r = \sqrt{\sum_{i=1}^{n} \left( (x_i - a)^2 - (y_i - b)^2 \right) / n}.$$
(4.7)

Therefore, the overall curvature is obtained as the reciprocal of the averaged radius of curvature defined in the sense illustrated above. The OAD-grown structures swim according to speed and arm length which is a result of hydrodynamics at low Reynolds number. Each nanomotor shown in Fig. 4.7 exhibits a similar yet different swimming pattern when placed in the same concentration of  $H_2O_2$  (10%) due to the various drag forces and torques applied to the arm corresponding to each length. Figure 4.10 (a) and Fig. 4.10 (b) are a 2-D plots showing representative experimental and simulational trajectories for nanomotors with various arm lengths respectively. The samples shown are typical for each arm length. To clearly compare the

![](_page_98_Figure_0.jpeg)

Figure 4.12 Experimental (black symbol  $\Box$ ) vs. simulational (red symbol  $\Delta$ ) data for speed vs. curvature  $\kappa$ . For the experiment, there exists a roughly linear increase of curvature with respect to speed (the speed is increased by increasing the concentration of H<sub>2</sub>O<sub>2</sub>). For the simulational results, a similar trend is seen for low speeds, but the curve flattens at higher speeds as opposed to staying linear.

different trajectories each was adjusted to have a mutual center at the origin of the graph (0 µm, 0 µm). All trajectories show roughly circular motion. The structure with the shortest arm (l = 0.86 µm, Fig. 4.7 (b)) moves with a relatively large radius in comparison to the other lengths; as the length of the arm increases, the radii of curvature become smaller. The nanomotors swim in a roughly circular pattern when the oxide arm is present. For each rotation with radius of curvature r, the structure spins once as it moves about the circular trajectory. Figure 4.11 (a) and Fig. 4.11 (b) compare the experimental values (black symbol  $\Box$ ) against the simulational values (red symbol  $\Delta$ ) for arm length vs. curvature  $\kappa$  and arm length vs. angular frequency  $\omega$  respectively, showing similar trends. Figure 4.12 compares experimental values (black with symbol  $\Box$ ) against simulational values (red symbol  $\Delta$ ) showing how  $\kappa$  is affected by variations in nanomotor speed for the l = 3.5 µm case. The speed is altered by changing the concentration of H<sub>2</sub>O<sub>2</sub>. Discussion of the comparison of experiment and simulation is presented below.

The nanomotors move just above the surface of the slide so surface-particle interactions and coupling are most likely present; however, for simplicity, in the following analysis these interactions are not considered here, and we only consider particle-fluid interactions which primarily cause the swimming behaviors observed. In this case, we expect that the nanomotor will move in a circular pattern, and this is in fact what is observed.

To estimate the resistance matrix elements, the nanomotor is considered to be a cylinder coupled to a sphere, and we neglect hydrodynamic coupling between the two parts. The centerof-mass for the entire structure is given by

$$\mathbf{x}_0 = \frac{m_a \mathbf{x}_a + m_s \mathbf{x}_s}{m_a + m_s} \tag{4.7}$$

where  $m_a, \mathbf{x}_a, m_s, \mathbf{x}_s$  are the mass and center of the sphere and the mass and center of the cylinder (arm) respectively. The velocity for the combined parts is  $\mathbf{v} = \frac{d}{dt} \mathbf{x}_0$ .  $\boldsymbol{\tau}$  is the torque with respect to the total center of mass  $\mathbf{x}_0$ . For the steady state,  $\mathbf{F} + \mathbf{F}^{\rm D} = 0$  where  $\mathbf{F}^{\rm D} = \mathbf{F}_{\rm a}^{\rm D} + \mathbf{F}_{\rm s}^{\rm D}$  in which  $\mathbf{F}_{\rm a}^{\rm D}$  and  $\mathbf{F}_{\rm s}^{\rm D}$  are the drag forces on the sphere and the cylindrical arm respectively and  $\mathbf{v}_{\rm s} = \frac{d}{dt} \mathbf{x}_{\rm s} = \mathbf{v} + \mathbf{\omega} \times (\mathbf{x}_{\rm s} - \mathbf{x}_0)$  which leads to

$$\mathbf{F}_{s}^{D} = -6\pi\eta a [\mathbf{v} + \mathbf{\omega} \times (\mathbf{x}_{s} - \mathbf{x}_{0})]$$
(4.8).

Defining a unit vector that is aligned with the arm,  $\mathbf{f}$ , the drag on the cylinder is given by  $\mathbf{F}_{a}^{D} = -R_{\parallel}\mathbf{f}(\mathbf{f}\cdot\mathbf{v}_{a}) - R_{\perp}(\mathbf{\tau}-\mathbf{f}\cdot\mathbf{f})\cdot\mathbf{v}_{a}$  where the coefficient for drag parallel and perpendicular to

fluid flow 
$$R_{\parallel} = -\frac{2\pi l \eta}{\ln(4l/d) - 0.72}$$
 and  $R_{\perp} = -\frac{8\pi l \eta}{\ln(4l/d) + 0.5} \mathbf{v}$  respectively in which *l* and *d* are

the length and diameter of the arm respectively. The velocity of the arm  $\mathbf{v}_{a} = \mathbf{v} + \mathbf{\omega} \times (\mathbf{x}_{a} - \mathbf{x}_{0})$ leads to the expression for the drag force on the arm

$$\mathbf{F}_{a}^{D} = -\left[R_{\parallel}\mathbf{f}\cdot\mathbf{f} + R_{\perp}(\boldsymbol{\tau}-\mathbf{f}\cdot\mathbf{f})\right]\cdot\left[\mathbf{v}+\boldsymbol{\omega}\times\left(\mathbf{x}_{s}-\mathbf{x}_{0}\right)\right]$$
(4.9).

Combining eq. (4.8) and eq. (4.9) gives the total drag force for the nanomotor and can be put into the form  $\mathbf{F} = \mathbf{A} \cdot \mathbf{v} + \mathbf{\tilde{B}} \cdot \mathbf{\Omega}$ .

Similarly the torque balance is in the form of  $\mathbf{\tau}_0 + \mathbf{\tau}_0^D = 0$  where  $\mathbf{\tau}_0$  is the external torque and  $\mathbf{\tau}_0^D$  is the drag torque. The torques on the arm and sphere with respect to  $\mathbf{x}_0$  is given by  $\mathbf{\tau}_0^D = \mathbf{\tau}_{a,0}^D + \mathbf{\tau}_{s,0}^D$ . For the sphere  $\mathbf{\tau}_{s,0}^D = \mathbf{\tau}_{s,s}^D + (\mathbf{x}_s - \mathbf{x}_0) \times \mathbf{F}_s^D$  where  $\mathbf{\tau}_{s,s}^D = -8\pi\eta a^3\boldsymbol{\omega}$  is the torque on the sphere with respect to  $\mathbf{x}_s$ . The torque on the sphere about the center of the structure is given by  $\mathbf{\tau}_{s,0}^D = -8\pi\eta a^3\boldsymbol{\omega} - 6\pi\eta a(\mathbf{x}_s - \mathbf{x}_0) \times [\mathbf{v} + \times(\mathbf{x}_s - \mathbf{x}_0)]$ , and for the arm  $\mathbf{\tau}_{a,0}^D = \mathbf{\tau}_{a,a}^D + (\mathbf{x}_a - \mathbf{x}_0) \times \mathbf{F}_a^D$  where  $\mathbf{\tau}_{a,a}^D = -[S_{\parallel}\mathbf{f}\cdot\mathbf{f} + S_{\perp}(\mathbf{\tau} - \mathbf{f}\cdot\mathbf{f})]\cdot\boldsymbol{\omega}$  is the torque with respect to

# $\mathbf{x}_{a}$ . The torque balance equation becomes

$$\boldsymbol{\tau}_{0} = 8\pi\eta a^{3}\boldsymbol{\omega} + 6\pi\eta a(\mathbf{x}_{s} - \mathbf{x}_{0}) \times [\mathbf{v} + \times (\mathbf{x}_{s} - \mathbf{x}_{0})] + [S_{\parallel}\mathbf{f} \cdot \mathbf{f} + S_{\perp}(\boldsymbol{\tau} - \mathbf{f} \cdot \mathbf{f})] \cdot \boldsymbol{\omega}$$

$$+ (\mathbf{x}_{a} - \mathbf{x}_{0})[R_{\parallel}\mathbf{f} \cdot \mathbf{f} + R_{\perp}(\boldsymbol{\tau} - \mathbf{f} \cdot \mathbf{f})] \cdot [\mathbf{v} + \boldsymbol{\omega} \times (\mathbf{x}_{s} - \mathbf{x}_{0})]$$

$$(4.10)$$

which can be put into the form  $\tau = \mathbf{B} \cdot \mathbf{v} + \mathbf{C} \cdot \mathbf{\Omega}$ .

Figure 4.10 (a) demonstrates experimental results for swimming trajectories corresponding to arm length for four different lengths (excluding  $l = 0 \mu m$  and  $l = 3.5 \mu m$  for clarity). The graph in Fig. 4.10 (b) shows the simulational results. It should be noted for the experiments that roughly constant velocity is observed for each arm length, and that each system

is observed at steady state at which the applied force and torque is exactly countered by the force and torque of the drag and friction. In the absence of any Brownian fluctuations, the simulated trajectories are found to be closed circles with constant curvature, whose radius decreases with increasing arm length. With Brownian motion, the trajectories deviate from perfect circles and instead take the form of irregular orbits that are qualitatively similar to those observed in the experiments. The increase in the mean trajectory curvature with arm length is also consistent with the experimental observations. This is shown more quantitatively in Fig. 4.11, where experimental values (black symbol  $\Box$ ) are compared with simulational values (red symbol  $\Delta$ ) for  $\kappa$  (Fig. 4.11 (a)) and  $\omega$  (Fig. 4.11 (b)). For the experimental results in Fig. 4.11 (a), as the arm length increases,  $\kappa$  slightly increases in a roughly linear fashion up until the  $l = 3.5 \,\mu m$  case which does not follow this trend; the simulation data follow a roughly linear increase with respect to l. In Fig. 4.11 (b),  $\omega$  is similar to  $\kappa$  with the  $l = 3.5 \,\mu\text{m}$  value not following the same trend as the rest of the data points; the simulational data starts linearly, but begins to level as lincreases. The large error bar for both the curvature  $\kappa$  and angular frequency  $\omega$  may account for the outliers. It is expected that  $\kappa$  and  $\omega$  will both reach a limiting value since increasing the arm length will eventually decrease the two values along with the velocity, i.e. at a certain length, the driving force will only rotate the structure and no translational motion will be present (no circular motion present, only rotation); as  $l \to \infty$ ,  $\omega, \nu \to 0$ . The two graphs have similar trends and values, but the simulations seem to show that  $\omega$  and  $\kappa$  are beginning to reach a limiting value for  $l > 3.5 \mu m$  while this is unclear for experimental data. Similar trends are observed for the curvature vs. speed for experimental (black symbol  $\Box$ ) vs. simulational (red symbol  $\Delta$ ) results shown in Fig. 12, where we find that good agreement is obtained at lower speeds, while the behavior at high speeds is not captured as accurately by the simulations. The experimental data points are following a linear increase while the simulational values appear to be reaching a limiting value as the speed increases.

As a control experiment, we alter the position of the oxide arm on the microbead and observe the swimming trajectories. We have shown in a previous study with Pt-coated microbeads that increasing the concentration of  $H_2O_2$  increases the speed of the microbeads and their trajectories due to symmetry are linear [28].

![](_page_102_Figure_2.jpeg)

Figure 4.13 (a) Schematic of a GLAD-grown structure; (b) SEM.

For the GLAD structures explained in the fabrication section, a schematic and an SEM are shown in Fig. 4.13 (a) and Fig. 4.13 (b) respectively, when the speed is modulated with the addition of various concentrations of  $H_2O_2$ , increasing speed should have little effect on the trajectories of the GLAD-grown structures since symmetry still exists; this is in opposition to the OAD-grown structures' trajectories which have greater average curvature with increased speed. The OAD-grown structures are expected to have greater torque since the drag increases concurrently with velocity. We subject the OAD-grown and the GLAD-grown structures to the same concentrations of  $H_2O_2$  to see whether curvature is altered for the two. OAD-grown speed plots are shown in Fig. 4.12 (a); as we increase the speed of the OAD nanomotor, the curvature increases monotonically which is expected while Fig. 4.14 shows the curvature remains roughly

![](_page_103_Figure_0.jpeg)

Figure 4.14: Speed vs. curvature for the GLAD-grown structure showing roughly constant curvature for all speeds.

constant as the speed is increased. The best-fit line for Fig 4.12 (a) gives a slope of  $7.2 \times 10^{-2}$  s/µm<sup>2</sup> while the slope for the GLAD structure motion in Fig. 4.14 is  $1.5 \times 10^{-2}$  s/µm<sup>2</sup>. The speed should have no effect on the GLAD structure being that the arm should have no effect on the torque, and Fig. 4.14 suggests this is indeed occurring. Intuitively, a swimmer that is symmetric and is being propelled along its axis of symmetry should not have any torque applied; the GLAD structure swims in a straight line as expected. This result strengthens the idea that the geometry of catalytic nanomotors has a major impact on swimming behavior and that modulation of behaviors is possible through systematic design.

Using the dynamic fabrication method using OAD and GLAD, we have studied the effects of geometry on catalytic nanomotors moving at low Reynolds number. The trajectories of the particles are highly dependent upon the geometry, and OAD/GLAD allows easy modulation

of nanomotor morphology. The special case that we study is a nanomotor consisting of a spherical microbead head and an oxide arm that is off-centered to the driving force arising from the chemical reaction. We change the length and angle of this structure, and compare the experimental results to results from a simulational model. The two sets of results are very similar, and discrepancies can be attributed to the absence of Brownian dynamics in the simulational model. As the field of catalytic nanomotors matures, engineers and scientists must consider the shape-dependence upon swimming behaviors in order to design better structures in the future.

# **4.3 Conclusions**

Dynamic shadowing growth is an effective method for the control and manipulation of catalytic nanomotors swimming at low Reynolds number. By programming the geometries of the particles, desired swimming behaviors can be achieved. The two examples above show that both rotational and translational motions are easily engineered for the same structure simply be placing the Pt catalyst in a different location. Also, by modulating the length of the structure, various swimming behaviors arise as well. Since catalytic nanomotors are autonomous swimmers, geometry-oriented design is an effective way to control nanomotor behavior without the application of external forces.

### CHAPTER 5

## SELF-ASSEMBLED NANOMOTOR STRUCTURES

Most research focuses on the analysis and control of single component nanomotors exhibiting either translational or rotational motion. The incorporation of multiple individually moving parts working in coordination would be a major step forward in this emerging field. One route to realize such a complex nanomotor system is to assemble individual parts that function together as seen in everyday machinery. A "nuts-and-bolts" assembly process is likely to be tremendously tedious for large-scale production or outright impossible with current technology when one works at these length scales. An advanced fabrication technique would require one to combine conventional and nonconventional fabrication techniques together to design complex nanostructures. As an example, flexible nano-hinges were fabricated by the electrodeposition of Pt/Au/Pt segments into a nanorod structure and then the nanorod was encapsulated with a polymer through a layer-by-layer deposition [56]. The Au was then etched, leaving two Pt segments on the ends linked by a flexible joint. For direct assembly of a complex nanomotor system, two methods may exist: a directed assembly method, and a self-assembly or selforganization method. For directed assembly, one could use external forces to manipulate one or two particles and link separate particles together.

Self-assembly refers to systems of molecules or particles that organize themselves into more complex arrangements without external influences. One example of microscopic selfassembly was presented by Dreyfus et al. in which they utilized biotin-streptavidin conjugation to link magnetic microbeads into a long filament and attached this tail to a red blood cell, and the filament beats back and forth in a magnetic field causing it to swim [78]. Multi-component nanomotors have also been constructed using conjugation methods including linking structures with bridging ligands [79] and electrostatic interactions [57]. At the length scale of current catalytic nanomotor research, Brownian motion does not allow for much interaction between micron-sized structures, but the active autonomous motion characteristic of catalytic nanomotors increases particle-particle interaction greatly increasing the incidence of self-assembly. Whitesides et al. presented an excellent study of the aggregation and self-organization of autonomous motion macroscopic plates consisting of both hydrophilic and hydrophobic sides proliferated by the active motion [41]. Self-organization is a realistic method for building nanomotor systems with higher complexity.

In our experiments, we have observed structures that have self-organized themselves into entities consisting of multiple independent particles. The motion of these structures is very different from those of individual nanomotors. Although the frequency of observation of some of these structures is low, many are seen often enough to warrant investigation. We find that complex nanomotors can either self-assemble via random Brownian-induced movement, or the assembly is facilitated by the active motion resulting from the catalyzed decomposition of hydrogen peroxide. By intentionally introducing long range interactions such as magnetic interactions, the yields of formation of desired nanoclusters can be greatly enhanced. In this study, we present the formation of a randomly assembled spinning cluster of tadpole nanomotors and their behavior. Also, with the introduction of magnetic interactions, intentionally assembled "helicopter" nanomotors of two separate structures are formed, and the two parts move autonomously and independently. Lastly, with the addition of joints and flexibility, a flexible nanoswimmer system can perform complex motion such as maneuvering around stationary objects. All of these nanomotor system exhibit interesting, if not surprising, motion not seen by the individual constituent particles. Our experiments demonstrate that the concept of selforganized, complicated catalytic nanomotors consisting of more than one individual part can be realized with careful experimental design, and this is the first step towards designing complex, autonomous, and multifunctional nanomachinary systems.

# **5.1 Spinning Clusters**

The SEM image in Fig. 5.1 (a) shows an individual tadpole-shaped swimmer consisting of a 2.01  $\mu$ m-diameter spherical silica bead and a ~ 3  $\mu$ m long amorphous TiO<sub>2</sub> arm that acts as a rudder. The silica bead is half-coated with Pt which propels the structure when immersed into aqueous H<sub>2</sub>O<sub>2</sub> as a result of an increased reaction rate at the catalyst site. The TiO<sub>2</sub> rudder is asymmetrically deposited onto the Pt-coated half-sphere. We reported in detail the fabrication and the analysis of a similar structure in section 4.2 (with Pt coating on the TiO<sub>2</sub> arm rather than on the silica bead [22]). To fabricate the tadpole structures, we first drop-cast a 3 µL colloidal suspension of 2.01 µm silica microbeads (Cat.# SS04N/7829, Bangs Laboratories) (diluted in methanol with a 1:5 ratio) onto clean 4  $\text{cm}^2$  silicon substrates tilted at an angle of 5°. This procedure allows the beads spread into a self-assembled monolayer. The bead-coated substrates were loaded into a vacuum chamber and a 2 nm Ti adhesion layer and 50 nm Pt were deposited by electron beam evaporation in a vacuum environment  $(10^{-6} \text{ Torr})$  at a vapor incident angle of 0°, resulting in roughly half-coated beads. Then a TiO<sub>2</sub> rudder is grown upon the coated microbeads by a dynamic shadowing growth (DSG) configuration with a vapor incidence angle of  $86^{\circ}$  with respect to the vapor incidence direction, taking advantage of the shadowing growth effect. The TiO<sub>2</sub> was deposited at a rate of ~ 0.5 nm/s, read by a quartz crystal microbalance (QCM), facing directly toward the incident vapor, until reaching a QCM reading of  $\sim 6 \,\mu m$ .




surface; (b) frames of a movie taken with an optical microscope to show a typical circular trajectory of a single structure; (c) SEM of an interlocked two-tadpole nanomotor; (d) rotational motion for the interlocked structures; the arrow indicates progress in time in which each image is a snap shot of the same location at ~ 1/4 sec; (e) example trajectory for a single swimmer (black) moving in circles, and the trajectory of a linked structure (red) taken for ~ 5 sec. intervals (from Ref. [61]).

Depending upon their orientation, the swimmers may move clockwise or counterclockwise, but are always propelled away from their catalyst site, as indicated by the force vector in Fig. 5.1 (a). A typical trajectory of such a swimmer in 5% H<sub>2</sub>O<sub>2</sub> is shown in Fig. 5.1 (b) and Fig. 5.1 (e) and is a circular motion with a drifting center and a radius of curvature of  $\sim 6 \,\mu m$ . The rotation frequency is  $\sim 0.4 \,\text{Hz}$ . The majority of the swimmers remain unattached to other particles, but occasionally two of the structures adhere to one another with the head of each nanomotor attached to the tail of the other as shown in Fig. 5.1 (c), where two tadpole swimmers interlock together to form a shape similar to an ancient Chinese Taiji symbol. This cluster can be formed by two possible ways: either by forming during the sonication of the nanomotors from the substrates or by forming through interaction caused by the active swimming motion. Without adding H<sub>2</sub>O<sub>2</sub>, the probability of 2-tadpole cluster formation is about 1% - 2% (3 trials counting 108, 69, 49 particles, all the statistics were performed by an optical microscope while the structures remained in the liquid), but with the addition of  $H_2O_2$  higher probabilities of 3% - 5% are obtained (3 trials of 99, 49, 49 particles). This likely occurs due to the greater interaction caused by the propulsion of the individual particles. The percentage of particles involved in aggregation was significant (20-30%); however, most of the aggregates were randomly oriented and consisted of more than 2 particles per cluster. The most prominent single aggregation was the two-component spinning cluster. The nature of the interaction between individual nanomotors is not clear; however, we suspect that the Van der Waals force is the main cause.

Figure 5.1 (d) shows movie frames of a clockwise spinning cluster in which the selected movie frames are taken in the same location; moving from left to right, each image shows the progress of ~ 1/4 sec in 5% H<sub>2</sub>O<sub>2</sub>. This cluster spins at ~ 0.5 Hz. The average rotational frequency for 5 spinning clusters was measured to be  $0.4 \pm 0.1$ Hz. A typical spinning trajectory



Figure 5.2: The driving forces are equal and opposite but off-centered leading to a torque,  $\vec{\tau}_{drive}$ , applied to the cluster. The force direction is taken to be perpendicular to the plane separating the two hemispheres of the microbead, and the distance between the two microbead centers is d.  $\theta$  is the angle between the plane and the arm of the structure. The center of rotation is represented by

the small circle half way along the vector  $\vec{d}$ . A drag torque is supplied to the structure that is equal to the driving torque in equilibrium which is not depicted in the scheme (from Ref. [61]).

is shown by the red curve in Fig. 5.1 (e) labeled "interlocked", with small center drift compared to a single swimmer. The motion changes from large sweeping circular trajectories for the individual swimmers to almost exclusively rotational motion (with very little translational motion) when two individual nanomotors are coupled together. This is due to two symmetric driving forces acting onto the cluster as shown in Fig. 5.1 (c), which balance the spinning of the structure. Thus, such coupling changes the motion of the nanomotor cluster, as compared to a single tadpole nanomotor.

Figure 5.2 illustrates the forces acting on the 2-nanomotor cluster. This model is idealized by assuming that the two tadpole nanomotors are exactly the same. The two forces on the microbead result in a torque on the cluster causing it to spin about an axis perpendicular to the cluster plane and through the center of mass. This torque can be estimated with our experimental data. For a particle moving with constant velocity and constant rotation in a low Reynolds number fluid we have [37, 38],

$$\vec{F} = A\vec{v} + \widetilde{B}\vec{\omega} , \qquad (5.1)$$

$$\vec{\tau} = B\vec{v} + C\vec{\omega} , \qquad (5.2)$$

where  $\vec{F}$  is the hydrodynamic force,  $\vec{\tau}$  is the hydrodynamic torque,  $\vec{\omega}$  is the angular velocity, and *A*, *B*, and *C* are second-order tensors dependent upon the swimmer's geometry. Due to the complex geometry involved, we only consider the empirical data, and use rough estimates to determine if the correct order of magnitude of frequency may be obtained. Under equilibrium, we have a constant angular frequency which results from  $\vec{\tau}_{drive} = \vec{\tau}_{drag}$ . By assuming the cluster is a single spinning cylinder (which we believe to be acceptable since the geometry of a closelypacked cluster approximates a cylinder), we can greatly simplify the calculations. The drag torque for a cylinder has been shown to be

$$\vec{\tau}_{drag} = \frac{\pi \mu l^3}{3\ln(2l/a) - 0.8}\omega,$$
(5.3)

where *l* is the length and *a* is the diameter of the cylinder,  $\mu$  is the viscosity and  $\omega$  is the angular frequency. Since the microbead is half-coated with Pt, the value of the driving force *F* can be estimated as  $F = \pi b^2 \chi c$ , where  $b \sim 1 \mu m$  is the radius of the microbead,  $\chi \sim 0.001 \text{ N/m}^2$  per percentage concentration, is the force per unit area per unit hydrogen peroxide concentration in

previous experiments [67], and *c* is the percentage concentration of H<sub>2</sub>O<sub>2</sub>. Since the Pt is coated on insulating silica microspheres, the driving force is not electrochemical as seen in Au/Pt nanomotors, and we believe the force arises from bubble propulsion by O<sub>2</sub> gas generation at the surface of the catalyst. From Fig. 5.2, we calculate the driving torque by setting the center of rotation halfway across the vector  $\vec{d} = d\hat{r}$ , placing the center at  $\vec{r} = (d/2)\hat{r}$ . The drive torque can then be calculated as

$$\bar{\tau}_{drive} = 2\bar{F}_{drive} \times \bar{r} = Fd\cos(\theta/2), \tag{5.4}$$

where  $\theta$  is the angular difference between the line separating the two hemispheres of the spherical microbead and the dashed line drawn through the arm of the structure. Setting Eqs. (5.3) and (5.4) equal, we obtain the frequency,

$$f = \frac{3Fd\cos(\theta/2)[\ln(2d/a) + 0.8]}{2\pi^2 \mu l^3}.$$
 (5.5)

Using the following values:  $F = \pi \times 10^{-15}$  N,  $d = 4 \mu m$ ,  $l = 4 \mu m$ ,  $\theta = \pi/4$ ,  $a = 1 \mu m$ ,  $\mu = 10^{-3}$  Ns/m<sup>2</sup>, we obtain  $\omega = 0.8$ s<sup>-1</sup>. The predicted value is consistent (correct order of magnitude) with our experimental value f = 0.4s<sup>-1</sup>.

#### 5.2 Randomly Self-Organized "Helicopter" Nanomotor Systems

Slightly resembling a micro-scale helicopter, the nanohelicopter structure consists of two constituent self-assembled components. The two parts are the main body, which is a tadpole-shaped nanomotor that resembles the cabin and tail boom, and the main rotor or blades of which



Figure 5.3: (a) A schematic of the helicopter-shaped multi-structured nanomotor showing the axis and direction of rotation of the top component; (b) a schematic of the top component pivots along with rotation as well; (c) the movie frames in ~ 1/5 sec. interval, from left to right, showing the rotation of the top nanomotor in the clockwise manner if viewed from the top. The whole structure only drifts slightly while the rotor spins.

consist of a self-assembled conglomeration of fragmented nanorods. The comparison of this structure to a helicopter is for imagery only as the rotor does not provide lift for the structure and there is no tail rotor. A schematic of the parts are presented in Fig. 5.3 (a) showing how the rotor spins clockwise atop of the main body and the junction of the two parts also has the ability to pivot from side to side along with rotary motion shown in Fig 5.3 (b). The helicopter nanomotor remains stationary with the exception of Brownian motion, thermal or chemical gradients, or surface tension; it does not actively swim, however. The only active motion exists at the rotor atop of the body. This motion may be seen in Fig. 5.3 (c); from left to right, the position of the camera remains constant as time progresses by  $\sim 1/5$  sec. per frame illustrating the slow clockwise rotation and pivot of the rotor. The rotor rotates at a frequency of  $\sim 0.1$  Hz. How this

structure self-assembles together is not clear; however, using the OAD method, we have devised a method to manufacture similar structures with the help of magnetic materials.

# 5.3 Magnetic Self-Organized "Helicopter" Nanomotor Systems

Clearly, using random assembly as shown above, the yield of the formation of desired cluster structures is very low. In order to increase the yield of desired structures, we can take advantage of magnetic interaction between individual particles. We mix two magnetized structures to induce self-assembly. The half-coated Ni microbeads were fabricated in the same manner as outlined previously. The V-shaped nanomotors have two linked arms grown from TiO<sub>2</sub> by two consecutive DSG depositions at a vapor incident angle of 86° and a QCM reading of 6 µm for each arm. After the first arm was deposited, a thin 100 nm layer of Ni was deposited onto the ends of the first TiO<sub>2</sub> arm. The substrate was quickly rotated 180° azimuthally, and another 100 nm Ni was deposited. The second arm was then grown atop of the Ni layer. A Pt layer with a QCM reading of 50 nm was deposited at a vapor incidence angle of 10° after rotating the substrate azimuthally by another 90°. To mimic such a complex structure in section 5.2, we mix the two magnetized structures, a V-shaped nanomotor (as the main rotor) and a halfcoated Ni silica microbead (as the body). Using DSG, we have fabricated the V-shaped nanomotors containing Ni films on the elbow. Figures 5.4 (a) and 5.4 (b) show SEM images of an individual V-shaped nanomotor removed by sonication and dried on a Si substrate and a top view of an array of the V-shaped nanomotor structures grown on a Si substrate, respectively. By depositing a thin layer of Ni on the elbow of the V-shaped structures, we are able pin the elbow to the surface of the substrate by a magnetic field and have it stand upright. A thin catalyst layer



Figure 5.4 (a) A representative SEM image of an individual V-shaped structure; (b) topview SEM image of the V-shape nanorod array; (c) a schematic of V-shaped structure showing the Ni on the elbow that allows the magnetic field to pin the structure to the substrate surface. The Pt causes clockwise rotation of the structure. The images on the right show an example structure spinning clockwise; (d) self-assembly by the interaction of magnetic dipole moments of the two structures. The SEM image shows an individual Nicoated microbead, and the images on the bottom are optical microscope video frames showing the two components coming together and spinning as shown in the schematic. Each frame from left to right shows the advancement of ~ 1 sec. (from Ref. [61]).

of Pt is deposited in an asymmetrical manner (90° azimuthal rotation) in order to induce rotational motion about the axis through the center of nanomotor in solutions of H<sub>2</sub>O<sub>2</sub> as shown in Fig. 5.4 (c). By manipulating the V-shaped structure with a bar magnet, we can tell clearly with an optical microscope that the structure does in fact stand on its elbow. The video frames of the right inserts of Fig. 5.4 (c) show the advancement of 1/3 sec., and depict a spinning V-shaped structure with the elbow pinned to the substrate by a rotating permanent magnetic bar (in this video, we chose images of the structure slightly tilted in order to show the structure's shape. In order to make a multi-component helicopter nanomotor, we use magnetic interaction to organize a V-shaped nanomotor atop a Ni-coated silica bead. We deposited a thin layer of ~ 50 nm Ni onto 2.01 µm diameter silica microbeads, and sonicated them from the substrate into a DI water mixture. We magnetized both structures while attached to the substrate in opposite directions so that they would assemble into a structure as shown in Fig. 5.4 (d). Then the magnetized Ni Vshaped nanomotors were added to and mixed with the Ni-coated microbeads. The SEM image in the insert of Fig. 5.4 (d) shows an individual Ni-coated microbead, and the images on the bottom show frames from an example video for an assembled structure moving in 5%  $H_2O_2$ . As we move from left to right, time increases by  $\sim 1$  sec. in each frame, and the two self-assembled structures adhere to one another under the influence of their respective magnetic dipole moments. Due to the complexity, the entire structure initially starts to rotate while the Ni coated bead performs a relative spinning motion with respect to the V-shape nanomotor. Then the entire structure flips over, and one can observe that the top V-shaped nanomotor spins slowly on the Ni coated microbead. This complicated motion is due to the complicated relative motion of the two structures in liquid: Ni is also a catalyst for the breakdown of hydrogen peroxide, thus the microbead is itself spinning and moving in the solution of hydrogen peroxide, while the V-shape

nanostructure rotates, and we see other types of motion besides the V-shaped structure simply spinning on the microbead.

The magnetic interaction greatly increases the yield of the helicopter structures compared to clusters without magnetic interaction. We observed 100 microbeads for 3 different cases: mixing magnetized structures with and without  $H_2O_2$ , as well as a control experiment with non-magnetized structures; we find that adding the structures together when the two are magnetized significantly increases the occurrence of helicopter structures from 0% (with no Ni on the bead) to ~20% - 25%. Interestingly, the addition of  $H_2O_2$  appears to slightly increase the occurrence of the desired helicopter-structure which we believe emerges from the increased interaction caused by active swimming as observed in the 2-tadpole cluster case as well. We believe that we have successfully fabricated a multi-component helicopter-shaped nanomotor using magnetic interactions, and this process may be used for future fabrication of more complex and functional structures.

## **5.4 Flexible Joint Swimmer**

Once two or three moving parts can be integrated together, advanced and complex motion can be achieved. The previous two sections show that a nanomotor system (2-tadpole cluster) can change the motion behavior, or different parts of a system (helicopter) can conduct different types of motion. With the addition of joints and flexible components into a system, one could greatly advance the motion complexity. Such a structure is the flexible joint swimmer. We have repeatedly observed a specific structure with a flexible joint resulting from the self-organization of the same tadpole nanomotors as described above. These structures bend at a joint and even have the ability to maneuver around stationary objects as shown in Fig. 5.5 (b). These



Figure 5.5 (a) The illustration of a three-component structure pivoting about the point of contact between the tail of the leader and the middle of the two heads of the trailer allowing the bending of ± α; (b) The movie frames, ~ 1/8 sec. interval, from left to right showing the structure colliding with a stationary particle (a structure similar to the trailer) then turning to maneuver around the object; the position of the images are taken at different locations to follow the trajectory of the particle; (c) a representative SEM image of the trailer consisting of two tadpole swimmers likely fussed by the deposition process; (d) a representative SEM image of a structure similar to the three-component structure described with both the leader and trailer; (e) the flex angle α defined by the difference in angle between the trailer and the leader; (f) a plot of the flex angle α vs. time during the maneuver showing the flexibility of the structure (from Ref. [61]).

structures, shown in Figs. 5.5 (a) and 5.5 (b), consists of two fused tadpole swimmers on the back end of the structure making one rigid section (an individual fused swimmer is shown in Fig. 5.5 (c)), which we call the trailer, and it is towed by one individual swimmer, called the leader, in front of the trailer as shown in Figs. 5.5 (a) and 5.5 (b). When the structure is immersed in a

 $H_2O_2$  solution, the leader swims and turns along the surface of the glass slide, and the trailer follows by pivoting at the joint between the two separate sections. The junction exists in between the two adjacent heads of the trailer (micro-beads) where the tail of the leader is positioned in the gap so that the joint has the ability to pivot from side to side. The relative frequency range for 3 trials (45, 34, 40 structures counted) are as follows: single structures: 75% - 77%, trailers only: 5% - 9%, trailer-leader complexes: 0% - 3%, and other aggregates: 14% - 20%. The movie frames in Fig. 5.5 (d) show such a motion: the trailer-leader structure interacts with a stationary particle also on the glass surface. The images in Fig. 5.5 (b) from left to right are frames from a video showing the advancement of ~ 1/8 sec. The stationary particle is the same structure as the trailer consisting of two swimmers adhering to one another and is not actively swimming (Fig. 5.5 (c)). The leader brushes the stationary particle, and then the trailer collides with it diverting the trajectory of the flexible structure to the right; this motion is allowed by the pivot of the joint and allows the swimmer to move around the obstacle while continuing to pull the trailer. To characterize this motion, we define a flex angle  $\alpha$  as shown in Fig. 5.5 (e): by drawing a line (solid) through the middle of the trailer (tangent to both beads) and another line (dashed) from the junction (the contact between the trailer beads) to the head of leader (the center of the leader bead), the flex angle is the angular difference between the two lines. In Fig. 5.5 (e), since the structure is not bent,  $\alpha = 0$ . Figure 5.5 (f) shows  $\alpha$  as a function of time as the structure collides with the stationary particle.  $\alpha$  increases as the cluster starts to strike the stationary particle until  $\alpha$ reaches a maximum flex angle  $\alpha \sim 32^{\circ}$  in the middle of the collision, then begins to decrease and returns to  $\alpha = 0$  as the structure straightens. One also notices that the stationed object has tilted slightly in comparison to its orientation before the collision. How these two parts adhere to one another and how this flexible action is allowed are under current investigation. Future

fabrications may take advantage of such designs to carry cargo through narrow channels or through obstacle-ridden paths.

# **5.6 Conclusions**

In conclusion, we have demonstrated that self-organized catalytic nanomotors consisting of more than one individual part can be formed through random self-organization or directed self-assembly. The self-organized structures consist of separate parts that cause the system as a whole to act in unique ways not exhibited by individual particles. We have shown three such examples: the spinning 2-tadpople cluster, the helicopter nanomotors with separate moving parts, and the flexible swimmer that can maneuver around stationary objects. To design advanced nanomotor systems, one not only needs to design different nanomotor parts, but also improve the clustering technique. Self-organization is promising for the fabrication of multi-component catalytic nanomotors with independent parts working in coordination. Combining current nanofabrication techniques with self-organization with the manual manipulation of particles with magnetic and electric fields, thermal and chemical gradients, and other methods, a way to realize complex nanomachinery is obtained, which may allow for major technological advances in the nano and microscopic realms. This topic warrants further investigation.

#### CHAPTER 6

## CONCLUSIONS AND FUTURE WORK

Catalytic nanomotor research has quickly become a very interesting topic in the nanotechnology field. The ultimate goal of this research is to manufacture micro and nanoscale autonomous robotic machinery that can perform intricate tasks at these scales. Gaining a broader understanding of how they operate and how to engineer these devices will allow for the first functional nanomachines.

In order to gain a more fundamental understanding, future research should focus on the ways to make catalytic nanomotors bio-compatible. Currently, the easiest fuel for study is hydrogen peroxide, which is toxic at the levels to the body at the concentrations used in these experiments. By using bio-compatible enzymes such as glucose oxidase and catalase instead of inorganic catalysts, applications in biology and medicine will become more practical. Also, combining the physics and engineering branches of this research with other biochemical processes will allow for more advanced applications such as the selective binding to certain cells such as cancer cells. In this case, the nanomotors could seek invasive intruders in the body and destroy them. Other more intricate applications such as the implanting of DNA segments into cells so that the cell will produce some desired effect. Clearly, future applications could have tremendous applications in medicine and biology.

Research must also focus upon the fine tuned control and structural design. The method presented in this thesis expands upon the types of geometry available for researchers to fabricate desired shapes, but there are still limitations to this method. Newer, more advanced fabrication techniques will have to work in combination with DSG and TDEP to develop even more sophisticated designs. Ideally, in the future, any type of shape at the nanoscale will be possible. Advances in conjugation will also have profound influences on this field. Fabricating multicomponent nanomotors is a major challenge, and a number of different fields of expertise will have to collaborate in order to have functional machines with independently working parts. The control over swimming behaviors is clearly another demand in this field. The combination of autonomous motion with external magnetic and/or electric fields (including light) will allow for the precise manipulation. This field is rapidly growing, and the advances have been tremendous over the past decade. Future researchers have many challenges to face, but this exciting field is rich with possibilities for future applications.

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