#### BUBBLE DRIVEN CATALYTIC MICROMOTORS

by

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#### (Under the Direction of Prof. Yiping Zhao)

## ABSTRACT

This year (2014) we celebrate a decade anniversary of catalytic micromotors, in which they have come to represent one of the important technical advances, having shown promise in many important functions in biomedical and engineering fields such as sensing, detection, drug delivery, oil spill cleanup, etc. Catalytic nano-/ micromotors are structures that convert chemical energy present in the surrounding aqueous environment into mechanical work through a catalytic reaction induced by an asymmetrically placed catalyst. This dissertation focuses on the fundamental study of the motion mechanics of catalytic motors.

Diffusiophoresis is the motion of motors due to diffusion of reaction entities, such as the fuel or by-products of the catalytic reaction. Small Janus catalytic motors i.e., spherical microbeads half coated with catalyst metal, utilize the diffusiophoresis mechanism. Introduction of a hydrophobic front surface in Janus catalytic has been observed to make them appreciably faster due to changes in reaction kinetics.

The bubble propulsion mechanism is observed when the bubbles formed on the catalyst surface eject or burst. The motion of bubbles provides an opposing thrust to the motor. We have studied the motion of bubble propelled big Janus motors using a fast CCD camera. The formation of bubbles depends closely on the nucleation energy, which also is related to surface curvature. It is predicted that bubbles are easier to nucleate on a concave shaped surface than on a convex shaped surface. Thus, bubble propulsion can be easily seen in concave motors. The predictions were confirmed with nanoshell catalytic motors with catalyst coated inside the shell. Similarly, if the catalyst is coated in the inner surface of a tube, a tubular motor can be produced. We used graphene oxide nanosheets (GO) as templates and the stress effect in the multilayer of metal thin films to create microtubes.

Finally, collective motion has been observed with 5-µm diameter Janus motors. These motors are too small for bubble propulsion to occur, but collectively they produce bubble and perform a synchronized motion. The collective motion is a result of Marangoni effect.

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#### CHAPTER 1

## INTRODUCTION

In 2001 Whiteside's group opened a new door for a field that was less explored and even less excitable. They created millimeter scale objects partly coated with Pt thin film, which self-propelled at an air water interface with the help of H<sub>2</sub>O<sub>2</sub> decomposition on one of its edges [1]. This was the first example of manmade catalytic motors. These structures could convert chemical energy from their surroundings and turn it into kinetic energy for their movement in an aqueous solution. The visions of such motors had long been prophesized; one notable example was Dr. Richard Feynman's challenge of creating a micrometer scale motor in 1959 [2]. One engineer by the name of William McLellan, engineered a microscopic motor to win the challenge shortly after. A long time after that, this field was neglected, until scientists started using advanced microfabrication techniques to realize microeletromechanical systems (MEMS). This branch of science is still progressing and the devices are getting smaller and more efficient. Using the MEMS technology to make structures that could swim in water is what some great scientists such as E. M. Purcell had envisioned [3].

Movement is essential and all the living organisms, from nanosized viruses to megasized animals, need it to survive. All these locomotive creatures have developed special organs and body parts to make them able to move efficiently. Nature has had millions of years to perfect the mechanism through evolution and the researchers have just begun the journey to catch up with her. Towards the beginning of the century, scientists developed micromotors that use fuels from surrounding environment and are not under any external field. In other words scientists were able to make true autonomous motors. Before one can study manmade motors, one has to look at what nature has been able to achieve in terms of micro and nanomotors.

### 1.1 Natural Nano- / Micro- motors

There are plenty of examples of micro and nanomotors in nature. One can make a broad classification of them as DNA, protein, and chemical based motors (Fig. 1.1) [4].

An example of DNA based and protein based motor is organelle ribosome containing rRNA and protein. Using both components, they read messenger RNAs and translate that information into proteins. Other examples of protein-based motors are kinesins, dyneins, and myosins which are used in various functions within the body. They harness the chemical energy (ATP) and perform different functions. A bacterium can be considered as a chemical based motor, and one well known example is Listeria monocygenes. This bacterium acquires it motion by burning its surrounding fuel asymterically. It does so with the help of asymmetric distribution of proteins on its surface, which produce actin filaments. Although these filaments are immobile, the asymmetry in the protein location on the cell surface leads to the asymmetric production of actin filament clouds, which, once dense enough, contribute to the recoil motion of the Listeria through recoil motion [4]. Another example is E. Coli [2]; it uses the helical bacterial flagella (which is ATP driven) to generate motion towards a food source or away from toxins. The flagellum is attached to a molecular motor that drive the flagellum according to proton gradient, which is maintained by the hydrolysis of ATP. As this motor spins, it creates a torque, which is used by the flagella to convert into linear motion. If one analyzes these motors closely, the structure of these biological motors is very intricate and its not as straightforward as the locomotion of macrosized creatures who use cyclic motion of limbs or wings or fins. This is due to the special circumstances the motors are subjected to when they move in this aqueous motion. Because of their size and the viscosity of the environment around the motor, the motion of the micro and nanosized motors becomes complicated. The inertial forces at this level do not produ-



**Figure 1.1:** Examples of nanomotors. (a) Construction and operation of the molecular tweezers; (b) the twin heads of a kinesin alternately bind the microtubule as the protein moves. (c) Schematic representation of ATPase and its hybrid analogue (d). (e) Molecular components required for actin-based motility of bacterium Listeria monocytogenes [4].

-ce any motion. We shall see the reasons in the next section.

Some of the chemical based motors, i.e. molecular machines are similar to electric motors and other human anologues. For example,  $F_0F_1$ -ATP synthase is a protein complex that synthesizes ATP from ADP and its rotary design resembles a manmade electric motor. However, all these biological motors can survive only in a liquid environment.

### 1.2 Challenges Faced by Micromotors- Low Reynolds Number Hydrodynamics

Considering a small volume element in a flowing fluid, we can write equation of continuity as,  $\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{U})$ , where  $\rho$  is the local density of the fluid around this element, and  $\vec{U}$  is the averaged local mass velocity. This equation can be derived by considering a balance

over a macroscopic volume V fixed in space,

$$\frac{d}{dt} \int_{V} \rho dV = -\int_{S} \rho \vec{U} \cdot \vec{n} dS \,. \tag{1.1}$$

The left side of eq. (1.1) represents the rate of change of mass accumulated in V and the right side represents the change in this accumulation via mass entering or leaving the through the surface S, which satisfies mass conservation. Applying the divergence theorem one gets,

$$\int_{V} \left( \frac{\partial \rho}{\partial t} + \nabla \cdot \left( \rho \vec{U} \right) \right) dV = 0.$$
(1.2)

This result applies to all volumes and therefore the integrand in eq. (1.2) must be identically zero and one obtains the equation of continuity. In fact, it is possible to derive the equation of continuity if one uses the surface moving with material points or material surface. The substantial or material derivative is defined by the operator equation as,

$$\frac{D}{Dt} = \frac{\partial}{dt} + \vec{U} \cdot \nabla \,. \tag{1.3}$$

Applying this operator to the equation of continuity,

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \vec{U} \,. \tag{1.4}$$

If one only considers the incompressible fluids, the density  $\rho$ , will be constant and therefore one has,

$$\nabla \cdot \vec{U} = 0. \tag{1.5}$$

Following the mass conservation, one can also look at momentum conservation and the equation is,

$$\rho \frac{D\vec{U}}{Dt} = \nabla \cdot \boldsymbol{\sigma} + \rho \vec{f} , \qquad (1.6)$$

where,  $\sigma$  is the stress tensor and  $\vec{f}$  is the external body force per unit mass. Applying the divergence theorem, one obtains,

$$\frac{\partial \left(\rho \vec{U}\right)}{\partial t} + \nabla \cdot \left(\rho \vec{U} \vec{U}\right) = \nabla \cdot \boldsymbol{\sigma} + \rho \vec{f} .$$
(1.7)

For a constant dynamic viscosity  $\mu$  and constant density  $\rho$ , the above equation reduces to,

$$\rho\left(\frac{\partial \vec{U}}{\partial t} + \left(\vec{U} \cdot \nabla\right)\vec{U}\right) = -\nabla \vec{p} + \mu \nabla^2 \vec{U} + \rho \vec{f}, \qquad (1.8)$$

where  $\vec{p}$  is simply the pressure acting on the surface. Equation (1.8) is also known as the *Navier-Stokes equation* [5]. The linearized Navier-Stokes equations for steady motion are also known as the creeping motion equations where  $\rho \vec{U} \cdot \nabla \vec{U}$  will be smaller than  $\mu \nabla^2 U$ . The approximate solutions for this equation can be worked out. These solutions are more accurate when the ratio of inertial forces to viscous forces  $lU\rho/\mu$  (here *l* is the characteristic length of a body in such a flow), i.e., the Reynolds number,  $R_e$ , is smaller. For a creeping flow with a low Reynolds number ( $R_e \ll 1$ ), we can neglect the inertial terms, and eq. (1.8) then reduces to,

$$\nabla \cdot \vec{U} = 0. \tag{1.9}$$

Solution to this equation gives the drag acting on a body in such a creeping flow. For a sphere with radius R and a linear speed v, one obtains,

$$\vec{F}_{drag} = 6\pi\mu R\vec{U}. \tag{1.10}$$

Thus, in equation of motion, no inertial forces appear at this low Reynolds number regime. In other words, both acceleration term and mass term are missing. This is the reason why a scallop motion would not generate any displacement at low Reynolds number environment. For its motion, a scallop opens its shell slowly and closes it fast, squirting out water and generating motion. At low Reynolds number environment the opening and closing of the shell would produce exactly the same and opposite displacements. For structures like these, when a force is applied on them, by means of limbs, rudders, wings, or fins, it does not produce actual motion, since the displacement achieved by moving these organs (referred to as deformation of a body) is cancelled out when the organs move in opposite way to return to original position. A body under external force would stop moving immediately after the applied force is stopped. This is a real challenge faced by the micro and nanomotors, since they cannot "swim" in a traditional sense using their own mass to generate acceleration.

To produce motion in such an environment, therefore, a body should deform in a noncyclic way and should not use a motion of its body parts that has only two steps (backwards and forwards or open and close). A body deforming in a circular or a helical way would be far more successful in such environment since the force applied is continuously in one direction. Therefore to produce motion in low  $R_e$  fluid, we have to design the motors while keeping the geometry and shape of the motors in central focus. To produce and maximize the motion under such environment, we can execute following steps,

1. Reduce the cross sectional area along the motion direction.

2. Avoid reciprocal motion.

3. Apply continuous asymmetric force.

4. Reduce effective viscosity experienced by the motor surface.

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We shall see in the following sections and then chapters how we and others have worked towards this goal using these guidelines to make micromotors smarter, faster and more efficient. We have reached a level where we can produce motors that can move even faster than the fastest biological micromotors in nature.

#### 1.3 Origin of Catalytic Nanomotors and Their Different Classes

It was almost 43 years since the famous speech by Richard Feynman, "Plenty of room at the bottom", that Whiteside's group developed the first manmade, chemical based motor. The structure they created was not in micro or nanoscale [1]. It was a centimeter-sized disk that floated on  $H_2O_2$  solution and converted the chemical energy from the solution into their motion via a catalytic reaction  $2H_2O_2 \rightarrow 2H_2O + O_2$ . This reaction takes place on the surface of catalyst situated on the disk. The  $O_2$  generated due to reaction formed into bubbles and pushed the disk forward through a recoil mechanism. In 2004, the first nanoscale motor using the same catalytic reaction was first reported in two landmark papers by the group of Thomas Mallouk at Pennsylvania State University and the Geoffrey Ozin at University of Torronto reported similar motors [6-7]. They reported motors made of Pt-Au (Fig. 1.2) and Ni-Au nanorods, synthesized by electrodepostion, termed 'striped nanorods'. These nanorods showed autonomous motion in the aqueous solution of  $H_2O_2$ . This is where the term '*catalytic motor*' was born. This year we celebrate a decade of research and innovation in this field and look back at how we developed



Gold

Platinum

Figure 1.2: Representation of Striped catalytic nanomotor, size of the nanorod is about 370 nm in diameter and 1  $\mu$ m in length

our understanding and design of motors. The motion of striped nanorods was continuous and non-Brownian and it was the result of electrochemical decomposition and charge exchange between Au and Pt part of the rod (Fig. 1.3). This motion mechanism was later improved by introducing carbon nanotubes in the Pt part, which resulted in huge increase in acceleration of nanowires (Fig. 1.3) [8].

The motors can be designed to perform certain predefined motion. Mallouk group demonstrated that the motors can perform rotational or circular motion. They used a trimetallic nanorotor consisting of Au, Ru and Pt [9]. The added third metal gives a perpendicular component to the motion, which produces ultrafast rotation. Using a different approach, our group showed that manipulating geometry could enhance and control motion of the micromotors. We reported the tadpole shaped motors, in which a multicomponent motor that had a Pt coated TiO<sub>2</sub> arm attached on top of a silica microsphere, using dynamic shadowing growth (DSG) (Figure 1.4a). Depending on the placement of Pt and changing geometrical parameters on the



**Figure 1.3:** Modified striped Au-Pt nanorods. The Pt part is infused with carbon nanorods. The green arrow points to the propulsion direction and red arrow shows the direction of charge exchange. The accompanying plots show the trajectory comparison with the striped nanorods [8].



**Figure 1.4:** (a) Different lengths of  $TiO_2$  arms are fabricated using DSG. (b) Trajectory of motors in 2-D top view for different arm lengths. (c) Trajectory of motors keeping the arm length fixed and changing the concentration of  $H_2O_2$  [10].

structure, one can produce different kinds of motional behaviors (Figure 1.4b and c) [10].

Besides bar, rod or microsphere, other shaped motors can designed as well. Recently more and more complex and advanced motors have been reported. In 2009, Schmidt's group developed a new motor, which consists of a microtube with Pt coating on the inner walls. These tubes or microjets produce  $O_2$  bubbles on the Pt surface and expel them from one of its ends, thereby giving it a thrust in the opposite direction. The microjets could produce astonishing speeds. The microtubes were made by using photolithography, wherein nanomembranes were deposited in patches which would rollup into tubes upon removal of photoresist. This method is summarized in Fig. 1.5 [11].

Following this report, many groups developed methods to fabricate microjets. Wang group developed a template method [12]. In this method, commercially available porous



**Figure 1.5:** Process flow for positioning rolled-up nanomembranes. a) Top and cross-section view of patterned photoresist layer on a substrate; b) Schematic diagram of the tilted deposition method exploiting the ballistic shadow effect; c) SEM image of rolled-up Ti/Au nanomembranes fabricated according to (b). d) Detailed process flow for rolling up deposited films with high conformity; e) optical microscopy image of rolled-up  $Al_2O_3$  nanomembranes obtained following the procedure in (d) [11].

conical template is used. The outer wall of the microjet is formed by polymerization of

polyaniline (PANI) film. Pt is then plated inside the tube using galvanostatic methods (Fig. 1.6).



**Figure 1.6:** (a) Template-assisted fabrication of tubular structure for microengine. Polyaniline (PANI) and Pt were electrodeposited sequentially into the commercial Cyclopore polycarbonate membrane. (b) Cross view of a PANI/Pt microtube [12].

## **1.4 Propulsion Mechanism**

From all the methods of fabricating and designing micromotors, it is clear that the motional behaviors vary significantly depending on the geometry as well as the propulsion mechanisms of the motors. Some move fast whereas the others move slower. Some move in the direction opposite to that facing the catalyst and others move in the direction that the catalyst is facing. Various theoretical models have been proposed to account for the propulsion mechanisms.

In general the main propulsion mechanisms include: diffusiophoresis, bubble propulsion, interfacial tension gradients and self-electrophoresis. There are other emerging mechanisms as well, such as self-acoustophoresis, self-thermophoresis, etc. We shall briefly look at some of these mechanisms below. A couple of review articles would give a fair idea of these mechanisms and how our understanding has changed [2, 4, 13-14].

#### **1.4.1 Diffusiophoresis**

As the name suggests the motion of the motors is directly linked to diffusion (of the fuel and by-products of the reaction). The asymmetrically placed catalyst on the motor creates asymmetric distribution of by-products from the catalysts as well asymmetric concentration profile of fuel around the surface of the motor. Goldstein et al suggested that the diffusion of high concentration of the products at the reaction sites generate a force to propel the nanomotor to move away from the diffusion gradient direction, as given by eq. (1.11),

$$\partial_t \rho(\vec{r}, t) - D\nabla^2 \rho(\vec{r}, t) = \frac{dN_p(t)}{dt} \delta^3(\vec{r} - \vec{r}_s), \qquad (1.11)$$

where  $\rho$ ,  $\vec{r}$ , D,  $\vec{r_s}$ , and  $\frac{dN_p(t)}{dt}$  are the density, position vector, diffusion coefficient for the reaction particles, location of the catalyst site and reaction products release rate respectively [15]. Since the reaction is continuous, the gradient and hence the diffusion is constantly maintained. This gives the motors the means to move continuously and autonomously. We shall discuss this mechanism in Chapter 3 in detail.

#### **1.4.2 Self-Electrophoresis**

The term electrophoresis describes the transport of particles in a liquid medium under an electric field, internal or external. If E is the field acting on the particle and v is the velocity of the particle then according to the Smolunchowski equation,

$$v = \frac{\zeta \varepsilon}{\mu} E \,, \tag{1.12}$$

here,  $\zeta$  is the zeta potential of the particle,  $\varepsilon$  is the permittivity of the medium, and  $\mu$  is the dynamic viscosity [13].

When catalytic motors are made from two metals to form a bimetallic junction, one of them could act as an anode and the other as cathode, depending on their relative electronegativity



**Figure 1.7:** Au-Pt composite nanorods. Schematic of redox reaction on anode and cathode. The direction of propulsion is denoted by the green arrow [13].

during the catalytic reaction as shown in Fig. 1.7. Unlike electrophoresis, the bimetallic motors do not respond to external fields, rather, they generate their own local field, which moves with the motors. The mechanism is termed self-electrophoresis for this reason. The best example of these motors, is the striped nanorod motors discussed earlier. As shown in Fig. 1.7, the oxidation of H<sub>2</sub>O<sub>2</sub> occurs at the Pt end (anode), while the reduction of H<sub>2</sub>O<sub>2</sub> happens at the Au end (the cathode). This reaction makes the rod negatively charged and leaves a high concentration of protons near the Pt end. Since there is a concentration gradient of protons from the Pt end to the Au end, an electric field is generated pointing from anode to cathode. Naturally, this electric field drives the negatively charged motor towards the Pt end. Another example of self-electrophoretic motors is the bimetallic Janus motors created by Dr. Gibbs in our lab. Using dynamic shadowing growth, silica microbeads were coated with varying overlap of Au and Pt layers (Fig. 1.8) [16]. It was found that the average speed of the motor *v* and exposed area of Au *A* followed a non-linear relation of  $v \propto A^{3/2}$ .

One could also use the same principle to create micropumps. Instead of free moving nanorods, if a nonmoving structure with a similar bimetal overlap is created, the electric field generated would force the protons to move to cathode, thus creating a continuous flow (Fig. 1.9). This structure was reported by the Mallouk and Sen group in 2005 [17].



**Figure 1.8:** Self-electrophoretic spherical micromotors. Using DSG, Au and Pt are deposited on different areas of the bead, producing desired area of exposed Au and overlapped Au [16].



**Figure 1.9:** Catalytic Micropump. Since the Au-Ag, cathode-anode structure is non-motile, the transfer of protons from anode to cathode creates a convective flow [17].

## **1.4.3 Bubble Propulsion**

Even before the direct evidence of bubbles from catalytic micromotors was observed, the possible existence of bubble and the resulting propulsion mechanism was proposed [2]. This is due the fact that certain motors, such as the motors with insulator-metal junction moved in the direction that is opposite to their bimetallic counterpart, i.e., they moved away from the catalyst surface. This and the fact that there must be a continuous source of force acting on the motor in order to produce motion, led researchers to believe that there must be tiny bubbles of  $O_2$  coming off of catalyst surface. These bubbles, while leaving the catalyst surface, impart an opposite thrust and that is how the motors move away from the catalyst surface [18]. Even though the direct observation of  $O_2$  nanobubble coming off of catalyst was not available, circumstantial evidence such as AFM images of nanobubbles suggested the presence of bubbles [2]. The reasons for the lack of bubbles are buried in the geometry of the motors and would be discussed in Chapter 4 in detail. In 2008, Schmidt's group demonstrated microtubular motors that ejected bubbles from one of its ends and provided the thrust to move forward [11]. They proposed an empirical model to explain the motion of the microtubes. The microtube while expelling the



**Figure 1.10:** The microtube motor gets a forward thrust due to series of deformation from Stage 1 to Stage 4, and then back to Stage 1 [11].

bubble goes through a series of deformations, which are cyclic but not reversible. As shown in Fig. 1.10, in Stage 1 the microtube is in "motor with a bubble inside" stage. As the bubble is expelled, the motor goes through deformation from "motor with bubble just outside" to "motor with a detached bubble" (Stage 4). This model is summarized into the expression  $v \approx f \times r_b$ , where v is the average velocity of the microtube, f is the frequency of bubbles expelled and  $r_b$  is the radius of the bubble.

## **1.5 Collective Behavior**

So far we have seen examples of motors that are independently autonomous and move without the presence of any external fields. It is also not Brownian since we see a clear trend of deterministic trajectories. Although some motors use external source as an excitation trigger, they still move autonomously since the motors convert the fuels locally [13]. In many cases, the external control on maneuvering the motors is desired. For instance, a motor carrying a drug targeted to a specific area is desired to reach there via some external controls. This can be achieved by adding components to the motors that respond to external fields without interfering with the propulsion mechanism. For example, one can add Ni to the composition of the motors and control their motion with the help of external magnetic field. However, it is also (and arguably) more beneficial to have motors that can perform tasks independently and without supervision. These tasks could include sensing and reporting of DNAs, pathogens, cleaning up impurities in their surroundings etc. These functions and many more require not one but many motors working together, collectively achieving the goals. Therefore, autonomous behavior is the foundation of collective behaviors such as schooling or swarming.

Collective behavior occurs in nature everywhere. In the macroworld, one can observe two kinds of collective behaviors, swarming, in which the individuals aggregate towards one common goal and schooling, in which a group moves in unison, in one direction at any point in time. Examples of swarming can be, group of predators hunting a pray or ants following other ants towards one food source. For schooling, there is schools of fish. They move with incredible speed and agility in a group maintaining their shape of a group. They also change direction responding to environment instantaneously as a whole group. The collective behavior can happen only if there is a communication between the individuals of the group. It gives vast advantages to the members of the group to survive and prosper. It is a classic case of 'whole being greater than the sum of its parts'. These collective behaviors give rise to something called 'emergent behavior', where in the communication within the group makes the movement appear to have a autonomy of its own. One of the important features of this behavior is that there is no central command. No one individual is responsible for taking the decision for the whole group.

Collective behaviors are also seen in nature in the microworld. Bacteria move towards a food source or away from a harmful agent. Their preferential movement was first discovered and

reported by Engelmann and Pfeffer in 1880 [19]. This motion was termed as chemotaxis. The bacteria can sense the gradient in the concentration of chemicals and can move towards the higher concentration or lower, depending on the nature of the chemicals. Gradually, an emergent behavior occurs as colonies of bacteria develop around food source. The motion of bacteria could be considered as semi-autonomous since they are acting under an external chemical field, but not totally controlled by the field.

Learning from nature and driven by the necessity to make catalytic motors more application ready, researchers have started studying the collective behaviors in motors. The first account of nonbiological chemotaxis was reported by Hong et al in 2007 [19]. They used a hydrogel soaked with H<sub>2</sub>O<sub>2</sub> and placed it in at the center of an enclosed chamber filled with Au-Pt nanorod motors as shown in Fig. 1.11a. The gel slowly creates a concentration profile in the chamber, with highest concentration of H<sub>2</sub>O<sub>2</sub> at the center to lowest concentration at the edges of the chamber. They observed that the nanorods demonstrated autonomous motion but with temporal sensing. Over time, the nanorods accumulated towards the hydrogel due to 'active diffusion' as shown in Fig. 1.11b. The nanorods in the presence of H<sub>2</sub>O<sub>2</sub> start performing active motion, but it is totally random at start. We know that the average speed of nanorods is proportional to the concentration of the fuel. Therefore, in one random tumble if a nanorod moves towards higher concentration of fuel, its speed will increase, and inversely, if it moves towards a lower concentration of fuel its speed will decrease. As a result, the nanorod will have more displacement going towards the higher concentration than the lower concentration regions. This preferential motion is summarized in the following equation,

$$X(\tau + \delta\tau) = X(\tau) + (1 + \varepsilon X)\cos\theta(\delta\tau) + \delta X(\delta\tau), \qquad (1.13)$$



**Figure 1.11:** (a) Schematic of the chemotaxis experiment. (b) Plot of fraction of rods as a fuction of time, showing the slow aggregation towards the gel [19].

where  $X(\tau)$  is the position of the rod at time  $\tau$ ,  $\theta$  the direction and  $\varepsilon$  is the concentration gradient. Since then researchers have used mechanisms other than self-electrophoresis to produce collective behavior in micromotors, such as diffusiophoresis and bubble propulsion.

In 2009 Sen's group reported swarming behavior using diffusiophoresis [20]. They used AgCl particles in their study. Under UV light, in water, those AgCl particles undergo a reaction, which produces charged ions. The reaction that takes place under UV light is,

$$4\text{AgCl} + 2\text{H}_2\text{O} \longrightarrow 4\text{Ag} + 4\text{H}^+ + 4\text{Cl}^- + \text{O}_2$$

The autonomous motion is a result of asymmetric photo decomposition of the AgCl particles, which could arise from non-uniform exposure to UV or due to surface abnormalities. This leads to diffusiophoresis similar to the motors discussed earlier. Since the AgCl particles themselves produce the electrolyte gradient and are also driven by the gradient, they tend to form schools of particles. These particles exhibit 'predator-prey' like behavior when charged, chemically inert microspheres are introduced to the mixture. The spheres inside the gradient are pushed towards the AgCl particles. When UV light is turned on, these spheres actively seek AgCl particles. If the sphere is negatively charged, they maintain an 'exclusion zone' (repulsion like dispersion)

around the negatively charged AgCl particles, and when the spheres are positively charged, they are attached to the AgCl particles (schooling).

Later, the same group reported reversible collective behavior [21]. Silver orthophosphate microparticles ( $Ag_3PO_4$ ) show transitions between exclusion and schooling. These behaviors are triggered by shifting the chemical equilibrium by addition or removal of ammonia or in response to UV light.

Schmidt group has reported collective behavior of bubble propelled microtube motors [22]. They have observed that autonomously moving microtubes could self-organize into complex configurations. Sometimes, the tubes bind themselves together in parallel i.e. one bubbling end next to bubbling end of the other or anti-parallel configurations i.e. bubbling end next to non-bubbling end. A large number of motors can also form complex clusters, with complex swimming patterns. These conditions depend on the  $H_2O_2$  concentration and the concentration of microtubes.

#### **1.6 Applications**

All the above mentioned different motion designs and mechanisms can be used to tailor into amazing applications.

Sensing and detection: Wangs's group has showed a few interesting applications using micromotors. One is detecting DNA and ribosomal RNA using micromotors [23]. The new motion-driven DNA-sensing concept relies on measuring changes in the speed of unmodified catalytic nanomotors induced by the dissolution of silver nanoparticle tags captured in a sandwich DNA hybridization assay. Along the same lines they have also shown rapid and selective isolation of nucleic acid targets from untreated samples and cancer cells in complex
media using functionalized micromotors [24-25]. The transport properties of single-strand DNA probe-modified self-propelling micromachines are exploited for "on-the-fly" hybridization and selective single-step isolation of target nucleic acids from "raw" microliter biological samples. The rapid movement of the guided modified microrockets induces fluid convection, which enhances the hybridization efficiency, thus enabling the rapid and selective isolation of nucleic acid targets from untreated samples. Sen's group also showed micromotors can be used for bone-crack detection, targeting, and repair using ion gradients [26]. Bone cracks can be detected by utilizing the damaged target itself as the trigger and the driving force. A crack in a bone creates a high local mineral content, these minirals can be selectively targeted and the micromotors swarm towards the crack. This can be utilized for active targeting and treatment by functionalized micromotors.

*Cargo (Drug) transport and delivery:* Catalytic motors have also been demonstrated to be used to pick up, transport, and release common drug carriers including biocompatible and biodegradable polymeric particles and liposomes [27]. Small magnetic particles coated with common drugs are instantaneously attached to micromotors that are functionalized with iron oxide particles due to weak magnetic interactions. The motors then travel a predesigned path controlled by external magnetic field and a rapid reversal of magnetic field releases the drug at the desired location. Molecularly imprinted polymer-based catalytic micromotors could be used for selective protein transport [28]. The surface of micromotors is polymerized in the presence of a target analyte. Due to this, the micromotors selectively concentrate the protein and gets attached to the surface. In another report, Sen's group has demonstrated the use of photochemical stimuli for the drop-off of cargo from load-bearing catalytic Pt-Au nanomotors [29]. Pt-Au nanorods are modified to have an additional silver segment. The nanorods are then attached with

a polystyrene microspheres with the help of electrostatic interactions. When these motors are introduced in a chloride environment and exposed to UV light stimulus, the silver segment dissolves and the cargo of polystyrene microspheres is delivered. Schmidt group has demonstrated the magnetic control of tubular catalytic microbots for the transport, assembly, and delivery of micro-objects as well as transporting multiple cells into specific locations were demonstrated [30].

*Environmental Applications:* Catalytic motors can also be potentially used for oil spill cleanup by using superhydrophobic alkanethiol-coated microsubmarines for effective removal of oil [31]. Here the surface of the micromotors is made superhydrophobic. This surface shows a strong adhesion to self assembled monolayers (SAM) of alkanethols. These SAMs show continuous interaction and adsorption of oil droplets in the surrounding media. Another report showed that micromotors can be used for cleaning water by degrading organic pollutants in water via the Fenton oxidation process [32]. In this report, the microjets inner walls are coated with Pt and the outerwalls are made up of Fe. The ions created in the catalytic breakdown of  $H_2O_2$  helps Fenton reaction with Fe to degrade organic pollutants.

### 1.7 Contents of Dissertation

In this thesis, I have focused on the understanding of the bubble driven micromotors and their collective behavior. This dissertation consists of 6 chapters. Chapter 1 contains the updated history in recent developments of catalytic micromotors and thesis motivation. We discuss the nature's version of micro and nanomotors and how the millions of years of trial and error of evolution has given the researchers the guidelines to built artificial motors. Physical challenges faced by motors in viscous medium are also discussed briefly. Chapter 2 discusses

diffusiophoresis in detail. The Stoke's solution for drag on a sphere is examined. We demonstrate that Janus motors with hydrophobic coating can make the diffusiophoretic motors more efficient. Chapter 3 includes detail discussion of bubble propulsion mechanism with both experiments and theory. We observe the bubble propulsion in large Janus motors and study the motion behavior in detail. The motion of the Janus motors is associated with bubble growth and burst. We also examine the effect of curvature on bubble nucleation. We find that concave motors can easily form bubbles to induce bubble based propulsion. Experimentally, we have demonstrated this principle through a multi-step fabrication process.

In chapter 4 a simple new method to fabricate microjet motors is presented. Strain engineered microtubes are built based on graphene oxide nanosheets and bimetal thin films. The resulting microjets are also propelled by bubbles. We have developed a mass transport model to describe the bubble formation process, and it predicts a qualitatively correct trend compared with the experimental data.

Chapter 5 contains a brief account of collective behavior in bubble propelled spherical Janus motors. Janus motors with 5-µm diameter, are observed to follow diffusiophoresis mechanism individually. However, at high motor density and high fuel concentration, they are observed to follow a collective motion, in which, the motors form a ring like structure and collectively form bubbles at the center of the circle. The bubble then grows and bursts, making the motors move cyclically inwards and outwards. The theoretical reasons are investigated. It is predicted that the temperature difference between the top and the bottom of the bubble generates a surface tension gradient which creates a Marongoni flow. Numerical simulations confirm that the strength of these effects would indeed generate such fast motion of motors in the collective

motion. At last, Chapter 6 gives the conclusion of the work done in this dissertation, and possible future experiments and applications.

#### CHAPTER 2

## DIFFUSIOPHORETIC MOTORS WITH SURFACE MODIFICATION

#### 2.1 Introduction

Of all the propulsion mechanisms of the catalytic nano/ micro motors, diffusiophoresis is one that closely resembles motion of natural nanomotors. Quite simply put, the motion is derived from the chemical gradient around the motor created by the asymmetrically distributed reaction products. In nature we observe such mechanism due to chemical gradients in bacteria, as they move towards a food source or move away from a detrimental entity. This is the origin for chemotaxis.

For catalytic motors, the chemical gradient is created due to the asymmetric placement of catalyst. Typically the catalyst breaks down the chemical fuel in the environment. The concentration of the fuel will be lowest at the surface of catalyst while; the concentration of the by-products will be highest. This creates diffusion of fuel and by-products towards and away from the catalyst, which in turn creates flows that help the motors to move in the opposite direction of catalyst surface. Different geometries of nanomotors have been designed that make use of this mechanism to create different motional behaviors [9].

The diffusiophoresis mechanism in catalytic motors is typically seen for motors with metalinsulator junctions, such as, Pt coated silica microspheres. The diffusiophoretic micromotors are typically in the size range of sub-micron to 10  $\mu$ m. The speeds of these nanomotors are below 100  $\mu$ m/s, although highest speed of such motors has been recorded at ~150  $\mu$ m/s [33].

Here I will focus on non-electrolyte diffusiophoresis. In general, the phoretic transport is the movement of colloidal particles due to a field that interacts with their surface. In our case the field is due to the gradient of chemical concentration created due to diffusion of reaction

products. A general expression for the speed (U) of the colloidal particle under a chemical gradient  $\nabla C_{\infty}$ , where  $C_{\infty}$  is the concentration of the solute at infinity, is given by,

$$U = \frac{k_B T}{\eta} K L^* \nabla C_{\infty}, \qquad (2.1)$$

where,  $k_B$ , T,  $\eta$ , K, and  $L^*$  are Boltzmann's constant, temperature, viscosity of the fluid, adsorption length on the colloid surface, and first moment of the solute distribution (directly related to potential energy arising from the surface interactions) respectively [34]. For our specific study we consider a silica microsphere ( $< 10 \mu m$  diameter), half coated with Platinum (Pt). This is an insulator-metal heterojunction motor. This kind of motor is also known as the Janus catalytic motor. This motor is then immersed in an aqueous solution of  $H_2O_2$ . The catalytic reaction happens on the Pt surface and H<sub>2</sub>O and O<sub>2</sub> are produced. Janus catalytic motors, perform a statistically constant directional motion. Usually, the constant speed U of a JCM is considered as a result of the balance of the driving force,  $F_m$ , a monotonically increasing function of the H<sub>2</sub>O<sub>2</sub> reaction rate, and the hydrodynamic drag force,  $F_{drag} = f_{drag}(\eta_{\infty}, l_s)U$ , where the drag coefficient  $f_{drag}(\eta_{\infty}, l_s)$  is a function of bulk viscosity  $\eta_{\infty}$ , local interfacial slip length  $l_s$ , and the size and shape of the motor, so that  $U = F_m/f_{drag}$ . When the radius *a* of the JCM is small, the motor is propelled by the diffusiophoresis mechanism, i.e., the concentration gradients of O<sub>2</sub> and  $H_2O_2$  around the Pt surface due to catalytic reaction generate a diffusiophoretic force  $F_m$  that moves the particle away from the Pt coated side [15, 35]. Assuming no slippage and uniform Newtonian flow, often  $f_{drag} = 6\pi \eta_{\infty} a$  for a spherical particle is applied, which is due to the normal and the shear interactions of a particle with fluid [5]. However, if the non-Pt surface of the JCM is chemically functionalized into a hydrophobic surface, two potential effects could be introduced: a slippery boundary with a finite  $l_s$  at the hydrophobic surface, and a change to the

reaction and/or diffusion kinetics at the Pt surface due to the presence of a hydrophobic surface coating and the possibly high concentration of gaseous O<sub>2</sub> resulting from catalytically decomposing H<sub>2</sub>O<sub>2</sub>. Intuitively, if the entire surface of a spherical particle is completely slippery, i.e.,  $l_s = \infty$ , according to Ref [5].  $f_{drag} = 4\pi \eta_{\infty} a$ , due only to the normal interaction between the motor and the fluid. This implies that under the slippery condition the effective moving speed of the motors could be increased provided that  $F_m$  remains a constant. At a hydrophobic surface, water energetically favorably forms a depletion layer [36], which can lead to an imperfectly bonded interface and/or significantly varying viscosity near the interface, and hence induce a large slip length  $l_s$  [37]. This depletion layer may also result in faster O<sub>2</sub> transport tangent to the motor surface than perpendicular to it. It would serve as a sink to drain O<sub>2</sub> tangentially away from the Pt side to the hydrophobic side and then release O<sub>2</sub> into the bulk solution. This mechanism may enhance the effective reaction rate and increase the phoretic driving force  $F_m$ . Therefore, in this chapter we attempt to answer two fundamental questions: First, how would a slippery boundary condition alter the motion dynamics? Second, would the hydrophobic modification alter the reaction/diffusion kinetics and consequently modify the motion dynamics? Here we have designed experiments to answer these questions.

# 2.2 Experiments and Results

For this study we use two different sized motors (2  $\mu$ m and 5.2  $\mu$ m in diameter). Each size motors are further divided into two groups: hydrophobic motors and hydrophilic motors (To emphasize, only the non-Pt side is functionalized). The fabrication process is as follows. Silica microbead suspensions of 2.01  $\mu$ m and 5.20  $\mu$ m (Catalog No. SS04N, SS06N, Bangs Laboratories) were first diluted to a 1:3 volume ratio in methanol, and a 2  $\mu$ l droplet of the

mixture is spread onto a  $2 \times 2$  cm<sup>2</sup> cleaned silicon surface. The substrates are then transferred to the chemical evaporation chamber for (HeptadecaFluoro - 1, 1,2, 2 - tetra-hydrodecyl) TrichloroSilane (HFTS) surface modification. The HFTS (catalog No., SIH5841, Gelest, INC.) deposition is a self-limiting process and usually results in a monolayer coating. Then the HFTS treated beads and bare silica beads are loaded into an electron beam evaporation system with a base pressure of about ~  $10^{-6}$  Torr. An adhesion layer of 10 nm of Ti is deposited on the beads at a deposition rate of 0.05 nm/s (measured by a quartz crystal microbalance), followed by 25 nm of Pt deposition at 0.05 nm/s. After the deposition, Janus motors with hydrophobic/catalytic surfaces and hydrophilic/catalytic surfaces are realized simultaneously. The as-deposited micromotors are suspended in 18 MQ·cm de-ionized water by ultra-sonication. The observation of motor motion is done as follows. Figure 2.1 (a) shows some representative trajectories of 5.2µm hydrophobic and hydrophilic JCMs moving in 5% H<sub>2</sub>O<sub>2</sub> in a 10 s interval. For a better comparison, the initial locations of all the JCMs are set to origin (x = 0, y = 0). The trajectories show that the hydrophilic JCMs move considerably shorter distances compared to that of the hydrophobic JCMs. A better picture of how hydrophobic surface modification affects the motion is obtained by studying the variation of motor speed U with bulk  $H_2O_2$  concentration  $C_{hp}^{\infty}$ , as shown in Fig. 2.1 (b). Each data point in Fig. 2.1 (b) is an average of at least 20 individual JCMs under the same condition. The horizontal straight lines represent the Brownian motion speed  $U_B$ , with ~ 1.3  $\mu$ m/s for 2  $\mu$ m JCMs and ~ 1  $\mu$ m/s for 5.2  $\mu$ m JCMs. Brownian motion is simply the motion exhibited by the motors in the absence of any directional force (in the absence of H<sub>2</sub>O<sub>2</sub>). This motion is exhibited by the motors due to the kinetic energy from heat at the room temperature. Brownian motion play an important role in the motion of motors. The motors undergo rotational as well as translational diffusion. The mean squared displacement  $\langle r^2 \rangle$  -t



**Figure 2.1:** (a) Representative trajectories of 11 hydrophilic and hydrophobic 5.2  $\mu$ m JCMs in 5% H<sub>2</sub>O<sub>2</sub>.  $\Delta x$  and  $\Delta y$  represent motor displacements in *x*- and *y*- directions, respectively. (b) Plots of average speeds *U* of 2 and 5.2  $\mu$ m hydrophilic and hydrophobic JCMs versus bulk H<sub>2</sub>O<sub>2</sub> concentration  $C_{hp}^{\infty}$ . The black solid symbols and the red open symbols represent hydrophobic and hydrophilic JCMs, respectively. The green and blue dotted lines represent respective Brownian motion speeds. The curves are the fitting results using Eq. (3.4).

relationship is always a good tool to differentiate the Brownian and active motion. For a Brownian motion,  $\langle r^2 \rangle$  -*t* follows the Einstein's relation,  $\langle r^2 \rangle = 4Dt$ , where  $D = k_B T / (6\pi\eta R)$ . Using literature values of physical constants such as viscosity ( $\eta = 0.00102$  Nm/s<sup>2</sup> for water), Boltzmann's constant ( $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{kg/s}^2 \text{K}$ ) etc., at room temperature, we get  $D = 8.2 \times 10^{-14} \text{ m}^2/\text{s}$  for a 5 µm spherical particle. Experimentally, for both hydrophilic and hydrophobic Janus motors,  $\langle r^2 \rangle$ -*t* appears linear with time (See Fig. 2.2). From the fitting parameters, one obtains  $D_{\text{phobic}} = 5.3 \pm 0.1 \times 10^{-14} \text{ m}^2/\text{s}$  and  $D_{\text{philic}} = 3.4 \pm 0.1 \times 10^{-14} \text{ m}^2/\text{s}$ , which are of the same order of the calculated *D*.



Figure 2.2: Mean squared displacement  $\langle r^2 \rangle$  for Janus motors as a function of time.

For the non-Brownian particles (in the presence of H<sub>2</sub>O<sub>2</sub>), the  $\langle r^2 \rangle$ -t, relation is given

by 
$$\langle r^2 \rangle = 4Dt + U^2 \tau_r t + \frac{U^2 \tau_r^2}{2} \left[ e^{-\frac{2t}{\tau_r}} - 1 \right]$$
, with  $\tau_r = 6\pi\eta R^3 / k_B T$  and  $\tau_r = 72$  s for a 5  $\mu$ m spherical

particle. As shown in Fig. 2.2, by fitting the  $\langle r^2 \rangle$ - *t* curve with the above equation, we get  $U^{philic}$ = 2.92 ± 0.02 µm/s, and  $U^{phobic}$  = 3.95 ± 0.06 µm/s. These values are very close to the

experimental results ( $U_{exp}^{philic}$  = 3.1 ± 0.2 µm/s, and  $U_{exp}^{phobic}$  = 4.2 ± 0.6 µm/s).

Below are the plots of  $\langle r^2 \rangle$ - *t* for 5 µm beads, averaged from at least 20 motors. Figure 2.2 is the experimentally measured data for HFTS treated and untreated beads. As we can see, in the absence of H<sub>2</sub>O<sub>2</sub> the HFTS treated and untreated particles behave the same way (purely Brownian).

Figure 2.1 (b) reveals three interesting phenomena: First, when  $C_{hp}^{\infty}$  is low (< 3% for 2 µm motors and < 1% for 5.2 µm motors), the speed difference of the hydrophobic and hydrophilic motors is indistinguishable. Second, at high  $C_{hp}^{\infty}$ , the speed of hydrophobic JCMs is always

greater than that of the hydrophilic JCMs. For  $C_{hp}^{\infty} = 5\%$ ,  $U^{phobic} = 3.4 \pm 0.6 \,\mu\text{m/s}$  and  $U^{philic} = 2.3 \pm 0.2 \,\mu\text{m/s}$  for 5.2  $\mu\text{m}$  motors; but  $U^{phobic} = 7.2 \pm 0.6 \,\mu\text{m/s}$  and  $U^{philic} = 6.6 \pm 0.5 \,\text{m/s}$  for 2  $\mu\text{m}$  motors. The difference is significant (48%) for larger particles, while it is marginal (9%) with smaller ones, showing size dependence. Note that the corresponding Brownian motion speeds ( $U_B$ ) are subtracted from the measured speeds. Third, the speed of the larger motors is always smaller than that of the smaller motors, regardless of whether the motor is hydrophilic or hydrophobic.

### 2.3 Discussions and Theoretical Considerations

To understand the motion of the particles we have to consider the mass transport and the gradients of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> that are generated as a result. We start by assuming that concentration fields of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> are similar but opposite, and are dominated by catalytic reaction on Pt. The mass transport problem, i.e. the concentration field  $C_i$  ( $i = H_2O_2$  or O<sub>2</sub>) around the motor is further simplified by the fact that diffusion length of either H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> are much larger than motor travel distance. The diffusion lengths can be calculated using Einstein's relation  $\sqrt{D_i t}$  to be ~ 45 µm in 1 second (~ time scale of our experiments) in water, where  $D_i$  is diffusion coefficient and *t* is time. The micromotor travels a few micrometers in the duration. This results in Laplace's equation,  $\nabla^2 C_i = 0$ . To solve this equation, we need to understand the geometry of the motor. For the Pt surface of the motor, the catalytic reaction, H<sub>2</sub>O<sub>2</sub> + Pt  $\rightarrow$  Pt(H<sub>2</sub>O<sub>2</sub>)  $\rightarrow$  H<sub>2</sub>O  $+ \frac{1}{2}O_2 + Pt$  is a two step reaction. In the first step, H<sub>2</sub>O<sub>2</sub> is adsorbed onto the Pt and in the second step the catalytic reaction releases O<sub>2</sub>. This creates a uniform H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> flux [38]. The flux can be written as follows,  $J_{hp}^{(P_1)} = k_{hp}C_{hp}^{\infty}(1-\Theta)$ , and  $J_{O_2}^{(P_1)} = k_{O_2}\Theta$ , where  $\Theta$  is the H<sub>2</sub>O<sub>2</sub> coverage

on the Pt surface,  $k_{hp}$  and  $k_{O_2}$  are the reaction rate constants for H<sub>2</sub>O<sub>2</sub> surface adsorption and O<sub>2</sub> production/desorption, respectively. With mass conservation and steady state reaction, one can relate both fluxes as,

$$J_{hp}^{(Pt)} = 2J_{O_2}^{(Pt)} = 2k_{O_2}C_{hp}^{\infty} / \left( \left( 2k_{O_2} / k_{hp} \right) + C_{hp}^{\infty} \right).$$
(2.2)

On the right hand side of the above equation, the H<sub>2</sub>O<sub>2</sub> concentration field  $C_{hp}$  is replaced by  $C_{hp}^{\infty}$ by realizing the fact that the amount of consumed H<sub>2</sub>O<sub>2</sub> is small due to high  $C_{hp}^{\infty}$  within the relatively short period of time in experiment. On the non-Pt surface,  $J_{hp}^{(non-Pt)} = J_{O_2}^{(non-Pt)} = 0$ .

The diffusion-induced hydrodynamics is assumed to follow the Stokes creeping-flow theory at low Reynolds number [5]. For a JCM, the O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> molecules interact with the motor surface, generate a pressure field, cause a local osmotic flow around the motor, and propel the motor to move [34]. The governing equations are  $\nabla \cdot \boldsymbol{\sigma} = 0$ ,  $\boldsymbol{\sigma} = -p\mathbf{I} + \eta_{\infty} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T]$ , and  $\nabla \cdot \mathbf{u} = 0$ , where  $\boldsymbol{\sigma}$ , p, and  $\boldsymbol{u}$  are the stress tensor, the pressure, and the velocity of the fluid, respectively.  $\boldsymbol{I}$  is the identity matrix, and superscript T indicates the transpose of a matrix. By assuming the continuity of tractions across the fluid-solid interface, the equilibrium conditions of the motor subjected to no external force or moment imposes additional constraints:  $\int_{\boldsymbol{\sigma}} \boldsymbol{\sigma} \cdot \mathbf{n} dS = 0$ ,

and  $\int_{S} \mathbf{r} \times (\mathbf{\sigma} \cdot \mathbf{n}) dS = 0$ , where *S* is the motor surface, and **r** is the position vector from the motor center to the motor surface. According to the classical theory of osmosis/phoresis [34], this diffusion-induced hydrodynamic process can be effectively modeled by using a slip velocity **u**' as a boundary/interfacial condition meanwhile treating the surrounding liquid as a Newtonian fluid, as illustrated in Fig. 2.3, where  $\mathbf{u}' = \mathbf{U} + \mathbf{\Omega} \times \mathbf{r} - \mathbf{u}$ , **U** and  $\mathbf{\Omega}$  are the linear and angular velocities of the (rigid) motor. If the fluid-solid interface is slippery (in the sense of Navier's slip), additional slip velocity can emerge in the presence of the shear stress  $\tau = (\mathbf{I} - \mathbf{nn}) \cdot (\mathbf{n} \cdot \boldsymbol{\sigma})$ . The net slip velocity  $\mathbf{u}'$  at motor surface is expressed as [34, 39]

$$\mathbf{u}' = \left(\mathbf{I} - \mathbf{nn}\right) \cdot \left[\frac{l_s}{\eta_{\infty}} \mathbf{n} \cdot \boldsymbol{\sigma} - \frac{k_B T}{\eta_{\infty}} \sum \Gamma_i \nabla C_i\right],\tag{2.3}$$

where  $k_B$  is the Boltzmann constant, T is the temperature,  $l_s$  is the local interfacial slip length,  $\eta_{\infty}$  is bulk viscosity and  $\Gamma_i$  is the second moment (a constant characterizing the interaction between  $O_2/H_2O_2$  and the motor surface [34]). The velocity U is related to  $\mathbf{u}'$  as its area average over the motor surface,  $\mathbf{U} = \frac{1}{4\pi a^2} \int_S \mathbf{u}' dS$ . Equation (2.3) can be traced back to the original work by



**Figure 2.3:** Illustration of slip due to Navier's slip boundary condition with a finite slip length ls(upper left) and diffusiophoresis with a solute (e.g., O2) concentration gradient, over the motor surface (upper right) on both the Pt and non Pt side of the motor shown below. Here, the blue arrows represent the tangential velocity components. Here r and  $\theta$  represent the position vector and the polar angle respectively.

Maxwell on thermal creep of rarefied gas at a solid surface [39]. The term,  $(\mathbf{I} - \mathbf{nn}) \cdot \left(\frac{l_s}{\eta_{\infty}} \mathbf{n} \cdot \boldsymbol{\sigma}\right)$ ,

is the dissipation due to the Navier slip boundary condition with a finite  $l_s$ , in analogy to friction [40-45]; whilst the term, , representing the osmotic driving force, induces a slip velocity according to Anderson [34].

It may be worth noting that in the literature, these two terms are often treated separately: for phoresis/osmosis, only the second term is considered [34], while for boundary conditions in micro- and nano-fluidics, only the first term is elaborated [40-45]. Under the assumption that concentration fields are dominated by the catalytic reaction on the Pt surface, the above boundary value problems of diffusion and diffusion-induced hydrodynamics are solved by using a boundary element method (by our collaborators in UTA). For example, Fig. 2.4 (a) shows the

normalized O<sub>2</sub> concentration,  $\tilde{C}_{O_2} = \frac{D_{O_2}}{J_{O_2}^{(Pt)}a}C_{O_2}$ , and normalized concentration gradient,



**Figure 2.4:** The plots of the normalized O<sub>2</sub> concentration field  $\tilde{C}_{O_2}$  (solid black curve) and concentration gradient  $\partial_{\theta} \tilde{C}_{O_2}$  (dashed red curve) versus the polar angle  $\theta$  of a JCM. (b) The plot of  $\tilde{U}$  as a function of the slip length  $l_s^{(non-Pt)} / a$  of a hydrophobic JCM.

 $\partial_{\theta} \widetilde{C}_{O_2} = \frac{D_{O_2}}{J_{O_2}^{(Pt)} a} \partial_{\theta} C_{O_2}$ , versus angle  $\theta$  (the polar angle on the plane perpendicular to the equator

plane of the Janus sphere, see Fig. 2.3).  $\partial_{\theta} \tilde{C}_{O_2}$  is symmetric with respect to the Pt/non-Pt dividing plane ( $\theta = 90^\circ$ ). The apparent singularity at  $\theta = 90^\circ$  is of the logarithmic order as a result of the stepwise flux boundary condition. Such a  $\partial_{\theta} \tilde{C}_{O_2} - \theta$  distribution causes both the shear stress and slip velocity concentrated at  $\theta = 90^\circ$ . Since  $C_{hp}^{\infty} - C_{hp}$  is proportional to  $C_{O_2}$ , the

normalized speed 
$$\widetilde{U} = \frac{\eta_{\infty}U}{k_{B}T} \sum \frac{D_{i}}{\Gamma_{i}J_{i}^{(Pt)}}$$
 for the JCM with varying  $l_{s}^{(non-Pt)} / a$  (while holding  $l_{s}^{(Pt)}$ 

= 0) is shown in Fig. 2.4 (b). It can be seen that  $\widetilde{U} \ (\approx 0.25)$  is nearly constant when  $l_s^{(non-Pt)}/a < 0.1$ , but increases gradually with  $l_s^{(non-Pt)}/a$ , and approaches to a constant value ( $\widetilde{U} \approx 0.28$ ) when  $l_s^{(non-Pt)}/a \rightarrow \infty$ . Such an increment in speed from a hydrophilic JCM to a hydrophobic JCM is estimated at 11%. In addition, as demonstrated by Huang et al, [46] for most experimental and theoretical works, the slip length of water on a hydrophobic surface should be less than 20 nm, regardless of the contact angle, which makes  $l_s^{(non-Pt)}/a \ll 0.1$  (even though there are few measurements which showed that  $l_s^{(non-Pt)}$  could be up to 1-2 µm [46]). Thus, the effect of the slip boundary condition at the non-Pt surface on the speed of the JCMs is not significant when applied to particle sizes less than 10 µm and can be neglected.

Therefore, the second term in Eq. (2.3), i.e., the diffusophoresis, should dominate the motor speed, and in this case, explicitly one has,  $\mathbf{u}' \propto \frac{k_B T}{\eta_{\infty}} \sum \Gamma_i \nabla C_i$ . According to Eq. (2.1), the

H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> flux  $J_i^{(Pt)}$  is a constant on the Pt surface, and U is an area average of  $\mathbf{u}'$ , one has,

$$U = U_{\infty} C_{hp}^{\infty} / \left( K + C_{hp}^{\infty} \right), \tag{2.4}$$

Motor Size (µm)	$U^{philic}_{\infty}$ ( $\mu$ m/s)	$U^{phobic}_{\infty}$ ( $\mu$ m/s)	<i>K<sup>philic</sup></i> (mol/m <sup>3</sup> )	<i>K<sup>phobic</sup></i> (mol/m <sup>3</sup> )	$k_{O_2}^{ m phobic}$ / $k_{O_2}^{ m philic}$	$U^{\it phobic}_{\infty}$ / $U^{\it philic}_{\infty}$
2	8.4 ± 0.6	9.4 ± 0.5	$1.1 \pm 0.2$	$1.4 \pm 0.2$	$1.3 \pm 0.3$	$1.1 \pm 0.1$
5.2	2.6 ± 0.1	$4.85 \pm 0.3$	$1.1 \pm 0.2$	$2.4 \pm 0.3$	$2.2 \pm 0.5$	1.9 ± 0.2

Table 2.1: Fitting parameters obtained for Eq. (2.3) from experimental data.

where 
$$U_{\infty} = \frac{Mk_B T \Gamma k_{O_2}}{\eta_{\infty} D}$$
 (with  $\frac{\Gamma}{D} = \frac{2\Gamma_{hp}}{D_{hp}} - \frac{\Gamma_{O_2}}{D_{O_2}}$ ),  $K = \frac{2k_{O_2}}{k_{hp}}$ , *M* is a proportionality constant

generally depending on slip length  $l_s$ , and  $\Gamma_i$  is assumed to be uniform over the entire motor surface. All of these observations directly support eq. (2.3). Fitting results when eq. (2.3) is curve fitted with the data of Fig. 2.1 (b), is listed in Table 2.1. This is a significant increase (48%) in the speed of the motors. In the previous section we already learned that this increase could not have been due to the increase in slip length. Therefore, this increase must be attributed to change in parameters listed in eq. (2.3). One can see that for the same sized JCMs,  $U_{\infty}^{\text{philic}} < U_{\infty}^{\text{pholic}}$ , and  $K^{philic} < K^{phobic}$ . In addition, for the same sized JCMs, it is expected that  $k_{hp}$  is the same for both hydrophobic and hydrophilic motors; thus,  $K^{phobic}/K^{philic} \approx k_{O_2}^{phobic}/k_{O_2}^{philic}$ . As shown in Table 1, for 2 µm motors,  $k_{O_2}^{phobic} / k_{O_2}^{philic} = 1.3 \pm 0.3$ , and for 5.2 µm motors  $k_{O_2}^{phobic} / k_{O_2}^{philic} = 2.2 \pm 0.5$ . That is, for both sized motors, the apparent reaction rate is indeed increased for hydrophobic JCMs. Also, the reaction rate enhancement is more significant when the motor size is larger. On the other hand, based on the ratios of  $U_{\infty}^{phobic}/U_{\infty}^{philic}$  and  $k_{O_2}^{phobic}/k_{O_2}^{philic}$  in Table 1 and the assumption that both  $\eta_{\infty}$  and  $D_i$  remain unchanged, one can obtain  $(M\Gamma)^{phobic}/(M\Gamma)^{philic} = 0.85$  and 0.86 for 2  $\mu$ m and for 5.2  $\mu$ m motors, respectively. In both cases,  $M\Gamma$  decreases due to the introduction of



**Figure 2.5:** Video frames of  $O_2$  bubbles generated by a 400-µm diameter Pt diskon (a) a HFTS treated Si (hydrophobic) substrate and (b) a clean Si (hydrophilic) substrate, submerged in 2%  $H_2O_2$ .

a hydrophobic non-Pt surface. Thus, the experimental data reveal an apparent enhanced reaction rate and a decrease in  $M\Gamma$  with the hydrophobic motors. The enhanced catalytic reaction rate on the hydrophobic JCMs is verified by an independent experiment. Two flat 400 µm diameter Pt disks (50 nm Pt) were fabricated; one on a clean Si (hydrophilic) substrate and the other on a HFTS treated Si (hydrophobic) substrate. These two samples were then submerged in 2% H<sub>2</sub>O<sub>2</sub> solutions. The O<sub>2</sub> bubble generation and growth were observed and recorded. Figure 2.5 shows some video frames from both the hydrophobic sample and hydrophilic sample. The O<sub>2</sub> bubbles start to nucleate immediately after the introduction of H<sub>2</sub>O<sub>2</sub> to the Pt surface on both samples. However, the hydrophobic sample shows more and larger bubbles compared to the hydrophilic sample at the same time. This observation indicates that  $k_{O_2}^{phobic} / k_{O_2}^{philic} > 1$ . In fact, by assuming that the bubbles are hemispherical, one obtains that the O<sub>2</sub> generation rate  $R_{O_2}^{phobic} = 3.15 \times 10^{-11}$ mol/s while  $R_{O_2}^{philic} = 1.38 \times 10^{-11}$  mol/s (for simplicity, the bubbles outside the Pt disk are not considered for this calculation), thus the ratio  $k_{O_2}^{phobic} / k_{O_2}^{philic} = 2.28$  for 2% H<sub>2</sub>O<sub>2</sub>.



(a) Hydrophilic surface

(b) Hydrophobic surface

**Figure 2.6:** Schematics of  $O_2$  flux produced around a Pt surface coated on (a) a hydrophilic surface; and (b) a hydrophobic surface. $D_{eff}$  is the effective  $O_2$  diffusion coefficient along the depletion layer. The  $O_2$  generated at a Pt surface would diffuse much faster along the depletion layer on a hydrophobic surface, inducing a greater area for  $O_2$  release, and causing a higher effective reaction rate.

When introducing the hydrophobic surface, the local concentration of O<sub>2</sub> around the Pt surface may be altered. The catalytically generated O<sub>2</sub> molecules are hydrophobes and are strongly attracted to a hydrophobic surface [47]. The depletion layer and the strong hydrophobic interaction of O2 with a hydrophobic surface in combination may have a positive effect on the reaction kinetics. The O2 molecules produced at the Pt surface can spread along the depletion layer to the hydrophobic side, effectively increasing the area for their release to the bulk solution as shown in Fig. 2.6. This effectively lowers  $C_{o_2}$  at Pt surface, which is similar to the interfacial polarization effect discussed by Anderson [34]. By lowering  $C_{0}$ , at the Pt surface, the O<sub>2</sub> production rate on a hydrophobic JCM should be enhanced compared to a hydrophilic one. Such a depletion mechanism as shown in Fig. 2.6 would reduce the concentration gradient of O<sub>2</sub>. Meanwhile, the enhanced  $O_2$  production rate would increase the concentration gradient of  $O_2$ . The net result of these two competing processes effectively makes gradients of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> larger, and thus increases the speed of the hydrophobic JCMs. The depletion layer alters the boundary conditions for the above boundary value problems of diffusion and diffusion-induced hydrodynamics, and further study is needed to fully understand the detailed process.

The reduction in  $M\Gamma$  could also be reasonably explained by the depletion mechanism. Since O<sub>2</sub> is attracted more to a hydrophobic surface,  $\Gamma$ , which measures the local osmotic driving force, should be increased for the hydrophobic motors. Thus, the change of  $\Gamma$  should not explain the decrease of  $M\Gamma$ . However, as shown in Fig. 2.6, O<sub>2</sub> is drained along the depletion layer from the Pt side tangent to the hydrophobic side, and can partially level off the high O<sub>2</sub> concentration gradient at the Pt surface edge, and hence decreases  $M\Gamma$ . Thus, the depletion mechanism could explain both experimental observations of enhanced  $k_{O_2}$  and reduced  $M\Gamma$ .

### **2.4 Conclusions**

In summary, we developed a theory by combining some excellent work done by Anderson and others. The two approaches gave a solid theoretical foundation and we tested it experimentally. We have experimentally observed that the hydrophobic JCMs move appreciably faster than hydrophilic JCMs under large fuel concentration, especially for larger sized motors. From numerical analysis, the slip boundary condition on the hydrophobic JCMs shows negligible effect on the motion speed, and the experimental data reveal that the catalytic reaction rate is enhanced. It is explained to result from the water depletion layer around the hydrophobic surface and the strong hydrophobic interaction between the generated  $O_2$  and the hydrophobic surface. This way to modify the motion of the catalytic motor provides an alternative method to design more efficient motors.

#### CHAPTER 3

## BUBBLE PROPULSION IN SPHERICAL MOTORS

In the field of micromotors, it has been well established now that the bubble propulsion mechanism can generate the fastest motors. However, the understanding of the bubble propulsion mechanism is not comprehensive. It is imperative that this mechanism needs to be studied in detail. The simplest micromotor geometry to study is the Janus catalytic motors. In particular, previous theoretical treatments of bubble propulsion [18] suggest that the bubbles leave the catalyst surface, impart a net momentum on the surface, and drive the motors. However, previous studies of spherical nanomotors, i.e. Janus particles, have not directly confirmed such a phenomenon. Only very recently rolled-up tubular microjets have been observed to eject bubbles from one end, acting as thrusters, with a maximum translational speed of 10 mms<sup>-1</sup> [48-50]. However, the tubular structure has a very different mass transport and bubble formation mechanism than the spherical micromotor since the catalyst is inside the tubular structure, and the detailed geometry of the tubes such as the symmetry of the tube, the size and shape of tube openings, and the tube length, controls the H<sub>2</sub>O<sub>2</sub> fuel supplying process. According to Fletcher [51], the large curvatures of previously studied spherical nanomotors resulted in large bubble formation energies, which made it difficult for bubbles to nucleate, grow, and detach from the catalytic surface. Therefore, in order to allow the bubbles to grow and form on a catalytic surface, the motor must possess a smaller curvature.

The effect of geometry and in particular, the effect of curvature on the nucleation is studied in detail. We find that we need to fulfill some constrains in order for the motors to travel via the bubble propulsion mechanism.

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## 3.1 Bubble Propulsion for Convex Catalyst - Quasioscillatory Motion

## **3.1.1 Experiments and Results**

We have performed a systematic study on the kinematic behavior of spherical catalytic micromotors with different diameters, 2 µm, 3 µm, 5 µm, and a distribution of beads between 10-50  $\mu$ m, to investigate the size dependent propulsion mechanism by fixing the H<sub>2</sub>O<sub>2</sub> concentration (5%). The bubbles begin to appear on the micromotors when the diameter of the beads is larger than 10 µm. With increasing bead size, the bubbling occurs more readily. Surprisingly, the motion kinematics of these larger motors are very different from those of previously reported small motors; the trajectory follows a quasi-oscillatory pattern rather than a linear motion. Such a process demonstrates a novel propulsion mechanism for catalytic micromotors. With a fast CCD camera, a systematic study has revealed that the motion of the micromotor coincides with the bubble growth/disappearance process: when the bubble grows and evolves on the catalytic surface, the motor moves away from the center of the bubble due to the bubble growth force; once the bubble reaches a maximum radius, it suddenly disappears (within 50 µs). Such a sudden disappearance, referred to as a bubble burst process, generates a local pressure depression that pulls the bead back towards the bubble location, and imparts a large impulse on the bead. Although the motion due to bubble bursting on a larger scale has been observed [1], this rocking motion induced by the bubble growth/burst has not been observed and understood before, to the best of our knowledge. To investigate in detail on this phenomenon, we have intentionally fabricated JCM with larger diameters ranging from 10 - 50 µm. The motors were fabricated with the following process. Silica beads with mean diameters of  $10 - 50 \,\mu\text{m}$  are uniformly spread on a Si substrate with the help of a double-sided tape. An ~10 nm adhesion layer of Ti is deposited on these beads in an electron beam evaporation system at a growth rate of



**Figure 3.1:** (a) A SEM image of the resulting Pt-coated Silica Janus bead. (b) Snapshots of a microbead (~ 25  $\mu$ m) in 5% H<sub>2</sub>O<sub>2</sub> solution at approximately every 200 frames (time interval of 0.01 s) showing the bubble growth/burst processes and the bead motional behavior. (c) The trajectory of the bead extracted from a 20,000 fps video. The red arrows denote the direction of trajectories of the bead after bubble burst and the green arrows represent direction the trajectories of the bead during bubble growth.

0.05 nm/s (measured by a quartz crystal microbalance), then a layer of Pt with a thickness of  $\sim$  25 nm is deposited at 0.05 nm/s. After the deposition, the substrates with coated beads are soaked in Hexane for about 20 minutes. This separates the beads from the tape with the help of tweezers. Most of the hexane is then pipetted out after centrifuging the mixture at 3000 rpm, leaving the beads at the bottom of a vial. Then Toluene is introduced to the vial in order to remove hexane and any leftover of tape glue residue on the beads. The mixture is again centrifuged. This process is repeated three times to ensure that the hexane is completely replaced by Toluene. To replace Toluene with water, the mixture has to go through intermediate steps of re-suspensions. After centrifuging the mixture, Toluene is replaced by Isopropanol followed by

Ethanol and then water. Finally, the beads are suspended in 18 M $\Omega$  de-ionized (DI) water. Figure 3.1(a) shows a scanning electron microscope (SEM) image of one such bead. A droplet (5  $\mu$ l) containing a few beads is then observed under the microscope, 10% peroxide (5  $\mu$ l) is then added to the droplet. Isolated single beads are randomly selected in order to observe independent motion. The motion of the beads is recorded at 1000, 5000, and 20,000 fps with a CCD camera (Phantom v9.1) using 10× magnification objective lens of a Mitituya FS110 microscope.

Figure 3.1(b) shows the representative snapshots at every 0.01 s for one complete cycle of bubble growth/burst process extracted from one video. The t = 0 s frame shows a bead of diameter ~ 45  $\mu$ m and an attached maximally sized bubble with a diameter of 73 ± 2  $\mu$ m. At t = 0.01 s, the big bubble disappears (burst), and multiple small bubbles start to grow on one side of the bead (catalytic surface), and some small bubbles coalesce and become a big bubble. Such a big bubble does occasionally detach from the bead, as shown in the frame t = 0.02 s,and then reattach back to the bead (t = 0.03 s). The big bubble continues to grow at the expense of small bubbles due to the Ostwald ripening effect (t = 0.04 s to 0.07 s) [52], until it reaches a maximum size (t = 0.08 s). The bubble bursts (t = 0.09 s), and the entire process repeats. The entire repeated process takes about 0.06 - 0.12 s. During the big bubble growth, the center of the big bubble displaces towards the bead slightly (~ 3 to 7  $\mu$ m) after the bubble reattachement, while the bead is pushed to a distance  $\sim 30 \,\mu\text{m}$  away from the bubble (toward the up-right direction in Fig. 3.1(b)). When the bubble bursts (from t = 0 s to 0.01 s, or from t = 0.08 s to 0.09 s), the center of the bead moves toward the center of the previous bubble (to the lower-left direction in Fig. 3.1(b)). Figure 3.1(c) shows the trajectory of the center of the bead after four such bubble growth/burst cycles. It demonstrates a quasi-oscillatory translational motion behavior: the bubble growth process pushes the bead forward while the bubble burst process pulls the bead back.

However, the growth process produces a larger overall displacement compared to that of the burst process; therefore, there is a net displacement of the bead in the forward direction. The dynamics of the bead motion during the bubble growth/burst process were studied in detail by 20,000 fps videos. By careful examination of the high speed video, we find that the bubble burst induced bead motion is accompanied by small timescale wave generation due to bubble collapse. Figure 3.2(a) shows four consecutive images taken at/after the burst of the bubble. With respect to the first image, at  $t = 50 \ \mu$ s, a wave pattern is generated around the bubble-bead system; at  $t = 100 \ \mu$ s, the bubble is gone and a propagating wave front is observed. At  $t = 150 \ \mu$ s, the wave pattern disappears, indicating the short life of the bubble burst event.



**Figure 3.2:** (a) Waves observed at the moment at/after the bubble bursts. (b) Numerically calculated normalized bubble radius R(t)/R(0) (dashed curves) and bubble pressure  $P_l(t)/P_*$  (solid curves) after bubble burst.

#### 3.1.2 Bubble Growth and Burst Model

The bubble burst and the generation of the wave pattern are the result of bubble shrinkage due to mass transport of  $O_2$  at the gas-liquid boundary. The bubble growth/shrinkage is governed by the Rayleigh-Plesset equation [53],

$$P_{b} = P_{\infty} + \frac{2\sigma}{R} + \frac{4\eta}{R}\dot{R} + \rho \left(R\ddot{R} + \frac{3}{2}\dot{R}^{2}\right), \qquad (3.1)$$

where  $P_{b}$ ,  $P_{*}$ , R,  $\sigma$ , and  $\rho$  are the pressure of gas inside the bubble, the pressure of the liquid at remote distances ( $\approx 101$  kPa, the atmospheric pressure), the radius of the bubble, the surface tension, and the mass density of water, respectively. Assuming that the gas inside the bubble follows the ideal gas equation,  $P_bV_b = n_bR_gT$ , where  $n_b$  is the mole number of gas molecules,  $R_g$  is the gas constant, and T is the temperature. At the moment of the burst, the O<sub>2</sub> flux flowing into the bubble supplied by the catalytic reaction is smaller than the flux leaking from the bubble to the liquid. At the boundary of the bubble, the net O<sub>2</sub>flux from the bubble into the water $\alpha$  is assumed to be a constant,

$$\dot{n}_b = -\alpha A_b \,, \tag{3.2}$$

where  $A_b = 4\pi R^2$  and  $V_b = 4\pi R^3/3$ . The fluid pressure at the bubble boundary,  $P_l = P_b - 2\sigma/R$ , determines how the bead would move. By solving Eqs. (3.1) and (3.2) numerically, the time dependent normalized R(t)/R(0) and  $P_l/P_*$  for  $\alpha = 10$ , 30 and 50 moles/(s·m<sup>2</sup>) (From the shrinking of the bubble, experimentally  $\alpha$  can be estimated as  $\alpha \approx 24$  moles/(s·m<sup>2</sup>)) are plotted in Fig. 3.2(b). For  $\alpha \ge 30$  moles/(s·m<sup>2</sup>), the bubble shrinks to zero in 50 µs .Such a shrinkage is accompanied with temporal oscillations of R and  $P_l$ . These oscillations could explain the observed wave pattern. When  $P_l/P_* < 1$ , a pressure depression region appears around the bubble, and liquid will flow inbound; when  $P_l/P_* > 1$ , the high  $P_l$  will push the liquid out of the bubble region. However, Fig. 3.2 (b) shows that within 50  $\mu$ s (time interval between two consecutive video frames), the  $P_l / P_z < 1$  region is greater than  $P_l / P_z > 1$  region, giving an effective depression. It indicates that the bead is pulled back towards the bubble location during the burst process.

The back-pull on the micromotor due the bubble burst produces negative displacement. Figure 3.3(a) shows the instantaneous velocity U(t) of the bead as a function of time t extracted from three burst events. The negative sign indicates that the velocity is against the net displacement. After the bubble burst, the initial speed of the bead can reach as high as 14 cm/s, which corresponds to a speed to body length ratio of 1,000. Such an initial speed imparts an effective impulse of  $I= 1.26 \times 10^{-11}$  Ns, or a pressure of 1.3 Torr on the bead, at the moment of bubble burst. Additionally, the Reynolds number jumps instantaneously to ~ 3, then falls to ~ 10<sup>-2</sup> within 0.1 ms.



**Figure 3.3:** Instantaneous speed U(t) of the micromotors as a function of time t: (a) after bubble burst and (b) during the bubble growth. The symbols are experimental data and the curves are the fittings. The insets show the free-body diagrams of the bead-bubble system for each case.

With the small Reynolds number, the motion of the bead is governed only by the drag force,  $F_{drag}$ , which results from the viscosity effect and potential wall effect due to proximity to the substrate stage [5],  $F = -F_{drag}$ , where

$$F_{drag} = 6\pi\eta R_m U \left( 1 + \frac{R_m}{\sqrt{\pi \upsilon t}} + \frac{9}{16} \frac{R_m}{\lambda} \left( \frac{\upsilon t}{3\lambda^2} \right) \right), \tag{3.3}$$

for a spherical bead of radius  $R_m$  and mass *m* moving with a velocity *U* at a vertical distance (from the center of the bead)  $\lambda$  to the wall, in a fluid with viscosity  $\eta$ , density  $\rho$ , and kinematic viscosity *v*. The velocity of the bead *v* can be expressed as,

$$U = U_0 e^{-k \left(At^{1/2} + t + Bt^2\right)},$$
(3.4)

where  $A = \frac{2R_m}{\sqrt{\pi v}}$ ,  $B = 3R_m v / 32\lambda^3$ , and  $k = 6\pi \eta R_m / m$ . By fitting the experimental data in Fig.

3.3(a) using Eq. (3.4), as shown in the dashed curves, one obtain  $\eta = 0.0011 \pm 0.0002 \text{ Ns/m}^2$  and  $\lambda = 40 \pm 3 \mu\text{m}$ , i.e., the viscosity is approximately the value of water, while  $\lambda$  is close to the radius of the maximum bubble (diameter ~  $73 \pm 2 \mu\text{m}$ ). This implies a possibility that the bubble is lifting the bead during the bubble growth, and the bead is moving horizontally on top and close to the observation substrate. After the large bubble bursts, small bubbles start to nucleate and grow on the catalytic surface again as shown in Fig. 3.1 (c), and the velocity of the bead instantaneously reaches a high positive value (~ 0.4 - 1.2 cm/s) as shown in Fig. 3.3 (b), and then decreases quickly within 10 ms. This behavior is closely associated with bubble growth. Figure 3.4 plots the measured radius *R*(*t*) of the big bubble and relative distance *S*(*t*) travelled by the bead versus time *t* for three separate cycles. Interestingly, the *S*-*t* relationship follows the pattern of *R*(*t*), which suggests that the movement of the bead is closely related to the advancing of the bubble boundary. According to Thorncroft et al [54], during the bubble growth, the *R*-*t* 



**Figure 3.4:** The plots of the bubble radius R(t) (open symbols), the accumulative bead travelling distance S(t) (solid symbols), and the accumulative bubble travelling distance  $S_b(t)$  (after bubble reattaching to the bead) (cross symbols) versus time *t*. The symbols are experimental data for different bubble growth cycles, and the dashed curves are the fitting results.

relation can be approximated by a power law,  $R = \gamma t^n$ , where *n* is the growth exponent and  $\gamma$  is the proportionality constant. If the rate of O<sub>2</sub> flow, *Q*, into the (major) bubble (at the expense of surrounding small bubbles *via* Ostwald ripening) is assumed to be a constant, then for the bubble volume, V = Qt. Thus, for a spherical bubble one should expect n = 0.33. Indeed, the big bubble on the catalyst surface follows above power law, with  $n = 0.36 \pm 0.01$  (see Fig. 3.4). The corresponding S - t curves also follow similar power law (Fig. 3.4). The driving mechanism for the bead during the bubble growth process is the result of two opposite forces,

$$F = F_{growth} - F_{drag}.$$
(3.5)

The growth force  $F_{growth}$  is due to bubble growth [55],  $F_{growth} = \pi \rho R^2 \left(\frac{3}{2}C_s \dot{R}^2 + R\ddot{R}\right)$ , where

 $C_s$  is an empirical constant that modifies the growth force, and the drag force,  $F_{drag} = 6\pi\eta R_m U$ , is

due to the motion of the bead as shown in the inset of Fig. 3.3(b). Considering the power law behavior of bubble growth, the velocity of the bead can be expressed as,

$$U = \left(\beta \int_{0}^{t} t^{4n-2} e^{kt} dt\right) e^{-kt}, \qquad (3.6)$$

where  $\beta = \gamma^2 \frac{\rho \pi}{m} \left[ \frac{3}{2} C_s(\gamma n)^2 + \gamma^2 n(n-1) \right]$ . By solving Eq. (3.6) numerically we can obtain the

fitting for bead velocity v(t) as shown in Fig. 3.3(b) with  $C_s = 900 \pm 140$ . The outliers shown in Fig. 3.3(b) are instances when random coalescing between bubbles occurs and when the bubble detaches and re-attaches to the bead (See Fig. 3.1(c) for t = 0.02 s). Equation (3.6) describes the bead motion very well for the bubble growth process. In the meantime, the bubble grows steadily and moves slowly with low Reynolds number (~ 10<sup>-7</sup>). Using Stokes law,  $F_{growth} = F_{drag}^b$ , and  $R = \gamma t^n$  with  $F_{drag}^b = 6\pi\eta Rv_b$ , we obtain the velocity of the bubble  $v_b = Et^{-1}$  with  $E = \frac{\gamma^3}{6v} \left(\frac{1}{6}C_s - \frac{2}{9}\right) = (9 \pm 3)\mu m$ . The bubble displacement is expressed as  $S_b = E \ln(t/t_0)$  with the bubble reattachment time  $t_0 \approx 0.04s$ . This equation can be used to fit the experimental data as shown in Fig. 3.4, and the best fit gives  $E \approx 6 \mu m$ , which is consistent with the above prediction.

# 3.1.3 Conclusion

In summary, we report the first reported bubble propulsion of spherical catalytic micromotors. We have observed new quasi-oscillatory translational motion dynamics of big Janus micromotors. The observed motional behavior is due to bubble growth and burst processes occurring during the catalytic reaction. The competition between these two processes creates a different and complicated driving mechanism for catalytic micromotors: the bubble growth

process imposes a growth force to move the micromotor forward while the burst process induces an instantaneous local pressure depression to pull the micromotor backward. The physical origins for this motion have been identified and the proposed models fit the experimental data very well. It is expected that these models could be used to describe other bubble propelled micro/nanomotors.

### **3.2 Bubble Nucleation**

We have demonstrated that Janus particles with a large enough diameter can be propelled by bubbles, but bubble propulsion for Janus particles of size less than 10  $\mu$ m does not occur readily. Bubble nucleation on spherical Janus nanomotors could reliably be observed only if their size is above certain critical value. This is because, for bubbles nucleation on a solid surface in an aqueous environment, the accumulated O<sub>2</sub> needs to reach a critical energy called the heterogeneous nucleation energy. This nucleation energy depends on the O<sub>2</sub> saturation concentration and the curvature of the surface. Bubbles require less energy to form on a flat solid surface than on a convex surface (referred to as positive curvature hence forth) and even less energy on a concave surface (referred to as negative curvature hence forth).

When H<sub>2</sub>O<sub>2</sub> molecules decompose on a Pt surface, O<sub>2</sub> bubble embryos are formed first. The embryos are formed only when the O<sub>2</sub> concentration in water reaches a saturation level and the accumulated O<sub>2</sub> has enough energy to transform into a new phase. The bubble embryo generation rate *J* is largely determined by the embryo formation energy  $\Delta G$ ,  $J = J_0 e^{-\frac{\Delta G}{k_B T}}$ , where  $J_0$  is the embryo generation rate when  $\Delta G = 0$ , *T* is the temperature, and  $k_B$  is the Boltzmann constant. Since *J* is exponentially decreasing with respect to the embryo formation energy  $\Delta G$ ,  $\Delta G$  dominates the bubble formation kinetics.

For heterogeneous nucleation, the formation energy  $\Delta G$  can be calculated according to Volmer's classical model [56]. Consider a small embryo forming on a flat surface. The energy required to produce an embryo of a new third phase is given by,

$$\Delta G = \Delta G_{\nu} V_{Total} + \sigma_{21} S_{21} + (\sigma_{13} - \sigma_{23}) S_{23}, \qquad (3.7)$$

where G is the nucleation free energy,  $\sigma_{ij}$  is the interfacial tension between the phases *i* and *j* and  $\Delta G_v$  is the Helmholtzfree energy difference per unit volume of the nucleated phase between supersaturated liquid at pressure *p* and bulk liquid at the equilibrium pressure above a flat surface of the condensed phase,  $S_{ij}$  is the area of the interface and. Assuming that the catalyst surface on which the nucleation takes place is hydrophobic, the embryo forms a spherical cap as shown in Fig. 3.5. The contact angle for the liquid is determined by Young's relation,

$$\cos\theta = \frac{\sigma_{23} - \sigma_{13}}{\sigma_{12}}.$$
(3.8)

The total volume of the embryo, with a critical radius  $r_c$  would be,

$$V_{Total} = \frac{1}{3} \pi r_c^3 g , \qquad (3.9)$$

where,

$$g = \left(2 - 3\cos\theta + \cos^3\theta\right),\tag{3.10}$$

The interfacial area Sij between phases i and j are,

$$S_{12} = 4\pi r_c^2 \left(\frac{\cos\theta - 1}{2}\right),$$
(3.11)

and

$$S_{23} = \pi \left( r_c \sin \theta \right)^2. \tag{3.12}$$

The nucleation energy for an embryo is given by,

$$\Delta G = V_{Total} \Delta G_{\nu} + S_{12} \sigma_{12} + S_{23} \sigma_{23}.$$
(3.13)



Figure 3.5: 3-D Rendering of a small bubble on a concave surface and its cross-section.

Putting eq. (3.8), and (3.12), in (3.13) one obtains,

$$\Delta G = \frac{4\pi\sigma_{12}^3}{3(\Delta G_{\nu})^2}g.$$
(3.14)

When  $\theta = 180$ , the nucleation becomes homogenous and the equation reduces to homogeneous

nucleation energy, 
$$\Delta G_{\text{hom}} = \frac{4\pi\sigma_{12}^3}{3(\Delta G_v)^2}$$
.

However, if the surfaces are not flat, the expression for  $\Delta G$  will be different. Fletcher [51] derived the nucleation energy for spherical convex surface,

$$\Delta G = \frac{16\pi\sigma_{12}^3}{3(\Delta G_v)^2} f_c, \qquad (3.15)$$

where  $f_c$  is known as the shape factor for convex surface and is given by,

$$f(m,x) = \frac{1}{2} \left\{ 1 + \left(\frac{1+mx}{g}\right)^3 + x^3 \left(2 - 3\left(\frac{x+m}{g}\right) + \left(\frac{x+m}{g}\right)^3\right) + 3mx^2 \left(\frac{x+m}{g} - 1\right) \right\},$$
(3.16)

here,  $m = \cos\theta$  and  $g = \sqrt{1 + x^2 + 2xm}$ . For a concave surface, a similar expression can be derived. Consider a bubble nucleating on a concave surface as shown in Fig. 3.5. It is similar to a spherical cap on top of a flat surface. However, there is an additional spherical cap which is part



Figure 3.6: (a) Cross-section of droplet displaying and (b) same cross-section displaying defined angles.

of the concave surface itself that we need to take into account. Consider the cross-section of Fig. 3.5 in Fig 3.6. Here we define the phases and the interfacial tensions accordingly as shown in the figure, i.e. 1: water, 2: bubble (vapor), 3: solid.

Considering the triangle ABC, since AB – radius of big circle, is perpendicular to  $\sigma_{23}$  and BC is perpendicular to  $\sigma_{21}$ ,  $\angle$  ABH =  $\pi$ - $\theta$  and,  $\angle$  ABC =  $\theta$ . To calculate the volume  $V_{total}$ , we need to calculate the volume of the segments, BEDB ( $V_1$ ) and BFDB ( $V_2$ ).

Let  $\angle CBD = \alpha_1$  and  $\angle ABD = \alpha_2$ , then the volume of spherical cap  $V_1$  and  $V_2$  is given by,

$$V_{1} = \frac{1}{3}\pi r^{3} \left( 2 - 3\sin\alpha_{1} + \sin^{3}\alpha_{1} \right), \qquad (3.17)$$

or, 
$$V_1 = \frac{1}{3}\pi r^3 \left(2 + 3\cos\psi - \cos^3\psi\right).$$
 (3.18)

and 
$$V_2 = \frac{1}{3}\pi R^3 \left(2 - 3\cos\phi + \cos^3\phi\right)$$
 (3.19)

So the volume of the embryo is,

$$V_{Total} = \frac{1}{3}\pi r^3 \left(2 + 3\cos\psi - \cos\psi^3\right) + \frac{1}{3}\pi R^3 \left(2 - 3\cos\phi + \cos\phi^3\right).$$
(3.20)

The interfacial areas covered by volume  $V_1$  and  $V_2$  are,

$$S_{21} = \int_{0}^{2\pi,\pi-\psi} r^{2} \sin\theta \,d\theta \,d\phi \,,$$
  

$$S_{21} = 2\pi r^{2} \left(1 - \cos\left(\pi - \psi\right)\right)$$
  

$$S_{21} = 2\pi r^{2} \left(1 + \cos\psi\right) \qquad (3.21)$$

and,

$$S_{23} = \int_0^{2\pi,\phi} r^2 \sin\theta \, d\theta \, d\Phi$$
$$S_{23} = 2\pi R^2 \left(1 - \cos\phi\right) \tag{3.22}$$

The free energy of the embryo, following eq. (3.13), is given by,

$$\Delta G = \Delta G_{\nu} \left[ \frac{1}{3} \pi r^{3} \left( 2 + 3\cos\psi - \cos\psi^{3} \right) + \frac{1}{3} \pi R^{3} \left( 2 - 3\cos\phi + \cos\phi^{3} \right) \right], \qquad (3.23)$$
$$+ \sigma_{21} \left[ 2\pi r^{2} \left( 1 + \cos\psi \right) \right] + \left( \sigma_{23} - \sigma_{13} \right) \left[ 2\pi R^{2} \left( 1 - \cos\phi \right) \right]$$

where,

$$\cos \psi = \left(\frac{R\cos\theta - r}{AC}\right) = \left(\frac{mR - r}{AC}\right),$$
$$\cos \phi = \frac{R - r\cos\theta}{AC} = \frac{R - mr}{AC},$$
$$AC = \sqrt{R^2 + r^2 - 2Rr\cos\theta} = r\sqrt{1 + x^2 - 2xm}$$

and  $r = -\frac{2\sigma_{21}}{\Delta G_v}$  is the critical radius for nucleation. Let  $\cos\theta = m$ ,  $g = \sqrt{1 + x^2 - 2xm}$ , and  $x = \frac{R}{r}$ ,

with  $\sigma_{23} - \sigma_{13} = \sigma_{21} \cos \theta$ , one obtains,

$$\Delta G = \frac{16}{3} \frac{\pi \sigma_{21}^3}{\Delta G_v^2} \frac{1}{2} \left\{ 1 - \left(\frac{1 - mx}{g}\right)^3 - x^3 \left(2 - 3\left(\frac{x - m}{g}\right) + \left(\frac{x - m}{g}\right)^3\right) + 3mx^2 \left(1 - \left(\frac{x - m}{g}\right)\right) \right\}.$$
 (3.24)

Thus, G for bubble on a concave surface is,

$$\Delta G = \frac{16}{3} \frac{\pi \sigma_{21}^3}{\Delta G_v^2} f_0(m, x), \qquad (3.25)$$



**Figure 3.7:** The plot of the shape factor  $f(x^{-1}, m)$  for free energy of bubble embryos, verses  $x^{-1}$  at m = 0.8.  $x^{-1} > 0$  represents convex surfaces, and  $x^{-1} < 0$  represents concave surfaces.

where, 
$$f_0(m,x) = \frac{1}{2} \left\{ 1 - \left(\frac{1-mx}{g}\right)^3 - x^3 \left(2 - 3\left(\frac{x-m}{g}\right) + \left(\frac{x-m}{g}\right)^3\right) + 3mx^2 \left(1 - \left(\frac{x-m}{g}\right)\right) \right\}.$$
 (3.26)

Note that the expression for nucleation energy on a concave surface eq. (3.26), is very similar to the one for convex surface eq. (3.16), with only a slightly difference in the shape factor. Plotting the nucleation energy for both concave surface (r < 0) and ending with convex surface (r > 0) is given in equation the Fig. 3.7. It plots f(m,x) versus  $x^{-1}$  at m = 0.8. Here, x is defined to be negative for a concave surface in order to make the curve continuous at x = 0. Note that, when f = 1, the nucleation energy on the surface is same as that for homogenous nucleation. As shown in Fig. 3.7, f increases quickly with  $x^{-1}$  when a curvature is positive while for negative curvature, f approaches to zero. Thus, it is possible that for the same radius, the bubble embryo generation rate for a concave surface is almost instantaneous while for a convex surface, the nucleation rate could approach to zero. Thus, a concave surface can easily generate bubbles for motor propulsion, i.e., concave micromotors would have a better performance.

#### **3.3 Concave Catalytic Nanoshell Motors**

### 3.3.1 Nanoshell Motor Fabrication

It is expected that if Pt is coated on the inner surface of a spherical shell, it can perform better. The nanoshell motors are fabricated using a combination of e-beam deposition and wet chemical etching. Figure 3.8 summarizes the fabrication process. First, silica beads are casted on the Ti coated Si substrate a method similar to that described in Section 2.2 except that silica bead suspensions were diluted in methanol with a volume ratio of 1:50 to ensure that the beads were far apart. Then, the bead-coated substrates were loaded into a custom built electron beam evaporation chamber. A Pt layer of 50 nm was first deposited at a vapor incident angle of 70°


**Figure 3.8:** Fabrication procedures of nanoshell motors. (a) Spread SiO<sub>2</sub> beads on Ti-coated Si substrate. (b) A layer of 50 nm Pt film was first deposited on the beads substrate at a deposition angle  $\theta = 70^{\circ}$ . The substrate was rotated at an azimuthally constant speed. (c) A layer of 400 nm Ag was deposited. The deposition conditions were the same as (b). (d) A 100 nm Au film was deposited at the same deposition condition. (e) Tri-metal layer coated beads were lifted off from the substrate by sonicating in a liquid media for 30 s. (f) The SiO<sub>2</sub> core was removed by 10% HF etching for 2 hours. The remaining was the nanoshell motors with the Pt surface inside.

and with a substrate azimuthal speed of 2 rpm as shown in Fig. 3.8 (b). Since the beads are separated in a large distance, the azimuthal rotation during the deposition can ensure a continuous coating on the side of the beads. The Pt was deposited at a rate of  $\sim 0.05$  nm s<sup>-1</sup>, monitored by a quartz crystal microbalance (QCM) facing directly toward the incident vapor. Then a layer of 400 nm Ag at a rate of  $\sim 0.2$  nm s<sup>-1</sup> and a layer of 100 nm Au at a rate of  $\sim 0.05$  nm s<sup>-1</sup> were deposited subsequently under the same substrate configuration and rotations as



**Figure 3.9:** Representative SEM images of nanoshell motors. (a) Before HF etching, the trimetal layer is coated on a 2  $\mu$ m SiO<sub>2</sub> bead excluding a small top area. (b) A nanoshell motor of a diameter  $D = 2 \mu$ m and an opening diameter (indicated by white arrow)  $D_0 \approx 0.8 \mu$ m. (c) A nanoshell motor with  $D = 5\mu$ m and  $D_0 \approx 2.7 \mu$ m. (d) Two shell motors close to each other. The upper one has  $D \approx 17.9 \mu$ m and  $D_0 \approx 11.4 \mu$ m, and the other one wit h $D \approx 20.2 \mu$ m and  $D_0 \approx 11.6 \mu$ m.

shown in Fig. 3.8 (c) and (d). After the deposition, the coated 2  $\mu$ m and 5  $\mu$ m beads were sonicated off from substrate into DI water (Fig. 3.8 (e)), then filtered by using a filter paper (3 ~ 4  $\mu$ m hole size for 2  $\mu$ m beads, 7  $\mu$ m hole size for 5  $\mu$ m beads). Then all the water suspended beads were emerged in 10% HF for 2 hours to remove SiO<sub>2</sub> core (Fig. 3.8 (f)). After etching, the suspended bead mixture was washed by DI water three times to remove HF. The method is similar to methods proposed by Whitesides group with slight modification [57]. Figure 3.9 shows some representative scanning electron microscope (SEM) images of different sized nanoshell motors. A silica bead of ~ 2  $\mu$ m diameter coated with metal layers (Au/Ag/Pt from



**Figure 3.10:** Snapshots of the motion of nanoshell motors in 5% H2O2 solution. (a) A nanoshell motor with  $D = 34 \mu m$ . The arrow indicates the direction of velocity. The motors moved in a straight line. (b) A nanoshell motor with  $D = 33 \mu m$  followed by an intact bubble. At t = 0.2 s, the nanoshell motor is pulled back due to the merging of two bubbles.

outside to inside) after physical vapor deposition is shown in Figure 3.9 (a). The inner most layer is a Pt catalyst layer. The middle layer is Ag, which acts a backbone to the structure. The outer layer is a thin Au layer, acting as a protection layer that prevents the direct contact of  $H_2O_2$  and Ag.

Figure 3.9 (b) shows a nanoshell with diameter  $D = 2 \ \mu m$  after HF etching. The shell opening has a diameter of  $D_o = 0.8 \ \mu m$ . The  $D = 5 \ \mu m$ nanoshell shown in Figure 3.9 (c) has an opening diameter of  $D_o = 2.7 \ \mu m$ . Two large nanoshell motors are shown in Figure 3.9 (d), with  $D = 17.9 \ \mu m$  and  $D_o = 11.4 \ \mu m$ ,  $D = 20.2 \ \mu m$  and  $D_o = 11.6 \ \mu m$ , respectively. From the shadowing growth mechanism point of view,  $D_o/D = \cos \theta = \cos 70^\circ = 0.342$ , where  $\theta$  is the deposit angle show in Fig. 3.9. The experimental  $D_o/D$  value obtained is between  $0.4 \sim 0.64$ . The mismatch between the predicted and experimental  $D_o/D$  could be due to the fact that the thickness of the metal tri-layer at the edge of the shell is extremely thin and delicate, and could have been removed during the wet HF etching process.

## 3.3.2 Motion Behavior and Bubble Growth

In 5% H<sub>2</sub>O<sub>2</sub> solution, spherical Janus motors with D = 2 and 5 µm move autonomously away from the Pt coated side without bubble generation. Bubbles begin to appear when the diameter of Janus motor D is greater than 10 µm. In this situation, the Janus motor moves away from the center of the bubble due to growth force exerted by the bubble as it grows on the catalytic surface. The motor is recoiled back when the bubble bursts. This is due to a local



Figure 3.11: The plot of the speed U of the nanoshell motors and Janus motors verses motor size D. The dashed lines represent the average speed for non-bubble and bubble driven motors,  $U_{non-bubble}$  and  $U_{bubble}$ , respectively.

pressure depression created by the sudden disappearance of the bubble. However, since the Pt surface coverage exceeds a hemisphere, multiple bubbles begin to grow and then eject/burst on the Pt surface simultaneously. On the other hand, all nanoshell motors are observed to be propelled by bubble ejection or burst. Nanoshell motors exhibit straight or circular motion. Figure 3.10 (a) shows the video frames of the motion of a nanoshell motor with  $D = 34 \,\mu\text{m}$ . Since the nucleation and early state of the bubble growth happens inside the shell, the bubble is visible only from the shell opening after t = 0.1 s on the bursting of a previous bubble. The bubble takes another 0.6 s to grow, and then bursts at about t = 0.7 s. The bubble and the motor could also exhibit complicated interactions. Figure 3.10 (b) shows one example for a nanoshell motor of  $D = 33 \,\mu\text{m}$ . When a bubble grows to a certain size, it detaches from the shell without bursting. This bubble stays in the vicinity of the shell when a new bubble starts to grow from the shell. Once the new bubble grows to a certain size, the previously ejected bubble could merge back with the new bubble on the shell.

By tracing the trajectories of the motors, one can obtain the average speeds of the motors. Figure 3.11 summarizes the speeds U of both the nanoshell motors and spherical Janus motors versus the motor diameter. For both structures, the speeds of bubble driven motors are significantly faster than those of non-bubble driven motors, and range between 20 - 300  $\mu$ m s<sup>-1</sup>. The speeds are comparable to those reported for microtube motors [12, 50]. The fastest speed record for catalytic microjets is ~1400  $\mu$ m s<sup>-1</sup> (~180 body length s<sup>-1</sup>) in 5% H<sub>2</sub>O<sub>2</sub> solution for microtube engines reported by Wang's group [12]. Under similar experiment conditions, nanoshell motors with  $D = 2 \mu$ m, can move as fast as 210  $\mu$ m s<sup>-1</sup> (105 body length s<sup>-1</sup>) and  $D = 5 \mu$ m ones, can move at 270  $\mu$ m s<sup>-1</sup> (54 body length s<sup>-1</sup>). Besides of microjets, the nanoshell motors could be an additional choice that suitable for applications where smaller sizes are critical.

#### 3.3.3 Bubble Propulsion Model

As in section 3.1 similar motion and force analysis was done starting with equation (3.3) and (3.4). The speed of bubble driven motors is closely related to the bubble burst frequency  $f_b$  and the maximum radius of the bubble  $R_{max}$ . The motor with higher  $f_b$  and larger  $R_{max}$  generally move faster. For nanoshell motors, their motion is driven by the bubble growth-burst cycle. During bubble growth, the motion of the motor is directed by the expansion of the bubble since the center of the bubble is stationary. When the bubble bursts, the motor will gain a sudden large displacement due to the instantaneous impulse. The force that is applied to the motor during bubble growth is,

$$F_{growth} = \pi \rho R_b^2 \left[ \frac{3}{2} C_s \left( \frac{dR_b}{dt} \right)^2 + R_b \frac{d^2 R_b}{dt^2} \right], \tag{3.27}$$

where  $\rho$  is the density of H<sub>2</sub>O<sub>2</sub> solution,  $R_b$  is the radius of the bubble, and  $C_s$  is a constant. The motion of the catalytic motors during bubble growth is the result of two competing forces,

$$\vec{F}_{net} = \vec{F}_{growth} + \vec{F}_{drag}, \qquad (3.28)$$

The drag force  $\vec{F}_{drag}$  is mainly due to the viscosity of the solution with the magnitude  $F_{drag} = 6\pi\eta RU$ , where  $\eta$ , R, U are the viscosity, the radius, and the speed of the motor, respectively. The force analysis suggests the displacement of motor  $\Delta x_1$  during bubble growth process is,

$$\Delta x_1 = \int_0^{T_0} \left[ \left( \int_0^t \frac{F_{growth}}{m} e^{\frac{6\pi\eta R}{m}t} dt \right) e^{-\frac{6\pi\eta R}{m}t} \right] dt , \qquad (3.29)$$

where *m* is the mass of the motor and  $T_0$  is the total time of a bubble growth. The integral above is solvable if we assume that the bubble growth follows a power law,  $R_b = \gamma t^{\frac{1}{3}}$  [54]. Given the initial and final conditions x(t = 0) = 0, U(t = 0) = 0,  $R_b(t = T_0) = R_{max}$ , the displacement during the growth period can be rewritten as,

$$\Delta x_1 = C_1 \int_0^{R_{\text{max}}^3} \left( y + R_{\text{max}}^3 \right)^{\frac{1}{3}} e^{-ky} dy, \qquad (3.30)$$

where  $C_1 = \frac{27\rho\pi}{\gamma^2 m} \left(\frac{1}{2}C_s - \frac{2}{3}\right)$  and  $k = \frac{6\pi\eta R}{m\gamma^3}$ . The displacement induced by bubble bursting  $\Delta x_2$ 

is small compare to  $\Delta x_1$  and is assumed to be a constant,

$$\Delta x_2 = C_2, \tag{3.31}$$

Thus, the total displacement  $\Delta x$  during a complete bubble growing/bursting cycle is,

$$\Delta x = C_1 \int_0^{R_{\text{max}}^3} \left( y + R_{\text{max}}^3 \right)^{\frac{1}{3}} e^{-ky} dy + C_2, \qquad (3.31)$$

Experimentally,  $\Delta x = UT_0 = U/f_b$ ; thus, the relation of  $U/f_b$  versus  $R_{max}$  should follow Eq. (3.31). Although  $C_1$ ,  $C_2$  and k vary among motors, it is still possible to estimate the trend of  $\Delta x$  empirically by solving Eq. (3.31) numerically. Figure 3.12 shows the  $U/f_b$  versus  $R_{max}$  plot and the solid curve is the estimated trend curve with parameter  $C_1 = 3 \times 10^{-4}$ ,  $C_2 = 9.28$  and k = 0.13. The experimental data follows the theoretical trend predict by Eq. (3.31). One important question for nanoshell motors is how the H<sub>2</sub>O<sub>2</sub> solution inside the shell sustains continuous generation of bubbles. The experimentally observed maximum bubble radius for a 2 µm, 5 µm and 33 µm nanoshell motor are  $R_{max} = 4$  µm, 8 µm and 17 µm, respectively. The maximum amounts of O<sub>2</sub> that could be produced by decomposing all of the H<sub>2</sub>O<sub>2</sub> solution inside the shell are  $3.49 \times 10^{-15}$  mol,  $5.45 \times 10^{-14}$  mol and  $1.57 \times 10^{-11}$  mol, respectively. Assuming that the O<sub>2</sub> inside the bubble is at  $P = 1.01 \times 10^5$  Pa (1 atm),  $T = 25^{\circ}$ C and follows the ideal gas law, then the amount of O<sub>2</sub> that



**Figure 3.12:** The plot of  $v/f_b$  verses maxima bubble size  $R_{max}$ . The solid curve is the fitting according to Eq. (10)

would be required to form a spherical bubble with  $R_{max} = 4 \ \mu m$ , 8  $\mu m$  and 17  $\mu m$  are  $1.05 \times 10^{-14}$  mol,  $8.38 \times 10^{-14}$  mol and  $8.04 \times 10^{-13}$  mol, respectively.

Thus, for 2  $\mu$ m and 5  $\mu$ m nanoshell motors, the amounts of H<sub>2</sub>O<sub>2</sub> inside the shells could not sustain the generation of a single bubble. This suggests that for the 2  $\mu$ m and 5  $\mu$ m nanoshell motors, the opening is not totally sealed by the bubble. However, for the 33  $\mu$ m nanoshell motor, the amount of H<sub>2</sub>O<sub>2</sub> inside the shell is sufficient to produce multiple bubble growth. On the other hand, if the opening is sealed by the bubble, the dynamics of bubble growth could depend on the remaining H<sub>2</sub>O<sub>2</sub> concentration within the shell. Catalytic decomposition of H<sub>2</sub>O<sub>2</sub> is a first order reaction, and the concentration of H<sub>2</sub>O<sub>2</sub> inside the shell is expected to obey

$$C_{H_2O_2} = C_0 e^{-Kt} , (3.32)$$

where  $C_0$  is the concentration of H<sub>2</sub>O<sub>2</sub> at t = 0, and K is the reaction rate constant. Assuming that the bubble is spherical with a radius  $R_b$  and the O<sub>2</sub> inside the bubble follows the ideal gas law,



**Figure 3.13:** Bubble radius  $R_b$  of nanoshell motors of different size verses time *t*. The solid curves are the fitting results using Eq. (13).

one has

$$R_b = R_0 \left( 1 - e^{-Kt} \right)^{\frac{1}{3}}, \tag{3.33}$$

where  $R_0 = \sqrt[3]{\frac{3R_gTVC_0}{4\pi P}}$  and V is the volume enclosed by the shell. In Figure 3.13 we plot the

measured bubble radius  $R_b(t)$  versus time t, where t = 0 is set at the moment when the previous bubble bursts. We note that Eq. (3.33) does not produce a good fit for the bubble growth data. Instead, the data can be fit well by the power law,

$$R_{b} = \gamma (t - t_{0})^{\frac{1}{3}}, \qquad (3.34)$$

as shown by the solid curves in Figure 3.13. Such a bubble growth dynamics is a result of the constant accumulation of O<sub>2</sub>, i.e. the flux of the O<sub>2</sub> toward the bubble is constant. This flux is generated by the surface catalytic reaction,  $J_{O_2} \propto A \cdot C_{H_2O_2}$  where A is the inner surface area of the shell. In order to keep  $J_{O_2}$  a constant,  $C_{H_2O_2}$  must also be a constant. However, according to



**Figure 3.14:** The bubble sealed and un-sealed nanoshell motors. Mass transport could occur through the gaps between the opening and the bubble for the un-sealed motors.

Eq. (3.32),  $C_{H_2O_2}$  will exponentially decay with time if the opening of the shell is sealed by a bubble. Therefore, the bubble cannot completely seal the shell as shown in Figure 3.14. The rough edges of the opening may facilitate the mass exchange, as transfer can take place within the gaps between the shell and bubble. Such a narrow opening will decrease the effective H<sub>2</sub>O<sub>2</sub> concentration inside the shell due to diffusion limited mechanism. For example, if one assumes that the reaction constant *K* of H<sub>2</sub>O<sub>2</sub> per unit area at a Pt surface is  $2.41 \times 10^{-5}$  m s<sup>-1</sup>, for the 2 um nanoshell motor shown Figure 3.13, the equilibrium  $C_{H_2O_2}$  inside the shell is estimated to be 1.8 wt. % which is less than 5 wt. % H<sub>2</sub>O<sub>2</sub> concentration outside the shell.

## **3.3.4 Conclusion**

In conclusion, we look into the nucleation process closely and study the effect of surface curvature of the catalyst on the nucleation energy. The theory predicts that the nucleation process readily occurs when the catalyst surface has a concave curvature. We test this theory by fabricating nanoshell micromotors in which the catalyst is placed on the inner walls of the shell. A unique fabrication method to make catalytic nanoshell motors is presented. The results show that nanoshell motors can generate bubbles easily at much smaller sizes than JCMs. The motion speed of the bubble propelled motors depends closely on the size and frequency of the bubble generated, and we have obtained an empirical relation that can fit the experimental data very well.

# **3.4 Conclusion**

Bubble propulsion is studied experimentally and theoretically for spherical catalytic motors: Janus catalytic motors and nanoshell motors. For Janus motors, we observe the bubble propelled motion for the first time for large motors. The motion of the motors is closely associated with bubble kinetics. Following this, nucleation on curved surfaces is studied from a theoretical point of view. The theory predicts that the bubble nucleation can occur more readily on a concave surface. This prediction is successfully tested on nanoshell motors in which the catalyst is coated on the inner walls. The motion of the motors is analyzed and found to be superior than Janus motors.

#### **CHAPTER 4**

# BUBBLE PROPULSION IN MICROJETS

We have mentioned the bubble propelled microjets a number times earlier, citing that they are the fastest manmade motors and have demonstrated a number of applications such as DNA sensing and detection [23], transport of cargo such as drugs [29-30], isolating nucleic acid targets [24]. However, the microjets, given their violent motions of bubble growth and collapse or expulsion, is one of the least efficient mechanisms [13]. Therefore, it is imperative to understand its manufacturing process, the geometry and how we can make the microjets as efficient as possible to maximize the motion to fuel consumption ratio. In this chapter, we propose a novel way to make microjets. In addition, in spite of the recent attention given to microjets, little is known regarding the detailed propulsion mechanisms of these microjets. Mei et al. have recently proposed a simple model, the body deformation model, which is based on the experimental observation that the average speed of a microjet is approximately equal to the product of the bubble radius and the bubble ejection frequency [58]. The model assumes that the system consisting of the microjet and the bubble undergoes a deformation from 'bubble inside the tube' to 'bubble detached from the tube'. Only the state of the deformation, in which the bubble starts to expel out of the microjet until its detachment from the microjet, contributes to the forward thrust of the microjet. This phenomenological model is sufficient to explain only the average speed of a microjet in certain cases. However, the detailed theoretical considerations of mass transport and its effect inside the microjet, along with the geometrical parameters on the motion of the microjets, have not been considered. The nucleation and growth of the bubble, along with how the bubbles eject from the microjet, have not been included in the model, which could be very important for bubble-governed dynamics. We already saw that these parameters

are important for the motion of bubble propelled spherical motors. Therefore, we studied the effects of these parameters on the motion of microjets as well in this chapter.

## 4.1 Microjets Fabricated by Graphene Oxide Nanosheets

Here we develop a simple inexpensive method in which multilayered heterostructures that contain graphene oxide (GO) nanosheets and exhibit spontaneous rolling behavior. The functions of the GO are to act as a support for the metallic multilayer and to provide an easily cleavable interface between the substrate and the vapor- deposited metal layers, which allows the heterostructures to detach from the surface and roll into freestanding scrolls. To our knowledge, this design strategy has not been applied to self- rolling nanostructured scrolls, despite the



**Figure 4.1:** Representative SEM images: (a) GO on the Si substrate before Ti/Pt coating, (b) GO on the Si substrate after Ti/Pt coating and (c) a typical GO/Ti/Pt scroll with 10 nm Ti and 10 nm Pt from a tilt view. Images (d) and (e) show typical GO/Ti/Pt scrolls with 10 nm Ti/10 nm Pt and 10 nm Ti/25 nm Pt.

advantages, which include the fact that it extends the range of material components in such structures and it is experimentally convenient (because it eliminates the need for an etching step, uses an aqueous dispersion of GO, and does not require epitaxially grown or lithographically defined starting materials). The microjets consists of GO, titanium, and platinum (GO/Ti/Pt). To fabricate this multilayed structure, we first drop-cast an aqueous dispersion of GO nanosheets on a silicon wafer and then used electron-beam evaporation to coat the GO with Ti (10 nm) followed by Pt (10 nm). Scanning electron microscopy (SEM) images before and after coating (Figure 4.1 (a) and (b)) show that there are no scrolled structures at these points, only wrinkles originating in the GO layer.

Upon sonication of the GO/Ti/Pt-coated wafer in water, the multilayer film fragments into multimicrometer-sized pieces that detach from the surface and spontaneously roll into full or partial scrolls (Figure 4.1 (b), and (c)). A size distribution analysis of more than 100 scrolls reveals that their diameters are typically  $1 - 2 \mu m$  (average diameter:  $1.4 \pm 0.4 \mu m$ ), and their lengths are  $10-20 \mu m$  (average length:  $15 \pm 7 \mu m$ ) (Figure 4.2). Furthermore, we have tuned the



**Figure 4.2:** (a) Diameter (*D*) and (b) length (*L*) distribution of 114 GO/Ti/Pt scrolls. The average diameter =  $1.4 \pm 0.4 \mu m$  and the average length =  $14.9 \pm 6.6 \mu m$ .



**Figure 4.3:** SEM images showing large areas with many scrolls for comparison. (a) Scrolls with 10 nm Ti and 10 nm Pt. (b) Scrolls with 10 nm Ti and 25 nm Pt.

diameters of the scrolls by varying the thickness of the platinum layer from 10 to 25 nm (Figures 4.3a and b). For example, Figure 4.1 (d) and (e) shows a SEM image of a typical scroll containing 10 nm Ti and 25 nm Pt. The average diameters of such scrolls are larger than those of scrolls with 10 nm Pt. In fact, the average scroll diameter (D) as a function of Pt thickness (t) plotted in Figure 4.4 (a) shows a monotonic increase of D with t. No obvious dependence of average scroll length (L) on t was observed. This is expected because the size distribution and



**Figure 4.4:** (a) Average scroll diameter *D* as a function of Pt thickness *t* and the best fit (red curve) using the stressed composite plate theory. (b) A plot of the scroll aspect ratio L/D versus the Pt thickness *t*.

shape of GO nanosheets in all experiments are statistically the same, and these parameters should determine the length of the scrolls. Thus, the calculated scroll aspect ratio (L/D) versus t shows a decreasing trend (Figure 4.4 (b)). The trends we observe in Fig.4.4 can be explained by applying Kirchhoff plate theory. The heterostructured GO/Ti/Pt film can be modeled as a composite plate undergoing cylindrical bending, where the three layers of GO, Ti, and Pt are perfectly bonded together and the residual stresses are considered as the dominant driving force of the rolling. The equilibrium condition of the nanosheet upon detachment from a substrate surface and rolling, [] states that  $\kappa = A\sigma_{Ti}^* + B\sigma_{Pt}^*$ , where  $\kappa$  is the film curvature upon bending, equal to the inverse of roll radius,  $\sigma_{Ti}^*$  and  $\sigma_{Pt}^*$  are the residual stresses in the Ti and Pt layers, and A and B are the constants determined by the Young's modulus and thickness of each layer [59]. For our multilayer structures, the Ti thickness is fixed at 10 nm, and the Pt thickness varies from 10 to 25 nm. The Young' s moduli (E) and Poisson ratios (v) for Pt, Ti, and GO are given by  $E_{Pt}$ =140 GPa and  $v_{\text{Pt}}$  = 0.38;  $E_{\text{Ti}}$  = 90 GPa and  $v_{\text{Ti}}$  = 0.32; and  $E_{\text{GO}}$  = 208 GPa, and  $v_{\text{GO}}$  = 0.16. The thickness of the GO layer and the residual stresses of Ti and Pt are the fitting parameters in the model. In order to fit the experimental data in Figure 4.4 (a), we find the best-fit curve using a total GO thickness of 1.6 nm with  $\sigma_{Ti}^* = 3.6$  GPa and  $\sigma_{Pt}^* = 6.9$  GPa. Note that the residual stresses in the Ti and Pt layers are different by a factor of 2, but the corresponding residual strains are approximately the same, 0.027 and 0.030, respectively. Here, we assume that the residual stress in each layer is homogeneous. The calculated residual stresses are reasonable and comparable to previously reported values [60]. In addition, this model allows us to estimate the thickness of GO incorporated in the scrolls. The atomic force microscopy measurements show that the thickness of individual GO nanosheets is approximately 0.8 nm; thus, the GO is incorporated into each scroll as a bilayer, on average. Such GO bilayers in the scrolls relate to the interaction between



**Figure 4.5:** XRD data collected from graphite flakes (starting materialfor GO), exfoliated GO nanosheets on Si, GO/Ti/Pt layers on Si, and annealed (120 °C) GO nanosheets on Si.

GO and the metal coatings. In fact, our further characterizations using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy all indicate that the nature of the GO changes after metal deposition. For example, Figure 4.5 shows the changing XRD patterns collected along the fabrication process, from (1) graphite starting material to (2) asprepared GO nanosheets to (3) GO/Ti/Pt multilayers (not yet scrolled). The XRD pattern of the GO nanosheets exhibits a characteristic (002) peak at 12.5°(black curve), which can be correlated to an interlayer spacing of 0.807 nm. For comparison, the original graphite flakes exhibit a sharp peak at 31°(green curve), corresponding to an interlayer spacing of 0.335 nm. This change in basal plane d -spacing is typical for graphite versus GO [61]. However, after metal deposition, the (002) peak of GO clearly shifts to 15°, consistent with GO reduction. In this sample, the Pt (111) peak at 46°(red curve) also is visible. To corroborate GO reduction, GO nanosheets on Si were heated to 120 ° C for 24 h. This annealing process resulted in a diffraction

pattern typically exhibited by partially reduced GO, characterized by broad peaks shifted to higher angles of  $2\theta$ , 17.5°, and 26°(blue curve in Figure 4.5) [62]. [] Additional data from XPS and Raman spectroscopy further support a GO reduction mechanism. To summarize, XPS shows a shift in relative intensity from C=O to C-C bonding after metal deposition, consistent with the observation by Ajavan and co-workers [63], and Raman spectroscopy indicates enhanced localized  $sp^3$  defects, which is characteristic of reduction. We conclude that metal deposition has a mild reducing effect on the GO nanosheets, causing the loss of predominantly carbonylcontaining functional groups and dissociation of water molecules [62]. [] Thus, the GO in GO/Ti/Pt appears to be intermediate in chemical and crystallographic character between asprepared GO and fully reduced GO. Such a reduction effect should have two consequences; first, it suggests that the Ti layer interacts strongly with the adjacent GO layer, which leads to strong adhesion between the Ti and contacted GO monolayer; second, the reduction is a local effect confined to only the Ti-GO interface and immediately adjacent GO layers. Thus, the Ti acts as "glue" to attach approximately two GO monolayers and the Pt layer tightly within this layered structure.

In the GO/Ti/Pt structure, each material layer contributes to the overall scrolling behavior. The highly anisotropic dimensions of GO nanosheets ( $nm \times \mu m \times \mu m$ ) cause them to assemble in parallel stacked arrangements within concentrated dispersions or dried forms [64]. The titanium layer enhances the adhesion between GO and Pt, and it induces GO reduction within approximately the first two contacted monolayers. These effects make the bilayer GO/Ti/Pt a tightly bonded three-component system. The residual stresses from the Ti and Pt layers cause this heterostructure to curl due to the relatively weak van der Waals interactions between GO nanosheet layers, which then allows the facile separation of the heterostructure from



**Figure 4.6:** (a) A series of static frames extracted from the video of a graphene-oxide/Ti/Pt scroll in motion. (b) Top view of the trajectory of this scroll in X-Y plane. (d) The plot of the distance in dependence of time calculated from 3(b) and the linear fitting result.

the substrate and further curling into scrolls. We emphasize that the detachment mechanism in this system is a physical delamination process, where the cleavage plane is within the top few nanometers of a much thicker GO film. Through this process, approximately two monolayers of partially reduced GO are incorporated on the outer surface of the scroll while excess GO remains on the substrate. The additional residual stress introduced by the Pt layer can tune the scroll diameter, and this material also can provide catalytic activity. This stress model predicts that the Pt layer is wrapped inside the scroll, and thus, such a scroll can act as a microjet motor. We put the scrolls in aqueous  $H_2O_2$ . We observed the  $O_2$  bubbles generated and ejected from one of the ends of the microjets, confirming the prediction. Figure 4.6 (a) shows representative movie frames extracted from the video using a 50x magnification objective lens. An analysis of the trajectory of this microjet in the horizontal plane reveals circular/spiral type motion (Figure 4.6

(b)). By examining the total traveling distance  $S \left( = \sum_{i=2}^{n} \sqrt{\left(x_i - x_{i-1}\right)^2 + \left(y_i - y_{i-1}\right)^2} \right)$  versus time, as

shown in Figure 4.6 (c), we further show that the jelly roll moves at a nearly constant speed (*U*) of 138  $\mu$ m s<sup>-1</sup>, which is approximately twelve body-lengths s<sup>-1</sup>. This speed is comparable to flagellated bacteria, which are some of the fastest organisms on Earth [65]. [] In fact, even greater speeds (up to 200 to 350 body-lengths s<sup>-1</sup>) have been reported for microjets in previous studies.

#### 4.2 Mass Transport in Microjets

Microjets are cylindrical or conical in shape. The motion of microjets is a direct consequence of bubble growth and bubble burst/ejection at one end of the microjet, as the microjet is pushed away from the bubble burst/ejection site. Bubble generation results from the catalytic decomposition of  $H_2O_2$  into  $O_2$  along the inner wall of the microjet, which then diffuses



**Figure 4.7:** The geometry of the cylindrical microjet, an attached bubble and definitions of related geometric parameters. Horizontal forces acting on the microjet and the bubble during the bubble growth are also illustrated.

to a bubble nucleation center at one end of the microjet. Due to the geometric confinement of the microjet, the flux of H<sub>2</sub>O<sub>2</sub> into the microjet and mass transport of O<sub>2</sub> out of the microjet are restricted, and are only possible from the two open ends of the microjet. H<sub>2</sub>O<sub>2</sub>/O<sub>2</sub> is transported in/out of the microjet by means of diffusion. Thus, the mass transport of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> depends strongly on the physical dimension of the microjet. When immersed in an aqueous solution of H<sub>2</sub>O<sub>2</sub>, both ends of the microjet are open for H<sub>2</sub>O<sub>2</sub> intake immediately before the reaction starts to happen. Assuming that the diffusion of H<sub>2</sub>O<sub>2</sub> in and O<sub>2</sub> out of the microjet follows Fick's first law [66][],  $J_p = -D_p dC_p / dx$ , where  $J_p$  is the flux (number of moles of matter passing through a unit area in unit time),  $D_p$  is the diffusion constant,  $C_p$  is the concentration (number of moles per unit volume), and subscript 'p' denotes species, H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>. Consider a cylindrical microjet of radius R and length L as shown in Fig. 4.7, which has a cross-section of area  $A = \pi R^2$  and perimeter  $B = 2\pi R$ . At the inner Pt-coated surface of the microjet, reaction  $2H_2O_2 \rightarrow 2H_2O+O_2$  occurs, consuming H<sub>2</sub>O<sub>2</sub> while releasing O<sub>2</sub>. Considering the processes, Fick's second law (i.e., the law of mass conservation) requires

$$\frac{\partial C_{H_2O_2}}{\partial t} = D_{H_2O_2} \frac{\partial^2 C_{H_2O_2}}{\partial x^2} - \frac{BK}{A} C_{H_2O_2}, \qquad (4.1)$$

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2} \frac{\partial^2 C_{O_2}}{\partial x^2} + \frac{BK}{2A} C_{H_2O_2}, \qquad (4.2)$$

Where *t* is the time, and *K* is the reaction rate constant of  $H_2O_2$  per unit area at a Pt surface. It is assumed that the reaction rate is proportional to local  $H_2O_2$  concentration. We do not consider the effect of  $H_2O$  generated through the reaction for two reasons. First, we are using the waterbased solvent, which means the entire reaction takes place in water. The  $H_2O_2$  concentrations used in the experiments are usually small; particularly in our experiments, we use 5%  $H_2O_2$ . Compared to the solvent, the amount of water generated through the catalytic reaction is almost



**Figure 4.8**: Normalized  $C_{H_2O_2}$  and  $C_{O_2}$  by  $C_{H_2O_2}^{\infty}$  versus normalized location x/L inside the microjet for different radii *R* at fixed  $L = 60 \ \mu m$ .

negligible and will not affect the local concentration of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>. Second, the small amount of water generated in the reaction may cause convection, but this effect should be negligible compared to the bubble driven hydrodynamic flow. Considering that if the reaction is fast, the concentration distribution inside the microjet will rapidly approach a steady state, i.e.,  $\frac{\partial C_p}{\partial t} = 0$ .

Thus, Eq. (4.1) and Eq. (4.2) can be simplified into

$$D_{C_{H_2O_2}} \frac{\partial^2 C_{C_{H_2O_2}}}{\partial x^2} - \frac{BK}{A} C_{C_{H_2O_2}} = 0, \qquad (4.3)$$

$$D_{O_2} \frac{\partial^2 C_{O_2}}{\partial x^2} + \frac{BK}{2A} C_{H_2 O_2} = 0.$$
(4.4)

According to most of our experimental observations, we can assume that there is no bubble at one end of the microjet, say, the left end (x = -L/2), while a bubble grows at the other, right end (x = L/2), as shown in Fig. 4.7. Thus, we have the following boundary conditions,

$$C_{H_2O_2}\Big|_{x=-L/2} = C_{H_2O_2}^{\infty}, \frac{\partial C_{H_2O_2}}{\partial x}\Big|_{x=+L/2} = 0, \text{ and } C_{O_2}\Big|_{x=\pm L/2} = 0$$

Here we assume that any  $O_2$  produced is expelled into gaseous phase at the right end of the microjet, which contributes to the growth of the bubble. The bubble seals the right end of the microjet. The concentrations of  $O_2$  and  $H_2O_2$  at the microjet ends are those of the open environments, except  $H_2O_2$  at the bubble-sealed end. Solving Eqs. (4.3) and (4.4) along with the boundary conditions, one has

$$C_{H_2O_2} = \frac{C_{H_2O_2}^{\infty}}{\cosh\left(\beta L\right)} \cosh\left[\beta\left(x - \frac{L}{2}\right)\right],$$

$$(4.5)$$

$$D_{H_2O_2}C_{H_2O_2}^{\infty}\left(1\left(1 + \frac{1}{2}\right)\right) = 1 + \frac{1}{2} \left(1 + \frac{L}{2}\right)\right) = 0$$

$$C_{O_2} = \frac{D_{H_2O_2}C_{H_2O_2}^{\infty}}{2D_{O_2}} \left( \frac{1}{L} \left( \frac{1}{\cosh(\beta L)} - 1 \right) x + \frac{1}{2\cosh(\beta L)} + \frac{1}{2} - \frac{\cosh(\beta L - \frac{1}{2})}{\cosh(\beta L)} \right), (4.6)$$

where  $\beta = \sqrt{\frac{2K}{D_{H_2O_2}R}}$ . Figure 4.8 shows a few representative plots of normalized  $C_{H_2O_2}$  and  $C_{O_2}$ 

by  $C_{H_2O_2}^{\infty}$  along the microjetaxis (*x/L*) for various microjet opening radii *R* with a fixed microjet length  $L = 60 \ \mu\text{m}$ . Here, we use  $K = 6.83 \times 10^{-7} \ m/s$  (derived from Paxton et al. [6]),  $D_{H_2O_2} = 1.43 \times 10^{-9} \ \text{m}^2/\text{s}$ , and  $D_{O_2} = 2.06 \times 10^{-9} \ \text{m}^2/\text{s}$  [67]. [] The concentration of  $H_2O_2$ decreases monotonically with *x*, i.e., from the open end to the bubble end. With the increase of *R*, the overall  $C_{H_2O_2}$  value increases, which is the result of the decreasing effective reaction rate constant *BK/A* scaled inversely with *R* in Eq. (4.1). In contrast,  $C_{O_2}$  exhibits a maximum value near the center and hence the gradient for release of  $O_2$  out of the microjet. Here we assume that no bubbles will nucleate in the center of the microjet. The position of the  $O_2$  concentration maximum is given by,

$$x_{\max} = \frac{1}{\beta} \sinh^{-1} \left( \frac{1}{\beta L} \left( 1 - \cosh(\beta L) \right) \right) + \frac{L}{2}.$$
(4.7)

Figure 4.9 shows variations of normalized  $C_{H_2O_2}$  and  $C_{O_2}$  with *x/L* for various microjet lengths with fixed  $R = 6 \ \mu m$ . It shows that  $C_{H_2O_2}$  decreases more rapidly along the microjet as the microjet gets longer. This could be due to the fact that while the supply of H<sub>2</sub>O<sub>2</sub> is restricted by the microjet opening, there is more Pt available for decomposition of H<sub>2</sub>O<sub>2</sub> inside the tube. This results in greater consumption of H<sub>2</sub>O<sub>2</sub> and generation of O<sub>2</sub>. As the length of microjet increases, the maximum O<sub>2</sub> concentration becomes larger. This directly supports the fact that more H<sub>2</sub>O<sub>2</sub> is consumed for longer microjets resulting in greater O<sub>2</sub> production.



**Figure 4.9:** Normalized  $C_{H_2O_2}$  and  $C_{O_2}$  by  $C_{H_2O_2}^{\infty}$  versus normalized location x/L inside the microjet for different microjet lengths *L* at  $R = 6 \mu m$ .

#### 4.3 Bubble Growth at the End of the Microjet

The O<sub>2</sub> produced in the microjet accumulates and moves toward the right end. It is expelled into the bubble, as shown in Fig. 4.7. The oxygen generation, i.e., the flux of O<sub>2</sub> going into the bubble, can be obtained using Fick's first law,  $J_{o_2} = -D_{o_2} \frac{dC_{o_2}}{dx}$ ,

$$J_{O_2}\Big|_{x=L/2} = -\frac{D_{H_2O_2}C^{\infty}_{H_2O_2}}{2L} \left(\frac{1}{\cosh(\beta L)} - 1\right).$$
(4.8)

The total mass of O<sub>2</sub> released at the end of the microjet, the bubble growth rate  $G_{O_2}$ , can be written as  $G_{O_2} = J_{O_2}AM_{O_2}$ , where  $M_{O_2}$  is the molar mass of O<sub>2</sub>. From a good number of bubble growth studies, we know that the bubble volume grows linearly with time,  $V_b = \frac{4\pi}{3}\gamma^3 t$  so that the bubble radius  $R_b$  follows a power law with respect to the growth time t,  $R_b = \gamma t^{1/3}$  [54]. Since

 $G_{O_2}$  is the amount of oxygen blown into bubbles per unit time, one has,  $\gamma = \left(\frac{3G_{O_2}}{4\pi\rho_{O_2}}\right)^{1/3}$ , where

 $ho_{O_2}$  is the mass density of oxygen, thus,

$$G_{O_2} = -\frac{D_{H_2O_2}C^{\infty}_{H_2O_2}\pi R^2 M_{O_2}}{2L} \left(\frac{1}{\cosh(\beta L)} - 1\right),$$
(4.9)

$$\gamma = \left[ -\frac{3D_{H_2O_2}C_{H_2O_2}^{\infty}R^2M_{O_2}}{8\rho_{O_2}L} \left( \frac{1}{\cosh(\beta L)} - 1 \right) \right]^{1/3}.$$
(4.10)

Figure 4.10 shows  $J_{O_2}$  and  $G_{O_2}$  as a function of microjet length *L* for three different values of *R*.  $J_{O_2}$  is always greater for smaller openings at any fixed length. However,  $G_{O_2}$  is always smaller for smaller openings. It is clear that the openings of the microjet play an important role in bubble



Figure 4.10: Predicted  $J_{O_2}$  and  $G_{O_2}$  versus microjet length L for different microjet radii R.

growth. Figure 4.10 shows that for a microjet with  $R = 2 \ \mu m$ , there is a value of *L* for which  $J_{O_2}$  reaches a maximum. From Eq. (4.8), one can find the condition for this  $J_{O_2}$  maximum,

$$L = 1.506 \sqrt{\frac{D_{H_2O_2}}{2K}} R^{1/2} \,. \tag{4.11}$$

For the specific K values observed in Paxton et al [6], we have,

 $L = 4.87 \times 10^{-2} R^{1/2}$ . This gives a criterion for optimizing microjet design for maximizing the O<sub>2</sub> generation and could potentially maximize the speed of microjets.  $G_{O_2}$  is more relevant to the growth of large bubbles, while  $J_{O_2}$  is critical for bubble nucleation and early stage growth. Figure 4.8 shows that microjets with smaller openings have a higher concentration of O<sub>2</sub> at any point in the microjet than microjets of the same length but with bigger openings; this translates directly into flux,  $J_{O_2}$ . However, since the overall Pt area available for reaction is greater in microjets with larger openings, the total oxygen produced per unit time is greater, which directly translates into larger  $G_{O_2}$ . The amount of oxygen expelled from the microjet,  $G_{O_2}$ , can be used

to calculate the frequency f for bubble ejection or burst given the maximum radius of the bubble  $R_B$ ,

$$f = \frac{3G_{O_2}}{4\rho_{O_2}\pi R_B^3}.$$
(4.12)

## 4.4 Bubble Growth Induced Motion

During the bubble growth, there are different forces exerted on the microjet which could make the microjet move as discussed in Chapters 3. In particular, the bubble growth will exert a growth force on the object to which the bubble is attached, and this force pushes the object forward as shown in Fig. 4.7 (here we have neglected all the vertical forces since all observed motion is horizontal). The growth force, which arises from the formation and growth of bubble surface against the fluid environment, is the only driving force on the microjet. While moving in a liquid environment, a microjet also experiences a drag force. The net force on the microjet is given by

$$F_{net} = F_{growth} - F_{drag}, \qquad (4.13)$$

where,  $F_{growth} = \rho_w \pi R_b^2 \left( \frac{3}{2} C_s \dot{R}_b^2 + R_b \ddot{R}_b \right)$ , with  $\rho_w$  the mass density of water and  $C_s$  an empirical

constant, and the drag force,  $F_{drag} = \frac{2\pi\eta LU}{\ln\left(\frac{L}{R}\right) - 0.72}$  for a tubular micro-object. The above drag

force formula was originally derived for a solid cylinder of length L and radius R. [] We numerically verified its applicability to a thin-walled tube as well by using a boundary element method. Since  $R_b = \gamma t^{1/3}$ , the instantaneous speed U of the microjet during bubble growth can be expressed as,

$$U = \left(\beta \int_{0}^{t} t'^{-2/3} e^{kt'} dt'\right) e^{-kt}, \qquad (4.14)$$

where  $\beta = \gamma^4 \frac{\rho \pi}{m} \left[ \frac{3}{2} C_s n^2 + n(n-1) \right], \ k = \frac{2\pi \eta L U}{m \left[ \ln \left( \frac{L}{R} \right) - 0.72 \right]}, \ \text{and} \ m \text{ being the mass of the microjet.}$ 

The average speed of the microjet during the bubble growth can be expressed as,

$$U_{avg} = f \int_{0}^{1/f} \left( \beta \int_{0}^{t} t'^{-2/3} e^{kt'} dt' \right) e^{-kt} dt .$$
(4.15)

Equation (4.15) can be solved numerically.

# 4.5 Experiments and confirmation

We use the microjets described in Section 4.1. The length *L* and mean opening radius *R* of the microjet are 30  $\mu$ m and 2.5  $\mu$ m, respectively. Most of the microjets studied in these experiments have similar dimensions, with *L* varying from 15  $\mu$ m to 40  $\mu$ m and *R* varying from 1.5  $\mu$ m to 3  $\mu$ m. In order to study the motion behavior, 5  $\mu$ L of an aqueous dispersion containing the fabricated microjets was pipetted onto a clean Si substrate, followed by the introduction of 5  $\mu$ L of 10% H<sub>2</sub>O<sub>2</sub> to activate the motion. After a steady reaction rate was reached and observed (less than 1 min), pictures and videos of microjet motion were captured and analyzed according to the protocol of Section 4.1. The location of an observed microjet was marked using a copper mesh by recording its relative position to the mesh after the liquid had dried. This microjet was then observed by SEM and the geometric parameters were measured. Using this process, the motion of a particular motor could be directly linked to its morphological parameters. We observe that most of the microjets exhibit circular motion with bubbles coming from only one particular end of the microjet in the high speed and high resolution videos. Most of the microjet motions result from bubble burst, and only few are due to bubble ejection. We can directly obtain



Figure 4.11: Representative 2D trajectories of five different GO microjets.

the following information from the videos: the length *L* and radius *R* of the microjet, the bubble ejection or burst events, the dynamic change of the radius  $R_b(t)$  of the bubble, and coordinates x(t), y(t) of the microjet. From these measurements we can determine the motion trajectory, the instantaneous speed *U*, average speed  $U_{avg}$  of the microjet, the maximum bubble size  $R_B$ , the flux of O<sub>2</sub> at the end of the microjet  $J_{O_2}$ , oxygen generation rate  $G_{O_2}$ , the bubble ejection/burst frequency *f*, and the prefactor for bubble growth  $\gamma$ . All of the experimentally derived parameters are summarized in Table 1.

The average speeds of the microjets are in the range of 100 µm/s to 1000 µm/s. However, the instantaneous speed of the microjet is not constant due to bubble growth and burst/ejection. The instantaneous speed is calculated using,  $U_{inst} = \sqrt{(x_{i+1} - x_i)^2 + (y_{i+1} - y_i)^2} / \Delta t$  where  $\Delta t$  is the time interval between each adjacent frame. Fig. 4.12 (b) shows plots of the instantaneous speed versus time for three of the microjets. The plot exhibits a pattern of low speed and high speed jumps. The black filled symbols represent the microjet speed during bubble growth, while the



**Figure 4.12**: (a) Representative plots of accumulated distance *s* travelled versus time *t* by three different microjets. The linear fitting (red line) represents a constant average speed; (b) instantaneous speed v for three different microjets with gray circles representing bubble burst/ejection events.

grey open symbol represent speed right after the burst or ejection events. The high speed jumps that are marked by circles are due to the bubble ejection/burst events. The motional behaviors depicted in Fig. 4.12 (b) are discretized since the instantaneous speeds are obtained from frame to frame and we are limited by the spatial resolution of the CCD. For example, at 100  $\mu$ s temporal resolutions the movement of the microjet may not be discernible in the given spatial resolution in certain subsequent frames; hence, the instantaneous speeds are calculated as zero for these instances. From this plot, and the observation of bubble ejection/burst, we can determine the bubble ejection/burst frequency *f*, which is summarized in Table 4.1. Using the high speed CCD camera to capture both bubble growth radius *R*<sub>b</sub> and the microjet displacement we can verify whether the assumption in the model proposed by Li et al. is valid [58]. According to the model proposed by Li et al., the center of the bubble is stationary during bubble growth, so that the motion of the microjet is caused by the expansion of the bubble.

Therefore, the microjet displacement should be same as the radius  $R_b$  of the bubble. Figure 4.13 (a) plots the bubble radius  $R_b$  as function of time *t* for 5 cycles of bubble growthburst/ejection for one of the GO microjets along with the accumulated microjet moving distance *s* during the bubble growth. Clearly, the microjet moving distance s is significantly smaller than the bubble radius  $R_b$  at any given time. This is inconsistent with the assumption by Li et al. In addition, Eq. (4.15) shows that the relation between frequency *f* and average speed  $U_{avg}$  is not as simple and linear as depicted in Ref. [58]. Our experimentally observed  $U_{avg}$  versus  $R_B \times f$ relationship is only partially consistent with the model proposed by Li et al. In Fig. 4.13 (b), we compare the predicted and observed average speed in Ref. 23 with the average speed versus the product  $R_B \times f$ , observed in our experiments. We see that the average speed observed in our experiments do not match well with the theory predicted in Ref. [58].

In fact, from the model proposed in Section 2, all the parameters associated with microjet motion are related to  $G_{O_2}$ , i.e., the prefactor  $\gamma$  for the bubble growth. This  $\gamma$  can be extracted experimentally and compared to theoretical prediction. From Fig. 4.13, we find that  $R_b$ -t follows the relation,  $R_b = \gamma t^n$ , and according to Eq. (4.10), the parameter  $\gamma$  is directly related to the shape of the microjet and the reaction rate, K,

$$K = \frac{D_{H_2O_2}R}{2L^2} \left( \cosh^{-1} \left( \frac{3D_{H_2O_2}C_{H_2O_2}^{\infty}R^2M_{O_2}}{3D_{H_2O_2}C_{H_2O_2}^{\infty}R^2M_{O_2} - 8\gamma^3\rho_{O_2}L} \right) \right)^2.$$
(4.16)

By fitting the bubble growth curves shown in Fig.4.13. and using Eq. (4.16) we can estimate the reaction constant *K*. Table 1 summarizes the  $\gamma$  obtained by fitting the *K* values obtained from the experimental data along with the physical dimensions of each microjet for which the *K* was calculated. All the *K* values we obtained are in the order of 10<sup>-5</sup> m/s. Experimentally, Paxton et al. have determined *K* to be  $6.83 \times 10^{-7}$  m/s [6] while Li et al. obtained *K* to be  $8.4 \times 10^{-4}$  m/s [68]. Our *K* values are within the range of these two values, and can be considered as reasonable values. In addition, one can also measure the O<sub>2</sub> generation rate  $G_{exp}$  using  $G_{exp} = f \rho_{O_2} V_b$ , where

Mi cro jet	Lengt h <i>L</i> (um) (± 0.5 um)	Radius <i>R</i> (um) (± 0.25 um)	Maximu m bubble radius $R_B$ (um) ( $\pm 0.25$ um)	Bubble frequen $cy f(/s)$	Bubble growth prefact ory(m/s <sup>1/3</sup> )	Growth rate $G_{exp}$ = $\rho f V_b$ (kg/s)	Experime ntal reaction rate <i>K</i> (m/s)	Avera ge microj et speed $U_{avg}$ ( $\mu$ m/s)	Bubble ejection /burst mode
1	23.4	2.8	2.0	580 ± 2	$2.0 \times 10^{-5}$	$2.7 \times 10^{-14}$	3.06 × 10 <sup>-5</sup>	580	Burst
2	15.5	1.8	2.5	$300 \pm 5$	1.9 × 10 <sup>-5</sup>	$2.8 \times 10^{-14}$	5.41 × 10 <sup>-5</sup>	590	Burst
3	17	1.8	2.3	$310 \pm 3$	2.1 × 10 <sup>-5</sup>	$2.1 \times 10^{-14}$	1.80 × 10 <sup>-5</sup>	510	Burst
4	16	1.8	2.5	308 ± 1	1.7 × 10 <sup>-5</sup>	$2.9 \times 10^{-14}$	4.41 × 10 <sup>-5</sup>	960	Burst
5	25.8	2.5	2	$380 \pm 4$	1.7 × 10 <sup>-5</sup>	$1.8 \times 10^{-14}$	1.65 × 10 <sup>-5</sup>	470	Burst
6	21.6	2.3	2	206 ± 5	1.2 × 10 <sup>-5</sup>	9.8 × 10 <sup>-</sup>	1.04 × 10 <sup>-5</sup>	360	Burst
7	23	2.5	2	569 ± 5	1.7 × 10 <sup>-5</sup>	$2.7 \times 10^{-14}$	1.85 × 10 <sup>-5</sup>	580	Burst
8	24	2.9	2	740 ± 5	1.8 × 10 <sup>-5</sup>	$3.5 \times 10^{-14}$	1.65 × 10 <sup>-5</sup>	630	Burst
9	23	2	2	$268 \pm 4$	1.3 × 10 <sup>-5</sup>	$1.3 \times 10^{-14}$	$2.1 \times 10^{-5}$	400	Ejectio n
10	20	2.5	2	66 ± 3	$8.0 \times 10^{-6}$	$3.2 \times 10^{-15}$	$1.1 \times 10^{-5}$	87	Ejectio n

**Table 4.1:** Geometrical parameters of the individual tubes and the experimentally derived

 quantities for each tube.

 $V_b$  is the volume of a single bubble,  $V_b = \frac{4}{3}\pi R_B^3$ ,  $R_B$  is the maximum radius of the bubble, f is the measured bubble burst/ejection frequency. Here we assume that the O<sub>2</sub> gas density is the same as that at the atmospheric pressure. We can compare the measured O<sub>2</sub> rate  $G_{exp}$  with the predicted,  $G_{O_2}$  calculated using Eq. (4.9). The values of physical dimensions of the microjets and reaction



**Figure 4.13**: (a) Bubble radius  $R_b$  and microjet displacement *s* versus bubble growth time *t* during bubble growth. The dotted lines represent the fitting using  $R_b = \gamma t^n$ , which can be used to extract  $\gamma$  experimentally. (b) Microjet average speed  $v_{avg}$  versus  $R_B \times f$ . Predicted (dotted line) and experimental ( $\circ$ ) values from Ref. 29 with experimental values of average speed of microjets with burst mechanism ( $\blacksquare$ ) and that with ejection mechanism ( $\blacktriangle$ ).

rates *K* are obtained from Table 4.1. Figure 4.14 (a) shows the comparison of  $G_{exp}$  and  $G_{O_2}$  for microjets with different aspect ratios,  $\xi = L/2R$ . Although the exact values of  $G_{exp}$  and  $G_{O_2}$  are different for different  $\xi$ , these two parameters follow the same trend. The discrepancy in the values could be due to several reasons: (1) the accuracy in determining  $\gamma$  values, (2) the assumption that  $\rho_{O_2}$  is constant within the bubble, could be inaccurate, and (3) the accuracy in determining the bubble ejection/frequency *f*. Figure 4.14 (b) plots the comparison of predicted frequency of bubble ejection/burst with that of the measured values for different  $\xi$ . The predicted frequencies are calculated by Eq. (4.12) using the physical parameters such as *L*, *R*, *K* and *R*<sub>B</sub>, obtained from Table 4.1. Again the theoretical prediction follows the experimental trend very well.

The speed of the microjet depends closely on the dimensions of the microjet as well as the bubble's growing radius  $R_b$ , maximum bubble radius  $R_B$ , and frequency f as seen from Eq. (4.15). Note that the average speed in Eq. (4.15) is the speed of the microjet during bubble



**Figure 4.14:** Comparison between experimental value (**•**), theoretical prediction (**•**) of (a) bubble growth rate  $G_{O_2}$ , and (b) bubble ejection/burst frequency *f*.

growth; however, it does not consider the effect of thrust induced by bubble burst or bubble ejection. It is observed that the process of burst or ejection provides a much greater thrust to the microjets than the thrust provided during bubble growth, as is seen in Fig. 4.12 (b). Figure 4.15 shows the comparison of the predicted average speed  $v_p$  with the measured average speed  $v_{avg}$  of the microjets. The measured speeds are obtained from slopes of plots in Fig. 4.12 (a) for each microjet, while the estimated average speeds are calculated using Eq. (4.15) and the parameters from Table 4.1. The frequency f and parameter  $\gamma$  are obtained from Eq. (4.12) and (4.10), respectively. Figure 4.15 shows that both  $v_p$  and  $v_{avg}$  follow the same trend, although the predictions significantly underestimate the magnitude of the speed since the theory does not take into account the effect of burst or ejection. Figure 4.15 also shows average experimental speed  $v_{growth}$  during bubble growth obtained from measuring the motion of the microjet without the impact caused by bubble burst/ejection. The average speed without the impact of bubble burst/ejection are calculated by using  $v_{growth} = s/t$ , where s is obtained from Fig. 4.14. We see that the  $v_{growth}$  values are much closer to the predicted values  $v_p$ . The discrepancy in values could be attributed to same reasons given in the paragraph above.



**Figure 4.15:** The plot of the average speed of the microjet  $v_{avg}$  (**1**), the average speed of the microjet during bubble growth  $v_{growth}$  (**A**), and the predicted average speed  $v_p$  (**•**) versus the aspect ratio  $\xi$  of the microjets.

# 4.6 Bubble Detachment: Ejection Or Burst

During the motion of the microjets, it is observed that the bubble grown at one end of the microjet either ejects from the microjet or bursts (disappears instantly) when it reaches a maximum size  $R_B$ , and imposes a large impulse to make the microjet move in the opposite direction. We cannot predict the behavior of the bubble after it reaches  $R_B$  with the current one-dimensional mass transport model. In a quasi-steady state, there is a constant supply of O<sub>2</sub> at the end of the microjet. The maximum size of the bubble and how it leaves the end of the microjet are influenced by a number of factors. Below we discuss how bubble ejection or burst could occur.

According to Zeng et al. [55], the maximum diameter of the bubble before it detaches from a microjet depends on the rate of bubble growth, interfacial tension, liquid pressure, buoyancy, etc. Since the growth and departure of bubbles is a dynamic process, the momentum exchange between the bubble and the liquid must be considered. The force equation for a growing bubble in one dimension can be expressed as,

$$F_{net} = F_{\sigma} + F_{growth} + F_{buoy} + F_{excess} + F_{wake}, \qquad (4.17)$$

where  $F_{\sigma} = \left(\frac{2\sigma}{R_b}\right)\pi R^2$  is the force due to surface tension ( $\sigma$  is the interfacial tension),  $F_{buoy}$  is the

buoyant force on the bubble,  $F_{excess} = 2\pi R\sigma$  is the contact pressure force due to surrounding liquid, and  $F_{wake}$  is the force created by the preceding bubble. We can neglect the effect of buoyant force since the motion of microjets is only on a horizontal plane. In addition, the magnitude of  $F_{wake}$  is estimated to be  $F_{wake} = 10^{-4} F_{growth}$ ; thus, we can also neglect  $F_{wake}$ . Therefore, the total force acting on the bubble can be written as,

$$F_{net} = 2\pi R\sigma - \rho_w \pi R_b^2 \left(\frac{3}{2}C_s \dot{R}_b^2 + R_b \ddot{R}_b\right) + \left(\frac{2\sigma}{R_b}\right) \pi R^2.$$

$$(4.18)$$

In quasi-equilibrium condition,  $F_{total} = 0$ . Therefore, the condition for bubble detaching from the microjet is

$$2\sigma R\left(1+\frac{R}{R_b}\right) \le \rho_w R_b^2 \left(\frac{3}{2}C_s \dot{R}_b^2 + R_b \ddot{R}_b\right). \tag{4.19}$$

Using the relation  $R_B = \gamma t_B^{1/3}$ , where  $t_B$  is the time when  $R_b = R_B$ , one has,

$$2\sigma R\left(1 + \frac{R}{\gamma t_B^{1/3}}\right) = \rho_w \gamma^4 t_B^{-2/3} \left(\frac{1}{6}C_s - \frac{2}{9}\right).$$
(4.20)

$$t_{B} = \left(-\frac{R}{2\gamma} + \sqrt{\frac{R^{2}}{4\gamma^{2}} + \frac{\rho_{w}\gamma^{4}}{2\sigma R} \left(\frac{1}{6}C_{s} - \frac{2}{9}\right)}\right)^{3}.$$
(4.21)
Using  $R = 2 \times 10^{-6} m$ ,  $L = 25 \times 10^{-6} m$ ,  $\sigma = 72 \times 10^{-3} N/m$ ,  $\rho_w = 1000 kg/m^3$ ,  $C_s = 6.67$  from Zeng et al [55], we get  $t_B = 20$  ms, which is close to the values (~ 1 - 5 ms) obtained in our experiments.

The process of bubble burst could be explained by the pressure difference created by the greater gap in O<sub>2</sub> leak rate out of the bubble and O<sub>2</sub> flux flowing into the bubble. In our onedimensional model, we did not consider the effect of  $O_2$  leak from the bubble to the solution. There are at least two reasons for the burst. First, the bubble growth is a dynamic process, it starts from its critical nucleation size  $R^*$ ; at this point it cannot seal one end of the microjet entirely. This means that during the bubble growth, there is still H<sub>2</sub>O<sub>2</sub> flux coming from the bubble nucleation end. This could lead to higher production rate of O2 than that predicted by the current model. When the bubble becomes larger and covers more area of the microjet opening, the O<sub>2</sub> flux becomes smaller. Meanwhile, the O<sub>2</sub> in the bubble could have a tendency to dissolve back into the solution during bubble growth. This "leakage" effect can rapidly intensify as the bubble's surface area becomes larger and the O<sub>2</sub> concentration becomes smaller at the far side during the bubble growth. After the bubble is grown so large as to cover the microjet opening and hence prevent H<sub>2</sub>O<sub>2</sub> intake, the O<sub>2</sub> production would soon stop. At this point, the bubble would only lose O2 and the bubble can collapse abruptly, i.e., burst. The pressure inside the growing bubble is described by eq. (3.1) [53],

$$P_{b} = P_{\infty} + \frac{2\sigma}{R_{b}} + \frac{4\eta}{R_{b}}\dot{R}_{b} + \rho \left(R_{b}\ddot{R}_{b} + \frac{3}{2}\dot{R}_{b}^{2}\right),$$
(4.22)

where  $P_{b}$ ,  $P_{*}$ ,  $R_{b}$ ,  $\sigma$ , and  $\rho$  are the pressure of gas inside the bubble, the pressure of the liquid at remote distances ( $\approx$  101 kPa, the atmospheric pressure), the radius of the bubble, the surface tension, and the mass density of water, respectively. The bubble bursts when the O<sub>2</sub> flowing into the bubble supplied by the catalytic reaction is much smaller than the  $O_2$  flux from the bubble into the liquid. The solution to this question can be obtained by combining Eq. (4.21) with mass transport equation and dynamic boundary conditions.

# 4.7 Conclusion

We developed a facile technique to fabricate these microjets with a less complicated method. With the technique we fabricated multilayered, freestanding nanostructured scrolls, made of GO, Ti and Pt, inwhich each material has been tailored to make both structural and functional contributions. In particular, the GO layer makes a maximum contribution with a minimal thickness. We studied the mass transport in these structures in a two dimensional model. The theory predicted that the length and the jet opening diameter plays an important role in mass transport and bubble dynamics, which in turn affects the motion of the motors. The experimental observations match well with the predictions.

#### CHAPTER 5

## COLLECTIVE BEHAVIOR

### **5.1 Introduction**

Autonomous catalytic motors are the foundation of collective behavior in man made motors. There are various ways to achieve collective motion among the motors. In particular, one can use the propulsion mechanisms to advantage while designing motors that perform collective behavior such as self-diffusiophoresis and self-electrophoresis. A few examples are presented in Chapter 1. As observed in nature, the collective behavior is driven by the nearest neighbor interactions of the motors. In bubble propelled motors, particularly the microtube motors, the collective behavior is observed but in each case it depends loosely on the concentration of motors and the fuel in the environment. The results are not always reliable and predictable. Furthermore, the collective motion is not a direct result of the bubble growth collapse dynamics Here we report a phenomenon of ring like self-assembled structures from 5  $\mu$ m JCMs in H<sub>2</sub>O<sub>2</sub> environment. As noted in Chapter 4, no bubbles can be observed on individual 5 µm JCM beads. The critical nucleation energy cannot be reached on the surface of these motors. There are several factors responsible to achieve the critical nucleation energy. First is the curvature of the catalyst surface. As seen in Chapter 3, for a convex surface, if the curvature is large, the energy needed to achieve successful nucleation is slightly larger than for a flatter surface. Concentration of O<sub>2</sub> is another factor, which plays an important role in nucleation. Nucleation is forming of a new phase, in our case it is bubbles made of O<sub>2</sub>. The critical energy to nucleate is reached when the concentration of the new species reaches a critical concentration termed as the saturation concentration. For 5 µm JCMs the O<sub>2</sub> concentration does not reach the saturation value due to the fact that the amount of O<sub>2</sub> produced is limited by the available catalyst surface area. The

diffusiophoretic motion of the JCM also prevents the O<sub>2</sub> from accumulating and reaching the saturation concentration. The limitations faced by individual JCMs could be overcome collectively if the multiple JCMs are concentrated in a small region and have a high concentration of H<sub>2</sub>O<sub>2</sub> in the surroundings. The O<sub>2</sub> saturation concentration would be quickly reached within that region, since the O<sub>2</sub> produced by each motor would accumulate and be unable to escape that region. In this study, we observed that JCMs with  $\sim 5 \ \mu m$  diameter at a high concentration of H<sub>2</sub>O<sub>2</sub> were able to collectively nucleate bubbles and perform a collective motion around the bubble. When the JCMs are introduced in a reservoir containing H<sub>2</sub>O<sub>2</sub>, they initially perform the autonomous diffusiophoretic motion. However, when multiple beads get crowded in a small region, the bubbles start to nucleate. When a single bubble is nucleated, it starts the process of collective motion. During its growth, the bubble forces the participating beads to arrange around its base in a ring like structure and draws them towards the center of the ring in a coordinated fashion, until the bubble bursts. This process repeats until the fuel is exhausted. The dynamics of the process are much different than previously reported collective/ schooling behaviors and bubble propulsion among micromotors. This process is not activated by any external chemical or light trigger, and it occurs spontaneously. This motion has been observed to occur more readily if the non-catalyst face of the motors is made hydrophobic. Such multi-faceted motion - trigger free schooling, transition between diffusiophoresis and bubble propulsion, periodic motion, collective bubbling among micromotors - has not been previously reported to the best of our knowledge.

## 5.2 Experiments and Results

For this study we use two different sized motors (2  $\mu$ m and 5.2  $\mu$ m in diameter). Each size motors are further divided into two groups: hydrophobic motors and hydrophilic motors (To emphasize, only the non-Pt side is functionalized). The fabrication process is same as described in Chapter 2. After the motors are fabricated they are suspended in 18 M $\Omega$ ·cm de-ionized water by ultra-sonication. For the experiments, a droplet (5  $\mu$ l) containing a few beads is cast on a clean Si surface and observed under the microscope, 10 – 20 % peroxide (5  $\mu$ l) is then added to the droplet. The volume of the droplet selected is such that, the resulting reservoir does not evaporate quickly and can be changed without affecting the quality of observations. The observation and recording protocols mentioned in previous chapters is followed.

Initially no bubbles are observed and the JCMs exhibit autonomous diffusiophoretic motion. However after a short period of time (~ 30s - 1 min), a distinct internal flow is observed in the droplet. The JCMs no longer exhibit autonomous motion; instead they are dragged toward a seemingly random local point. The flow is not caused by any external stimulus and it is radially directed towards this local point in the reservoir. The point of aggregation is random since it is observed to occur repeatedly at different locations in the reservoir. Once the JCMs are aggregated O<sub>2</sub> saturation is reached and bubbles start to nucleate. The bubble forces the adjacent JCMs to arrange at its base in a circle. As the bubble grows it draws the JCMs at its base towards



Figure 5.1: Snapshots of microbeads as they get densely populated in a small region and the subsequent bubble and ring formations.

the center of the circle. Once the bubble grows to a critical  $R_{\text{max}}$  (typically between 50 – 75 µm) it bursts. However, the circular ring of JCMs is maintained and a new bubble starts to nucleate at the center of the ring. The local pressure changes due to bubble then attracts neighboring motors to take part in the synchronized growing and collapsing of bubbles and the motion is sustained. Figure 5.1 is a series of snapshots of a video taken during this process. It shows the process of initial swarming of beads, the bubble growth, and then the new bubble nucleation after previous one is burst. The new bubble also reaches approximately the same radius value,  $R_{\text{max}}$  before it bursts and the cycle continues. It is important to note that the bubble is not attached to the surface of any JCMs and all the JCMs seem to collectively feed the bubble with O<sub>2</sub> from their catalytic conversion of H<sub>2</sub>O<sub>2</sub>. It indicates that bubble forms on a flat Si surface, since homogenous nucleation is unlikely. As the time stamps indicate, the bubble growth and burst are observed. The



X Displacement (µm)

**Figure 5.2:** After the initial bubble burst, the beads are locked in the ring. They all travel towards the center of the bubble as it grows. The black lines highlight the trajectory of each motor.

JCM motion as a result is also fast (few hundred  $\mu$ m/s). The expected motion of catalytic micromotors, which is to travel in the opposite direction of the catalyst surface, is ceased and the micromotors are locked in these ring structures. Figure 2 shows the snapshot of a video sequence at a moment when the initial bubble of the cycle has just burst. Superimposed are the trajectories that each motor follows after this image is taken. The red arrows denote the direction of the JCM motion. The JCMs all travel toward a common point, which is the center of the bubble. The bubble itself is not necessarily fixed to a location on Si substrate and is sometimes observed to move in the horizontal plane, dragging the ring with it. The figure shows a couple of interesting points. 1) All the motors are arranged and locked in a virtual circle. 2) None of the motors are physically attached to the bubble, which suggests that all or most of the beads are feeding the bubble remotely. The bubble seems to feed from the surrounding supersaturated O<sub>2</sub> by means of Ostwald's ripening [52]. 3) None of the motors are facing away to towards the bubble center, which is the direction of the motion.

Different starting densities of JCMs were tested to determine the critical number of beads required to instigate this motion. Starting with  $7 \times 10^4$  motors/ml, the concentration of JCMs was increased to  $1.4 \times 10^5$  motors/ml and  $3 \times 10^5$  motors/ml. For hydrophilic JCMs the swarming of JCM and collective behavior only occurred with the highest motor density ( $3 \times 10^5$  motors/ml). For hydrophobic JCMs all the densities produced swarming and collective bubbling. There are other differences between the collective behavior in hydrophobic JCM and hydrophilic JCM as well. The average number of motors taking part in the collective bubbling differs significantly for hydrophobic JCM and hydrophilic JCM. The number of motors in a ring also shows some relation with the initial density of motors used. Figure 5.3 shows a plot of number of beads in a ring as a function of initial motors density. It shows that the average number of beads in the ring



**Figure 5.3:** Number of beads *n*<sup>0</sup> in a ring for different densities of motors/ml.

reduces as the initial density is increased for hydrophobic JCMs. However, for hydrophilic JCMs the number of beads in the ring is significantly more than the highest bead average for hydrophobic JCMs. It indicates that the number of beads required for collective bubbling is less for hydrophobic JCMs than for hydrophilic ones and it reduces as the initial density of JCMs (motors/ml) or in other words the number of motors in the reservoir (motors/m<sup>2</sup>) is increased.

### **5.3 Discussions**

The location of these nucleation sides are arbitrary and thus rule out the possibility of external factors such as currents due to air, pressure etc. The nucleation sites are determined by the local concentrations of  $O_2$ . If  $O_2$  concentration in a small area increases beyond supersaturation, the nucleation occurs. The concentration of  $O_2$ , given the diffusion laws, will be greater at the surface of the Pt initially, however, as the time passes, the  $O_2$  is unable to escape the ring created by the motors. This is because, the diffusion of  $O_2$  molecules is driven from

higher to lower concentration, and since at the circumference of the circle, the concentration is highest, the  $O_2$  starts to accumulate inside the ring, which leads to supersaturation.

The motion of the beads during the bubble growth and burst is synchronized and fast. Also, noted before, the orientation of motors does not influence the motion. This implies that diffusiophoresis is not the dominant driving mechanism. The motion analysis of nanomotors observed during bubble growth indicates that nanomotors move toward the bubble base with a speed of hundreds of micrometers per second. Such a collective movement of the nanomotors is too fast to be caused by diffusiophoresis. Such a movement is also not caused by the fluid flow induced by bubble growth. We hypothesize that the fast movement of nanomotors toward bubble base is caused by evaporation-induced Marangoni flow near the bubble [69]. The evaporation of water on the top surface of the liquid film induces a heat flux. During the bubble cycle, this flux causes the liquid at the bottom of bubble to be warmer than that at the top of the bubble. Since the surface tension of water decreases as temperature increases, the surface tension of water is higher at top of the bubble than at the bottom of the bubble. This variation of the surface tension along the bubble surface drives a Marangoni flow, which can entrain nanomotors near the substrate toward the bubble base. Preliminary numerical simulations suggest that this effect is indeed capable of producing speeds comparable to those observed in the experiments. More studies and experiments are still being done.

The difference between the collective behavior in hydrophobic and hydrophilic JCMs is interesting and could be explained by the  $O_2$  supersaturation. The catalytic conversion rate of Pt on the hydrophobic JCM is effectively larger than that for the hydrophilic JCM. This is because of the depletion later formed around the Pt surface that allows quick removal of  $O_2$  from Pt surface and dispersion into the liquid. This is studied in detail in Chapter 3. This results in quick build up of  $O_2$  inside the ring, and the number of motors required reach supersaturation is reduced drastically as seen in Fig. 5.3. Another consequence of the depletion layer in hydrophobic JCM is that the overall  $O_2$  content of the reservoir is also higher than for the reservoir containing hydrophilic JCMs. This could explain the decrease in the average number of motors in a ring.

## **5.4 Conclusion**

In conclusion we have observed a new trigger free schooling behavior followed by collective, periodic bubbling motion with spherical JCMs. The JCMs with 5  $\mu$ m diameters cannot produce bubble-propelled motion individually. However, with high motor density (motor/ml), the JCMs can collectively form bubbles and perform a collective synchronized motion. This motion is fast and the direction of motion is towards the center of the bubble, irrespective of the orientation of Pt on the JCMs. The diffusiophoresis mechanism does not contribute to this motion. It is proposed that the motion of motors towards the bubble center is caused by Marongoni flow effects. The numerical simulations show that the Marongoni effect can produce similar speeds observed in the experiments. The higher effective conversion rate of H<sub>2</sub>O<sub>2</sub> at Pt surface on hydrophobic JCM results in easier O<sub>2</sub> saturation and bubble formation than in the hydrophilic JCMs. This result could be expected to garner interest for collective task management with fewer size restrictions as far as bubble nucleation is concerned.

### CHAPTER 6

## CONCLUSION AND FUTURE WORK

Catalytic micromotors have fast become a hot topic of research. Many researchers around the world are doing research to find new and innovative ideas to design different kinds of motors and perform different kinds of motions, using different mechanisms. At the core of it all is the understanding of motion mechanisms. The fundamental physics of hydrodynamics and chemical kinetics is very important in understanding the mechanisms and helping us improve the design.

This dissertation has attempted to answer some fundamental questions about the motional behaviors of catalytic motors. In particular, the dissertation has focused on two propulsion mechanisms, diffusiophoresis and bubble propulsion. We have discussed how small motors that use chemical gradients and diffusion move in aqueous solution of  $H_2O_2$ . The reaction kinetics of catalyst around hydrophobic and hydrophilic surfaces is exploited to make faster micromotors.

Major part of the dissertation is dedicated to learning the fundamentals of bubble propulsion mechanism. The nucleation theory is developed and effect of curvature on production on bubbles is studied. The predictions of the theory is tested using spherical Janus motors with convex and concave catalyst surface are tested. We also tested the concave catalytic surface with microtube motors. We studied the mass transport of the fuel and by products inside the tube since it is an important aspect for improving the efficiency of motors. The effect of geometry on the mass transport is presented.

Along the way in this study we explored different techniques of fabrication of motors. Experimentally the method of making the motors hydrophobic is presented and the effect on the motion is studied. To test the theory concave shell motors were fabricated and their motion is observed. We also developed a method to fabricate microtube motors using a simple technique of strain engineering.

The future of catalytic motors lies in developing new systems and making them smarter. The research going forward should be three pronged. Design orientation, fundamental understanding, and application orientation. Design orientated motors are those which are manufactured with new materials and new physical designs that perform different kinds of motional behaviors. They are also the ones that borrow ideas from different fields. They use different chemical reactions and energy created in those reactions to convert it into motion. Understanding oriented research is what will give a guideline to the new designs of the motors. The application-oriented research develops and uses the motors to practical applications.

The collective behavior presents a promising avenue of research. It is important for the development of the field that we discover new ways to create motors that perform collective behaviors. Light induced collective behavior is used in number studies. The light is used to activate or accelerate some chemical reaction. The light source used is almost always UV. This is because only a limited number of chemical reactions are explored for this purpose and more study needs to be done. Visible light can also be used to invoke collective behavior in motors. It could be done using the semiconductor properties of Si substrate on which experiments are done. Very rarely are the properties of substrates ever exploited in this field of research and it needs more work. We have obtained promising results with metal semiconductor junctions on substrate activated by light. The motors respond to visible light and the motion appears synchronous to on-off switch of the light.

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