Synthetic model microswimmers near walls

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Summary

From flocks of birds in the sky and schools of fish in the water, to tiny colonies of bacteria in the soil and cells in the human body, living organisms have evolved to grow and to maintain themselves. A few examples of them are shown in Figure 1A-E. Scientists often think of these organisms as *living materials*. These materials have remarkable abilities: they can control their shape, assemble, organize, and even heal themselves, to name a few. Living materials use these abilities to respond to the stimuli they sense from their environment. Take bacteria for instance. Bacteria use a mechanism called chemotaxis[1]: To feed or to protect themselves, their bodies' tiny flagella sense if the amount of food molecules or of toxins increases in a certain direction. In the same way, sperm moves towards the egg, and neutrophils chase after bacteria.

Nowadays, scientists have found great inspiration in living materials. They use this inspiration to create microscopic *synthetic materials* that will likewise move autonomously inside complex environments. These materials, known as *synthetic microswimmers*, can be very useful for industrial applications. For example, they could be used in bio-medicine and micro-surgery to transport and deliver drugs at specific locations within the body, or they could be used in environmental remediation to locate and decompose the source of pollution inside contaminated waters.

In this work, we prepared in the laboratory synthetic particles with sizes of about three micrometers, as in Figures 1F-H. Particles of this size are called *colloids*: they are so small that they cannot be seen with the naked eye, but we can image them using a microscope. Normally, when we place the colloids inside a liquid they move randomly, an effect known as Brownian motion. Here, by tailoring the surfaces of the colloids, we suppressed their random motion and instead we made colloids that could direct their own motion: we covered half their surface with the metal platinum and then we placed them inside water that also contained a small amount of hydrogen peroxide. In this liquid, the platinum-coated colloids immediately propel themselves with the platinum side on the back because of a catalytic process that takes place on the platinum. For this reason they are named *catalytic microswimmers* and can be used in experimental studies as models for synthetic microswimmers.

[1] In ancient greek *τάξις*, from the verb *τάσσω* which translates as to arrange, order

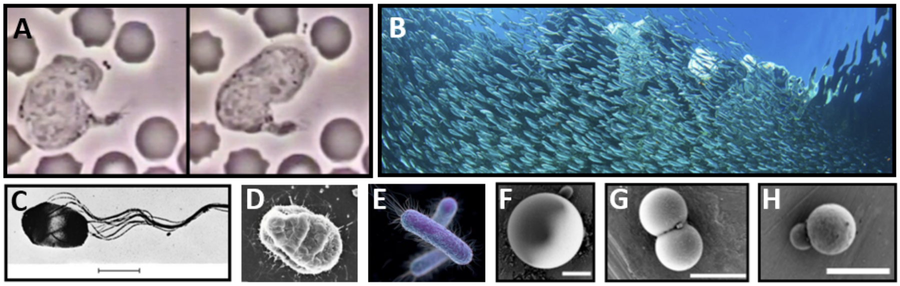

Figure 1: **Examples of biological (A-E) and synthetic (F-H) swimmers. A)** A white blood cell, called neutrophil, senses and chases after a bacterium. It moves between the red blood cells by constantly changing its shape. **B-E)** Examples of biological swimmers with different sizes and shapes. A school of fish (B), a *Salmonella* bacterium (C, the scale bar is 1 micrometer), a *Thiovulum majus* bacterium (D), and *Escherichia coli* bacteria (E). **F-H)** Examples of the synthetic microswimmers that we synthesized and studied in our laboratory. Our colloidal swimmers had sizes around 3 micrometers and were either spherical (F, scale bar is 1 micrometer) or shaped like dumbbells. The dumbbells were symmetric (G, scale bar is 3 micrometers) —the two lobes had the same size— or asymmetric (H, scale bar is 2 micrometers) — one lobe was smaller than the other.

Briefly, they achieve their motion as follows: the platinum acts as a catalyst that breaks down the hydrogen peroxide. This is a chemical reaction process, which creates reaction products around the platinum. These reaction products are colored green in Figure 2A. Simply put, hydrogen peroxide is the *fuel* that the colloid uses (consumes) to push itself forward. In essence, this happens because the reaction products interact with the colloid; this causes the liquid to move in one direction around the colloid and pushes (propels) the colloid forward. This mechanism of motion is similar to *self-phoresis* [2,3,4], but for these colloids the exact details of the mechanism are not known yet.

When we place the mixture of the synthetic swimmers and the liquid fuel inside a container, the swimmers tend to swim downwards towards the bottom. When they reach the bottom wall, they stay there and self-propel parallel to the wall, as sketched in Figure 2A. In **chapter 2**, we used a microscope to image the swimmers and to measure how fast they moved near the wall. We first used a wall

[2]In ancient greek *φόρησις* from the verb *φέρω* which loosely translates as to bring, carry
[3]In general, phoresis describes the migration of colloids inside a liquid
[4]The prefix *self-* is used here because the colloid causes its propulsion by itself without external driving

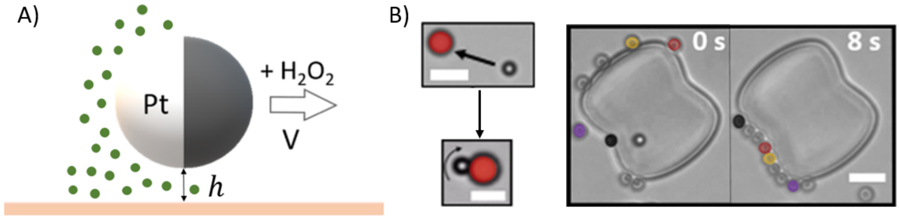

Figure 2: **A)** Our colloidal particles are half-coated with platinum (Pt) and self-propel with speed V parallel to a wall, and at a fixed height h from it, inside hydrogen peroxide (H_2O_2). The platinum breaks down the fuel (hydrogen peroxide) and creates reaction products (shown here as green dots). These drive fluid flows around the particle and the wall. **B)** We 3D-printed obstacles for the swimmers on the wall. The obstacles had circular (marked as red in the images on the left) or peanut shapes (images on the right). When the swimmers approached the obstacles they moved in orbits around them. The swimmers assembled themselves and formed long chains along the obstacles.

made of glass. Then, in some experiments we modified the surface of the glass wall, and in others we used walls made of other materials. We found that the swimmers moved with different speeds above the walls, sometimes faster and sometimes slower. We proposed that this happened because some walls were more slippery than others: slippery walls helped the liquid to flow along more easily. On the contrary, the liquid found a resistance along walls that were not slippery, which caused the swimmers above them to move slower. This work helped us to understand that nearby walls can affect the motion of synthetic microswimmers, as has already been known for biological microswimmers.

In **chapter 3**, we developed a simple method for measuring the distance (height) at which any swimmer (that is shaped like a sphere) moves above the wall. Our method uses quantitative mathematical relationships that connect the random motion (diffusion) of colloids to a height from the wall. Although for our swimmers random motion is suppressed, it is still present, and can be extracted from measurements taken by the microscope; afterwards, the height of the swimmer from the wall can be calculated from the diffusion. By using this method, we found that our swimmers move very close to the wall at heights of about 300 nanometers, a length that is much smaller than the size of the swimmers. To our surprise, we also found that the height remained almost constant when we changed various conditions in the experiments, for example the size of the swimmers or their electrical charge. We called the tendency of swimmers to move parallel to the wall and at fixed heights from the wall, ''ypsotaxis'' [5]. Our work

[5]From the greek word $\acute{\upsilon}\psi o\varsigma$ which means height

showed once again that walls influence the behavior of synthetic swimmers, and this helped us to put forward some new ideas about their motion mechanism.

In **chapter 4**, we used a 3D-printing technique to print and attach microstructures on top of the wall. These structures were larger than the swimmers and had either circular shapes or shapes that looked like peanuts, see for example Figure 2B. As the swimmers were moving parallel to the wall, they came across the structures and then started to orbit around them. We found that when more swimmers orbited the same structure, they were moving faster than when a swimmer was orbiting alone. It was very interesting to find a sense of cooperative motion between synthetic swimmers, because until now this was found only between biological swimmers like bacteria. In addition, the swimmers assembled themselves and formed long chains, which were orbiting around the structures. Finally, we found that the curvature of the structures affected the behavior of the long swimmer chains. This can be useful in the future for applications: we could think of strategies to use the curvature of the walls as a tool to control the motion of the swimmers.

In **chapter 5**, we developed a second method for measuring distances between colloids and walls. This technique was based on holographic microscopy. It can be used to measure the height from the wall for any colloid — not only the ones that look like spheres — as long as the surface of the colloid is the same everywhere. Because of this, we could not use it for the spherical swimmers with the platinum side, but instead we used it to study the random motion of colloids with more complex shapes. We studied colloids that looked like *dumbbells* after they settled above the wall. To make the dumbbells, we always attached together two spheres that had the same size. We found that the motion of the dumbbell above the wall depended on the size of the dumbbell. In water, the smaller dumbbells were positioned at preferred angles with respect to the wall. This did not happen when we used bigger dumbbells made of the same material: the bigger dumbbells oriented almost parallel to the wall instead. Our work showed that non-spherical colloids behave in complex ways near a wall. In the future, this can help us to develop models that will predict the movement of colloids with arbitrary shapes near walls.

In **chapter 6**, we were inspired by biological microswimmers which have non-trivial shapes. For biological microswimmers, shape is expected to be important: for example, different shapes may help the swimmers to navigate more easily inside complex environments. We were interested to see how shape affects the motion of synthetic swimmers. We used dumbbells with different morphologies as shown in Figure 3. We added platinum on one side of the dumbbells and then placed them in the hydrogen peroxide fuel. Symmetric dumbbells self-propelled in the direction away from the platinum in a straight motion. In contrast, asymmetric dumbbells were moving in circles. Our finding agreed with previous research and confirmed that the shape and coating of the swimmer controls its trajectory.

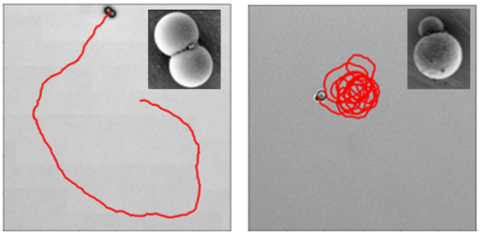

Figure 3: Dumbbell-shaped swimmers with symmetric lobes moved almost in a straight-like fashion (left). Swimmers with asymmetric lobes moved in circles (right panel). The red lines show the trajectories of the swimmers.

Overall, the work presented in this thesis helped us understand how synthetic swimmers behave and which factors affect their speeds and trajectories. This understanding may be useful when using catalytic swimmers as models for microswimmers in science, but also in future applications: since synthetic swimmers will be needed to perform tasks in complex environments, this work may help in predicting and controlling their motion inside different environments.