Controlled propulsion of artificial magnetic nano-structured propellers

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ABSTRACT For biomedical applications, such as targeted drug delivery and microsurgery, it is essential to develop a system of swimmers that can be propelled wirelessly in fluidic environments with good control. Here, we report the construction and operation of chiral colloidal propellers that can be navigated in water with micron-level precision using homogeneous magnetic fields. The propellers are made *via* nano-structured surfaces and can be produced in large numbers. The nanopropellers can carry chemicals, push loads, and act as local probes in rheological measurements.

Considerable progress has been achieved in manipulating nanoscale objects[1] on surfaces[2] and in high vacuum environments. Attaining a similar level of control in fluidic environments[3-7] could revolutionize many aspects of nanotechnology and open exciting possibilities in micro-fluidics and nano-rheology. At microscopic length-scales and therefore at low Reynolds numbers, reciprocal motion is absent as a potential means of locomotion (Scallop theorem[8]). Special swimming strategies are therefore needed. While propulsion in liquid crystal films[9], with electric fields[10], in magnetic field gradients[11], and with the aid of chemical decompositions[7,12] have been investigated, those that rely on a homogeneous magnetic field are especially promising as they can be operated from a distance in aqueous environments. Of particular scientific and technological interest are therefore magnetically actuated nano- and micro-structures that 'swim' similar to biological micro-organisms[13,14]. Two strategies that permit swimming at low Reynolds

number and that are used by living organisms are the flexible oar-like motions of spermatozoa and the cork-screw motion of bacterial flagella. Recently, the motion of spermatozoa was mimicked in an artificial magnetic swimmer of dimensions around 30 microns that executed some linear motion[4]. A variety of cork-screws have also been fabricated[5,15,16] with lengths from 30 microns to centimeters.

Here we describe a simple method of producing large numbers of nano-structured propellers and demonstrate the first fully controlled artificial swimmer that can be navigated with micron-level precision. Small size of artificial structures is especially beneficial, since colloidal length scales permit navigation in confined geometries and imply long sedimentation times. The propellers are typically 200-300 nm in width and about one to two microns long; they are driven by a homogeneous magnetic field. They are made of silicon dioxide (SiO_2) and are thus easily functionalized. Despite being Brownian in the absence of a driving force, their motion can be fully controlled when a small magnetic field is applied.

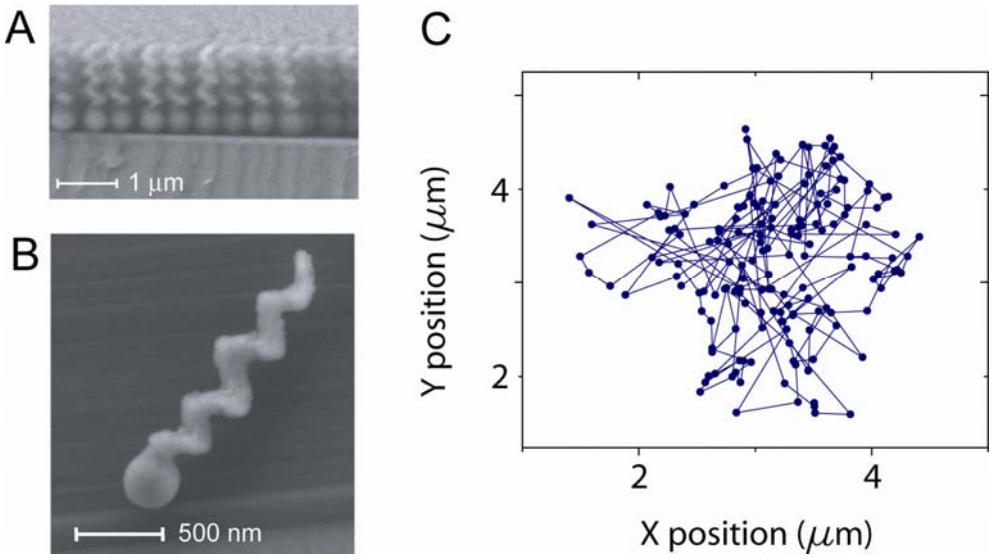

Figure 1. A) SEM image of a wafer section with a nano-structured film containing ~10^9 SiO_2 helices/cm^2. B) SEM image of an individual glass screw with nano-structured helicity. C) Translational Brownian motion is observed in a 25 second trajectory of a single colloidal glass propeller in water (recorded at 7 fps).

To fabricate the glass (SiO_2) nano-structured propellers, we use a shadow-growth method, known as glancing angle deposition[17], which permits the growth of a wide variety of nano-structured thin-films, including helical screw-like structures. A Si wafer (2 inch diameter) was first covered with a monolayer of silica beads of diameter 200-300 nm. The glass helices were then grown on the Si wafer by vapor deposition in an electron beam evaporator at a process pressure of 10^{-6} Torr. The SiO_2 vapor flux was incident at 87° and ~3 Å/s, while the wafer was rotated about its surface normal at ~0.07 rpm by a computer-controlled substrate manipulator. A wafer section of a vapor-deposited film with ~10^9 SiO_2 helical propellers per cm^2 is shown in Fig. 1A. The helices are freed from the wafer by sonication and laid onto a surface. A thin layer (30 nm) of a ferromagnetic material (cobalt) is deposited by thermal evaporation onto the surface and hence one half of the helices. The substrate with the cobalt covered helices is then placed between the pole-pieces of an electromagnet and the helices are magnetized, such that their magnetic moment is perpendicular to their long-axis (see also supporting information). An SEM image of a single glass propeller is depicted in Fig. 1B. To be able to track the swimmers, we coupled a fluorophore to the SiO_2 surface by mixing ~10 mg of (3-Aminopropyl) dimethylethoxysilane (United Chemical Techn.) with ~1 mg of Rhodamine B isothiocyanate (Aldrich) in 1 ml of dry ethanol at room temperature. In the absence of an external magnetic field, the propellers exhibit Brownian motion in water as can be seen in Fig. 1C.

A tri-axial Helmholtz coil is used to generate a homogeneous magnetic field of ~50 Gauss rotating at frequencies of up to 170 Hz, with full directional control in all 3-dimensions. The permanent magnetic moment of the colloid strongly couples with the rotating magnetic field of the coil, and for each rotation the helix executes about its body axis, it translates forward or backward by its pitch, depending on its helicity and the sense of rotation of the magnetic field. That rotation about the long axis is favored, follows from the respective rotational drag coefficients, which may be estimated if one takes the nano-swimmers to be approximately ellipsoidal. The ratio f, of the drag about the major axis a relative to the minor axis b is then given by[18]:

$$f = \frac{2b^2}{a^2}\left[\ln\left(\frac{2a}{b}\right) - \frac{1}{2}\right] \quad , \qquad (1)$$

where the dimensions are such that $a^2 >> b^2$. The ratio of the drag coefficients for the lengths of 1 to 2 microns is $f \sim 0.1$, implying that rotation about the long axis is ten times more efficient.

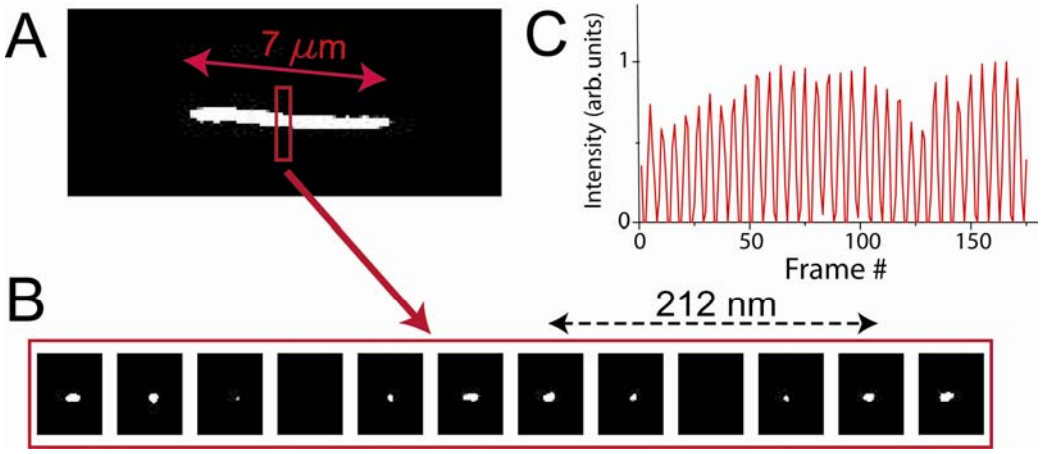

Figure 2. Images from a high-frame rate (low-resolution) video recording of A) 0.5 s trajectory (recorded at 350 fps) and B) individual images for a section of that trajectory. The swimmer is driven by a 60 gauss (6 mT) magnetic field rotating at 66 Hz in the plane orthogonal to its direction of translation. C) In the total distance of 7 μm traversed by the swimmer at 14 μm/s, it blinks 33 times, such that each full rotation corresponds to a forward movement of 212 nm through solution.

We can directly visualize the rotation/translation coupling in a single chiral colloid, as the magnetic layer, which only covers half of the body, is opaque, so that the fluorescence intensity is modulated as the screw rotates: bright as the dye faces the observer and dark when the magnetic film shields the dye. Two full rotations and the associated changes in fluorescence intensity are shown in the image sequence in Fig. 2, where for each revolution, the swimmer propels through solution by 212 nm. The full movie is available online.

Once driven with a rotating magnetic field, strong rotation/translation coupling was observed, such that the nano-structured swimmer moves forward by its full pitch, for each rotation it executes about its body axis. The torque due to the magnetic field was stronger than the viscous drag due to the environment, such that the rotation matched the rotational frequency of the applied rotating magnetic field for the entire frequency range (dc to 170 Hz) of our coil. For frequencies around 150 Hz, the chiral colloids can be propelled at speeds of ~40 μm/s. It is interesting to note that the artificial swimmers of this Letter are not only similar in size to a bacterial cell, but that they also move at similar speeds.

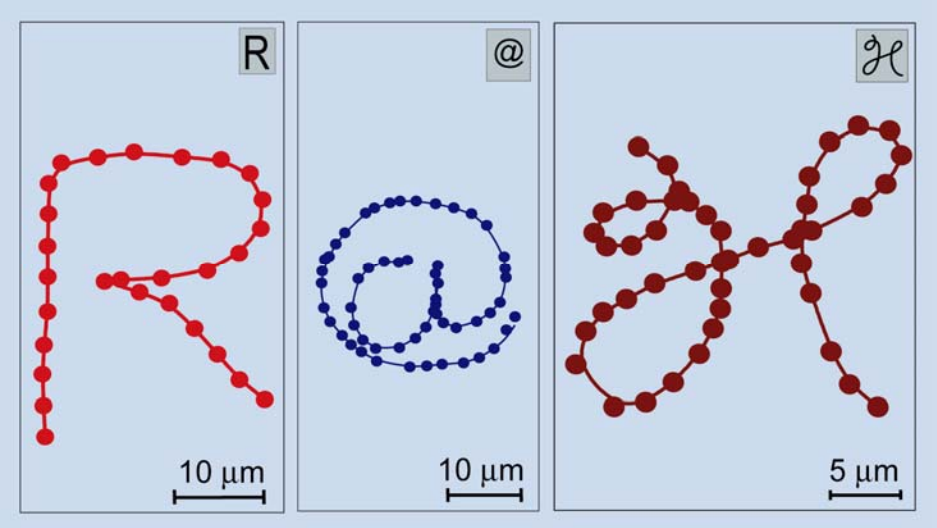

Figure 3. Trajectories of individual nano-swimmers in solution that navigate the pre-programmed "R@H" tracks that are shown in the insets. The points correspond to the position of the swimmer for each frame of the corresponding movie, while the lines show the entire track. The three corresponding movies and further details are available online at http://pubs.acs.org.

Apart from size and speed, a technologically important aspect of any nano-propulsion scheme is the degree with which the motion can be controlled. Since Brownian motion tends to dominate at these length scales it is important for the effect of the magnetic field, B, on the permanent magnetic moment, μ, of the colloid to be much stronger than thermal motion, i.e. $\mu B >> kT$, which is satisfied in the present system (see suppl. information).

The level of control observed with field strengths of 60 Gauss can be seen in Fig. 3, where we show the pre-programmed paths (inset) and the actual trajectory of a nano-swimmer in solution. The agreement can be seen to be excellent.

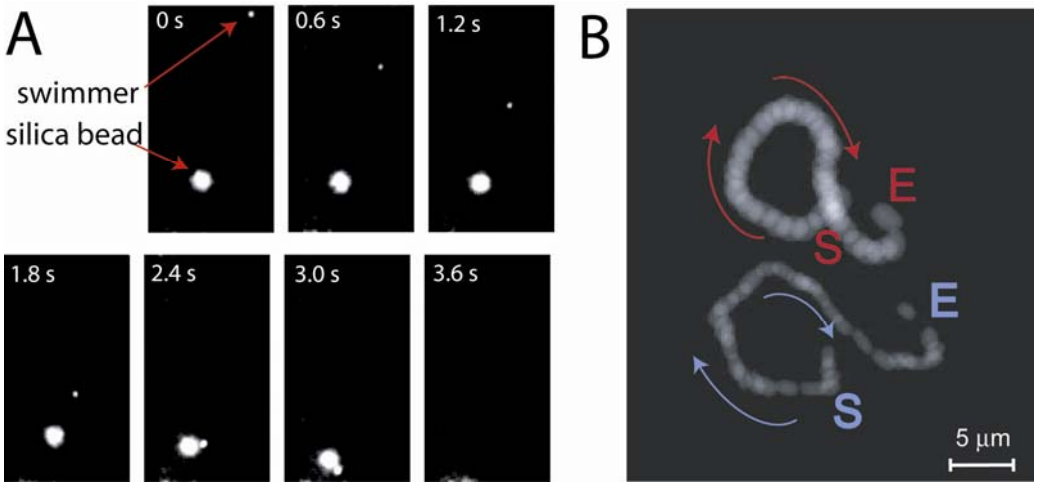

Figure 4. A) A silica bead (5 µm diameter) is being pushed by a swimmer (1.5 µm long, 200 nm wide). The images (from left to right) show how the swimmer approaches the bead and pushes it out of the field of view. A 40x microscope objective was used, and, the time gap between consecutive images is about 0.6 seconds. B) Compound image of two swimmers follow identical paths under the action of a magnetic field pre-programmed to follow a curved trajectory from start (S) to end (E).

The swimmers with nano-structured chirality we describe could find applications in rheological measurements at the micro and the nanoscale[19-21], and could either be used as passive local probes or for active manipulation at these length-scales. This is demonstrated in Fig. 4A where a 1.5 *µm* long swimmer is driven against a silica bead a thousand times its volume and pushes it out of the field of view of the microscope. Standard micro-rheological techniques used to manipulate small particles, such as optical tweezers or atomic force microscopes (AFM), do not work at long-range as they require proximity to a microscope objective or an AFM tip, respectively, whereas the nano-swimmers are readily controlled from a distance as the driving field is homogeneous. We

estimate the force, F, which can be generated by a swimmer from the drag it overcomes (taking its shape to be approximately ellipsoidal)[18]:

$$F = \frac{4\pi\eta a v}{\left[\ln(\frac{2a}{b}) - \frac{1}{2}\right]} \quad , \qquad (2)$$

where, a and b are respectively the dimensions along the major and minor axes, η is the viscosity of the surrounding medium and v is speed of the swimmer. For a 2 μm long helix with a diameter of 200 nm in traveling at 40 μm/second in water, the generated force (~ pN) is comparable to a weak optical trap. However, the diameter of the swimmer is approximately 200 nm and this results in a large applied pressure (~ few N/m^2), which could be advantageous for local manipulation, such as at biological membranes[22,23].

For certain applications in microfluidics[24], as well as in drug delivery, it may be important to be able to manipulate more than one propeller simultaneously. That this is possible is demonstrated in the image in Fig. 4B, where the tracks of two swimmers are seen that are simultaneously propelled with a high degree of control.

In summary, we have described the construction and operation of one of the smallest artificial swimmers to date. Due to their inherent chirality, the nano-structured swimmers presented in this Letter exhibit full coupling in their rotational and translational motions[25], and also make it possible to directly probe the use of hydrodynamic forces, such as shear[26] or vorticity[27] as a means of chiral separation. The fabrication method used to make the nano-structured helices can be used with a variety of materials and lends itself to large scale production. A variety of materials could be used, however the fabrication of glass propellers permits molecules to be easily attached to the SiO_2 body of the swimmer *via* standard silane coupling chemistry. The propulsion mechanism is similar to that of a rotating flagellum of a bacterial cell, where now the rotation of the chiral colloid is controlled using a homogeneous magnetic field. This allows the propellers to be powered from a distance, and permits full control in three dimensions. We expect that the simple method of realizing chiral colloidal swimmers in large numbers and the precise way with which they can be moved through solution will open up exciting possibilities and applications in micro-fluidics and nano-rheological studies,

in delivering and mixing of chemicals, and allow the potential use of artificial swimmers for biomedical applications to be explored.

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Supporting Information Available:

Description of experimental details and further information regarding the materials and methods used and movies: movie 1 showing object trajectory (slowed down 50 times and frames from this movie can be seen in Figure 2), movies 2, 3, and 4 showing the swimmer following the "R", "@", and "H" trajectories of Figure 3 (the magnetic field strength is ~60 G and the magnetic field vector rotates at frequencies ranging from 50 to 80 Hz), and movies 5 and 6 corresponding to parts A and B of Figure 4, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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