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Wafer-Scale Fabrication of Micro- to Nanoscale Bubble Swimmers and Their Fast Autonomous Propulsion by Ultrasound

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ACCESS Metrics & More Article Recommendations Supporting Information ABSTRACT: Fuel-free, biocompatible swimmers with dimensions smaller than one micrometer have the potential to

sions smaller than one micrometer have the potential to revolutionize the way we study and manipulate microscopic systems. Sub-micrometer, metallic Janus particles can be propelled rapidly and autonomously by acoustically induced fluid streaming, but their operation at acoustic pressure nodes limits their utility. In contrast, bubble-based microswimmers have an "on board" resonant cavity that enables them to operate far from the source of acoustic power. So far, they have been fabricated by direct writing techniques that limit both their minimum dimensions and the number that can be produced.



Consequently, the size scaling of the properties of bubble swimmers has not been explored experimentally. Additionally, 3D autonomous motion has not yet been demonstrated for this type of swimmer. We describe here a method for fabricating bubble swimmers in large numbers $(>10^9)$ with sizes ranging from 5 μ m to 500 nm without direct writing or photolithographic tools. These swimmers follow a previously proposed scaling theory and reveal useful phenomena that enable their propulsion in different modes in the same experiment: with magnetic steering, autonomously in 3D, and in frequency-specific autonomous modes. These interesting behaviors are relevant to possible applications of autonomously moving micro- and nanorobots.

KEYWORDS: bubble motors, microswimmers, nanoswimmers, atomic layer deposition, acoustic propulsion

icroswimmers are synthetic objects that can be propelled by power from external magnetic or electric fields,¹⁻³ chemical catalysis,⁴⁻⁶ light,^{7,8} or ultrasound^{9,10} or a combination of these methods. The development of diverse propulsion mechanisms for microswimmers has been driven in part by their emerging applications in materials science,¹¹ water purification,¹² medical diagnostics, and drug delivery.¹³ Additionally, collective phenomena arising from combinations of propulsion mechanisms are fundamentally interesting because they enable the control of self-organizing dynamic systems, which can be designed to perform certain predetermined tasks.^{14,15}

The propulsion of micrometer-size metallic Janus particles by ultrasound in the megahertz regime enables fast, autonomous motion, which can be combined with chemical or magnetic steering.^{16,17} Several studies have demonstrated the utility of these microswimmers for *in vitro* bioanalytical applications.¹⁸ However, because they must operate at an acoustic pressure node, their actuation is limited to a distance of a few wavelengths (typically hundreds of micrometers at megahertz frequencies) from the source of acoustic power. A promising alternative is to design systems in which an acoustic resonant cavity is trapped on board the swimmer in the form of a gas bubble.^{19–21} This allows for tunable and biocompatible actuation far from the source of acoustic power and at much faster speeds (up to millimeter per second) than are available by other propulsion mechanisms. With micrometer sized cup-shaped bubble-based swimmers operated at megahertz frequencies, the secondary Bjerknes force (F_B) holds the swimmer tightly to solid surfaces, so they move along the floor or walls of microfluidic devices.²² The placement of a tail²² or dorsal fin²³ on these swimmers can overcome this limitation and enable their movement in three dimensions (3D), but these complex designs require fabrication by direct writing

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Figure 1. Synthesis and operation of acoustic bubble swimmers. (A) Synthetic scheme for fabricating arbitrarily sized bubble swimmers. (B–E) High resolution SEM images of 3 μ m (B), 1 μ m (C), 600 nm (D), and 500 nm (E) bubble swimmers after scratching from the substrate. (F) Schematic of bubble swimmer. (G) General scheme for swimmer operation, requiring a source of acoustic input that generates streaming propulsion from the swimmer.

techniques that are limited both in resolution and throughput.^{20,24} A method for making swimmers of arbitrary size and in large numbers can enable researchers to study collective phenomena that are potentially useful in sensing, particle assembly, and other applications. Additionally, there are no examples of acoustic bubble-based swimmers that can move autonomously in 3D or even in 2D at dimensions below one micrometer.

In this work, we describe a wafer-scale, non-photolithographic method for the fabrication of cup-shaped bubble-based swimmers with dimensions ranging from a few micrometers down to 500 nm. Borrowing from earlier research on shadow nanosphere lithography, with subsequent etching and deposition steps, we fabricate entire wafers $(>10^9)$ of bubble-based swimmers and characterize their directed and autonomous motion in acoustic fields. These experiments reveal several interesting scale-dependent phenomena. The microswimmers can be dynamically switched between 2D and 3D swimming modes, can be actuated independently from one another, and have multiple bubble oscillation modes that lead to intriguing, well-defined behaviors. They can also be steered to manipulate and assemble microscopic objects with high precision and speed.

RESULTS AND DISCUSSION

The process flow for wafer-scale fabrication of microswimmers is shown in Figure 1 (see Experimental Section for full details). Polystyrene (PS) spheres of the desired size were spin-coated onto a silicon wafer at an appropriate concentration to yield well-separated spheres. A thin film of chromium was then evaporated to imprint the spheres' shape onto the wafer,^{25,26} serving both as a mask for reactive ion etching (RIE) and as a lift-off layer for atomic layer deposition (ALD) of HfO₂. The spheres were then removed and RIE was used to etch holes where the spheres had shadowed the deposition of Cr. With RIE, it was possible to adjust the shape of the resulting holes from conical (etching faster in the center than at the edges) to cylindrical to approximately spherical by simply changing the etching parameters. In order to obtain cup-shaped holes, low etching pressures (~40 mTorr) and medium powers (100-150 W) in a SF_6/O_2 plasma were used, giving an etch rate of ~500 nm/min. The Cr was then functionalized with an octadecylphosphonic acid (ODPA) self-assembled monolayer to enable clean lift-off of the ALD HfO2 layer.^{27,28} HfO2 was chosen as the material for the swimmers' shells because of its high density, optical clarity, low toxicity to mammalian cells,² high strength and rigidity, and tolerance to the etching chemistries of Cr and Si/SiO₂. Sonication in a Cr etchant following the ALD step enabled the removal of the HfO₂ and Cr layers on the unshadowed regions of the wafer, and the same RIE recipe that was used to generate the holes was then used to etch the Si sidewalls around the ALD layer and release the cup-shaped HfO₂ swimmers in an upright position. Finally, a 10 nm thick film of nickel was thermally evaporated onto the wafer, which was then cleaned in an air plasma before incubation in perfluorooctyltrichlorosilane (PFOTS) to render

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Figure 2. Behavior of swimmers at the volume resonance frequency. (A) Schematic and time-lapse image of a 3 μ m swimmer, showing selfalignment. (B) Schematic and time-lapse image of a 500 nm swimmer, showing no persistent self-alignment. (C) Predicted and experimental resonance frequencies showing agreement with theory. (D–G) Sequential image series and accompanying cartoons of a 600 nm swimmer pulling, steering, and assembling passive tracer particles.

the surface of the swimmers hydrophobic. At the end of the process, the diameter of the swimmers was slightly larger than that of the template spheres due to undercutting in the RIE step. The finished microswimmers were then scratched off the Si substrate with a water-filled micropipette tip and added to a fluid chamber for actuation. When the hydrophobic swimmers came in contact with water at this point, a bubble of ambient air was trapped inside. Owing to their hydrophobic exterior, they tend to float at the air-water interface, but tapping the wafer gently to agitate the liquid allowed the swimmers to sink into the liquid. As a proof of concept, we synthesized microswimmers templated from 3 μ m, 1 μ m, 600 nm, 500 nm, and 350 nm diameter polystyrene spheres. The methods used to acoustically actuate and magnetically steer the microswimmers are described in previous reports and are summarized in Figure 1G.^{19,20,22}

Following our earlier report on larger swimmers of similar shape,²² we set out to test the scaling relation for the resonant volume oscillation frequency of cylindrical bubble swimmers:

$$f_{0} = \frac{1}{2\pi} \left(\frac{\kappa P_{0}}{\rho (L - L_{b}) L_{b}} \left(1 + \frac{4\gamma L_{b}}{\kappa P_{0} a^{2}} \right) \right)^{1/2}$$
(1)

Here κ is the adiabatic index (~1.4), P_0 is the static pressure inside the bubble, ρ is the fluid density, L and L_b are the length of the cavity and bubble, respectively, γ is the surface tension (0.07 N/m) on the bubble surface, and a is the radius of the bubble. Due to the optical clarity of the shell material used and the reflectivity of the solid-air-water interfaces, it was possible to measure the size of the bubble directly by using optical microscopy (Figure S1). Although this became more difficult at swimmer sizes smaller than 1 μ m, we could still obtain reasonable values for the resonance frequency, which matched well with eq 1 (Figure 2C). Overall, we find agreement within a few percent between the experimental and predicted resonance frequencies, even for swimmers with more tapered ends. Thus, eq 1 provides a quick and convenient method for determining the primary resonance frequency of arbitrarily shaped bubble swimmers, at least down to dimensions of 500 nm. So far, our attempts to use this or other fabrication methods (including successful electrodeposition and ALD in anodic alumina templates) to generate functional swimmers below 500 nm have been unsuccessful. It should also be noted that, although swimmers fabricated on one wafer operate at approximately the same resonance frequency, minor inhomogeneities in size, shape, and the degree of hydrophobicity can change the size and shape of the bubble, leading to a degree of inhomogeneity in the resonance frequency and behavior among swimmers of the same batch, within a few tenths of a megahertz (shown as error bars in Figure 2C). Additionally, as shown in Figure 1B, particle dimers and multimers can result in twinned swimmers, which display anisotropic spinning behavior. It is unclear whether

there are separate bubbles trapped in each side or one large bubble in this case.

As noted in our previous report, both micrometer- and submicrometer scale swimmers are significantly attracted to the substrate at their primary resonance frequency, a consequence of the secondary Bjerknes force. This is especially evident for swimmers larger than 1 μ m, where vertical self-alignment is always seen, orienting the swimmer with its open end pointing toward the substrate (Figure 2A). Although this effect is also seen at 1 μ m and smaller sizes, Brownian forces become more dominant at that length scale and prevent the swimmers from achieving a steady orientation unless they are maintained in the vertical position with a magnetic field, which acts on the ferromagnetic Ni film inside the swimmer. As noted previously,²² the vertical self-alignment of the swimmers can be attributed to the fact that the Bjerknes force is strongest at the bubble interface and therefore results in a net torque around the center of mass of the swimmer. However, for smaller swimmers, both the Bjerknes force and the moment arm (i.e., the distance between the point of application of Bjerknes force and the center of mass of swimmer) are smaller, resulting in less torque on the swimmer. In this size regime, they typically take random walks on their side unless steered magnetically in a specific direction (Figure 2B). For 1 μ m and smaller swimmers, alignment perpendicular to the substrate and constrained actuation is not seen at any frequency below the volume resonance. The 500 nm swimmers appear to be in a regime where the secondary Bjerknes force is too weak to hold them to the substrate at any frequency, and if they are aligned vertically, or are randomly oriented in the absence of a magnetic field, they become free 3D swimmers. However, at 500 nm size, they are still easily steered in 2D and 3D by changing the orientation of an applied magnetic field, either down into the substrate or up and away from the substrate, respectively (Movie S1).

At their volume resonance frequencies, the swimmers can be propelled at high speeds (up to 1110 μ m/s, 306 μ m/s, 204 μ m/s, and 77 μ m/s for 3 μ m, 1 μ m, 600 nm, and 500 nm swimmers, respectively), even at low piezoelectric driving voltages. For these experiments, we chose a 10 MHz PZT transducer, which has its maximum power in the middle of the range of the volume resonance frequencies for 500 nm to 3 μ m swimmers. Because of the variation in transducer efficiency at different frequencies, we were not able to measure the pressure dependence of swimmer speeds quantitatively. Nevertheless, we find that their speed increases monotonically with input voltage over at least one decade of applied power and that their speed at a given applied voltage also scales with size (Figure S3). Of particular interest is the observation that the 600 nm swimmers are actually propelled backward, a marked departure from our expectation that the swimmers should move with their closed ends forward. When these swimmers are tilted on their side with an applied magnetic field, they always move with their open-end leading; but when they are oriented perpendicular to the substrate, typical closed-end forward swimming is seen, although the optical resolution at this length scale may be misleading. From scanning electron microscopy (SEM) images (Figure 1D), one can see that the likely source of this unusual swimming behavior is a lip of residual oxide, which is likely a defect across this batch of swimmers, leading to this interesting swimming behavior at every frequency (Movies S2 and S3), which will be studied in more detail in future work.

Additionally, we find that sub-micrometer bubble swimmers are particularly easy to steer in order to manipulate and assemble microscale objects without perturbing their surroundings. As a proof of concept, we compared 3 μ m and 600 nm swimmers for both pushing and pulling silica microspheres (Figures S4 and 2D-G, respectively). At low input voltages, that is, 50 mV_{pp} for 3 μ m swimmers, the secondary Bjerknes force on the silica tracer particles is small, and the swimmer is able to push the tracer particles without visibly perturbing their surroundings or dragging tracers behind them (Figures S4 and S5 and Movies S4 and S5). At higher input voltages, the secondary Bjerknes force becomes stronger, and the swimmers are able to attract and drag microscopic objects, assembling and moving several at once (Figure 2D-G, Movies S2 and S6). Given that they are not held to the substrate by the secondary Bjerknes force, we find unsurprisingly that the 500 nm swimmers do not, within the limits of our observations, attract or drag microscale tracer particles. With the large difference between their primary resonance frequencies, two swimmers of different sizes can be actuated independently of each other in the same experiment and thus controlled independently (Figure S6 and Movie S7).

In exploring the frequency dependence of microswimmer speeds, we discovered a family of propulsion modes that can be used to manipulate swimmer behavior by simply changing the driving frequency. As described in detail in the fluid mechanics literature, oscillating microbubbles have a number of resonant modes in addition to their well-defined primary, or volume, resonance.^{30–33} There exist nonlinear and shape oscillation modes that cause the swimmers to take different well-defined paths from their starting position based on the nature of the oscillation. These shape oscillations have been described using eq 2,³³

$$\omega_n = \sqrt{\left((n-1)(n+1)(n+2)\frac{\gamma}{\rho R^3}\right)}$$
(2)

which predicts that they should occur at frequencies higher than the volume resonance of the bubbles. In agreement with the observations of Rogers and Neild,³³ we observe attraction of the bubbles to the substrate and to microscale objects at their volume resonance. Also in agreement with their observations, we find that the shape resonance modes in fact appear at frequencies *below* the primary oscillation mode, especially at half the primary resonance frequency. As noted above, the secondary Bjerknes force traps the swimmers at the substrate due to close, in-phase oscillations of the bubble with its acoustic reflection. We can estimate the secondary Bjerknes force experienced by a bubble near the substrate as³⁴

$$F_{\rm SB} \approx \frac{\rho_{\rm f}}{4\pi d^2} \langle \dot{V}^2 \rangle \tag{3}$$

where *d* is the distance between the centers of the real and the imaginary bubble (equal to twice the distance of bubble center from the wall), *V* is the volume of the bubble, and \dot{V} is the time rate of change of the volume of the bubble. Under conditions of volume resonance, this can be further expressed as

$$F_{\rm SB} \approx \frac{\rho_{\rm f}}{4\pi d^2} \langle \dot{V}^2 \rangle \approx \frac{\rho_{\rm f}}{4\pi d^2} (4\pi a^2 \dot{a})^2 \tag{4}$$

where *a* is the radius of the bubble. Since the streaming force is known to scale as $F_{\text{streaming}} \approx \varepsilon^2 \rho_{\text{ff}} t^4 f^2$, the relative dominance of these forces on one other for volume resonance varies as F_{SB}/t^4



Figure 3. Isotropic, unbound streaming of swimmers leading to different behaviors. (A) Schematic and demonstration of a balanced 3 μ m swimmer being steered at volume resonance. (B) Schematic and sequential images of the same swimmer moving in 3D upon application of a 700 kHz acoustic field. (C, D) Paths of multiple swimmers, 500 nm (C) and 1 μ m (D), displayed as raw tracks for clarity under an isotropic resonance.

 $F_{\text{streaming}} \approx 4\pi \rho_{\text{f}} (a/d)^2$. However, for shape mode oscillations, the time rate of change of the volume of the bubble, \dot{V} is smaller and consequently the attractive Bjerknes force on the bubble is weaker.

Accordingly, we observe the following: at certain fractions of the volume resonance frequency, especially around half, isotropic modes are found that propel the swimmers strongly toward their closed ends but without strong attraction to the substrate. In this mode, the object is a free swimmer and can be steered precisely in 3D, as well as switched back and forth between constrained 2D and free 3D swimming (Figure 3A,B). As noted above, the 600 nm swimmers move with their open end forward in both their 2D and 3D swimming modes. Additionally, between these isotropic modes there exist various anisotropic streaming modes, which act to propel the swimmers in different directions when they are still attracted to the substrate, or to take well-defined, time-periodic paths in 3D (Movies S3, S8, and S9). As shown in Figure 3A,B, these observations with smaller swimmers prompted us to reexamine the behavior of our previously reported 5 μ m × 8 μ m

swimmers²² that were fabricated by two-photon direct writing techniques. We find that the tail fins we had added previously to lower the attraction to the substrate were a requirement for free swimming at the volume resonance frequency, but by activation of the swimmers in a shape resonance mode at around 480 kHz, they detached easily from the substrate and could be steered magnetically in 3D (Figure S7 and Movie S10).

Some of this behavior is similar to the phenomena described by Ahmed et al.,³⁰ where off-resonance modes in larger bubble systems caused out-of-plane oscillations that led to useful behaviors. Since the swimmers are free to travel in all directions in the absence of a strong secondary Bjerknes force or when they are displaced from the substrate, these outof-plane and shape oscillations manifest themselves as unique swimming behaviors. They are capable of breaking the symmetry of the "standing" position and of propelling the swimmers autonomously, or along well-defined paths such as closed loops or spirals. In the case of the 3 μ m swimmers, because $F_{\rm B}$ scales as R^4 , we see that at resonances close to the



Figure 4. Anisotropic streaming of swimmers and resulting phenomena. (A) Schematic diagram and trajectory of a 3 μ m swimmer being steered by changing the acoustic frequency. (B) Schematic and trajectory of a suspended 3 μ m swimmer moving in a 3D spiral upon application of a 1.18 MHz acoustic field. (C) Demonstration of a 600 nm swimmer dynamically switching from steered, 2D swimming to autonomous spiraling. (D) Trajectories of multiple 1 μ m swimmers along separate well-defined paths upon application of an anisotropic streaming frequency. (E, F) 2D Slice plots of streaming field around swimmer for symmetric (E) and asymmetric (F) placement near the wall.

volume resonance, the swimmer is still strongly attracted to the substrate but is propelled asymmetrically, even though $F_{\rm B}$ is still sufficiently strong to confine it to 2D trajectories (Figure 4A and Movie S11). For 3 μ m swimmers at frequencies very close to the volume resonance, these minor anisotropies drive the swimmer in an arbitrary direction but allow it to still attract other objects and even be steered by them as the streaming pattern is blocked by their presence; we demonstrate the autonomous assembly of 3 μ m silica particles in Movie S12. At 700 kHz, half the volume resonance frequency, we see that these swimmers do typically self-align with the substrate but are then detached from it and propelled into the third dimension. By then activating at an intermediate resonance, the unconfined, anisotropic swimming behavior can be observed as a 3D spiral, similar to behavior seen in some electric field driven colloids (Figure 4B).^{35,36} These behaviors are observed in swimmers of every size studied, suggesting that the effect is intrinsic to this size and shape regime or that all the swimmers are in some way anisotropic in shape. This effect enables the operator to dynamically tune among different autonomous and magnetically directed behaviors (Figure 4C). Unlike any other swimmer of this type, this can be done with cup-shaped objects without any physical modification and suggests possibilities for tunable, even fully autonomous motion in "swarms," which is demonstrated at the 1 μ m (Figure 3D) and 500 nm (Figure 3C) scales. At anisotropic resonances, the swimmers can be steered in different directions or along well-defined paths (Figure 4A,D).

We can also reproduce swimmer behavior in numerical simulations by instituting some static asymmetry in our model. The asymmetry drives out-of-plane oscillations that may be exaggerated in certain shape modes, giving rise to the oscillatory motion. Figure 4E,F shows the numerical simulation of the streaming flow patterns around a swimmer placed symmetrically and asymmetrically near a wall, respectively. As expected, the streaming patterns demonstrate perfect spherical symmetry around the axis of the swimmer for the symmetric case. In contrast, for the asymmetric placement of a swimmer near the substrate, the symmetry in the streaming pattern is disturbed, which can result in nonzero torque around the transverse axes of the swimmer. We postulate that their directional motion may have to do with weak standing waves or acoustic field anisotropies around the swimmers, leading to different directionalities at different frequencies. If the origin of this phenomenon can be understood in more detail, it may be possible to rationally design systems in which multiple swimmers can be steered very precisely with only the application of a multiplexed acoustic field.

CONCLUSIONS

By exploiting both shape and volume resonances, excitation at specific frequencies can be used to alter the trajectories of one or many swimmers at once. A key consequence of this, which is relevant to fundamental studies of autonomous movement and collective phenomena, is that bubble-based swimmers are can be driven into autonomous 3D motion at approximately half of their volume resonance (Figure 3). Exploiting both kinds of modes to switch between 2D and 3D trajectories may enable the combination of acoustic propulsion with chemical, photochemical, and magnetic signals for actuation and steering, as well as for hybrid and collective effects such as chemotaxis,^{37,38} rheotaxis,^{16,39} swarming, and predator-prey behavior.^{14,38} Although their speeds are lower at non-volumeresonance modes, the swimmers can still achieve speeds upward of 100 μ m/s, which is significantly faster than other synthetic swimmers in the same size regime. When they are far from any boundaries, intermediate modes drive the swimmers in time-periodic fashions ranging from spirals to closed loops (Figures S7 and S8). By tuning of the frequency and amplitude of the acoustic excitation, bubble swimmers of different sizes can be driven in a number of interesting and potentially useful ways, which can be designed based on a desired application.

In summary, we have demonstrated a simple fabrication method for acoustically powered bubble swimmers that are below the size limit of two-photon direct writing and can be quickly fabricated in large quantities. While these swimmers confirm and expand upon observations made in previous reports, we have extended their movement into an autonomous regime. At their volume resonance, these are the smallest swimmers that can move at speeds exceeding 100 μ m/s, and they can be used to manipulate and assemble microscopic objects. Below their volume resonance frequency, shape modes can be used to steer swimmers in 3D with no physical modifications or to actuate them in a time-periodic fashion that may be useful and interesting in studies of active matter. Future work will focus on combining these swimmers with chemical and light actuation to create hybrid nanovehicles capable of carrying out well-defined tasks, exploring the applications of fast nanoscale motors in biology and physics, examining their collective phenomena, and studying in depth the mechanism driving their behaviors.

EXPERIMENTAL SECTION

Materials and Instrumentation. Polystyrene microspheres were purchased from Alfa Aesar (1 μ m, 500 nm, catalog numbers 42715 and 42714, respectively), Fisher (600 nm, catalog number 09980035), or Polysciences (3 μ m, catalog number 17134-15). Prime grade silicon wafers were purchased from Addison Engineering Inc. (4P-006, (100), $R = 25.2-42.5 \Omega$ and used as received. 1H,1H,2H,2H-Perfluorooctyltrichlorosilane (97%) and octadecylphosphonic acid (97%) were purchased from Alfa Aesar. Thermal and e-beam evaporation processes were performed in Lesker PVD-75 systems, RIE was performed in an Oxford Plasmalab 80+, and ALD was performed in a Cambridge NanoTech S200. Scanning electron microscopy was performed in a JEOL 7500F HRSEM with EDAX EDX mapping. Swimmer experiments were carried out on an Olympus BX-60m microscope with a Flea-3 PointGrey camera and accompanying software. Ultrasound waveforms were generated using a Siglent SDG2122X function generator hooked to two wires: one was soldered to the back of a piezoelectric disc (PZT, purchased from Steminc, catalog number SMD10T02F412ST), while the other was embedded in a colloidal silver epoxy used to fix the transducer to a silicon wafer (for good acoustic transmission). Two 60 μ m thick Kapton polyimide spacers with a 5 mm inner diameter and a coverslip were used to trap about 6 μ L of water. The acoustic substrates were always cleaned in an air plasma prior to acoustic manipulation, performed in a Harrick Plasma PDC-001-HP, also used to clean samples at multiple steps in the synthesis. Magnetic fields were generated with a cylindrical magnet (DEE, K&J Magnetics INC. USA, 0.5 T at surface). Video analysis was performed using ImageJ and Tracker software

Swimmer Fabrication. Polystyrene microspheres of appropriate sizes were purchased from Alfa Aesar. Twenty microliters of a 2.5 wt % microsphere solution was diluted with 400 μ L of DI water and added to a fleshly plasma-cleaned silicon wafer or piece spun at 700 rpm to yield well-separated spheres. Then, a 50 nm thick chromium layer was e-beam evaporated onto the wafer to serve as a hard mask for RIE, with holes in the Cr layer where the spheres were; the spheres were dissolved in N-methyl pyrrolidone (NMP). RIE was then performed using 10 sccm O₂ and 50 sccm of SF₆ at 50 mTorr and 150 W power, giving an etch rate of 500 nm/min and straight sidewall etching with a rounded bottom. The chromium was then protected with an octadecylphosphonic acid (ODPA) SAM by first treating for 2 min in a plasma cleaner, then soaking for at least 2 h in a 1 mM solution of ODPA in toluene. This prevents significant buildup of ALD material on the chromium for easy removal later. ALD was used to deposit HfO₂ into the pores conformally, typically 600 cycles with tetrakis(dimethylamido)hafnium(IV)/H2O with 20 s purge times at 150°, which results in a 60 nm thick shell (~0.1 nm/cycle deposition), and the chromium mask was removed in chromium etchant 1020 from Transene, which typically requires 45 min of sonication in this solution. Finally, the same RIE recipe that was used to make the hole was used to remove the sidewalls and free the structures, as HfO₂ is resistant to the etching process. Finally, 10 nm

of nickel was thermally evaporated onto the surface of the wafer, followed by 2 min of air plasma cleaning treatment before a 15 min incubation in a PFOTS vapor at 85°. This yields hydrophobic swimmers that can be scratched from the surface with water in a micropipette tip and added to an acoustically active substrate for manipulation.

Swimmer Actuation. The acoustic manipulation substrate is described above and always plasma cleaned before use to make the surface hydrophilic (prevents sticking). A micropipette tip is filled with 6 μ L of DI water, which is deposited in a droplet to the wafer containing the swimmers. By scratching of the surface within the droplet with the tip of the micropipette and pulling up the entire volume, the swimmers are suspended within the tip and can be added to the acoustic substrate. By sweeping of the frequency of an arbitrary waveform generator hooked to the leads of the transducer, the resonance frequency of the swimmer can be quickly found, especially by calculation of its predicted resonance first. The swimmers are free to move to user defined positions by the application of a magnetic field (described above), which is tilted in the empty space below the stage of the microscope. This steers the swimmers, but they can also move autonomously, as described above.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03311.

Methods for numerical simulations of bubble motor streaming and supplemental figures illustrating the size and frequency dependent properties of the bubble swimmers (PDF)

Movie of 500 nm swimmer propelled and steered in 2D at 17.91 MHz and 1.5 V_{pp} (AVI)

Movie of 600 nm swimmer exhibiting ultrafast motion and precision steering at 10.9 MHz and 2 V_{pp} , capable of pulling silica microparticles (AVI)

Movie of 600 nm swimmer switched dynamically between curly (8.01 MHz) and straight motion (11.21 MHz) at a constant driving voltage of 2.1 V_{pp} (AVI)

Movie of pushing mode of 3 μ m swimmers at 50 mV_{pp} and 1.45 MHz (AVI)

Movie of pushing mode of 1 μ m swimmers (AVI)

Movie of pulling mode of 3 μm swimmers at 1.45 MHz and 150 mV $_{\rm pp}$ (AVI)

Movie of independent manipulation of two swimmers at two different frequencies, first 8.97 MHz and second 1.55 MHz, at a driving voltage of 200 mV_{pp} (AVI)

Movie of closed loop motion of 1 μ m swimmers at 4.89 MHz and 400 mV_{pp} (AVI)

Movie of spiral motion of a suspended 3 μ m swimmer at 1.18 MHz and 100 mV_{pp} (AVI)

Movie of 3D photolithographically printed swimmer (5 μ m × 8 μ m) swimming in 3D at 480 kHz and 500 mV_{pp} (AVI)

Movie of acoustically steered motion of 3 μ m swimmer bound to the surface, frequency swept from 800 to 1000 kHz at 500 mV_{pp} (AVI)

Movie of autonomous assembly of silica microspheres at a slightly anisotropic mode, driving the swimmer to move in one direction and pick up particles along the way, driven at 1.49 MHz and 600 mV_{pp} (AVI)

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Author Contributions

J.M.M. and T.E.M. conceived of the experimental concept. J.M.M. and J.M.B. carried out and characterized swimmer synthesis. J.M.M. analyzed and interpreted experimental data and swimmer properties. N.N. designed the numerical model and conducted simulations of streaming fields around swimmers. J.M.M., N.N., and T.E.M. wrote the manuscript, and all authors contributed to the final manuscript.

Notes

The authors declare no competing financial interest.

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