Electronic Supplementary Information

Acoustic Microcannons: Towards Advanced Microballistics

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1. Supporting Video Description

Video S1. Acoustic droplet vaporization of PFC emulsions after applying an US pulse to a PFC/silica nBs-loaded Mc (left) and control Mc without PFC emulsion (right).

2. Supporting Figures

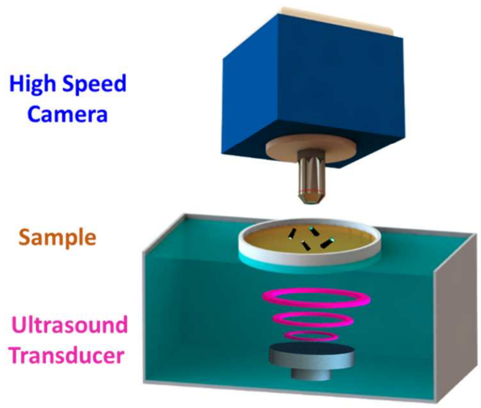

Figure S1. Schematic of the Ultrasound Set up: The operation consists of a piezoelectric transducer submerged in water, a petri dish which contains the sample, and the firing of the microcannons is recorded by a high-speed camera on top.

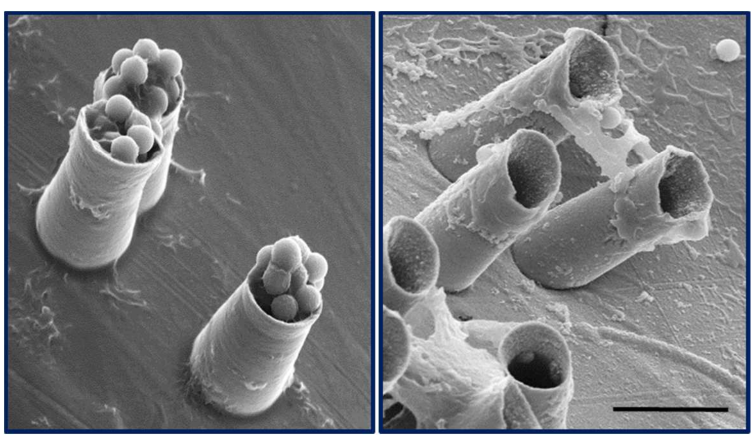

Figure S2. SEM images showing multiple nanobullet-loaded Microcannons before (left) and after (right) the Ultrasound-triggered firing (scale bar, 5 μm).

3. Modeled Speed of Microcannon and Nanobullet

Table S1. Geometry, design and density parameters for calculations.

	MICROCANNON	NANOBULLET
Length and Radius	13 μm and 5 μm	1 μm
Mass (kg)	2.72×10^{-13} kg	9.24×10^{-15} kg
k (kg/s)	8.8×10^{-8} kg/s	1.89×10^{-8} kg/s
V_0 (m/s)	**9.0**	**42.2**

The Mc displacement was captured using high-speed camera with an average speed for Mc (recording at 109,500 frames per second), by considering the change in position of the microcannon in the time considered lead to 1.05 ± 026 m/s average speed of the microcannons. The visualization of nB firing presents a technological challenge to image and measure its average speed, in part due to their small size and high speed. Therefore, a theoretical approach was used to predict how the nB will react upon ultrasound (US) triggered firing of a Mc free in solution, taking into consideration the forces acting on the MC, due to both Mc and nB are exposed to the same propulsion thrust of the PFC explosion. The calculation of an approximation of the nB speed was carried out considering that the force is only applied to one nB for simplicity. In order to know which forces dominate in this movement, whether viscous or inertial forces, the Reynolds number was calculated as follows:

$$R_e = \frac{\rho v L}{\mu} \qquad \textit{Equation S1}$$

Re is the Reynolds number that gives information about the type of flow of the object under study. Since the media of study is water and considering ρ, density of the water, 10^3 kg/m^3, μ, viscosity of the water, 1.0×10^{-3} kg m^{-1} s^{-1}, v the speed of the Mc 1.05 m s^{-1} and L, the length, in average 13 μm , Re was calculated to be 13.7.This low Reynolds number suggests that the Mc moves in a laminar flow where the viscous forces dominate the motion and the inertia of the microscale objects is no longer important. This fact was previously explored for other nano/micromachines. [1] Thus, the Mc moves due to the vaporization of the PFN and the expansion of the gas on the cavity, being this one the driving force, then, the primary force is the hydrodynamic drag force, the rest of the forces involved will not be considered. Furthermore, the nB is also experience by the same force, drag force. Consequently, the force applied to the Mc, F_{Mc} is the same that the one applied to the nB loaded in the Mc. The force of the nB will be defined as F_{nB}.

$$\vec{F}_{Mc} = \Sigma n_{nB} \cdot \vec{F}_{nB} \qquad \textit{Equation S2}$$

This force, defined by Stokes' law [2] is proportional to the velocity being the constant, k dependent on the shape and size of the object under study, and it is the responsible of the movement of both Mc and nB, then, the speed equation can be obtained from the integration of the force term being m the mass for the object. The Equation 1 expresses the speed of an object (Mc or nB), being the instantaneous and the initial speeds, v and v_0; the mass of the object, m; the drag force constant, k; and t the interval of time under study

$$F = -m\frac{dv}{dt} = kv \ \ ; \ \ \frac{dv}{v} = -\frac{k}{m}dt \ \ ; \ \ \int_{v_0}^{v} \frac{dv}{v} = \int_0^t -\frac{k}{m}t$$

$$Ln\left(\frac{v}{v_0}\right) = -\frac{k}{m}t \ \ ; \ \ v = v_0 e^{-\frac{kt}{m}}$$

$$v = v_0 e^{-\frac{kt}{m}} \qquad \textit{Equation 1.}$$

This *Equation 1* shows that the speed exponentially drops from the initial speed (v_0) achieved from the vaporization of the PFC. Considering that the speed is the rate of change in the position, the initial velocity of the Mc could be further described as follows:

$$v = \frac{dx}{dt} = v_0 e^{-\frac{kt}{m}} \ \ ; \ \ \int_0^x dx = \int_0^t v_0 e^{-\frac{kt}{m}} dt \ \ ; \ \ \Delta x = -\frac{1}{k/m} v_0 (e^{-\frac{kt}{m}} - 1)$$

Consequently, *Equation 2* defines the initial the Mc considering the hydrodynamic drag force the one responsible for the movement. This equation depends on the displacement that the Mc moves in a certain interval of time. Thus, *Equation describes the* Mc movement.

$$v_{0_{Mc}} = \frac{k_{Mc}\,\Delta x}{m_{Mc}\left(1 - e^{-\frac{k_{Mc} t}{m_{Mc}}}\right)} \qquad \textit{Equation 2}$$

The speed calculations herein estimated must be considered as an approximation because of the important instrumental limitations. Moreover, the measurement of the distance that the Mc moved in a short period of time should also be considered not completely accurate since it only possible to capture the bullet for 5 or 6 frames under 109,500 frames/s videos. For calculation of the drag factor, the microcannon was modeled with a cylindrical shape, as in previous papers of nano/micromotors fabricated with the same template-based methodology, [3] being the k factor obtained from the *Equation 3*. Considering the dimension of the Mc, L, length 13 µm, R, radius of 5 µm, k_{MC} was calculated to be 8.8 x 10^{-8} kg/s.

$$k_{MC} = \frac{2\pi\mu L}{Ln\left(\frac{2L}{R}\right) - 0.72} \qquad \textit{Equation S3}$$

The mass of each Mc was calculated considering the mass of the gold deposited, the graphene mass contribution was considered negligible o. For that, as the charge, Q, deposited was 1 C, and considering 100% efficiency for the electrodeposition, the mass of gold deposited was estimated using the gold molecular mass, M_{mol}, the number of electrons involved in the electrodeposition, n, 3 for gold and the Faraday constant, F, 96485 C mol^{-1}.

$$W_{metal} = \frac{M_{mol}\,Q}{n\,F} \qquad \textit{Equation S4}$$

The mass of gold deposited was 68 mg, considering that there are around 2.5 x 10^{6} pores in each membrane template, the mass of each microcannon was estimated to be around 2.72 x 10^{-13} kg. The mass contribution of graphene was considered negligible. The bullets are subjected to the same total force than the Mc, however, the sphere shape of the nB (silica particle) make that the drag constant, k_{Nb} be calculated as follows,

$$k_{NB} = 6\pi\mu R \qquad \textit{Equation s5}$$

Considering for a water medium, μ, the water viscosity (10^{-3} kg/m s) and R, the radii of the nB sphere, 1.0 μm, the drag constant, k had a value of k_{NB}= 1.89 x 10^{-8} kg/s. Knowing that the density of the silica particles is 2.2 g/cm^3 and the volume of a sphere, 4.2 x 10^{-18} m^3, thus the mass of a particle is 9.24 x 10^{-15} kg.

Another approximation should be required since the Mc and nB are propelled by the same force, drag force, which causes the movement of both objects, thus the initial velocity of the bullet was 42.2 m/s around 5 times faster than the Mc. This approximations were carried out considering the force is only applied to a single nB for simplicity, future studies will focus on developing a more precise theoretical simulation considering the greatest fraction of space occupied by spheres defined by Gauss to be a close-packing of equal spheres with a value of $\frac{\pi}{3\sqrt{2}}$ the maximum number of spheres which could be loaded will be 45 spheres.

References

1. Gibbs, J. G.; Zhao, Y.P. Design and Characterization of Rotational Multicomponent Catalytic Nanomotors. *Small*, **2009**, 5, 2304.

2. Happel, J.; Brenner, H. Low Reynolds Number Hydrodynamics with Special Applications to Particulate Media. Englewood Cliffs, NJ: Prentice-Hall, **1965**.

3. Li, J.; Huang, G.; Ye, M.; Li, M.;Liu, R.; Mei, Y. Dynamics of Catalytic Tubular Microjet Engines: Dependence on Geometry and Chemical Environment. *Nanoscale*, **2011**, 3, 5083.

4. Kagan, D.; Benchimol, M. J.; Claussen, J. C.; Chuluun-Erdene, E.; Esener, S.; Wang, J. Acoustic Droplet Vaporization and Propulsion of Perfluorocarbon-Loaded Microbullets for Targeted Tissue Penetration and Deformation. *Angew. Chem. Int. Ed.* **2012**, 51, 7519-7522.