High-Speed Propulsion of Flexible Nanowire Motors: Theory and Experiments (Electronic Supplementary Information)

On Shun Pak[‡],¹ Wei Gao[‡],² Joseph Wang,² and Eric Lauga¹

¹Department of Mechanical and Aerospace Engineering,

University of California San Diego, 9500 Gilman Drive, La Jolla CA 92093-0411.

²Department of Nanoengineering, University of California San Diego, 9500 Gilman Drive, La Jolla CA 92093-0448.

I. EXPERIMENTAL SECTION

A. Synthesis of the flexible Ni-Ag nanowires

The nanowire motors were prepared using a common template-directed electrodeposition protocol. A silver film was first sputtered on one side of the porous alumina membrane template containing 200nm diameter cylindrical pores and 25mm diameter (Catalog No 6809-6022; Whatman, Maidstone, U. K.) to serve as a working electrode. The membrane was then assembled in a plating cell with an aluminum foil serving as a contact for the sputtered silver. Copper was electrodeposited in the branch area of the membrane from a 1M $CuSO_4 \cdot 5H_2O$ solution, using a charge of 8C and a potential of -0.9V (vs. Ag/AgCl reference electrode, along with a Pt-wire counter electrode); subsequently, gold was plated next from the commercial gold plating solution (Orotemp 24 RTU RACK; Technic Inc.) at -0.9V (vs. Ag/AgCl), using a charge of 0.5C, which was used for protecting the Ni while dissolving the membrane later; nickel was deposited from a nickel plating solution containing $20gL^{-1}$ NiCl₂· $6H_2O$, $515gL^{-1}$ Ni(H₂NSO₃)₂· $4H_2O$, and $20gL^{-1}$ H₃BO₃ at -1.0V (vs. Ag/AgCl) for 6C, finally, silver was plated subsequently at -0.9V (vs. Ag/AgCl) for a total charge of 4.5C using a commercial silver plating solution (1025 RTU @ 4.5 Troy/gallon; Technic Inc., Anaheim, CA). The sputtered silver layer was mechanically removed from the membrane by polishing with 3-4 μ m alumina particles; and the copper sacrificial layer was dissolved using 20% HCl and 0.5 M CuCl₂. The membrane was then dissolved in a 3M NaOH solution for 30 minutes to completely release the nanowires. The nanowires were collected by centrifugation at 6000 rpm for 5 minutes and were washed repeatedly with nanopure water ($18.2M\Omega cm$) until a neutral pH was achieved. All nanowire solutions were stored in nanopure water at room temperature. Flexibility of the silver segment was achieved by its partial dissolution accomplished by mixing 10μ of the diluted Ni/Ag nanowire solution with 10μ of the 10% hydrogen peroxide solution for 1 minute. The nanowires were then washed on the glass slide using nanopure water (18.2 M Ω ·cm) until a neutral pH was achieved.

B. Characteristics of the nanowire motors

1. Distribution of nanowire lengths

A typical nanowire motor had a total length of 5.8μ m: 1.5μ m-long Ni head and a 4 μ m-long flexible Ag tail, with a 0.3μ m-long Au included (adjacent to the Ni segment) to protect the Ni segment from acid etching during the dissolution of the Cu sacrificial layer, and to allow functionalizing the motor with different types of biomolecules and cargos. The nanowires were electrodeposited in an alumina membrane template, which produced nanowires of very uniform length. After partial dissolution of the silver filament, the total nanowire length would vary slightly. A distribution of the total nanowire length (in sampling 40 nanowires) is shown in Fig. 1.



FIG. 1: Distribution of the total length of nanowires after partial dissolution of the silver segment. (Sample size, 40)

2. Effective nanowire motors

Millions of nanowires can be produced from one single membrane. However, very dilute samples were used in our experiment to avoid the magnetic aggregation of nanowires. A typical number density of nanowires in our experiment was ~ 50 per μ L. Around 40% of nanowires worked effectively in a sample drop of 20μ L. Typical sedimentation time of a nanowire was less than 1 minute. The speed measurement was taken when the image of the nanowire stayed focused under the microscope, indicating that the nanowire had reached an equilibrium position. The nanomotors could function throughout the entire process of an experiment (typically 20 minutes long), until the solution dried up. The same nanowire motor maintained similar propulsion characteristics before and after repeated on/off of the magnetic field (indicating the possibility of no plastic deformation along the silver filament). The speed was consistent for different periods under continuous actuation of the same nanomotor.

C. Magnetic driven movement

The magnetic field was achieved by a triaxial Helmholtz coil, consisting of one homogeneous rotating magnetic field a constant magnetic field which is perpendicular to the axis of the rotating one. The magnetic induction was measured using a Gaussmeter (Model 475 DSP Gaussmeter, Lake Shore Cryotronics, Inc, Westerville, OH). The locomotion of nanoswimmer in human serum samples were carried out by mixing directly with the nanomotor solution (1:1 ratio).

D. Motion of the Ni segment as a function of the actuation frequency

In this paper, we confine our studies to the regime where the nanowire follows synchronously the precessing magnetic field, rotating at the same angular frequency as the magnetic field about the z-axis. The motion of the magnetic field is assumed to be completely slaved to the magnetic field (the viscous force is subdominant) throughout the range of frequency explored in the experiments (0–35Hz). To validate this assumption, we measure the motion of the Ni head: the frequency of rotation and the radius (amplitude) of the cone swept by the Ni head in Fig. 2 for a typical magnetic field setup ($H_1 = 10$ G and $H_0 = 9.5$ G). In Fig. 2a, the rotational frequency was essentially indistinguishable from the actuation frequency (slope ≈ 1), except a slight difference at high frequencies (an actuation frequency of 30Hz drove the Ni head to rotate at 29Hz). In addition, in Fig. 2b, the radius of the cone swept by the Ni head



FIG. 2: Motion of the Ni segment as a function of the actuation frequency, with $H_1 = 10$ G and $H_0 = 9.5$ G. (a) Frequency of rotation of the Ni segment. (b) Radius (amplitude) of the cone swept by the Ni segment.

attained an almost constant value of 1.3μ m over all frequencies, with only a slightly decaying trend. Based on these observations, the assumptions made in our geometrical model are considered to be valid.

E. Equipment

Template electrochemical deposition of nanowires was carried out with a CHI 621A potentiostat (CH Instruments, Austin, TX). Scanning electron microscopy (SEM) images were obtained with Phillips XL30 ESEM instrument using an acceleration potential of 20kV. An inverted optical microscope (Nikon Instrument Inc. Ti-S/L100), coupled with a 40x objective, a Photometrics QuantEM 512/SC camera (Roper Scientific, Duluth, GA) and a MetaMorph 7.6 software (Molecular Devices, Sunnyvale, CA) were used for capturing movies at a frame rate of 30 frames per sec. The speed of the nanomotors was tracked using a Metamorph tracking module and the results were statistically analyzed using Origin software.

II. ESI VIDEO CAPTIONS

- ESI Video 1 : Two nearby Ni-Ag nanoswimmers under the actuation of the external magnetic field (20Hz). The scale bar is 10μ m.
- ESI Video 2 : Motion of Ni-Ag nanowire swimmer upon different frequencies (5-30Hz). The scale bar is $10\mu m$.
- ESI Video 3 : Motion of Ni-Ag nanowire swimmer ($U = 15 \mu m/s$) in an untreated human serum sample. The scale bar is $5 \mu m$.