Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Hydrogen-peroxide-fulled platinum-nickel-SU-8 microrocket with steerable propulsion using eccentric nanoengine

Liangxing Hu,[a] Kai Tao,[a] Jianmin Miao*[a] and Gerhard Grüber[b]

[a]School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b]School of Biological Sciences, Nanyang Technological University, 60 Nanyang Drive, Singapore 637551, Singapore

*Corresponding authors: *mjmmiao@ntu.edu.sg*

Equipment:

1. Advanced Vacuum/vision 310 MK II: gas 1 5% SiH_4/N_2 and flow rate 160 sccm, gas 2 N_2O and flow rate 1420 sccm, gas 3 N_2 and flow rate 240 sccm, pressure 800 mTorr, temperature 300 °C;
2. Fumehood for KOH etching: temperature 120 °C;
3. Karl Suss Deltta VPO Primer: temperature 100 °C;
4. Cee Spin Coater: speed 5000 rpm, spin duration 30 s;
5. Karl Suss MA56 mask aligner: expose type vacuum, expose time 5 s, power 275W;
6. Fumehood for photoresist development: room temperature;
7. Semitool/PSC-101 drying machine: speed 1600 rpm, spin duration 2 min;
8. Hot Plate/MODEL HP50: temperature 100 °C;
9. Hyper HAD color video camera;
10. Mitatoyo WF microscope: magnification 10;
11. HITACHI S-3500N scanning electron microscope: voltage 5 kV;
12. Magnetron sputter system: gas Ar and flow rate 20 sccm, base vacuum 3 mTorr, power 200W;
13. E-beam evaporator/EDWARDS FL 400: gas N_2, current 25 mA, voltage 4.96 kV, temperature RF, pressure 3.2 mTorr;
14. JEOL JSM-5600LV field emission scanning electron microscope: voltage 20 kV.

Materials:

1. HMDS (purchased from Clariant Pte Ltd, Singapore);
2. Photoresist (purchased from AZ Electronic Materials, Singapore);
3. AZ 300MIF developer (purchased from AZ Electronic Materials, Singapore);
4. N_2 gas (purchased from Soxal, Singapore);
5. Gold (purchased from Analytic Technologies Pte Ltd, Singapore);
6. Nickel (purchased from MOS Group, Singapore);
7. SU-8 (purchased from Teltec Semiconductor Pacific(s) Pte Ltd, Singapore);
8. SU-8 developer (purchased from Teltec Semiconductor Pacific(s) Pte Ltd, Singapore);
9. Acetone (purchased from Avantor Performance Materials, USA);
10. Iso-propyl alcohol (purchased from Avantor Performance Materials, USA);
11. Potassium hydroxide (purchased from Aik Moh Paints & Chemicals Pte Ltd, Singapore);
12. Hydrogen peroxide (purchased from Tee Hai Chem Pte Ltd, Singapore).

Software

1. SEMICAPS 2200C_3 imaging system;
2. Osprey swiftcap video capturing;
3. INCA software;
4. ImageJ.

Derivation of the driving force F_{drive} stemmed from the momentum change

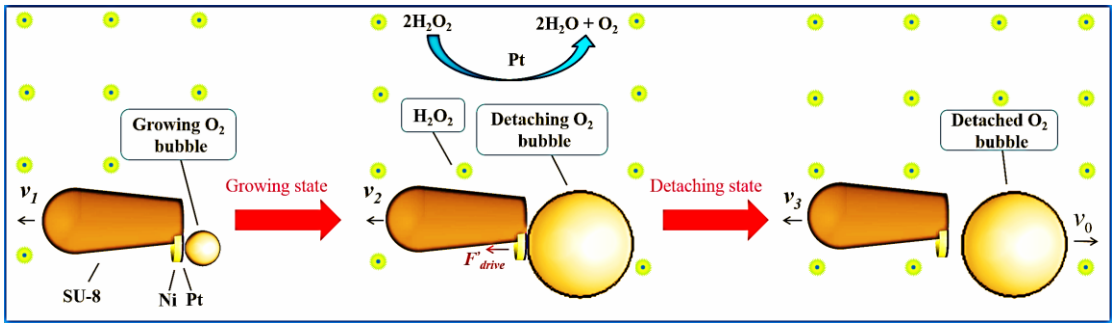
In general, hydrogen peroxide (H_2O_2) catalyzed by platinum (Pt) can be decomposed into water (H_2O) and oxygen (O_2) bubbles.[1,2] During the H_2O_2 decomposition, O_2 bubbles are generated at the surface of eccentric Pt nanoengines of microrockets and detached from microrockets. SI Figure S-1 demonstrates two states of a platinum-nickel-SU-8 (Pt-Ni-SU-8) microrocket-O_2 bubble integral system. In the beginning, O_2 bubbles are generated and attached to the surface of Pt, microrockets and O_2 bubbles have a joint velocity of v_1. The O_2 bubbles grow bigger and bigger, called *growing state*. At this state, microrockets and O_2 bubbles have a same velocity of v_2. After a short period of time of Δt, O_2 bubbles are detached from the rockets, called *detaching state*. After the detachment of O_2 bubbles, the rockets have a velocity of v_3, while O_2 bubbles have a distinct velocity, named v_0. According to the Momentum Conservation Law, one can obtain the following equation

$$(m+\Delta m)v_2 = mv_3 - \Delta m v_0 \quad \text{(SI-1)}$$

$$m(v_3 - v_2) = \Delta m(v_2 + v_0) \quad \text{(SI-2)}$$

where, m is the mass of one single Pt-Ni-SU-8 microrocket, Δm represents the mass of each individual detached O_2 bubble. According to the Momentum Theorem, the driving force F'_{drive} induced by one single detached O_2 bubble can be expressed as

$$F'_{drive} = m\frac{v_3 - v_2}{\Delta t} = \Delta m\frac{v_2 + v_0}{\Delta t} \quad \text{(SI-3)}$$



SI Figure S-1. Schematic diagram for illustrating the generation of the driving force F_{drive} induced by the detachment of O_2 bubbles.

After a period of time of Δt, if N O_2 bubbles are detached from the Pt-surface of one single rocket, the total driving force F_{drive} can be described as

$$F_{drive}=NF_{drive}^{'}=N\frac{\Delta m}{\Delta t}(v_2+v_0) \quad \text{(SI-4)}$$

At steady state, microrockets reach a constant velocity of v, namely $v_1= v_2= v_2 = v$. Hence, one can obtain

$$F_{drive}=N\frac{\Delta m}{\Delta t}(v+v_0) \quad \text{(SI-5)}$$

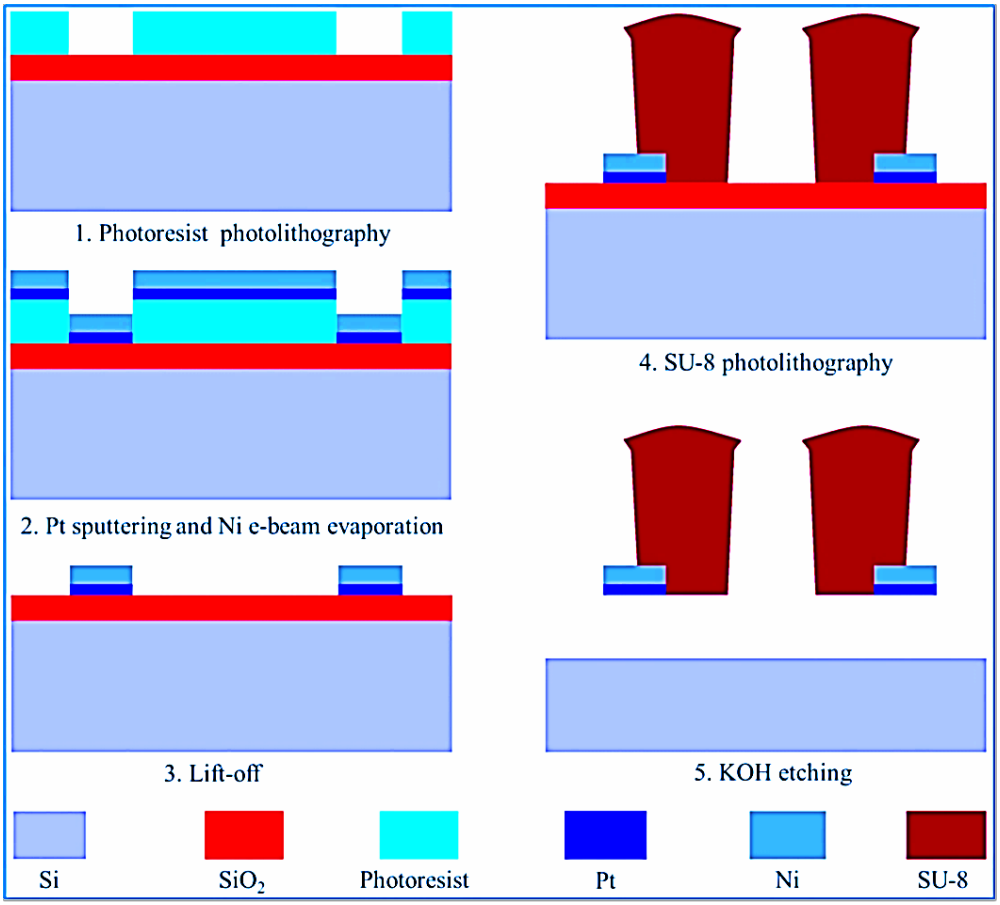
Fabrication of microrockets

A 4-inch silicon (Si) wafer was firstly immersed into sulfuric acid (H_2SO_4) to clean the surface at 120°C in 30 minutes. The Si-wafer surface was then deposited with a layer of 500 nm thick silicon dioxide (SiO_2) by plasma enhanced chemical vapor deposition (PECVD) at 300°C for 20 minutes. In order to improve photoresist adhesion onto oxides, SiO_2 coated Si-wafer was transferred into a prime oven for hexamethyldisilazane (HMDS) coating to form a strong chemical bond onto the oxide surface in 120 seconds. Afterwards, a layer of 1.5 μm thick photoresist was spin-coated on the SiO_2 surface at 5000 revolutions per minute (rpm) for 30 seconds. The pattern on the glass photomask was exposed onto the photoresist coated Si-wafer using 365 nm wavelength ultraviolet (UV) light over 4 seconds. The pattern was subsequently developed in an AZ 300MIF developer solution for 1 minute (step 1 in SI Figure S-2). The patterned Si-wafer was coated with a layer of 50 nm thick Pt by magnetron sputter in 4 minutes and following deposited with a layer of 100 nm thick Ni using e-beam evaporator for 15 minutes (step 2 in SI Figure S-2). The wafer was immersed in acetone etching off photoresist, called *lift-off* (step 3 in SI Figure S-2). Thereafter, the Pt-Ni-nanoengine patterned wafer was spin-coated with a layer of 15 μm thick SU-8 at 5000 rpm in 30 seconds, and the photolithography was performed once again. Pt-Ni-SU-8 microrockets with eccentric nanoengines were formed on the SiO_2-surface using the SU-8 developer to release the unexposed SU-8 over 3 minutes (step 4 in SI Figure S-2). Finally, the microrockets were released from the Si-wafer using potassium hydroxide (KOH) etching off 1 μm thick SiO_2 (step 5 in SI Figure S-2). The fabricated Pt-Ni-SU-8 microrockets, as shown in SI Figure S-3, were stored in a glass bottle for the following experiments.

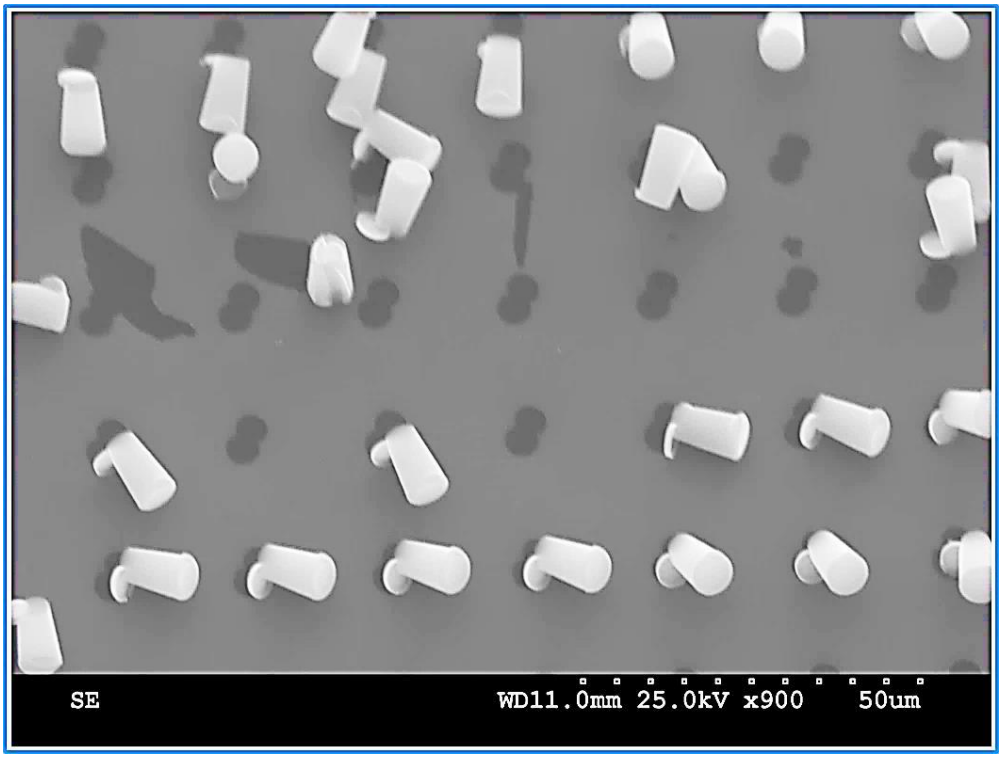
Experimental set-up

The experimental set-up, as shown in SI Figure S-4, was established for investigating the microrocket's self-steering motion. The set-up was mainly composed of four parts, including an optical microscope, sample stage, camera and computer.

The fabricated Pt-Ni-SU-8 microrockets, as shown in SI Figure S-3, were immersed into different concentrated H_2O_2 solution. The prepared samples were then dropped onto the surface of a glass slide using a pipette. Afterwards, the glass slide was transferred onto the m-



SI Figure S-2. Schematic diagram of the fabrication procedures of Pt-Ni-SU-8 microrockets with eccentric nanoengines. The microrockets are fabricated using a high-efficiency layer-by-layer method based on NEMS technology, including PECVD, photolithography, sputtering, e-beam evaporation, lift-off and KOH etching.



SI Figure S-3. SEM image of the fabricated Pt-Ni-SU-8 microrockets with eccentric nanoengines.

icroscope stage. Thereafter, the generation and detachment of the O_2 bubbles and the motion of microrockets were captured by the camera installed onto the microscope. Finally, the motion processes are recorded by the computer installed with a video recording software.

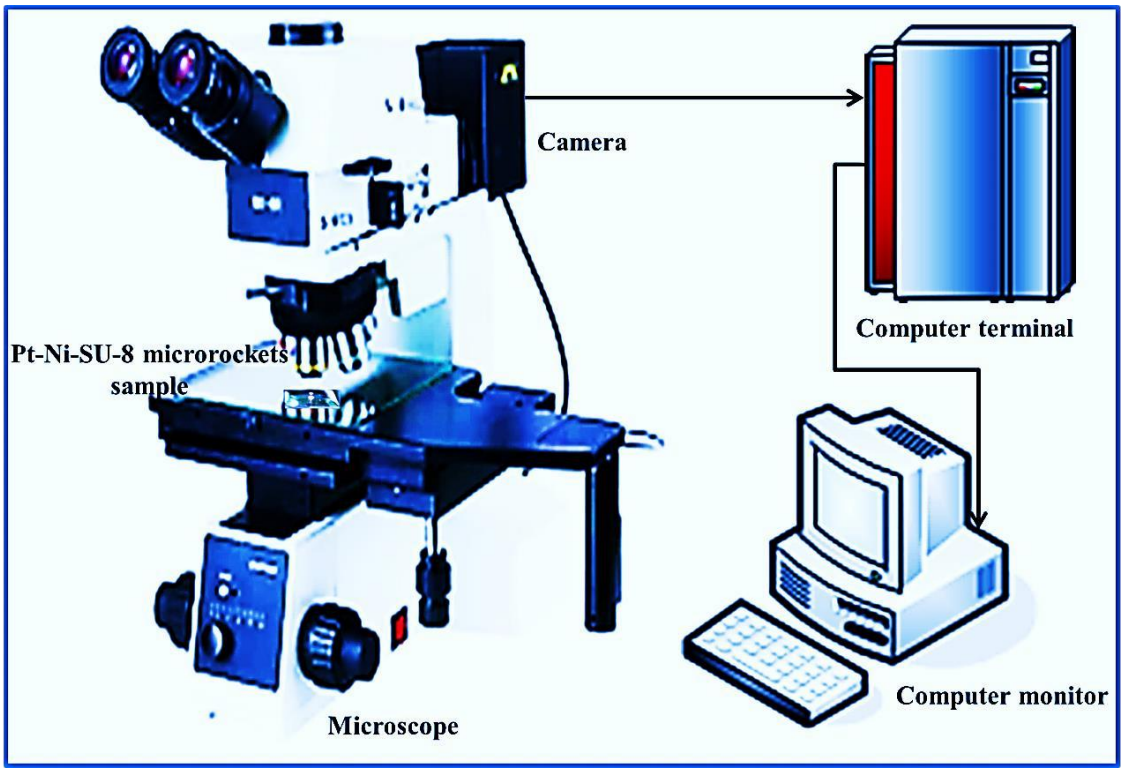
Brownian motion speed of microrockets

In micro- and nano regime, the linear diffused distance x of a micro/nanoparticle can be described as in one dimensional space[3]

$$<x^2>=2Dt_{diff} \quad \text{(SI-6)}$$

where, x, D and t_{diff} are the diffusion distance, diffusivity and diffusion time of the micro/nanoparticle, respectively. By differentiating equation (SI-6), one can obtain that the Brownian motion speed v_B of the particle can be described as

$$v_B=\frac{D}{\sqrt{2Dt_{diff}}} \quad \text{(SI-7)}$$



SI Figure S-4. Experimental set-up for characterizing the Pt-Ni-SU-8 microrocket's self-steering propulsion in diluted H_2O_2 solution. The set-up mainly includes a microscope, sample stage, camera and computer.

Moreover, Einstein and Smoluchowski showed that the diffusivity D of the particle moving in a specific fluid is related to the coefficient of the friction f, and the diffusivity can be expressed as[4]

$$D=\frac{K_bT}{f} \quad \text{(SI-8)}$$

where, k_b=1.3806488×10^{-23} m^2·kg/(s·K) is the Boltzmann constant and T is the absolute temperature. The coefficient of the friction f can be expressed as[5]

$$f = \frac{2\pi\mu L}{\ln(L/R)-0.5} \quad \text{(SI-9)}$$

where, $\mu = 0.001$ kg/(m·s) is the dynamic viscosity of the media (DI water), L and R are the effective length and radius of the microrocket. If t_{diff} = 1 s and T=300 K, the Brownian motion speed of the fabricated Pt-Ni-SU-8 microrockets is as follows

$$v_B \approx 0.482 \text{ μm/s} \quad \text{(SI-10)}$$

Calculation of catalytic reaction rate constant and adsorption constant

The pressure difference Δp at the interface between two fluids can be described by the Young-Laplace equation.[6] Hence, the pressure inside O_2 bubbles P_{O_2} can be calculated as follows

$$P_{O_2} = P_{atm} + 2\gamma/R_d \quad \text{(SI-11)}$$

where, $P_{atm} = 1.015 \times 10^5$ Pa is the atmospheric pressure, γ (0.072 N/m for DI water) is the surface tension of the solution and R_d is the radius of the detaching O_2 bubbles.

As seen, the radiuses of the detaching bubbles at higher concentrations are larger than those at lower ones, as shown in Fig. 6 (see paper). Meanwhile, the generation rate and the detachment rate of the O_2 bubbles at higher concentrations are higher. In our experiments, it is obtained that about five O_2 bubbles are generated and detached from the surface of one single microrocket in 10 mol/m^3 H_2O_2 solution over 1 second, as shown in Fig. 7 (see paper). The initial speeds of the detached O_2 bubbles from Pt-Ni-SU-8 microrockets are about 50 μm/s. Based on the values given above and the pressure P_{O_2} inside O_2 bubbles calculated by equation (SI-11), one can obtain that the catalytic reaction rate constant k is about 109.3 mol/(m^2·s) and the adsorption constant α is 0.087 m^3/mol, using the equations derived by Gibbs and his colleague.[7]

References

1 W. F. Paxton, K. C. Kistler, C. C. Olmeda, A. Sen, S. K. St. Angelo, Y. Cao, T. E. Mallouk, P. E. Lammert and V. H. Crespi, *J. Am. Chem. Soc.*, 2004, **126,** 13424.

2 S. Wang and N. Wu, *Langmuir*, 2014, **30,** 3477.

3 T. Mirkovic, N. S. Zacharia, G. D. Scholes and G. A. Ozin, *Small*, 2010, **6,** 159.

4 D. Patra, S. Sengupta, W. Duan, H. Zhang, R. Pavlick and A. Sen, *Nanoscale*, 2013, **5,** 1273.

5 Z. G. Wu, T. Y. Si, W. Gao, X. K. Lin, J. Wang and Q. He, *Small*, 2016, **12,** 577.

6 S. Wang and N. Wu, *Langmuir*, 2014, **30,** 3477.

7 J. G. Gibbs and Y. P. Zhao, *Appl. Phys. Lett.*, 2009, **94,** 163104.