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Full Paper

Characterization on Three-Dimensional Trajectory of Disk-Like Gold-Nickel-Platinum Nanomotor Using Digital Holographic Imaging

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Self-propelling disk-like nanomotor consisting of three metallic segments: a non-catalytic gold (Au), central magnetic nickel (Ni), and a catalytic platinum (Pt), is designed and fabricated with a high-efficiency layer-by-layer (LbL) deposition method based on the nano-electro-mechanical systems (NMES) technology. A bubble propulsion mechanism, resulting from bubble growth and collapse, is proposed to explain the locomotion of the nanomotor suspended in hydrogen peroxide (H₂O₂) solution. The autonomous propulsion of Au-Ni-Pt nanomotor is characterized by digital holographic imaging and analyzed using Matlab, revealing that oxygen (O₂) bubbles are generated and detached from the surface of Pt. In addition, the holographic images are for the first time used to reconstruct the instantaneously three-dimensional (3D) location and trajectory of the nanomotor.

1. Introduction

Nanomotor is a nanoscale device which has the capability to convert energy into either mechanical movement or force.^[1] In nature, living systems possess their own intelligent and efficient biomolecular motor proteins for various functions acquired through millions of years of evolution.^[2] For instance, linear biomolecular nanomotors such as kinesin, myosin and dynein, are capable of hydrolyzing adenosine triphosphate (ATP) into adenosine diphosphate (ADP) and phosphate (Pi) for lateral movement along the corresponding tracts (actin or microtubule filaments).^[3, 4] Moreover, some bacteria are able to propel forward using the flagella with powerful rotational molecular nanomotors, transforming ion motive force (IMF) into rotary kinematic movement.^[5] In addition, biological cells are equipped with molecular engines, which are required to generate the biological fuel ATP. These engines are the rotary molecular nanomotors, called F- or A-ATP synthases. Both of them consist of two distinct reversible rotary motors that can operate in different types of fuel.^[6, 7]

Inspired by naturally occurring molecular nanomotors, researchers have tried to design and fabricate tiny devices^[8-11], which could possess the ability to mimic the autonomous movement of biomolecular nanomotors in living bodies as described above. For example, Ismagilov and his co-workers firstly developed a millimeter-scale motion system driven by ejecting the oxygen (O₂) bubbles.^[12] This motion system consisted of a thin polydimethylsiloxane (PDMS) plate mounted with a piece of platinum (Pt) coated porous glass filter. The glass filter was fixed on the surface of the PDMS plate by a stainless steel pin. Afterwards, the assembled system was immersed in hydrogen peroxide (H₂O₂) solution. Pt catalyzed the decomposition of H₂O₂ to create O₂ bubbles detaching from its surface, which in turn introduced a driving force to propel the motion of the system. Gibbs and his colleagues reported a Pt-coated silica sphere, called Janus nanomotor.^[13]

The Pt-coated sphere could catalyze H_2O_2 to produce O_2 bubbles for propelling itself forward. Another similar work was carried out by Ebbens and his co-workers, in which a nonconductive Janus particle swimmer was proposed, which constituted a fluorescent polymer bead coated with a hemisphere of Pt.^[14]

The aforementioned artificial catalytic micro/nanomotors coated with Pt can autonomously propel forward in deionized (DI) water in the presence of H_2O_2 .^[12-14] The dynamics of these micro/nanomotors depends on the geometry and the material composition, due to the design and fabrication methods used. The propulsion direction of these micro/nanomotors can be along or opposite to the catalyst (Pt) site. Several mechanisms have been proposed to explain the propulsion phenomenon, such as self-electrophoresis^[15], interfacial tension^[16] and self-diffusiophoresis^[17]. These mechanisms are mainly focused on the chemical reaction process of H_2O_2 decomposition to explain the locomotion of micro/nanomotors. In this paper, we propose a bubble growth and collapse mechanism for the self-propelling nanomotor which is designed in the form of a disk, consisting of three metallic segments: gold (Au), nickel (Ni), and Pt. The propulsion of the nanomotor is originated from the growth of O_2 bubbles and subsequent bubble detachment/collapse at the Pt surface.

On the other hand, electrochemical deposition and rolled-up technique have been exploited to fabricate hollow cylindrical or conical nanomotors with high complexity, they need high-level fabrication skills.^[18, 19] The design and fabrication of the engineered micro and nanomotors is still considered an extraordinary challenge in nanotechnology. Hence, a long-term aim is to develop and fabricate catalytic micro/nanomotors in a low-cost and high-efficiency manner, as well as suitable for applications in biosensing^[20], environmental remediation^[21] and drug delivery^[22]. The disk-like Au-Ni-Pt nanomotor, proposed in this work, is fabricated using a high-efficiency layer-

by-layer (LbL) deposition method based on the nano-electro-mechanical systems (NEMS) technology. The previous works have focused on the two-dimensional (2D) characterization of nanomotors. In this work, the movement of self-propelling Au-Ni-Pt nanomotor in H₂O₂ solution is characterized using a digital holographic microscopy. The holographic data is used, for the first time to our knowledge, to reconstruct the instantaneously three-dimensional (3D) distribution and velocity of the nanomotor.

2. Bubble growth and collapse propulsion mechanism

The autonomous propulsion of disk-like Au-Ni-Pt nanomotor in H₂O₂ solution is produced through the growth and collapse cycle of O₂ bubbles from the Pt surface, as illustrated in Fig. 1. The H₂O₂ decomposition can be described as

where, Pt acts as a catalyst.^[12-14, 16] H₂O₂ is adsorbed onto the surface of Pt, and then decomposes into H₂O and O₂ bubbles.^[23-27]

Before adding H₂O₂, nanomotors are stationary in DI water. Once H₂O₂ is added into DI water, O₂ bubbles are generated (growing state) and then detached (detaching state) from the surface of Pt, as shown in supporting information Figure S1. During the bubble growth, the nanomotor accelerates and moves forward until the bubble reaches its maximum size. This remains the main cause of the propulsion of the nanomotor in the solution. After the bubble collapses, the nanomotor decelerates resulting from a low pressure generated due to surface tension and an imbalance of pressure inside the bubble and the surrounding liquid. At the steady state, the nanomotor reaches a constant velocity.

Fig. 1. Schematic diagram of the disk-like Au-Ni-Pt nanomotor's propulsion. The propulsion of the nanomotor is resulting from the bubble growth and collapse, due to the decomposition of H_2O_2 into H_2O and O_2 bubbles.

The digital holographic microscopy is a very powerful imaging tool, which is extremely beneficial for studying the 3D information of small objects. A digital hologram can be used to obtain the size, location and distribution of microscopic particulates.^[28] As shown in Fig. 2, a beam of the coherent laser light is used to illuminate a sparse sample. The directly transmitted light and scattered light from the particles interfere to make a hologram. A microscopy objective is used to collect the light, and holograms are recorded by a digital camera.

3. Results and Discussion

3.1 Characterization of disk-like Au-Ni-Pt nanomotor

The schematic of the material compositions, sizes and structure of the proposed nanomotor is shown in Fig. 3. The nanomotor consists of Au, Ni and Pt, which is shaped as a concentric disk

with 8 μm in diameter. The thickness of Au-, Ni- and Pt-disks is 200, 100 and 300 nm, respectively. Pt is used as the catalyst to chemically decompose H_2O_2 into both H_2O and O_2 bubbles.^[12, 23] Au is used as the non-catalyst and purposely to build asymmetric structure for ensuring autonomous propulsion in the micro and nanoscale regime.^[15, 16] Ni is a type of magnetic material for controlling the propulsion in future work. For instance, the motion direction of a Ni-contained nanomotor can be controlled under an external magnetic field.^[29, 30] The fabrication of the nanomotor has been carried out using the NEMS technology developed in the Micromachines Lab, School of Mechanical and Aerospace Engineering (MAE) at Nanyang Technological University (NTU), Singapore.^[31] The detailed fabrication steps are illustrated, as shown in supporting information Figure S2.

Fig. 2. Schematic diagram of the working principle of the digital holographic microscopy used to record the holograms of the nanomotor. A beam of the coherent laser light illuminates the sample. The directly transmitted light and scattered light from the sample interfere to make a hologram. A microscope objective collects the light and holograms are recorded by the camera.

Fig. 3. Schematic diagram demonstrating the structure, size and material composition of disk-like Au-Ni-Pt nanomotor. The proposed nanomotor has a form of a disk with 8 μm in diameter, consisting of three layers: 200 nm thick Au (top layer), 100 nm thick Ni (middle layer) and 300 nm thick Pt (bottom layer).

The scanning electron microscopy (SEM) image of the fabricated Au-Ni-Pt nanomotor on the silicon (Si) wafer surface is shown in Fig. 4. In order to confirm the material composition of the fabricated nanomotor (supporting information Figure S3), the energy dispersive spectrometry (EDS) analysis was performed. The EDS results of the nanomotor show that the nanomotor is made of three different metals: Au, Ni and Pt, as shown in Fig. 5.

Fig. 4. SEM image of single Au-Ni-Pt nanomotor on Si wafer substrate.

Fig. 5. EDS analysis results of Au-Ni-Pt nanomotor showing the material composition of the nanomotor.

The digital holographic microscopy system, as shown in supporting information Figure S4, was used for investigating the Au-Ni-Pt nanomotor propulsion and dynamics. From the experimental results, the O_2 bubbles were continuously generated at the Pt-surface with the addition of H_2O_2 into DI water, as shown in Fig. 6. As seen, Au-Ni-Pt nanomotor was suspended in H_2O_2 solution, and O_2 bubbles were detached from the Pt-surface after a short period of time. The recoil force, induced by the detachment of O_2 bubbles, thrusts the nanomotor to propel forward. The diameters of the detaching O_2 bubbles were approximated to be $170\ \mu m$ (Fig. 6). The results were consistent with those reported by Wang and Wu.^[32]

Fig. 6. Time lapses of the Au-Ni-Pt nanomotor's propulsion recorded by the holographic imaging microscope.

3.2 3D trajectory of disk-like Au-Ni-Pt nanomotor in H₂O₂ solution

In this work, we have demonstrated that H₂O₂ catalyzed by Pt is decomposed into O₂ bubbles which are responsible for the propulsion of Au-Ni-Pt nanomotor. These tri-metallic nanomotor is capable of self-propulsion in H₂O₂ solution. The dynamics of the nanomotor was visualized and characterized by digital holographic imaging. The 3D location and velocity of the nanomotor were obtained from the reconstructed images of a sequence of recorded holograms.

Since the dynamics of the nanomotor depends on the growth and collapse of O₂ bubbles at the surface of the nanomotor, we identified the location of a nanomotor from its proximity to the bubble. The growing bubble attached to the nanomotor can be easily imaged with the digital holography. From the holographic data, the position and dynamics of the nanomotor were analyzed by custom reconstruction algorithms. In particular, the compressive reconstruction method of the holographic data reduced the noise artifacts and allowed a faster image processing of the holographic data.

The fabricated Au-Ni-Pt nanomotor was immersed in the H_2O_2 solution to investigate the autonomous propulsion using the digital holographic microscopy. The time lapses for the propulsion of the nanomotor are characterized, as shown in Fig. 6. The recorded hologram data are used to reconstruct the 2D and 3D trajectories of the nanomotor using “ImageJ” and “Matlab”, as shown in Fig. 7 and 8, respectively. In detail, the displacement of the nanomotor in one bubble period is shown in Fig. 9.

Fig. 7. Time lapses of the reconstructed 2D trajectory of the Au-Ni-Pt nanomotor.

Fig. 8. Time lapses of the reconstructed 3D trajectory of the Au-Ni-Pt nanomotor.

3.3 Disk-like Au-Ni-Pt nanomotor's 3D velocity in H₂O₂ solution

The instantaneously 3D velocity of the nanomotor can be expressed as follows:

$$\vec{v}_{x_i} = \frac{\vec{x}_{i+1} - \vec{x}_i}{\Delta t_i} \quad (2)$$

$$\vec{v}_{y_i} = \frac{\vec{y}_{i+1} - \vec{y}_i}{\Delta t_i} \quad (3)$$

$$\vec{v}_{z_i} = \frac{\vec{z}_{i+1} - \vec{z}_i}{\Delta t_i} \quad (4)$$

$$\vec{v}_{t_i} = \sqrt{\vec{v}_{x_i}^2 + \vec{v}_{y_i}^2 + \vec{v}_{z_i}^2} \quad (5)$$

where, $\bar{x}_i$, $\bar{y}_i$ and $\bar{z}_i$ are the displacement of the nanomotor along x , y and z directions at the i^{th} moment, respectively. $\bar{x}_{i+1}$, $\bar{y}_{i+1}$ and $\bar{z}_{i+1}$ are the displacement of the nanomotor along x , y and z directions at the $(i+1)^{\text{th}}$ moment, respectively. $\bar{v}_{x_i}$, $\bar{v}_{y_i}$ and $\bar{v}_{z_i}$ are the velocity of the nanomotor along x , y and z directions at the i^{th} moment, respectively. $\bar{v}_{t_i}$ and Δt_i are the total speed of the nanomotor and the total time period at the i^{th} moment, respectively.

Fig. 9. The displacement of the Au-Ni-Pt nanomotor in one bubble period.

The Au-Ni-Pt nanomotor propulsion was studied in H_2O_2 solution, the concentration of H_2O_2 was 5 mol/m^3 (Fig. 6). Using equations (2) to (5), the 3D velocity of the nanomotor is calculated,

as shown in Fig. 10. In micro and nano realm, catalytic nanomotor in DI water without the presence of the fuel H_2O_2 would undergo thermal fluctuation motion, called Brownian motion. In such a case, there are no O_2 bubbles generated, and the nanomotor moves forward slowly and randomly (supporting information). As seen, the self-propelling speed of disk-like Au-Ni-Pt nanomotor is larger than the Brownian motion speed.^[33]

Fig. 10. The 3D velocity of the Au-Ni-Pt nanomotor.

3.4 Discussion on disk-like Au-Ni-Pt nanomotor propulsion

The bubble radius can be theoretically calculated by

$$R = \gamma t^n \quad (6)$$

where, R is the radius of the O_2 bubble, γ is the proportionality constant, n is the growth exponent ($n \approx 0.33$), t is the growth time of O_2 bubbles. The radiuses of the O_2 bubbles before detachment are experimentally characterized, as shown in Fig. 11. As can be seen, the experimental results are in good agreement with the theoretical ones.

The pressure between two fluids can be described by the Rayleigh-Plesset equation.^[32] Hence, the pressure inside the O_2 bubbles P_{O_2} can be calculated as follows

$$\frac{P_{O_2}(t)-P_{\infty}(t)}{\rho_L} = R\ddot{R} + \frac{3}{2}(\dot{R})^2 + \frac{4v_L\dot{R}}{R} + \frac{2\varepsilon}{\rho_L R} \quad (7)$$

where, $P_{\infty}(t)=P_{atm}=1.015\times 10^5$ Pa, is the atmospheric pressure; ρ_L is the density of the liquid, v_L is the kinematic viscosity, ε is the surface tension.

Fig. 11. Bubble radius variation with time. The experimental results are in good agreements with the theoretical ones.

In our experiments, it was obtained that about 7 O_2 bubbles were generated and detached from the surface of the nanomotor in 1 second, as shown in Fig. 11. The speed of the detached O_2 bubbles from the Au-Ni-Pt nanomotor was about 80 $\mu\text{m/s}$. Based on the values given above, the pressure inside O_2 bubbles can be calculated using equation (7). Employing the equation derived by Gibbs and his colleagues^[13], one can obtain that the catalytic reaction rate constant k is about 126.8 $\text{mol}/(\text{m}^2\cdot\text{s})$, and the adsorption constant α is approximately 0.069 m^3/mol . The results were in good agreement with those reported in reference 13. On the other hand, the speed of the nanomotor in our results was larger than those presented in reference 13, while it was lower than those studied by other researchers^[29, 30], due to the differences from the nanomotor's shape and

material composition. In such a case, one can learn the reasons in reference 13. In fact, there are several parameters which influence the speed of the nanomotor, giving us the guidance how to design and characterize the nanomotor in future work.

4. Conclusion

We have fabricated disk-like Au-Ni-Pt nanomotor which is capable of self-propulsion in H_2O_2 solution. H_2O_2 catalyzed by Pt is decomposed into O_2 bubbles that are responsible for the propulsion of the Au-Ni-Pt nanomotor. The dynamics of the nanomotor was visualized and characterized by digital holographic imaging. The 3D location and velocity of the nanomotor were for the first time obtained from the reconstructed images of a sequence of recorded holograms.

Supporting Information Summary Paragraph

Readers can find the supporting Information (i) materials, equipment and softwares used; (ii) the derivation of the driving force (Figure S1); (iii) fabrication of nanomotors (Figures S2 and S3), (iv) the experimental set-up (Figures S4), and (v) the Brownian motion speed of the nanomotor.

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Conflicts of Interest

The authors declare no conflicts of interest.

Keywords: disk-like nanomotor • growth-collapse propulsion • hydrogen peroxide • holographic imaging • three-dimensional trajectory.

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The Table of Contents Entry

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