X-ray-Powered Micromotors
Zhaoyi Xu,‡ Mojun Chen,‡ Hyeonseok Lee,† Shien-Ping Feng,‡ Jae Yeon Park,‡ Sangsul Lee,‡ and Ji Tae Kim*†

‡Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China
†Pohang Accelerator Laboratory, Pohang University of Science and Technology, Pohang 37673, Republic of Korea

Supporting Information

ABSTRACT: Light-powered wireless manipulation of small objects in fluids has been of interest for biomedical and environmental applications. Although many techniques employing UV–vis–NIR light sources have been devised, new methods that hold greater penetrating power deep into medium are still in demand. Here, we develop a method to exploit X-rays to propel half-metal-coated Janus microparticles in aqueous solution. The Janus particles are simultaneously propelled and visualized in real-time by using a full-field transmission X-ray microscope. Our real-time observation discovers that the propulsive motion follows the bubble growth enhanced by water radiolysis near the particle surface under X-ray irradiation. We also show that the propulsion speed is remotely controlled by varying the radiation dose. We expect this work to open opportunities to employ light-powered micro/nanomotors in opaque environments, potentially by combining with medical imaging or nondestructive testing.

KEYWORDS: micromotors, light-driven actuators, X-rays, water radiolysis, microbubbles

INTRODUCTION
Propulsive motion of small objects that outrun Brownian diffusion in fluids has long been regarded as an interesting research topic among scientists.1–3 Furthermore, the propulsion at small scales has been employed to drive artificial micro/nanomotors aiming at accomplishing microscopic tasks such as drug/cell delivery,4–9 microsurgery,10,11 environmental remediation,12 nanofabrication,13,14 and so on. Propulsion mechanisms that convert various forms of energy into directed motion include catalytic self-propulsion,15–17 external stimulation by electric and magnetic fields,18–22 light,23,24 and ultrasound,25,26 and combinations thereof.27,28

Light stimulation is wireless, reversible, tunable, and therefore is emerging as a powerful method to remotely control micro/nanomotors in fluids. Light–matter interactions with high spatiotemporal resolution can trigger chemical/physical reactions that enable propulsion with high precision and individual addressability.29,30 Examples include light-driven diffusiophoresis,31 electrophoresis,32,33 thermophoresis,34–37 bubble recoil,38 interfacial tension gradient,39 and selective deformation.40,41 Most of the light-responsive micromotors have successfully employed UV–vis–NIR light with diverse bandwidths.42–46 However, it is still a longstanding challenge to achieve the efficient transfer of light power to the micromotors in opaque environments. Conventional UV–vis–NIR light sources hold insufficient penetrating power deep into biological medium, which is limited to a few millimeters.47 Therefore, it is necessary to develop new propulsion methods that can improve the penetration.

Since their discovery by Röntgen,48 X-rays have long been regarded as the most celebrated light source for noninvasive imaging in medicine, biology, and materials science. In particular, the high penetrating power of X-rays enables whole-body, in vivo medical imaging and continuing scientific demands have advanced the radiation sources of X-rays, e.g., synchrotron sources, for improving brightness and coherence.39 Nevertheless, to the best of our knowledge, X-rays have never been employed as an external stimulus for propelling micro/nanomotors in fluids. We emphasize that the capability to steer and track micromotors under a whole-body imaging platform may potentially accelerate their clinical use. Here, we report on a method that exploits X-rays to generate propulsive motion of micromotors in an aqueous environment. Half-copper-coated silica (Cu/SiO2) Janus microparticles can be propelled under X-ray irradiation, resulting from enhanced radiolysis of water near the particle surface. To stimulate and visualize the propulsive motion at a single-particle level, we use a full-field transmission X-ray microscope (TXM)33–35 with synchrotron hard X-rays that hold excellent brightness and coherence. Our real-time microradiographic observation discovers that the radiolytic bubble growth propels the Janus particle and its motion coincides with the advancing of the bubble surface. We also show that the propulsion speed of the Janus particle is remotely controlled by the pulse width of X-rays.
associated with the amount of radiation dose, resulting in on-demand manipulation.

**Results and Discussion.** Figure 1a illustrates the experimental setup based on a TXM consisting of a focusing mirror system, a motorized sample stage, a zone plate, a phase plate, and an image detector. To propel and visualize Cu/SiO2 Janus particles, focused hard X-rays with an energy of 6.3 keV are illuminated onto a thin liquid chamber containing the particle suspension. The pulse width of X-rays in the range of milliseconds is controlled by a beam shutter with a constant period of 2 s. The X-ray driven propulsion mechanism is schematically illustrated in Figure 1b. When X-rays are irradiated onto a Cu/SiO2 Janus particle, a microbubble is formed on the Cu side of the particle. As the bubble grows, the particle is propelled toward the advancing of the bubble surface. We propose that the bubble growth may result from water radiolysis that is the decomposition of water molecules due to ionizing radiation. It is well known that hydrogen gas, H2(g), is one of the main radiolytic products. The chemical reactions that form H2 gas are as follows.56

\[ e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^- \]  
\[ e_{aq}^- + H^* + H_2O \rightarrow H_2 + OH^- \]  
\[ H^* \rightarrow H_2 \] 

where \( e_{aq}^- \) is the aqueous electron and \( H^* \) is the hydrogen free radical. To explain the formation mechanism of the bubble on the Cu side, it is necessary to consider the radiation dose transfer at the metal/water interface.57 It has been reported that the radiation dose transfer from metal to water is greater than that from silica to water due to larger stopping power difference. Therefore, the enhanced water radiolysis at the Cu/water interface accelerates the H2 bubble formation on the Cu surface.

Sequential microradiographs in Figure 1c–f (Movie S1, Supporting Information) show the propulsive motion of a Cu/SiO2 Janus particle with 6 μm diameter (Figure S1, Supporting Information) in aqueous solution (1:1 water/glycerol with 5 M acrylamide) under pulsed X-rays (pulse width: 70 ms, period: 2 s). (c) 0 s, (d) 2 s; the formation of a microbubble on the particle, (e) 4 s; translational motion driven by the bubble growth, and (f) 38 s.

**Figure 1.** X-ray-powered micromotors. (a) Schematic illustration of the experimental setup: A transmission X-ray microscope is utilized to propel and visualize a Cu/SiO2 Janus particle in a liquid thin chamber. The X-ray energy is fixed at 6.3 keV and the pulse width in the range of milliseconds is controlled by a beam shutter with a constant period of 2 s. (b) The Janus particle is propelled by bubble growth from water radiolysis under X-ray irradiation. (c–f) A series of transmission X-ray microradiographs and trajectories (in red) shows propulsive motion of a Cu/SiO2 Janus particle (diameter: 6 μm, thickness of Cu: 100 nm) in 1:1 water/glycerol solution with 5 M acrylamide under pulsed X-rays (pulse width: 70 ms, period: 2 s). (c) 0 s, (d) 2 s; the formation of a microbubble on the particle, (e) 4 s; translational motion driven by the bubble growth, and (f) 38 s.
X-ray irradiation (Figure S2a). Their representative trajectories are displayed in Figure S2c,d, respectively. The role of the Janus shape is to aid asymmetric bubble growth on the particle, promoting the directed motion of the particle. Our quantitative study in Figure 2 reveals that the propulsion dynamics of the Janus particle is governed by the radiolytic bubble growth under X-ray irradiation. Figure 2a plots the radius of the bubble $R(t)$, as a function of time $t$, induced by X-ray radiolysis on a Cu/SiO$_2$ Janus particle (the pulse width of X-rays: 70 ms, period: 2 s). The $R$–$t$ relation is approximated by a power law $R(t) \sim t^n$ with $n = 0.39 \pm 0.02$. Each plot is obtained from the individual trajectory of each bubble. (b) The plot of particle displacement, $S(t)$, as a function of time, $t$. Each plot is obtained from the individual trajectory of each Janus particle. (c) The plots of the bubble growth rate (circle) and propulsion speed (square) as a function of time, $t$.

![Figure 2](image)

$R(t) = Kt^n$  

(4)

where $n$ is the growth exponent and $K$ is the proportionality constant. The increase of $R(t)$ follows the power law with $n = 0.39 \pm 0.02$, which is similar to $n = 1/3$, implying that volumetric bubble growth rate on the particle is constant under the given X-ray irradiation. The displacement of the Janus particle, $S(t)$, has a similar trend with the $R(t)$ as shown in Figure 2b. This result provides the opportunity to control the particle motion by varying the bubble growth. The propulsion performance can also be evaluated by the instantaneous speed of the particle. Figure 2c plots the bubble growth rate, $dR/dt$ (circle), and particle propulsion speed, $v(t) = dS/dt$ (square), as a function of time, $t$. At the initial stage when the bubble starts to push the particle ($t < 3$ s), the propulsion speed, $v$, is gradually increased and it reached the maximum value of $\sim 0.85 \mu$m/s. The trend of the initial $v(t)$ is deviated from $dR/dt$ due to the drag force of the particle acting against the bubble growth force. In the later stage ($t > 3$ s), when the bubble is large enough, the particle speed, $v$, follows a similar trend to the bubble growth rate $dR/dt$ and gradually decreases with time. As a result of the transition between these two regimes, the maximum propulsion speed $v_{max}$ at $t \sim 3$ s is observed. This transition is suppressed as the particle size decreases (as experimentally shown in Figure S3, Supporting Information). The observation time was set up to 2 min because the neighboring bubbles could bother measuring the propulsion as their sizes increased. In this experimental condition, the bubble bursting or detachment from the particle was not observed due to high viscosity in the solution although they could provide oscillatory and consistent propulsion. Thorough investigations to control the bubble bursting/detachment (e.g., the use of a surfactant in Figure S4) are still underway.

One central question—can X-rays tune the motion?—motivates us to investigate the dependency of the propulsion dynamics on radiation dose. To change the radiation dose, the pulse width of X-rays was controlled by a mechanical shutter. To characterize the particle motion with constant image acquisition rate, the period of X-ray pulses was fixed at 2 s. First, Figure S5 (Supporting Information) plots the required time for initial bubble formation as a function of the pulse width of X-rays at a constant period of 2 s. It is clearly shown that the bubbles are formed earlier as the pulse width increases. More importantly, the particle propulsion driven by the bubble growth is governed by the radiation dose. Figure 3a plots the propulsion speed of the Janus particle, $v$, as a function of time at different pulse widths of X-rays from 50 to 110 ms. (b) The plot of the maximum speed of the Janus particles, $v_{max}(t)$ as a function of pulse widths of X-rays.

![Figure 3](image)

$\text{Figure 3. X-ray dose effect. (a) The plot of the propulsion speed of the Cu/SiO}_2\text{ Janus particles driven by radiolytic bubble growth, } v(t), \text{ as a function of time, } t, \text{ at different pulse widths of X-rays from 50 to 110 ms.}$

$\text{(b) The plot of the maximum speed of the Janus particles, } v_{max}(t) \text{ as a function of pulse widths of X-rays.}$
surface, which can enhance water radiolysis on the Cu side. The enhancement loses its effectiveness as the distance from the particle surface exceeds 1 μm.

CONCLUSIONS

In this work, we have demonstrated that X-rays can propel metal-coated Janus microparticles in an aqueous environment. The real-time TXM enabled us to study X-ray-driven propulsion dynamics at the single-particle level. We revealed that the propulsion mechanism is based on radiolysis of water: the particle motion follows the growth of H2 bubble on the particle under X-ray irradiation. We showed that the propulsion performance, i.e., the instantaneous speed, can be controlled by instant variation of the radiation dose. Although in this work performance, i.e., the instantaneous speed, can be controlled under X-ray irradiation. We showed that the propulsion particle surface exceeds 1 μm.

EXPERIMENTAL METHODS

Sample Preparation. SiO2 beads with a diameter of 6 μm were deposited on an Si wafer by two-step spin coating (200 rpm 10 s and 8000 rpm 5 s). The Si wafer was cleaned by rinsing with acetone, isopropanol, and deionized water under sonication for 5 min each and an O2 plasma process for 5 min. To produce Janus microparticles, 5 nm-thick Ti (as adhesion layer) and 100 nm-thick Cu were deposited on the hemispheres of the SiO2 beads by sputtering. The thickness of these deposited metals was carefully characterized by an atomic force microscope (AFM) (Bruker MultiMode 8). The wafer was sputtered for 1 minute to release the Janus microparticles into deionized water. A centrifuge process (10,000 rpm and 10 min) was performed to obtain sufficient concentration of the Janus microparticles. The particle suspension was prepared in a water/glycerol mixture (1:1 volume ratio) with 5 M acrylamide to tackle two technical challenges for stable observation: (1) High viscosity of the solution (η ∼ 100 mPa·s) suppresses gravity-driven sedimentation of the particles. (2) Acrylamide acts as a scavenger to reduce the byproducts of water radiolysis, thereby inhibiting the undesired random generation of bubbles in the solution. The prepared Janus particles were characterized using FE-SEM (LEO 1530, Zeiss) with EDX analysis.

X-ray Microradiography and Stimulation of Micromotors.

The experiment was carried out using a TXM consisting of a focusing mirror system, a motorized sample stage, a zone plate, a phase plate, a magnifying lens, and a CCD detector, installed at 7C X-ray Nano Imaging (XNI) beamline in Pohang Light Source (PLS-II). The beam current and storage energy of the synchrotron facility are 360 mA and 3 GeV, respectively. The X-rays were monochromated at 6.3 keV using a silicon (111) double-crystal monochromator and focused on the sample using a mirror system. The beam flux at the sample position was estimated to be ~10¹¹ photons s⁻¹. The exposure time of X-rays was controlled by a mechanical beam shutter with a constant period of 2 s. A 100 μm-thick liquid chamber with two SiN windows (purchased from Norcada) was used to contain 0.5 μL-volume particle suspension. The dimension of the SiN window was 500 μm (width) × 500 μm (height) × 100 nm (thickness). The off-axis illuminated Fresnel zone plate was used as an objective lens of X-rays with an outermost zone width of 50 nm and a diameter of 350 μm. The pinhole-type Zernike phase-contrast plate enhanced the image contrast from a 10 μm diameter hole in an aluminum film of 3.84 ± 0.04 μm thickness. X-ray images were detected in a Tb:LSO scintillator crystal (15 μm thickness), converted to optical images, and magnified with a ×20 objective. A CCD camera (Apogee Alta: 4096 × 4096 pixels, 9 μm pixel size, 16-bit digital resolution) was used.

Dose Calculation. We use the EGSnrc code for Monte Carlo simulation. EGSnrc can simulate the transport of photons with energy lying between 1 keV to several hundred GeV in any material or geometry. We use the EGSnrc C++ class library to write our application. A monoenergetic cylindrical shaped parallel beam with 10 μm radius is simulated and 1 × 10¹⁸ photons’ tracks were calculated. The energy of the beam is 6.3 keV and the energy absorption cut off we set is 1 keV. The target simulated here is a water/glycerol (1:1 volume ratio, intimately mixed, density 1.14 g/cm³) mixture sphere with 500 μm radius, and a 100 nm Cu-coated Janus particle with 6 μm diameter is placed in the center of the chamber.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b00174.

Figure S1. FE-SEM and EDX images of the Cu/SiO2 Janus particles; Figure S2. Cu/SiO2 Janus particle vs SiO2 particle under X-rays; Figure S3. Propulsion speed of Cu/SiO2 Janus particles with different diameters; Figure S4. Bubble bursting on a Cu/SiO2 Janus particle; Figure S5. Required time for bubble formation vs pulse width of X-rays; Figure S6. Au/SiO2 Janus particle vs Cu/SiO2 Janus particle under X-rays (PDF).

Movie S1. Propulsive motion of a Cu/SiO2 Janus particle in 1:1 water/glycerol solution with 5 M acrylamide under pulsed X-rays; Movie S2. Half-Cu-coated SiO2 Janus particles (left) and bare SiO2 particles (right) suspended in the solution under the same X-ray irradiation (AVI) (AVI).

AUTHOR INFORMATION

Corresponding Author

*E-mail: jtkim@hku.hk.

ORCID

Shien-Ping Feng: 0000-0002-3941-1363
Ji Tae Kim: 0000-0003-4662-0179
ACKNOWLEDGMENTS

This work was supported by the Early Career Scheme (HKU 27207517) and General Research Fund (HKU 17208218) from the Research Grants Council of Hong Kong, the Seed Fund for Basic Research from the University of Hong Kong (201611159002), the MOTIE (Ministry of Trade, Industry & Energy) (10080526), and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

REFERENCES


