

Nanoscopic Imaging of Self-Propelled Ultrasmall Catalytic Nanomotors

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ABSTRACT: Ultrasmall nanomotors (<100 nm) are highly desirable nanomachines for their size-specific advantages over their larger counterparts in applications spanning nanomedicine, directed assembly, active sensing, and environmental remediation. While there are extensive studies on motors larger than 100 nm, the design and understanding of ultrasmall nanomotors have been scant due to the lack of high-resolution imaging of their propelled motions with orientation and shape details resolved. Here, we report the imaging of the propelled motions of catalytically powered ultrasmall nanomotors—hundreds of them—at the nanometer resolution using liquid-phase transmission electron microscopy. These nanomotors are Pt nanoparticles of asymmetric shapes ("tadpoles" and "boomerangs"), which are colloidally synthesized and observed to be fueled by



the catalyzed decomposition of $NaBH_4$ in solution. Statistical analysis of the orientation and position trajectories of fueled and unfueled motors, coupled with finite element simulation, reveals that the shape asymmetry alone is sufficient to induce local chemical concentration gradient and self-diffusiophoresis to act against random Brownian motion. Our work elucidates the colloidal design and fundamental forces involved in the motions of ultrasmall nanomotors, which hold promise as active nanomachines to perform tasks in confined environments such as drug delivery and chemical sensing.

KEYWORDS: ultrasmall nanomotor, catalysis, self-diffusiophoresis, liquid-phase transmission electron microscopy, motion analysis, finite element simulation

INTRODUCTION

In 1959, Feynman depicted a future where devices at small scales can be swallowed into human body to do surgeries at target organs.¹ These devices, now called micro- or nanomotors that can move autonomously in fluid and powered by external forces such as chemical reactions, are receiving evergrowing interest due to applications in biomedicine, active sensing, fuel cells, and environmental monitoring and remediation.^{1,2} For example, catalytic motors such as micrometer-sized Pt-Ti Janus particles were shown as good catalysts for NaBH₄ decomposition, increasing H₂ generation rate by more than nine times compared to static particles for powering a fuel-cell car.³ Optical microscopy has been often used to image and analyze the motions of these micron-sized motors, to understand their propulsion mechanisms, and to achieve advanced design of micromotors with desired properties such as fast speed, high motion directionality, high durability, and high precision cargo transportation.⁴ In addition to micromotors, nanomotors (>100 nm) have also been studied extensively, mostly made out of top-down chemical or physical vapor deposition methods.⁵ Conventional or super-resolution optical microscopy were used to image their centroid positions but without nanoscale shape details. Recent work by Wan et al. innovatively used liquid-phase transmission electron microscopy (TEM) to videotape the directional motions of cadmium chloride particles ~200 nm in size, which underwent beaminduced self-decomposition to achieve propulsion.⁶

Meanwhile, even smaller motors, the ultrasmall nanomotors (<100 nm), heretofore referred to as U-motors, have recently attracted increasing research efforts considering their unique advantages: (*i*) large specific area for efficient catalysis, (*ii*) sufficiently small size for device miniaturization, for endocytosis to cross cellular membranes,^{7,8} and for facile, scalable colloidal synthesis, and (*iii*) their capability to couple with

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Figure 1. Colloidal synthesis of Pt U-motors and FEA simulation of the chemical gradient surrounding them in the presence of NaBH₄ fuel. (a) Schematic illustration showing the one-pot synthesis of Pt NPs with varied shapes, including asymmetric shapes such as tadpoles and boomerangs and symmetric shapes such as dendrites. (b) Schematic illustration showing the tracking of the self-propelled motion of Pt NPs in a liquid chamber for TEM imaging. The local concentration gradient of H₂ could drive a tadpole to move toward its head. (c) TEM images of Pt NPs (top) and simulated H₂ concentration (in the log scale, middle) and the magnitude of diffusioosmotic flow velocity (u, bottom) around them. The directions of propulsion force (F_p) on each NP are labeled by arrows (middle). White arrowed curves in the bottom panel depict the streamlines of the generated diffusio-osmotic flow. From left to right: tadpoles with a 50 nm tail, a 36 nm tail, a 30 nm tail and additional branches protruding on the head, and a boomerang standing on the substrate (represented as a gray bar). Scale bars: 50 nm. (d) Diffusion coefficients of Pt NPs in NaBH₄ and NaCl solutions measured by dynamic light scattering (DLS).

other size-defined properties (e.g., optical, magnetic, plasmonic) for multifunctionality. However, efforts on rational design of U-motors have remained very limited (literature studies summarized in Table S1) due to a lack of understanding of the propulsion mechanism at the nanoscale,^{9–15} which is fundamentally associated with the challenges to resolve the motions and shapes of U-motors with nanoscale details. Moreover, it is expected that Brownian force that randomizes motion directions scales inversely to particle size and can become hard for U-motors to counteract and to induce propelled motion. Thus, understandings are needed on the fundamental forces and mechanisms involved in the dynamics of U-motors.

Here, we report the design of U-motors based on colloidally synthesized Pt nanoparticles (NPs), which can be powered by catalyzing the decomposition of the NaBH₄ fuel in aqueous solutions, and achieve the direct imaging of their propelled motions with shapes simultaneously resolved under liquidphase TEM. Based on finite element analysis (FEA), through NaBH₄ decomposition, a H₂ concentration gradient can be generated around Pt NPs of asymmetric shapes (e.g., tadpoles and boomerangs in this work) and propel the NPs to move directionally. Such design of U-motors is verified by our liquidphase TEM imaging, where Pt NPs move with diffusion exponents as high as 1.4. The nanometer resolution imaging allows us to map the orientation and centroid positions of NPs, where a high correlation is consistently found between the NPs' orientation and moving direction, matching with our FEA prediction using experimentally resolved NP shapes as inputs. This match supports that self-diffusiophoresis induced by the local concentration gradient of catalyzed reaction products serves as the major propulsion mechanism, which is

fundamentally originated from the nanoscopic shape asymmetry of NPs. Meanwhile, other mechanisms such as selfelectrophoresis and ionic self-diffusiophoresis are also possibly responsible for the propulsion of our U-motors. Our comparative studies on the trajectories of more than 180 NPs (fueled vs unfueled) reveal that NPs need to have strong driving forces to counteract against Brownian force as Umotors. Our work integrates colloidal synthesis of U-motors, simulation of the propulsion mechanism, and liquid-phase TEM imaging of the propelled motions. Such integration invites future efforts in designing, understanding, and modulating U-motors that are colloidally synthesized and are promising for broad applications such as intracellular sensing and delivery, pollutant detection and degradation, and controlled self-assembly.

RESULTS AND DISCUSSION

Design and Colloidal Synthesis of Catalytically Powered U-Motors Driven by Self-Diffusiophoresis. We design and colloidally synthesize Pt NPs with asymmetric shapes as U-motors by utilizing their catalytic activity to produce a directional driving force. Different from electrochemical or vapor deposition methods adopted for larger motors,¹⁶ colloidal synthesis of NPs is scalable and capable of controlling shape details at the nanoscale. For example, the recent work by Kwon et al. used multistep colloidal synthesis to produce Au/Pt-egg-in-nest U-motors for drug delivery.¹⁴ In our work, we employ control of reaction kinetics to synthesize Pt NPs of asymmetric shapes in a one-pot reaction, with a focus on force imbalance originating from symmetry breaking of NP shapes. As shown in Figure 1a, asymmetric Pt NPs are synthesized by reducing Pt(II) precursor with glucose in the presence of cetyltrimethylammonium bromide (CTAB) and oleylamine. The NPs are small: tadpoles with a total length of 70-90 nm and boomerangs with arms about 7 nm-thick and 80 nm-long (Figure S1). Both shapes are asymmetric with large specific surface areas for catalytic reactions. Meanwhile, the synthesis also produces dendritic NPs highly symmetric in shape (Figure S2), which serves as a convenient comparison. Prior studies have indicated the influence of branching instability on the growth of Pt dendrites.^{17,18} Once a branch protrudes out of the region depleted of reactants, it can reach a higher concentration of Pt monomers and thus grows faster than shorter branches, resulting in the symmetry breaking of the branch lengths in the final product. Meanwhile, due to the limited amount of Pt(II) precursor in the reaction solution, only part of the dendrites grow into tadpoles or multipods, leading to a mixture of shapes in the final product. The assynthesized NPs further undergo ligand exchange with carboxylated thiols, which are negatively charged in neutral or basic aqueous solutions to keep the NPs dispersed due to electrostatic repulsion (Figure S3).^{19,20}

To visualize the motion trajectories and shape of U-motors simultaneously, two SiN_x microchips are used to sandwich an aqueous solution containing these Pt NPs for liquid-phase TEM imaging, where fresh fuel solution of NaBH₄ is flowed through the microfluidic channels (Figure 1b). Liquid-phase TEM enables tracking of the position and shape contour of NPs over time, from which the NPs' translational and orientational motion trajectories are extracted. A series of physical quantities are calculated, such as the motion speed, diffusion exponent, and correlation between motion direction and NP orientation, which altogether comprehensively capture the U-motor behaviors and the propulsion mechanism.

In this work, decomposition of $NaBH_4$ is chosen as the model reaction, which can be catalyzed by Pt_1^3

$$NaBH_4 + 2H_2O \rightleftharpoons 4H_2 + NaBO_2 \tag{1}$$

The as-generated $NaBO_2$ is further hydrolyzed into NaOH and H_3BO_3 ,

$$NaBO_2 + 2H_2O \rightleftharpoons NaOH + H_3BO_3$$
 (2)

resulting in an increase in the pH of the solution. It should be noted that $NaBH_4$ is also a promising hydrogen storage material due to its high hydrogen density, nonflammability, mild operation temperature, stability in alkaline solution, and nontoxic products. With Pt nanomotors serving as the catalyst, H_2 release from $NaBH_4$ decomposition can be significantly accelerated, providing a viable means to power a fuel-cell model car.³ Specific to this experiment, $NaBH_4$ is also compatible with our liquid-phase TEM holder in a wide range of concentrations varying over 0-132 mM.

Considering the presence of gas (H_2) and ions (BO_2^-, OH^-) in the products, four propulsion mechanisms can be potentially involved:²¹

(i) Bubble Propulsion. Particles are driven through a recoil force generated from the detachment of bubbles. Based on our FEA (Figure 1c, Methods), the highest concentration of H₂ generated by the catalytic reaction near the surface of Pt NPs is around 20 μ M, 40 times lower than its solubility in water (0.8 mM), suggesting that no gas bubbles are expected to form. This is further supported experimentally where no bubbles are observed on or close to the NPs under liquid-phase TEM, indicating that bubble propulsion is not critical for our system.²¹

(ii) Self-Electrophoresis. Charged particles are driven by a self-generated electric field as a result of asymmetric redox reactions on surface.²² In our system, the Pt tadpoles have different thicknesses in the head and tail, which can lead to different catalytic activity on these two ends and the generation of an electrochemical current flowing between them. The decomposition of NaBH₄ can split into two half reactions:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- (cathode)$$
(3)

$$BH_4^- + 4OH^- \rightarrow 2H_2 + 4e^- + BO_2^- + 2H_2O$$
 (anode) (4)

The thicker Pt end may potentially have stronger catalytic activity, which is the head of the tadpole in our case. However, the direction of the current generated from this effect remains debatable and is often derived from direct imaging in previous studies of micromotors.^{23,24} In Pt tadpoles, assuming that the thicker Pt serves as the anode, the surrounding local electric field will point from head to tail, driving the particle motion in the direction of tail to head (the zeta potential of the NP surface is negative), consistent with the prediction from neutral self-diffusiophoresis. If we assume the opposite, this mechanism can compete with neutral self-diffusiophoresis.

(iii) Ionic Self-Diffusiophoresis. Charged particles are driven by a concentration gradient of ionic species. Ionic selfdiffusiophoresis will occur if there is a concentration gradient of ions generated from chemical reactions on the NP surface. In previous studies,²⁵ the difference in the diffusivities of cations and anions leads to local concentration gradients of ions and thus the formation of a local electric field, which propels the motor. In our case, for the decomposition of NaBH₄, BH₄⁻ undergoes consumption while BO₂⁻ is produced, with the latter exhibiting a slower diffusivity than the former $(1.67 \times 10^{-5} \text{ and } 0.935 \times 10^{-5} \text{ cm}^2/\text{s}$ for BH₄⁻ and BO₂⁻, respectively).²⁶⁻²⁸ It leads to accumulation of negative charges around the surface of the particle, resulting in an inward direction of the local electric field that drives surface electroosmotic flow. Additionally, BO₂⁻ can be hydrolyzed and produce OH⁻, which has a faster diffusivity than BH₄⁻ (5.3 \times 10⁻⁵ cm²/s for OH⁻).²⁹ In this case, an inverse localized electric field is generated. As a result, ionic self-diffusiophoresis can contribute to propulsion as well.

(iv) Neutral Self-Diffusiophoresis. The motion of particles can also be driven by a concentration gradient of neutral molecules. We perform FEA simulations to map the chemical distribution and its induced diffusioosmotic flow around our asymmetric U-motors, evaluating the contribution from neutral self-diffusiophoresis on the U-motors and predicting their moving directions. Ensemble concentrations of different species evolving during reactions (eqs 1 and 2) are first calculated (Figure S4 and Supporting Information), at a starting concentration of 1.98 mM of NaBH₄ (detailed below as the optimal concentration in our experiment). The calculation shows a concentration of H₂ more than four times higher than those of BO_2^- , OH^- , and H_3BO_3 , indicating H₂ as the major contributor to neutral self-diffusiophoresis. The generation rate of H₂ is further estimated as 1.0×10^{-4} $mol/(m^2 \cdot s)$, with which we map the local concentration of H₂ around Pt NPs. Experimentally imaged contours of typical Pt NPs are used as the input NP shape in the FEA. The diffusion of H₂ molecules follows Fick's law, and the concentration field is calculated using the Laplace equation (Methods).



Figure 2. Liquid-phase TEM imaging and analysis of directional motions of long-tail tadpoles (denoted as T1 and T2) in NaBH₄. (a) Timelapse liquid-phase TEM images showing both the position and shape of T1 during movement. (b) MSD- Δt curve on the log-log scale and fitting (black line) to obtain the diffusion exponent. (c) Centroid position trajectory of T1 overlaid with instantaneous NP orientation. (d) Schematic illustration of the definitions of particle orientation (θ_p), instantaneous velocity direction (t to t + 0.1 s, θ_{sd}), and long-time velocity direction (t - 0.5 s to t + 0.5 s, θ_{ld}). The dashed line represents a possible trajectory. (e) θ_p , θ_{ld} , and instantaneous displacement (t to t + 0.1 s) of T1 in the time range of 0.4–10.4 s. (f) Time-lapse liquid-phase TEM images, (g) MSD- Δt curve on the log-log scale and fitting (black line) to obtain the diffusion exponent, and (h) centroid position trajectory overlaid with particle orientation of T2. (i) θ_p , θ_{ld} , and instantaneous displacement of T2 in the time range of 0.4–10.4 s. For ease of comparison, the data in (e) and (i) cover the same time period of the motions (10 s, i.e., 100 frames here).

As shown in Figure 1c, the asymmetric shape of Pt NP creates a H_2 concentration gradient and thus an osmotic pressure gradient near its surface, resulting in the generation of diffusioosmotic flow.³⁰ The flow stresses and propels the NP.

Though the rough surface and presence of small cavities make the flow complicated, the overall propulsion force is predicted to drive the tadpole to move toward its head and the boomerang to move toward its elbow (Figure 1c and Table S2). Note that for the boomerang, simulation is conducted on it standing on the substrate based on our observation under TEM (Figure S5). The produced H_2 will accumulate in the confined space between the lying arm and the substrate (Figure S1c). Together with the H_2 trapped between two arms, an overall propulsion force is generated, driving the boomerang to move on the substrate toward its elbow.

Both self-electrophoresis and ionic self-diffusiophoresis are sensitive to salt concentration, whose increase will reduce the strength of the local electric field generated by concentration gradients in these two mechanisms.²⁴ We measure the diffusivity of Pt NPs in 1.98 mM NaBH₄ (the fuel) mixed with 0–20 mM NaCl by DLS. As shown in Figure S6a, while fluctuation exists, no obvious decrease in diffusivity is observed. This suggests that neutral self-diffusiophoresis, which does not depend on the salt concentration, can serve as the leading propulsion mechanism. The asymmetric distribution of chemical species can occur around catalytic NPs due to asymmetry in the NP shape, composition, and reaction rate. For U-motors, the spatial profiles of the concentration are found sensitive to nanoscale shape details. The well-maintained shape of Pt NPs makes them distinct from the self-diffusiophoresis in cadmium chloride particles, where no catalytic reactions were present but an electron beam was speculated to induce self-decomposition of cadmium chloride, which are not sustainable.⁶ It is noteworthy that the heads of the tadpoles can also be asymmetric (e.g., the third tadpole in Figure 1c). In this case, in simulation, H_2 is accumulated at one side of the tadpole, leading to the generation of a torque and a deviation in the moving direction from its long axis. Such a deviation makes the motion less directional and dependent on the instantaneous orientation of the NPs.

Direct Imaging and Quantitative Analysis of Propulsion Trajectories of U-Motors by Liquid-Phase TEM. Selfpropulsion of Pt U-motors under the NaBH₄ fuel is first experimentally verified outside TEM by DLS, in aqueous solutions of NaBH₄ or NaCl with the same concentration ranging from 0.66 mM to 1.98 mM. While only slight variations in the NP diffusivity are noticed in NaCl, an apparent increase in the diffusivity of Pt NPs is observed with increasing concentration of NaBH₄, confirming self-propulsion (Figure 1d). Interestingly, the Pt NP diffusivity reaches a plateau when the concentration of NaBH₄ exceeds 1.98 mM, likely due to the increasing amount of NaBO₂ generated by the reaction which blocks the active sites of Pt catalysts.³ It should be noted that all of the data in Figure 1d are obtained using the same batch of Pt NPs. Since the majority (82.8%, Figure S2c) of the NPs are symmetric, 10% enhancement in diffusivity observed in DLS is significant to support the presence of the driving force. Considering the applications of our U-motors in biological media, the fueling mechanism using NaBH₄ still works in solutions containing low concentrations of salt (0.66 mM NaCl), with enhanced diffusivity of Pt NPs upon increased concentration of NaBH₄ (Figure S6b,c). However, further increasing the salt concentration to 154 mM, around the ionic strength of biofluids, may lead to NP aggregation. Nanoparticle surface modification to induce high surface charge or with additional steric hindrance from bulky ligands can be considered for mitigating such aggregation.¹⁵

In our liquid-phase TEM experiments, 1.98 mM NaBH₄ is used as the fuel and flowed at a low rate of 5 μ L/min to ensure a constant fuel supply while avoiding liquid flow-induced NP

drifting (Video S1). Effects from external liquid flow are negligible as discussed in previous liquid-phase TEM studies,³ which is also verified by our observation that tracking multiple NPs in different locations reveals independent motions without global drifting (Figure S7). Low dose rates of 14.3-35.4 e⁻/ $(Å^2 \cdot s)$ are used during imaging to minimize beam-induced NP reactions, water radiolysis induced bubble formation, and ligand stripping, thus allowing real-time and real-space observation of generic NP motion trajectories (Methods). Although H₂ is generated from the Pt-catalyzed NaBH₄ decomposition, we do not observe bubbles forming near our charged, hydrophilic NPs or in the solution. Earlier studies have also suggested that hydrophobic Pt particle surfaces favor bubble generation due to the reduced energy barrier for bubble nucleation.^{32,33} The NPs are of low concentrations in our experiments; the interaction between NPs can be neglected.34,35

Figure 2a shows a typical example of a tadpole (denoted as T1) with directional motion in 1.98 mM NaBH₄. Assisted by single NP tracking, the trajectory of the centroid positions (x, y) of T1 is traced and plotted in Figure 2c, which captures unidirectional motions of T1 over extended time (>10 s). Based on the tracked centroid positions, we calculate and plot the mean-squared displacement (MSD) versus time interval (Δt) curve for T1 (Figure 2b). For anomalous diffusion, the MSD can be described by the power law:

$$MSD = \langle |\mathbf{x}(t_i + \Delta t) - \mathbf{x}(t_i)|^2 \rangle = K_{\alpha} \Delta t^{\alpha}$$
(5)

where $\mathbf{x}(t_i)$ is the NP position vector at time t_i , $\mathbf{x}(t_i + \Delta t)$ is the position vector of the same NP at time $(t_i + \Delta t)$, K_{α} is the generalized diffusion coefficient, and α is the diffusion exponent. In this general relationship of MSD~ Δt^{α} (eq 5), α < 1 means subdiffusive motion often caused by local caging effect or molecular crowding, $\alpha = 1$ suggests normal diffusion (or Brownian motion) influenced by thermal fluctuation, and α > 1 highlights the dominance of certain directions in motions and denotes a superdiffusive, propelled motion in the presence of external forces. For T1, we obtain $\alpha = 1.4$ from fitting of the MSD- Δt curve to eq 5, consistent with the persistent directionality in motions observed in liquid-phase TEM images.

In addition to tracking centroid positions, we measure the contour and orientation of NPs during the motions, which are consistent with the prediction by FEA. We define a vector pointing from the tail of the tadpole to its head, and the direction of the vector is the orientation of the NP, θ_{p} (definition in Figure 2d and an enlarged view of T1 is provided in Figure S8). We define the instantaneous velocity direction from the displacement between neighboring frames (*t* to *t* + 0.1 s) as θ_{sd} (Figure 2d). Considering that NPs may be locally trapped from time to time and the instantaneous velocity direction might not always reflect its overall directionality, we also measure the long-time velocity direction from the displacement vector over a time span of 1 s (t - 0.5 s to t + 0.5 s) as θ_{ld} (Figure 2d). As summarized in Figure 2e and Figure S9a, a positive correlation is observed among θ_{p} , θ_{sd} , and θ_{ld} for T1, with nearly identical trends exhibited in θ_p and $\theta_{\rm ld}$. This highly positive correlation is consistent with our FEA simulation (Figure 1c): if the tadpole is propelled by a locally generated chemical gradient, $\bar{\theta_{p}}$, θ_{sd} , and θ_{ld} are highly consistent as the induced osmotic pressure drives the tadpole to move toward its head. Moreover, the persistent directionality in the motion of T1 is reflected by a constant θ_{ld} , which is



Figure 3. Directional motion observed in NPs of other asymmetric shapes. (a, e) Time-lapse liquid-phase TEM images showing the directional motion of (a) a tadpole with a shorter tail (T3) and (e) a boomerang standing on the substrate. (b, f) MSD- Δt curves on the log-log scale and their fitting (black lines) showing a diffusion exponent of (b) 1.2 for T3, (f) 0.7 (<1.1 s) and 1.3 (1.1-4.5 s) for the standing boomerang. (c, g) Centroid trajectories overlaid with particle orientations for (c) T3 and (g) the boomerang. (d, h) θ_{p} , θ_{ld} , and instantaneous displacement in the time range of (d) 0.4-10.4 s for T3 and (h) 1.4-11.4 s for the boomerang.

observed during 4.5–6.2 s with $\theta_{\rm ld}$ kept at ~54°, indicating the dominance of propelled motion.

Notably, in addition to the unidirectional motions (4.5-6.2 s), the trajectory of T1 also exhibits variations in moving direction before 4.5 s and confined motions at 7.3-9.5 s (Figure 2a,c), which we attribute to pronounced randomization effect on U-motors due to thermal fluctuation and chemically heterogeneous surface of the SiN_r substrate. On one hand, the translational diffusion coefficient of a Brownian particle scales with 1/r while its rotational diffusion coefficient scales with $1/r^3$. As a result, previously studied micron-sized motors are less affected by Brownian forces than NPs and tend to exhibit long-time directional motions.9 In comparison, the orientation of the NP may not always be consistent with its moving direction, but the deviation is generally less than 90°. On the other hand, the intermittent translational motions of NPs in liquid-phase TEM can lead to strong fluctuations in $\theta_{\rm p}$ and $\theta_{\rm sd}$, accompanied by loss of correlation between them (Figure S9a). Previous liquid-phase TEM studies have identified heterogeneous charge distribution on the SiN_x substrate and thus the presence of local pinning sites.^{36–38} The random distribution of surface charge varies the NPsubstrate attraction, leading to the random trapping of NPs for different time periods. As part of a NP is pinned to the substrate, the rotation of the NP overwhelms its translational motion, leading to frequent variation in θ_{p} .

Aside from MSD, we also verify the directional motion of T1 over the tracking period through vector addition of all instantaneous velocities (Figure S10). A net velocity of 21 nm/s with a direction consistent with particle orientation is obtained, supporting the overall directional motion of T1. The variation in velocity direction over the extended tracking period, on the other hand, also indicates the non-negligible influence of Brownian force and the resulting rotation of NPs in introducing randomness to their long-term trajectories. Note that DLS measures the generic motions of the NPs in solution. In comparison, diffusivities of NPs observed in liquidphase TEM imaging have been shown to be suppressed significantly by 3–8 orders of magnitude,¹⁹ due to factors such as the strong interaction between NPs and SiN_r substrate, pinning on the SiN_x substrate, highly viscous liquid layer near the substrate, and geometric confinement of the liquid cell.^{39,40} This leads to the 2,000-times (e.g., 4.4×10^3 nm²/s vs 9.8 × $10^6 \text{ nm}^2/\text{s}$) lower diffusivity measured from liquid-phase TEM compared to that from DLS.

Directional motion is also observed in other tadpoles with a shape similar to that of T1, exemplified by T2 shown in Figure 2f and Video S2 with a diffusion exponent of 1.3 derived from the MSD- Δt plot (Figure 2g). The simultaneous occurrence of long instantaneous displacement and relatively consistent θ_{ld} (at -129°) is observed in the first 2 s, demonstrating the propelled motion of T2. Similar directional motion with smaller displacements is also resolved at 6.5–8.4 s with θ_{ld} kept at -89° (Figure 2h,i). The similar shape of T2 to T1 (a tail length of 37 ± 2.7 nm for T2 vs 37 ± 2.4 nm for T1) and thus their comparable diffusion exponent (1.3 for T2 vs 1.4 for T1)



Figure 4. Statistical analysis of motion types for fueled and unfueled NPs. (a) Time-lapse liquid-phase TEM images showing the confined motion of the tadpole (TC1) in 1.98 mM NaCl. (b) MSD- Δt curve on the log-log scale and its fitting (black line) showing a diffusion exponent of 0.90. (c) Trajectory and its overlay with the particle orientation for TC1. (d) θ_p , θ_{id} , and instantaneous displacement of TC1 between 54.3 and 64.3 s. (e) Comparison between motions of NPs in NaBH₄ and NaCl, with a higher proportion of superdiffusive NPs observed in NaBH₄. The subdiffusive, diffusive, and superdiffusive motions are defined by diffusion exponents <0.9, 0.9-1.1, and >1.1, respectively. (f) Comparison of asymmetric NPs' motions in NaBH₄ and NaCl, with a higher proportion of superdiffusive NPs observed in NaBH₄. A threshold of 10 s is placed to exclude those fragmented trajectories.

further support the robustness of our U-motor design, where catalytic NPs with asymmetric shapes can be propelled by the chemical gradient confined to them. Different from T1 where $\theta_{\rm p}$ closely matches with $\theta_{\rm ld}$, more frequent deviations are observed in T2, together with an effective diffusivity ($D_{\rm eff}$) half of that of T1 (1.7 × 10³ nm²/s for T2 vs 4.4 × 10³ nm²/s for T1, Table S3). This difference can be potentially attributed to the variation in the detailed surface structures of the tadpoles, such as their surface protrusion and concavity, and in the surface charge of SiN_x substrate.^{37,38,41}

Extension of the U-motor Design to Other Asymmetrically Shaped NPs. This self-diffusiophoresis propulsion based on the shape asymmetry of Pt NPs can be extended to other NP shapes. For example, similar directional motions are observed in T3, a tadpole of a shorter tail $(21 \pm 1.7 \text{ nm for T3})$ vs 37 \pm 2.4 nm for T1, Figure 3a-d and Figure S11a, Video S3) and without long protrusions in the head. FEA simulation (Figure 1c) predicts that, with a similar shape, a short-tail tadpole experiences a suppressed osmotic pressure and exhibits a weaker propelled motion than a long-tail one, due to a smaller chemical gradient generated with a shorter tail.⁴² This prediction is supported by our experiment. The D_{eff} measured from the diffusive regime of the MSD- Δt curve and containing contributions from both Brownian motion and propulsion, for T3 is three times smaller than that of T1 ($1.3 \times$ $10^3 \text{ nm}^2/\text{s}$ for T3 vs $4.4 \times 10^3 \text{ nm}^2/\text{s}$ for T1, Table S3). The rotational randomization at 21 s also suppresses the net displacement of T3, resulting in a smaller diffusion exponent of 1.2. The strong correlation, on the other hand, still exists

among θ_{p} , θ_{sd} , and θ_{ld} , suggesting the chemical gradient as the major driving force; T3 also shares the same propulsion mechanism as T1.

In addition to tadpoles, the self-diffusiophoresis mechanism can be applied to other asymmetric shapes. Figure 3e-h and Video S4 show the directional motion of a boomerang that, interestingly, stands on the SiN_x substrate and projects a wedge shape under liquid-phase TEM imaging where the flipping of the boomerang is later observed (Figure S5). Notably, the MSD- Δt curve shows two regimes, with an increase observed in the diffusion exponent from 0.7 ($\Delta t < 1.1$ s) to 1.3 ($\Delta t > 1.1$ s). This transition from subdiffusive motion to directional, superdiffusive motion at crossover Δt suggests a short-time trapping effect that is overcome by directional motions. By defining the boomerang orientation as the orientation $\theta_{\rm p}$ of the vector pointing from the tip of the lying arm to the elbow (Figure S5c), a close correlation is observed between θ_{p} , θ_{sd} , and $\theta_{\rm ldt}$ suggesting the boomerang is mostly moving toward its elbow. Such an observation follows our FEA simulation (Figure 1c), where a high concentration of H_2 is trapped between two arms and the substrate. The induced chemical gradient propels the boomerang to move (from tips) toward elbow.

Statistical Trajectory Analysis Showing U-Motors Follow Subdiffusive Motions Without Fuels. Going beyond single NP trajectory analysis, we track more than 180 NPs in total, which are dispersed in the NaBH₄ (with fuel) and NaCl (without fuel) solutions at the same concentration of 1.98 mM, whose results show that fueled NPs have a significantly higher portion of propulsive motions. Here, the same concentration of NaCl is used as the control group to approximate the ionic strength of NaBH4 and thus the influence from substrate-NP interaction.¹⁹ In the unfueled NaCl solutions, only subdiffusive motions are observed in the tadpoles. Figure 4a and Video S5 show a typical tadpole (TC1) with a diffusion exponent of 0.90 derived from the MSD- Δt curve (Figure 4b). As evident from crowded translational and orientation trajectories (Figure 4c), frequent pinning of TC1 to the SiN_x substrate is observed over 10 s, accompanied by weak correlation between $\theta_{\rm p}$, $\theta_{\rm sd}$, and $\theta_{\rm ld}$, frequent changes in $\theta_{\rm ld}$, small D_0 (5.9 × 10² nm²/s for TC1 compared to (1.3–4.4) \times 10³ nm²/s for tadpoles and boomerang in NaBH₄), and small averaged instantaneous velocity (66 nm/s for TC1 compared to 80-110 nm/s for those in NaBH₄) (Figure 4d and Figure S12). Here, D_0 represents the diffusivity of an unfueled NP, measured from the diffusive regime of its MSD- Δt curve and without contribution from propulsion. Similar sluggish motion of tadpoles in NaCl is also seen in other tadpoles, regardless of the size. TC2 in Figure S13, for example, has a diffusion exponent of 0.67, highly uncorrelated $\theta_{\rm p}$ and $\theta_{\rm ld}$, and considerably slow averaged instantaneous speed (39 nm/s). In fact, no displacement is observed for TC2 from 5.5 to 10.0 s, indicating the attraction of TC2 to the substrate and the lack of strong force to free it to even just exhibit Brownian motion.

In liquid-phase TEM, the diffusivity of fueled tadpoles is more than twice higher than that of unfueled ones with similar shapes, similar for the averaged instantaneous velocity (Tables S3 and S4), which confirms the existence of a propulsion force in the presence of fuels. Moreover, independent motions of NPs are observed in different locations of the liquid cell, as shown in Figure S7, suggesting that the directional motion is not contributed by global drifting. The correlation between θ_{p} and θ_{sd} is also quantitively analyzed. As shown in Figure S14, compared to tadpoles in NaCl, those in NaBH₄ exhibit a higher consistency in $\theta_{\rm p}$ and $\theta_{\rm sd}$, represented by higher percentages of their θ_{sd} falling in the range of $\theta_p \pm 90^\circ$, 60° , and 45°. The Pearson's correlation coefficients for $\theta_{\rm p}$ and $\theta_{\rm sd}$ are calculated (Table S5). Higher correlation coefficients are observed in tadpoles in NaBH₄ compared with those in NaCl, providing supportive evidence for the propelled motion of Pt NPs in the presence of fuels.

Statistically, only 1.6% of the NPs in NaCl shows slightly superdiffusive motion (one dendrite among all the 66 NPs tracked with a diffusion exponent of 1.1), in comparison to 9.6% of the NPs in NaBH₄ showing diffusion exponents larger than 1.1 (Figure 4e and Figure S15). The directional motion of the one Pt NP in NaCl could be due to small concentrations of H₂O₂ generated from radiolysis of water under e-beam illumination (<0.6 mM based on the simulation shown in Figure S16),⁴³ which can also be catalyzed by Pt to induce O_2 gradient around Pt NPs. However, such propulsion is weak, considering the low concentration of H₂O₂ and the negligible amount of superdiffusive NPs in NaCl. If only asymmetric NPs are considered, no propelled motion is characterized in NaCl at all, while 16.7% of the NPs undergoes superdiffusive motion in NaBH₄ (Figure 4f). Such a difference supports the presence of propulsion force in NaBH4, which arises from its decomposition catalyzed by Pt. It should be noted that the diffusion exponents compared in Figure 4e,f are all derived from fitting of the MSD- Δt curve (on the log-log scale) in the range of 0.5 to 2.0 s, ensuring the reliability of the

comparison. The majority of NPs undergo subdiffusive motion in either NaBH₄ or NaCl, with similar proportions (\sim 75%). We attribute it mostly to the dominance of symmetric NPs (82.8%, Figure S2c) in the product from one-pot synthesis, which does not have enough propulsion to drive directional motions.

To further confirm that the propelled motion of our Umotors is not due to the surface heterogeneity of SiN_x substrates, we quantitatively compare the motions of tadpoles and spherical dendrites in the presence of chemical fuels. As shown in Figure S17, an obvious augmentation in superdiffusive motion is observed in tadpoles when compared to symmetric dendrites (a total of 37 NPs analyzed), validating that the observed superdiffusive motion is due to the presence of driving force. We also compare the motion of symmetric dendrites in 1.98 mM NaBH₄ in three independent liquidphase TEM experiments (Figure S18), given the possible variations in NaBH₄ decomposition and radiolysis of solvent that may affect the surface chemistry of SiN_x substrate and thus the motion of NPs. Subdiffusive motion is observed to dominate in all three experiments with symmetric dendrites, confirming the consistency in our experiments regardless of potential pH change or (local) ionic strength variation.

Motion Analysis for Passive and Active NPs in the Liquid Chambers. In a liquid chamber without fuel, a dilute solution of NPs that are considered as passive will experience two major sources of friction: (i) hydrodynamic Stokes drag due to the solvent and (ii) NP–substrate interactions which at long times will result in an additional contribution to the total friction constant. Qualitatively, this scenario can be described in a simple generalized Langevin equation (GLE) for the passive NP velocity:

$$M\frac{\mathrm{d}\nu}{\mathrm{d}t} \approx -\zeta_{\mathrm{s}}\nu + \delta f_{\mathrm{s}}(t) - \int_{0}^{t} \mathrm{d}t' K(t-t')\nu(t') + \delta f_{\mathrm{K}}(t)$$
⁽⁶⁾

where ζ_s is the hydrodynamic Stokes–Einstein friction constant due to NP–solvent interactions, $\delta f_s(t)$ is the corresponding fluctuating force, $-\int_0^t dt' K(t-t')v(t')$ is the systematic effective force from NP–substrate interactions where the memory function K(t) is proportional to the selfcorrelation of NP–substrate force between a certain time interval, and $\delta f_K(t)$ is the corresponding fluctuating force. Note that eq 6 is schematic in that it is not written in a vectorial manner and there is no dependence on distance from the substrate, *z*. These simplifications seem qualitatively reasonable, given that we track NPs moving close to the substrate and analyze their in-plane two-dimensional (2D) trajectories.

With TC1 serving as a representative example of passive NPs in NaCl (Figure 5a), we experimentally obtain a diffusion exponent of 0.9 at short times (<3 s) followed by a transition from subdiffusive to diffusive motion at longer times (>3 s). Thus, the MSD can be qualitatively described as

$$MSD = B\Delta t^{0.9}, \ \Delta t \ll \tau^* \tag{7}$$

$$MSD = 4D_0 \Delta t, \ \Delta t \gg \tau^*$$
(8)

Here, *B* is a constant with proper units, and τ^* is the crossover time from subdiffusion to normal diffusion. Such a behavior of the MSD would emerge from the above GLE if the memory function was of the form:



Figure 5. MSD- Δt curves of (a) TC1 and (b) a dendrite in 1.98 mM NaCl, (c) T1 and (d) T3 in 1.98 mM NaBH₄. The fittings of the curves as well as the diffusion exponents are labeled to different time periods.

$$K(t) \propto A\left(\frac{\tau_0}{\tau_0 + t}\right)^{0.9} \exp\left(-\frac{t}{\tau^*}\right)$$
(9)

where A is a constant with proper units, τ_0 is an elementary short time scale. When the observation time is long compared to τ_0 , but short compared to τ^* , such that the NP has experienced many types of interactions with the substrate, the memory function is of an inverse power law in time form with a fractional exponent, resulting in the subdiffusive MSD. However, if the observation time is long enough $(t > \tau^*)$, the NP-substrate interactions result in an additional frictional drag force (ζ_K) on the NP, which follows the well-known relation

$$\zeta_{\rm K} \propto \int_0^\infty {\rm d}t K(t) \propto \tau^{*0.1} \tau_0^{0.9} \tag{10}$$

In our physical system, this extra friction constant reflects the retardation of NP motion due to its interaction with the substrate, and the corresponding long-time NP diffusivity (D_0) is

$$D_0 = \frac{k_{\rm B}T}{\zeta_{\rm s} + \zeta_{\rm K}} \ll \frac{k_{\rm B}T}{\zeta_{\rm s}} \tag{11}$$

In our experimental results, D_0 obtained from liquid-phase TEM is 3 orders of magnitude smaller than that measured from bulk dilute solution test (DLS), suggesting that the friction arising from NP-substrate interaction is much larger than the hydrodynamic drag force from pure solvent, as indicated by the inequality in eq 11. Similar motion is also observed in symmetric dendrites with a transition from subdiffusive to diffusive motion captured at ~4 s (Figure 5b). The diffusion exponent and transition time may vary among NPs due to the variation in NP shape, local surface charge and roughness of the SiN_x substrate, and NP-substrate interactions.

It should also be noted that NPs commonly follow a "stickand-slip" motion in the liquid cell as the SiN_x surface is not homogeneous.^{36,37,41,44} In this case, the NPs are expected to show subdiffusive motion at a small time scale due to temporary adsorption onto the substrate and diffusive motion at a long time scale due to the ultimate averaging of the consequence of NP–substrate jumps. Moreover, the time scale for NP desorption is likely characterized by a distribution of the adsorption energies and barriers. This quenched disorder could serve to induce a continuous time random walk (CTRW) behavior that underlies the fractional temporal power law decay of K(t) on intermediate time scales and hence subdiffusive MSD– Δt behaviors.⁴⁵

For the propelled NPs in NaBH₄, an additional propulsive force is added, leading to superdiffusive motion observed at short time scales (generally <2 s based on experimental observation shown in Figure 5c,d). Such a superdiffusive regime cannot be observed in passive NPs in NaCl, differentiating the two systems with and without driving force. As time extends (>4 s), stochastic fluctuations eventually randomize the direction of propulsion force due to NP interactions with the solvent molecules or adsorption/ desorption events at the surface, which both can induce NP rotation. For tadpoles with weaker driving force (T3, Figure 5d), a subdiffusive regime can be observed between 3 s and 4 s, which can be attributed to the attenuated impact from propulsion overcome by that from thermal fluctuation and NP-substrate interaction. It is clear that with all the different forces considered, the analysis of the MSD- Δt curves still clearly differentiates the behaviors of passive, nonfueled NPs in comparison with fueled NPs undergoing propelled motions. We foresee our analysis on the nonmonotonic evolution of MSD over time will benefit further investigations into the motion of passive or active NPs under liquid-phase TEM.

CONCLUSIONS

We integrate liquid-phase TEM imaging and FEA simulation to understand the propulsion mechanism of U-motors, which have remained otherwise underexplored. The reaction system is carefully designed, with asymmetric Pt NPs (<100 nm) chosen as the U-motors and H₂ gradient arising from decomposition of NaBH4 as the driving force. Benefiting from the nanometer resolution, the trajectory, MSD, particle orientation, and its consistency with moving direction can all be extracted from TEM movies, which are further utilized to verify the underlying self-diffusiophoresis mechanism as well as an anatomy of the components of the motions. Based on the statistics of more than 180 NPs, we show how self-catalyzed decomposition of NaBH4 can serve as a sustainable driving force over Brownian forces. Compared to micromotors, the motion of U-motors is influenced more strongly by Brownian force, as indicated by the inverse scaling of translational and rotational diffusivities with particle size.

In general, for U-motors, surface heterogeneity, either from geometric asymmetry or variation in surface composition, is required for the generation of driving force, which is necessary for overcoming thermal fluctuations and directing the motion of the NP.⁴ For monocomponent nanomotors, exemplified by the Pt tadpoles and boomerangs in this work, symmetry breaking in NP shape (e.g., aspect ratio, surface facet, curvature, and roughness) is of great significance in inducing an asymmetric distribution of chemical species around the NP to induce propulsion. For a more pronounced chemical gradient and controlled NP velocity, the confinement effect brought by the concave surface can be considered, which concentrates chemicals near the surface of the NP. The confinement of H₂ between the dendritic heads and elongated

tail of the tadpole as well as the two arms of the boomerang is crucial for inducing a sufficiently strong gradient to propel the directional motion of NPs. When the NP-substrate interaction is also considered, NPs with smaller contact area with the substrate may experience a reduced trapping effect and thus a higher probability for exhibiting diffusive or super-diffusive motion in the presence of a driving force (Figure S19).

As to future work, more stable fuel, NPs with higher catalytic reaction rates and more pronounced shape asymmetry or surface composition variation, and solvents with different dielectric constants and viscosities can be considered.^{4,46} For example, NPs featuring concave cavities such as nanotubes and nanobowls can be expected to exhibit stronger propulsion force due to the confinement of chemicals within the cavity and thus the generation of a larger chemical gradient.¹² Janus NPs serve as another promising candidate, where catalytic reactions occur at one end of the NP. A more asymmetric distribution of chemicals is anticipated with enhanced propulsion force exerted on the NP. In addition, by utilizing viscous liquid with high dielectric constant, such as glycerol and glycerol carbonate, the electron beam effect can be reduced and a consistent diffusivity measured in liquid-phase TEM and DLS may be achieved.⁴⁶ We see our work as the stepping stone for more colloidal design of asymmetric NPs as active ultrasmall nanomachines, for more liquid-phase TEM studies to significantly advance our understanding of their morphology-performance relationship, and for more studies into these nanomachines and their applications in broader fields such as biomedicine and energy storage.

METHODS

Chemicals. Sodium hexachloroplatinate(IV) hexahydrate (98%, Na₂PtCl₆·6H₂O, Sigma-Aldrich), D-(+)-glucose (≥99.5%, C₆H₁₂O₆, Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB, for molecular biology, ≥ 99%, C₁₉H₄₂BrN, Sigma-Aldrich), oleylamine (technical grade, 70%, C₁₈H₃₇N, Sigma-Aldrich), sodium borohydride (99%, NaBH₄, Sigma-Aldrich), sodium chloride (≥99.0%, NaCl, Fisher Scientific), acetone (≥99.5%, C₃H₆O, Fisher Scientific), 2-(2-(2-(11-mercapto-undecyloxy)-ethoxy]-ethoxy)-ethoxy−ethoxy− et h o x y − e t h o x y − a c e t i c a c i d (≥ 9 5 %, H S - (CH₂)₁₁(OC₂H₄)₆OCH₂COOH, Prochimia Surfaces), sodium phosphate monobasic monohydrate (molecular biology grade, ≥99%, NaH₂PO₄·H₂O, EMD Millipore), sodium phosphate dibasic anhydrous (≥99%, Na₂HPO₄, Acros) were purchased and used without further purification. Throughout the experiments, we used deionized (DI) water with a resistivity of 18.2 MΩ·cm at room temperature.

Synthesis of Pt NPs. In a standard protocol, 8.9 μ mol of Na₂PtCl₆·6H₂O, 0.25 mmol of glucose, and 0.05 mmol of CTAB were mixed with 2.5 mL of oleylamine in an 8 mL glass vial. The vial was closely capped, transferred to an oil bath set at 95 °C, and preheated for 30 min under vigorous stirring, during which time the solution turned clear. It was then transferred to a second oil bath set at 167 °C and reacted for another 4 h followed by cooling down to room temperature. The product was collected by mixing the reaction solution with 7.5 mL of acetone, centrifuged at a speed of 5000 rpm for 5 min, washed one more time with acetone (5000 rpm for 5 min), and redispersed in 2 mL of water.

Thiol Modification of Pt NPs. The thiol modification of Pt NPs was conducted following our previous work.²⁰ Typically, 1 mL of the Pt NPs was centrifuged at 7000 rpm for 7 min followed by removing all of the supernatant and redispersed in 3.05 mL of water. As the next step, $44.26 \ \mu$ L of aqueous thiol solution (HS-(CH₂)₁₁(OC₂H₄)₆OCH₂COOH, 7.93 mM) was added, mixed with Pt NPs, and incubated for 30 min for the ligand exchange. The solution was then sonicated for 5 s and added to 0.163 mL of 1 M

phosphate buffer solution (PBS, pH = 8, composed of 70 mM sodium phosphate monobasic monohydrate and 930 mM sodium phosphate dibasic anhydrous). The solution was left undisturbed for 1 week, waiting for the Pt NPs to sediment to the bottom of the tube. 12 μ L of the sediment was then pipetted out, diluted in 100 μ L of water, and centrifuged at a speed of around 2000 rpm for 1 min. Finally, 82 μ L of supernatant was removed, and 10 μ L of water was added. The solution was well mixed by a pipet and later used for liquid-phase TEM.

Tracking NP Motion Using Liquid-Phase TEM. Liquid-phase TEM imaging was performed on a Hitachi 9500 TEM with a LaB₆ emitter at 200 kV, and a spot size Micro 1 was used for TEM imaging. Movies were captured by a Gatan Orius fiberoptically coupled CCD camera with an exposure time of 0.1 s at a rate of 10 frames per second (fps). A liquid flow TEM holder (Hummingbird Scientific) was used. In a standard protocol, 0.1 μ L of thiol-coated Pt NPs was dropped onto a SiN_x spacer chip (window: 50 μ m × 200 μ m × 50 nm, 250 nm spacer, Hummingbird Scientific) and overlaid with a window chip (window: 30 μ m × 650 μ m × 50 nm, Hummingbird Scientific). Both chips were pretreated with oxygen plasma (Harrick Plasma Cleaner PDC23G) at a low radio frequency level for 27 s to clean their surfaces and render them hydrophilic. Water was first flown into the liquid chamber for 10 min at 5 μ L/min followed by 1.32 mM NaBH₄ for 30 min and 1.98 mM NaBH₄. Videos were taken after flowing 7 min of 1.98 mM NaBH₄, and the flow speed was kept at 5 μ L/min during video recording. Due to the small thickness of spacer and the slow flowing rate, the liquid was supposed to slowly penetrate into the chamber and its influence on the movement of NPs could be negligible. The different moving directions of NPs in NaBH₄ also indicated the weak influence of the flowing liquid, which was overwhelmed by self-propulsion. A dose rate of 35.4 $e^{-}/(A^2 \cdot s)$ was used throughout the experiment, unless specifically mentioned.

Different concentrations of NaBH4 were also tested to verify the presence of propulsion and the behavior of NPs. In pure water absent of NaBH₄, NPs stayed attached to the substrate and negligible motions were observed (Figure S20). Due to the balance of input and output charges, the surface of the SiN_x chip is supposed to be positively charged under beam illumination,^{37,47} leading to an electrostatic attraction confining the negatively charged Pt NPs to the substrate. When a 1.98 mM NaBH₄ solution was flowed into the liquid chamber, the increased ionic strength and thus counterion screening of the NP-substrate attraction as well as the fueling reaction released the NPs from the substrate, allowing them to move freely near the substrate. A higher concentration of NaBH₄ (2.64 mM) also promoted NP motions. However, the more effective screening of counterion attraction made NPs easily escape from the substrate and diffuse out of focus, making the trajectory tracking difficult. According to previous works, beam-induced radiolysis reactions will lead to slight increase of the ionic strength in the illuminated area, further releasing the NP from the substrate attraction.

Structural Characterizations, Diffusivity, and pH Measurement. Hitachi 9500 TEM with a LaB₆ emitter at 200 kV was used to characterize the size and shape of the Pt asymmetric NPs. The diffusion coefficients and zeta potentials of thiol-coated Pt NPs in water, NaCl, and NaBH4 were measured using a Zetasizer Nano (Malvern). To mimic the environment in a liquid cell, where radiolysis of water contributes to the generation of H⁺ and a solution pH of 4.5 in the absence of NaBH₄, the NaCl and NaBH₄ solutions used for DLS measurements were all prepared by HCl solution with a pH of 4.5. Specifically, 0.053, 0.058, 0.065, 0.074, 0.18, and 0.24 mL of 13.2 mM NaBH₄ or NaCl were added to 1 mL of Pt NP suspension (in HCl solution) sequentially to reach a final concentration of 0.66, 1.32, 1.98, 2.64, 3.96, and 5.28 mM, respectively. The pH change was measured by a pH Meter FiveEasy F20 (Mettler Toledo). Specifically, 5 μ L of thiol-coated Pt NPs was mixed with 10 mL of 1.98 mM NaBH₄ and the change of pH was recorded until it stabilized. The control experiment was conducted using the same procedure but in the absence of Pt NPs.

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13)

Finite Element Simulation of H_2 Gradients Around Pt NPs. COMSOL Multiphysics (version 5.4a) was used to simulate the chemical concentration gradient and resulting diffusioosmotic flow around U-motors (Figure 1c). The contours of the U-motors were extracted from TEM images¹⁹ and used for simulation. For tadpoles, the simulation plane was parallel to the substrate, while for the boomerang, the simulation plane was vertical to the substrate and parallel to particle propulsion direction since it stood up. The 2D contour of the U-motor was placed in a 250 nm × 250 nm plane filled with DI water as media. In simulation, COMSOL expanded the plane to a three-dimensional (3D) column with infinite thickness and simulated the 3D flow, whose cross-sectional view is shown in Figure 1c. The simulation involved modules of transport of diluted species and creeping flow, both are built-in functions in COMSOL:

$$\nabla \cdot \boldsymbol{J} + \boldsymbol{u} \cdot \nabla \boldsymbol{c} = \boldsymbol{0} \tag{12}$$

$$J = -D\nabla c \tag{(1)}$$

$$\mu \nabla^2 \boldsymbol{u} - \nabla \boldsymbol{p} = 0 \tag{14}$$

$$\nabla \cdot \boldsymbol{u} = \boldsymbol{0} \tag{15}$$

where **J** is the flux of H₂, **u** is the diffusioosmotic flow velocity, *c* is the concentration of H₂, *D* is the diffusivity of H₂ in water set as $10^{-9} \text{ m}^2/\text{ s}$, $r^{29} \mu$ is the dynamic viscosity of water set as $1 \text{ mPa}\cdot\text{s}$, r^{29} and *p* is pressure. The H₂ generation rate on U-motor surface was set as $10^{-4} \text{ mol}/(\text{m}^2\cdot\text{s})$ based on experiments (Supporting Information). Due to asymmetric shape of U-motors, the concentration of produced H₂ was expected to be nonuniform, where such a gradient will induce self-diffusiophoresis, described by boundary condition of the particle:⁴⁸

$$\boldsymbol{u}_{s} = \boldsymbol{M}(\boldsymbol{I} - \boldsymbol{n}\boldsymbol{n})\boldsymbol{\nabla}\boldsymbol{c} \tag{16}$$

where u_s is the surface velocity, M is the mobility of H_2 set as $10^4 \text{ nm}^2/(\text{s}\cdot\text{mM})$,⁴⁹ and (I - nn) defines the chemical gradient of H_2 tangential to the U-motor surface with I representing the identity matrix and n as the local normal unit vector to particle surface.^{48,49} The diffusioosmotic flow gives stress (σ) to the particle and propels the particle. The propulsion force (F_p) on the U-motor is calculated as

$$F_p = \int_s \boldsymbol{\sigma} \cdot \boldsymbol{n} ds \tag{17}$$

$$\boldsymbol{\sigma} = -p\boldsymbol{I} + \mu(\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^{T}) \tag{18}$$

where s is the surface area. The numerical simulations presented above enable us to predict the propulsion of the shaped U-motors qualitatively.

TEM Movie Processing and Single NP Tracking. For all TEM videos captured in .avi format with the size of 1144-by-1144 pixels, ImageJ was used to resize each frame in the videos to 512-by-512 pixels, and the frames were saved in ".tif" format. A custom MATLAB code was used to track the motions of the NPs in two steps. (1) Segmentation was performed on each frame to find the centroid coordinates of the NPs. In this step, the images were first denoised by the built-in function "imgaussfilt.m" with a sigma of 5 pixels and then binarized by the built-in function "adaptthresh.m" with a sensitivity of 0.7. After the segmentation, the isolated regions connected to the image boarder were deleted using the built-in function "imclearborder.m" to ensure the correct detection of centroid coordinates. The centroid coordinates of the NPs were finally given by the built-in function "regionprops.m". (2) Due to the presence of multiple NPs in each frame, the trajectory of the same NP has to be linked from its coordinates in different frames. This step was done using a custom MATLAB code developed by the literature.⁵⁰ During this step, the maximum displacement of NPs between neighboring frames was set to 120 pixels to save computational cost. Meanwhile, the NPs were allowed to be missing in maximum five consecutive frames to prevent the trajectory from being interrupted by the missed frames due to the motion blur effect. After this automatic tracking, a few trajectories might still be disconnected to give several segmented trajectories or

swapped in the middle. To solve the issues, each trajectory was then inspected and manually corrected.

For tadpoles, the rotation of NPs may lead to the loss of tracking of their tails due to fast motion or being out of focus. In this case, we utilized the centroid of the head to track the position of tadpoles, and each trajectory was inspected and manually corrected after automatic tracking to ensure the centroid accurately corresponds to the tadpole head. For boomerangs, either standing or lying on the substrate, their larger contact area with the substrate makes it harder for them to rotate out-of-plane. Thus, tracking the center of mass of their 2D projections is accurate enough to show their trajectory.

MSD Calculation. For each trajectory, the MSD is defined and calculated as $\frac{1}{N} \sum_{i=1}^{N} |\mathbf{x}(t_i + \Delta t) - \mathbf{x}(t_i)|^2$, where $\mathbf{x}(t_i)$ represents the NP position at *i*th time point sampled in the trajectory; $\mathbf{x}(t_i + \Delta t)$ represents the position at time Δt after t_i ; and N is the total number of time points that can be sampled from this trajectory when time interval is Δt .⁴⁰ The slope of each MSD- Δt curve (on the log-log scale) was calculated by using the linear regression method from the MSD and Δt values in the range of 0.5–2.0 s.

To assess the statistical significance for the MSD analysis, we calculated the standard error (SE) of MSD: 51,52

$$SE = \frac{STD}{\sqrt{N}}$$
(19)

where STD is the standard deviation of MSD and N is the number of displacements (within a certain time interval) used for MSD calculation. Using T1 as an example, relatively small errors are observed, as shown in Figure S21. In the case where bias might be introduced using overlapping intervals, with T3 as an example, we compared the MSD derived from both independent and overlapping intervals (Figure S22). A similar diffusion exponent of 1.2 was obtained from both methods, suggesting their negligible difference in interpreting NP motion in our case.

Orientation Measurement. For orientations of displacements in the trajectory, θ_{sd} and θ_{ld} were calculated using the built-in function "atan2d.m" which returned the four-quadrant inverse tangent expressed in degrees of the displacement vector. The $\theta_{sd}(t)$ is defined as $atan2d(\mathbf{x}(t + 0.1 \text{ s}) - \mathbf{x}(t))$ and $\theta_{ld}(t)$ is defined as $atan2d(\mathbf{x}(t + 0.5 \text{ s}))$, where $\mathbf{x}(t)$ represents the NP position at time t. Due to the noise and the possible motion blur effect in the movies, the orientations of NPs (θ_p) in each frame were measured manually by "angle tool" in ImageJ.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.3c12590.

Literature summary of synthetic and characterization methods of U-motors, literature summary of NP motions observed under liquid-phase TEM, characterization of Pt NPs, calculation of H_2 generation rate, DLS measurements in a mixture of NaBH₄ and NaCl, simulation of propulsion force, simulation of H_2O_2 concentration, additional liquid-phase TEM images and data analysis (PDF)

Video S1: Liquid-phase TEM video (left) and corresponding centroid position trajectory overlaid with instantaneous NP orientation (right) showing the directional, self-propelled motion of T1 in 1.98 mM NaBH₄; dose rate: 35.4 $e^{-}/(Å^2 \cdot s)$ (AVI)

Video S2: Liquid-phase TEM video (left) and corresponding centroid position trajectory overlaid with instantaneous NP orientation (right) showing the directional, self-propelled motion of T2 in 1.98 mM NaBH₄; dose rate: $35.4 \text{ e}^-/(\text{Å}^2 \cdot \text{s})$ (AVI)

Video S3: Liquid-phase TEM video (left) and corresponding centroid position trajectory overlaid with instantaneous NP orientation (right) showing the directional, self-propelled motion of T3 in 1.98 mM NaBH₄; dose rate: 35.4 $e^{-}/(Å^2 \cdot s)$ (AVI)

Video S4: Liquid-phase TEM video (left) and corresponding centroid position trajectory overlaid with instantaneous NP orientation (right) showing the directional, self-propelled motion of a standing boomerang in 1.98 mM NaBH₄; dose rate: $35.4 \text{ e}^-/(\text{Å}^2 \cdot \text{s})$ (AVI)

Video S5: Liquid-phase TEM videos showing the subdiffusive motions of TC1 (left) and TC2 (right) in 1.98 mM NaCl; dose rate: $35.4 \text{ e}^{-}/(\text{Å}^2 \cdot \text{s})$ (MP4)

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Notes

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