ACS APPLIED MATERIALS & INTERFACES

Letter

Cite This: ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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Catalytic Micromotors Moving Near Polyelectrolyte-Modified Substrates: The Roles of Surface Charges, Morphology, and Released Ions

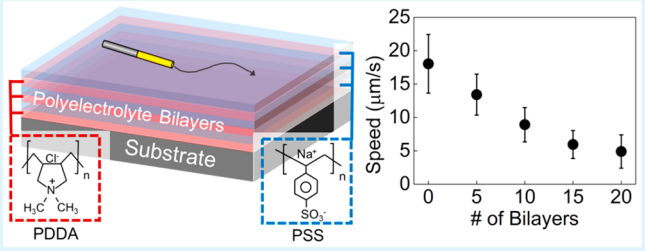
Mengshi Wei,[†] Chao Zhou,[†] Jinyao Tang,[‡] and Wei Wang*[,†]

[†]School of Materials Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055,China

[‡]Department of Chemistry, University of Hong Kong, Hong Kong SAR 999077, China

Supporting Information

ABSTRACT: Synthetic microswimmers, or micromotors, are finding potential uses in a wide range of applications, most of which involve boundaries. However, subtle yet important effects beyond physical confinement on the motor dynamics remain less understood. In this letter, glass substrates were functionalized with positively and negatively charged polyelectrolytes, and the dynamics of micromotors moving close to the modified surfaces was examined. Using acoustic levitation and numerical simulation, we reveal how the speed of a chemically propelled micromotor slows down significantly near a polyelectrolyte-modified surface by the combined effects of surface charges, surface morphology, and ions released from the films.



KEYWORDS: *micromotors, electroosmosis, simulation, ultrasound manipulation, self-assembled wrinkles*

Recently, there have been strong research interests in synthetic microswimmers ("micromotors") as model systems to understand living active matter,[1−4] and increasingly so on their dynamics near confinements.[5−12] This is an important issue because both the individual dynamics and collective behaviors of a microswimmer critically depend on its interaction with boundaries.[13] In a more practical sense, applications with living or synthetic microswimmers almost always involve a wall near which the particles accumulate, such as those encountered in microfluidic chips and blood vessels.[14−17] Recent experimental studies show that micromotors, especially those powered by chemical gradients, are very sensitive to geometrical obstacles; they can be steered by walls, trenches, and large spheres, and accelerate in narrow channels.[6−11,18−20] These topological features, however, are often produced by physical means, while chemical modification remains a fertile ground that is largely unexplored. Here we show substrates coated with charged polyelectrolyte bilayers significantly slow down catalytic micromotors moving nearby, and, with the help of acoustic levitation technique and numerical simulations, reveal the role of surface charges, ionic strength, and surface wrinkles in such an effect.

Bimetallic (such as gold−ruthenium, or AuRu) micromotors are chosen as a model system for our study.[21] When exposed to hydrogen peroxide solutions, the gold end of the AuRu rod preferentially catalyzes the oxidation of H_2O_2 into O_2, which (along with H_2O_2) reduces into H_2O at the Ru end. The production and consumption of protons during this process establishes a localized electric field, in which the negatively charged microrod moves.[22,23] This so-called self-electrophoresis mechanism is one of the most successful and consistent operating mechanisms for micromotors, and its operation crucially depends on the local distributions of chemical concentrations, electrical potential and fluid flows, all of which can be altered by nearby boundaries. Moreover, metal particles are heavy and sediment closer to the bottom, making them more sensitive to the presence of boundaries. For these reasons, bimetallic micromotors qualify as a good model system to study the boundary effects.

Previously, it was shown that such kind of bimetallic micromotors moved substantially more slowly near a charged glass substrate than in the bulk.[24] This observation was qualitatively attributed to the electroosmotic flow near the charged substrate. To elaborate, because bimetallic micromotors move phoretically in a self-generated electric field, the same field can also couple to a charged and nearby substrate (e.g., glass) that induces electroosmosis and hinders the motor if both the particle and the substrate carry the same type of charges (Figure 1a). Furthermore, charges on these two surfaces dictate the magnitude of their electrical interactions and therefore their separation, which determines the degree of confinement for micromotors. Similar boundary effects were also noted in two previous studies where bimetallic micromotors were found to speed up in tightly confining micro-

Received: December 4, 2017
Accepted: January 4, 2018
Published: January 4, 2018

DOI: 10.1021/acsami.7b18399
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

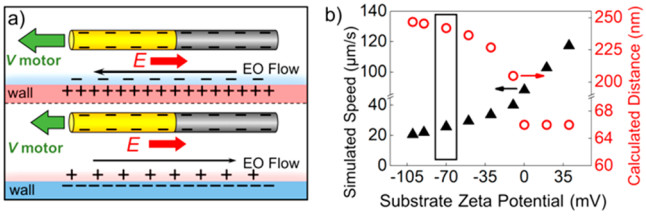


Figure 1. Micromotor dynamics near charged substrates. (a) Schematic showing the difference in separation distance, electroosmotic (EO) flow direction, and motor speeds (V_{motor}) between AuRu motors moving on a positively (top panel) and a negatively charged substrate. (b) Simulated motor speeds (black triangles) increase as the substrate zeta potential is arbitrarily changed from negative to positive, while the calculated separation distance between the rod and the substrate (red circles) decreases. Values in the black box correspond roughly to experimental conditions. See the Supporting Information for detailed calculations.

channels,[19] but slow down when only confined by one wall.[6] To exploit such a boundary effect to systematically manipulate micromotor dynamics, finite element simulation was first performed to provide guidance. Figure S7 presents the distribution of electric fields and fluid flows near an active bimetallic rod and a charged substrate. By arbitrarily varying the substrate surface zeta potential, the direction and magnitude of the surface electroosmotic flows change (Figure S8). So does the distance between the rod and the bottom. Taking these into consideration, our simulation suggests that a bimetallic rod would move faster above a less negatively charged surface, and even more so on a positively charged surface (Figure 1b).

Can we experimentally modify the surface charge and test our simulation results? This can be accomplished by a simple and well-developed technique called layer-by-layer (LBL) assembly (Figure 2a), where oppositely charged polyelectrolyte films are sequentially deposited on a substrate through electrostatic forces. By stopping the assembly at the right layer, a modified surface with positive or negative charges can be obtained. In our experiments, positively charged poly(diallyldimethylammonium chloride) (PDDA), and negatively charged poly(sodium-*p*-styrenesulfonate) (PSS) constituted one bilayer,[25] and such a LBL assembly was repeated up to 20 times to obtain uniform coating of ∼200−300 nm thickness. Details of the coating process and characterization of the film can be found in the Supporting Information. Surface zeta potential of the uncoated glass substrate was measured to be −72.9 mV, whereas it changed to −25.6 mV and +32.4 mV for bilayers ending with PSS and PDDA, respectively. In a typical experiment, AuRu bimetallic rods of ∼3 μm long and ∼300 nm in diameter were electrochemically synthesized and suspended in 15 vol % H_2O_2 solution in an experimental cell of ∼200 μm in height. The bottom of these cells is made of functionalized substrates, and the dynamics of micromotors moving near the substrate were tracked by optical microscopy, their speeds calculated and compared.

Somewhat surprisingly, speeds of bimetallic micromotors on polyelectrolyte surfaces were rather inconsistent with our simulation. For example, negatively charged bimetallic microrods moved consistently more slowly than near pristine glass surfaces, with lower speeds as more bilayers were present (Figure 2b). In addition, the majority of motors became stuck on layers ending with PDDA (+), whereas those that remained motile moved slightly slower than on layers ending with PSS (−) (Figure S4). These results do not agree with the simulated trend in Figure 1b, which suggests that motors move faster near PSS ending films than on pristine glass, and PDDA ending films should be even more helpful. How do we rationalize the speed decrease of motors on functionalized surfaces when numerical models based on surface charges and electroosmotic flows suggest they should move faster?

A closer look revealed that solution conductivity, σ, increased significantly after the surface functionalization (Figure 3). Our measurement (see the Supporting Information for details, information inferred from bulk measurement) indicated that upon immersion of functionalized surface to water, σ increased monotonically over time (Figure 3a, inset), reaching a maximum value that was higher for substrates coated with more bilayers. Such a substantial increase in σ is suspected to originate from Na^+ and Cl^- ions that leached out of the polyelectrolyte films and diffused into the solution. According to electrokinetic theories, the speed V of catalytic nanomotors decreases following $V \approx 1/\sigma$.[22] As a result, the thicker the film, the more ions it potentially releases, and the slower the motors, which agrees qualitatively with the experimental data in Figure 2b.

Having established that solution conductivity strongly affected motor behaviors, it is interesting to see if we can decouple this effect from surface features. The basic idea is that, if motor speeds decreased on LBL films exclusively due to released ions, then their speeds should scale with $1/\sigma$ regardless of whether it moved near the bottom or in the bulk.

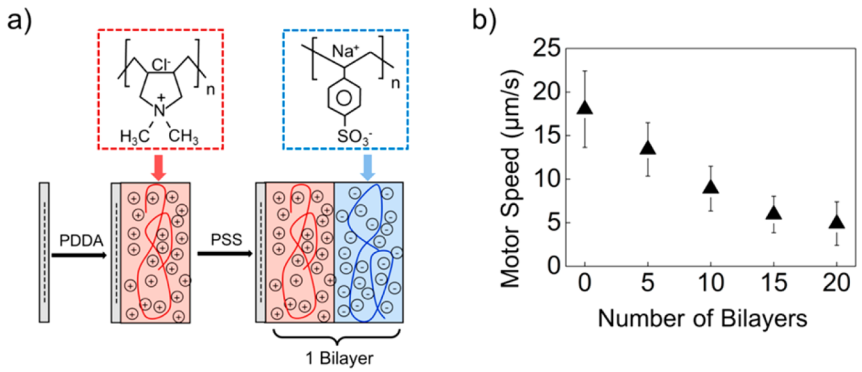


Figure 2. Functionalization of glass substrates with polyelectrolytes. (a) Glass substrate with intrinsic negative surface charges is modified sequentially by PDDA and PSS polyelectrolyte films in a LBL process. (b) Motor speeds monotonically decreased as more polyelectrolyte bilayers were coated on the glass.

DOI: 10.1021/acsami.7b18399
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

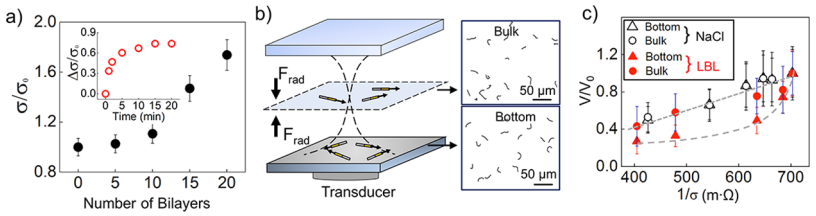


Figure 3. Effect of ionic conductivities on motor speeds. a) Solution conductivity σ increases with the number of bilayers, and with the time the film is immersed in the solution (inset). σ is normalized by σ_0, which was measured near a pristine glass substrate under a typical experiment condition. (b) Acoustic radiation force (F_{rad}) traps microrods in a levitation plane at the center of the acoustic chamber, where they are considered to be moving in the bulk. Motor trajectories during 1 s after the ultrasound was turned off are compared to the trajectories of the motors moving at the bottom. (c) Speeds of bimetallic motors scale roughly to $1/\sigma$, where σ is varied by either adding NaCl to the solution (hollow data points) or modifying the substrate with polyelectrolyte films (LBL, solid data points). In each case, motors were tested both near the substrate (triangles) and levitated to the bulk by ultrasound (circles). Dashed lines are for eye-guiding purpose only.

Experiments with micromotors moving in the bulk is often technically challenging, because commonly studied micromotors are often heavier than water and readily sediment. Acoustic levitation turns out to be a powerful tool to overcome this limitation (illustrated in Figure 3b).[26] With an appropriate selection of ultrasound frequency and chamber dimensions, micromotors can be lifted away from any boundaries, enabling the in situ comparison between particle dynamics moving in the bulk and that near a boundary.[27,28] Normalized experimental data in Figure 3c show that, the speeds of motors moving in the bulk above a LBL functionalized substrate (red filled circles, measured after the ultrasound was turned off and while the rods were settling) scales with $1/\sigma$ in the same way as motors in NaCl solution of known conductivity (empty symbols). However, data in Figure 3c also suggests that motors near LBL films (red filled triangles) not only moved more slowly than the ones in the bulk (red filled circles), which is expected because of surface charge effects; their speeds do not follow the $1/\sigma$ scaling well either. Additional effects could play a role, such as the morphology, elevated viscosity, and polymer−rod interactions near the functionalized surface.

So far, we have assumed that micromotors moved on a smooth surface, but it might not always be the case. For example, one striking feature of the LBL-assembled polyelectrolyte films was microscopic and wormlike wrinkles that became obvious beyond ∼10−15 bilayers. These topological features, which have been reported previously,[29,30] are captured under atomic force microscope (AFM) in Figure 4a. Although there is no global order or periodicity, the amplitude of the wrinkling instability (characterized by average roughness by AFM) is consistent across the surface and changes with the number of bilayers (Figure 4b).

The wrinkling patterns in Figure 4a are such a prominent feature that it is reasonable to suspect that it could serve as tortuous "speed bumps" for motors moving across the surface. Such a possibility finds support in recent experimental studies where micromotors, especially those powered by chemical gradients, are very sensitive to geometrical obstacles such as walls, trenches and large spheres.[6−11,18−20] To test if such an effect applies to our polyelectrolyte wrinkled films, we levitated motors away from the substrate by ultrasound, and compared its dynamics in the bulk to that near the wrinkled surface. Figure 4c shows that, although motors moved slower near the surface than in the bulk, the magnitude of the speed decrease is not beyond that can be attributed to surface charges. This is perhaps not surprising. Even though the typical wavelength of wrinkles (estimated to be 1 μm or less) on these films is

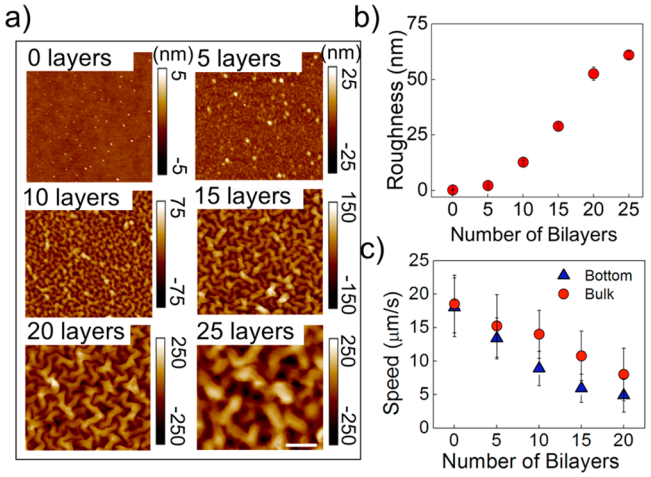


Figure 4. Self-assembled wrinkles on polyelectrolyte films. (a) Atomic force micrographs of films of various numbers of bilayers. The scale bar is 1 μm and applies to all panels. (b) Surface roughness as a function of the number of bilayers. (c) Motor speeds near the surface of films of various thickness (triangles), compared to that when levitated in the bulk (circles).

comparable to the micromotor size, their roughness is on the order of tens of nanometers, much smaller than the microrod diameter. Motors therefore might not be able to "feel" these wide and shallow grooves and respond. This is also consistent with a previous study where steps lower than 10% of the motor size were not able to effectively rectify their trajectories.[10] Although further increasing the number of bilayers could intuitively produce deeper features that are more effective to guide micromotors, we found a similar surface roughness and less defined patterns for substrates with 30 bilayers. Optimization in the LBL process is possibly needed.

To conclude, we have studied the speeds of bimetallic microrods moving on chemically modified surfaces. Compared to pristine glass, micromotors moved significantly slower on surfaces functionalized with bilayers of positively and negatively charged polyelectrolytes, inconsistent with simulation based solely on surface charges. Solution conductivity due to ions diffusing out of the polyelectrolyte films is proposed to be primarily responsible for such a speed decrease, while self-assembled surface wrinkles, although a prominent feature, plays a negligible role. Additional effects, such as viscosity change and polymer−particle interactions near the functionalized surface, are difficult to probe directly at this point, but could play a minor role in modifying the motor dynamics.

DOI: 10.1021/acsami.7b18399
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b18399.

Microrod synthesis, motor experiments and ultrasound setup, surface modification with polyelectrolyte films, solution conductivity measurement, numerical simulation (PDF)

Video S1, bimetallic micromotors levitated in the bulk vs. moving near the bottom (AVI)

Video S2, bimetallic micromotors moving near substrates functionalized with 0, 5, 10, 15, and 20 bilayers of polyelectrolyte films that end with PSS (negative) (AVI)

Video S3, bimetallic micromotors moving near substrates functionalized with 0.5, 5.5, 10.5, 15.5 and 20.5 bilayers of polyelectrolyte films, where " .5" indicates that the film ended with PDDA (positive) (AVI)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: weiwangsz@hit.edu.cn or wwang.hitsz@gmail.com.

ORCID

Jinyao Tang: 0000-0002-0051-148X

Wei Wang: 0000-0003-4163-3173

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project is financially supported by the National Natural Science Foundation of China (11774075 and 11402069), Natural Science Foundation of Guangdong Province (2107B030306005), and the Science Technology and Innovation Program of Shenzhen (JCYJ20170307150031119). We gratefully acknowledge the helpful discussions with Dr. Mihail N. Popescu.

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DOI: 10.1021/acsami.7b18399
ACS Appl. Mater. Interfaces XXXX, XXX, XXX–XXX