Abstract: The motion of catalytic tubular micromotors are driven by the oxygen bubbles generated from chemical reaction and is influenced by the resistance from the liquid environment. Herein, we fabricated a rolled-up graphene tubular micromotor, in which the graphene layer was adopted as the outmost surface. Due to the hydrophobic property of the graphene layer, the fabricated micromotor performed a motion pattern that could escape from the attraction from the bubbles. In addition, Escherichia coli and Staphylococcus culture experiments proved that the graphene outer surface displays antibacterial property. Considering the bubble-avoiding and antibacterial properties, the rolled-up graphene tubular micromotor holds great potential for various applications such as in vivo drug delivery and biosensors.

Introduction

Artificial self-propelled machines at the micro/nanoscale with various structures, for example, bi-metal rods,[1] Janus particles,[2] tubes,[3] and helices,[4] have drawn much attention over the past decade. Among those different structures, micro/nanotubes are studied for their asymmetric inner and outer surfaces.[5] In 2009, we brought up the concept of catalytic tubular microrockets fabricated by rolled-up nanotechnology, which set up the foundation of catalytic tubular micromachines.[6] Oxygen bubbles produced by H₂O₂ catalytical decomposition on the inner surface with catalytic property, such as for example, Pt, Ag, and catalase, eject from one end of the tubular structure, and propel the tubular micromotor to move forward. Micromotor with this driving fashion was soon developed to be a promising candidate in multiple applications, such as cargo delivery and releasing,[7] environmental remediation,[8] bio-sensing,[9] etc. In most applications, the ability of avoiding the interference from surrounding environment like bubbles is required.[10] Especially, the micromotor attached to the large bubble will be hard to escape from the surface tension of the bubble. In most cases, surfactants are added in the H₂O₂ solution to decrease the surface tension of the inner wall and to increase the bubble propulsion frequency of micromotors. The correspondingly decreased size of oxygen bubbles leads to reduced influence from bubbles as obstacles.[11] However, surfactants can only decrease the size but not the amount of the bubbles, and micromotors are still hindered by the small bubbles in surrounding environment. In addition, ultrasonication was also used to removing oxygen bubbles generated from the catalytic reaction. Nevertheless, the fast elimination of oxygen bubbles propelled led to decreased micromotors’ speed.[12]

Graphene is a promising two dimensional material with outstanding electronic and optical properties.[13] Numerous studies on applications of graphene in flexible electronic devices,[14] molecule detecting,[15] energy storage,[16] and energy storage[17] have been published. Previous studies have combined graphene-based materials and tubular micromotors to take advantage of the excellent properties of graphene and its derivations and explored new applications for micromotors. In general, two approaches are engaged for the fabrication of tubular micromotors, i.e., rolled-up nanotechnology and template-assisted fabrication, and the rolled-up nanotechnology has the advantage of producing tubular structures with various materials and their combinations.[18] Graphene-related micromotors were previously fabricated via both approaches.[16] For instance, Y. P. Zhao et al.[16] reported a graphene oxide (GO)/Ti/Pt tubular micromotor fabricated by rolled-up nanotechnology, where sonica-
GO was electrochemically reduced when it was in solution so the graphene/Ti/Cr/Pt nanomembrane was remade. The antibacterial property of graphene would much improve the situation. Researchers have reported the antibacterial property of graphene and graphene derivatives. The antibacterial property of graphene based materials is considered as a result of (1) oxidative stress that can interfere with the metabolism of bacteria associated with reactive oxygen species or charge transfer generated by graphene; (2) physical harm to bacteria cell membranes by the sharp edges of graphene nanoflakes that lead to the leakage of intracellular substances; and (3) graphene as a flexible thin film wrapping and trapping bacteria cell membrane. In order to verify the antibacterial property of our graphene tubular micromotors, we cultured the micromotors with *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) on Ge substrate. By analyzing the surviving situation of bacteria on graphene covered surface and area without graphene, we proved that the outer surface of tubular micromotors could prevent bacteria multiply. With hydrophobic and antibacterial surface, this rolled-up monolayer graphene tubular micromotor could have great potentials for in vivo applications as man-made micro/nanomachines.

### Results and Discussion

The catalytic tubular graphene micromotor was fabricated by rolled-up technology as illustrated in Figure 1a. The monolayer graphene was first grown on Ge substrate by chemical vapor deposition (CVD) with H₂ and CH₄. Then, Ti and Cr layers were deposited on graphene sequentially by e-beam evaporation with differed deposition rates and thicknesses, which introduced internal strain into the multilayer nanomembrane system. The e-beam evaporation was also used to deposit a thin Pt layer for about 2 nm to be the inner catalytic layer of the tubular micromotor. Thus, graphene/Ti/Cr/Pt four-layered nanomembrane was fabricated. Later on, a standard photolithography procedure followed by ion beam etching (IBE) was applied to create patterns on graphene/Ti/Cr/Pt nanomembrane. Afterwards, the remained photoresist was removed by acetone and Ge substrate was partially etched by H₂O₂ solution so the graphene/Ti/Cr/Pt nanomembrane was released and rolled up under the control of the built-in strain. At last, critical point drying was engaged in order to prevent structure collapse caused by the surface tension of liquid. For comparison, micromotor without graphene decoration was also prepared. In such case, the outer surface of the micromotor is Ti.

The obtained rolled-up tubular micromotors were characterized by scanning electron microscopy (SEM) and the results are shown in Figure 1b. The two pits under the rolled-up micro-

![Figure 1](https://example.com/image1.png)
tube was generated from the anisotropic corrosion on the single crystal Ge substrate by H$_2$O$_2$ solution.$^{[24]}$ The fabricated micromotor has a fine and straight tubular structure with the diameters of 3.4 and 3.6 µm for left and right ends (Figure 1b), respectively. Here, due to the imperfection of the rolling process, the diameter of the right end is slightly larger than the diameter of the left end. This asymmetry is actually important for micromotor application, since the generated oxygen on the inner surface of the micromotor would gather to form bubbles and migrate to the lager end under the influence of capillary force.$^{[25]}$ In addition, energy-dispersive X-ray spectroscopy (EDX) mappings of the samples were carried out to check the elemental distribution, and typical results are presented in Figure S1. One can see that Ti and Cr distribute evenly on the tube wall. While the Ge signal is slightly weakened on the position of the tubular micromotor, for that the micromotor shields part of the Ge signal. However, the monolayer graphene and Pt layer (≈0.2 nm) are too thin for EDX signal collection. In order to prove the existence of graphene layer, Raman spectroscopy was adopted. Figure 1c demonstrates the Raman spectra of bare graphene on Ge substrate (black line) and the rolled-up graphene/Ti/Cr/Pt microtube (red line), which indicates the existence of graphene on the outer surface of the rolled-up tubular micromotors. In addition, it could be noticed in Figure 1c that the characteristic peaks of graphene microtube has a slight blue shift compared to those of planar graphene. This phenomenon indicates that the graphene layer is in compression due to the rolling process, which leads to blue shift of Raman characteristic peaks.$^{[26]}$ In addition, the wettabilities of the outer surfaces of micromotors were studied by means of contact angle (CA) measurement. As shown in Figure 1d and e, the CAs of flat monolayer graphene and Ti nanomembrane are 53° and 93°, respectively, proving that the Ti surface is hydrophilic and monolayer graphene surface is hydrophobic.

When H$_2$O$_2$ solution as the fuel was filled in the microtube and catalytically decomposed on inner Pt surface, the generated O$_2$ bubbles thrusted out from larger end of the tubular structure and propelled the tubular micromotor to move forward. In present work, the motion behavior of the fabricated graphene micromotor in H$_2$O$_2$ solution was characterized in detail by optical microscopy, as shown in Figure 2a and b. The optical images in Figure 2a show the circular motion of a tubular graphene micromotor with a speed of $\approx 612$ µm s$^{-1}$ in 15% H$_2$O$_2$ and 0.01 wt.% surfactant (Sodium dodecylbenzenesulfonate, SDBS) solution. The red line denotes the motion trajectory in 3 s. Linear motion of a graphene micromotor was also observed in Figure 2b, with a speed of $\approx 602$ µm s$^{-1}$ in the solution of the same composition. Time lapse images of a fast motion of a graphene micromotor at a speed of $\approx 1667$ µm s$^{-1}$ in solution with higher H$_2$O$_2$ concentration are also presented in Figure S2. Theoretically, tubular micromotors would have linear motions by the driving force generated from the ejection of bubbles, whose direction is along the central axis of the tubular structure. However, the rolled-up procedure is not always ideally controlled, which leads to imperfection of the tubular structure. The flaws of the structure of micromotors such as the opening not being perfectly circle would much influence the motion trajectory, resulting in the circular motion.$^{[16a,27]}$ In addition, physical changes of the liquid environment such as the excitation of eddy flow will also lead to the motion trajectory change of micromotors.$^{[28]}

Figure 3 a and b show the motion behaviors of micromotors with and without graphene at the outer surfaces. In Figure 3a, the micromotor without graphene modified surface moving with bubbles attach to its surface. In Figure 3a, one can see that the motion speed of the micromotor without graphene decoration reduces from 19.2 to 13.3 µm s$^{-1}$ in 1.5 s, demonstrating a speed loss of more than 30% after the attachment of the bubble. The influence of the bubble as obstacle is remarkable. On the other hand, it could be noticed that for the micromotor with graphene decoration, no bubble is attached to the surface of the micromotor when it moves through a string of bubbles (Figure 3b). The images in Figure 3b show that when the graphene micromotor encountered the bubbles, the motion speed rapidly decrease to less than half of the original speed. After $\approx 2$ s, the micromotor passes through the string of the bubbles, and the motion speed quickly recovers to the original value. Figure 3c denotes a graphene micromotor bypassing a large bubble in its motion trajectory. When the graphene micromotor meets the bubble, the motion is hampered and speed decreased to less than 50%. Propelled by the ejection of oxygen bubbles, the graphene micromotor moves around the large bubble for more than a semi-circumference, then escapes from the micromotor-bubble interaction. The quick speed recovery after detachment can also be observed.

![Figure 2](image-url)  
**Figure 2.** Circular motion (a) and linear motion (b) of graphene micromotors in solution of 15% H$_2$O$_2$ and 0.01 wt.% SDBS. Scale bar: 100 µm.
in this case. It should be pointed out that high concentration of H$_2$O$_2$ was used in current experiments for better demonstrating the interaction between the hydrophobic surface of graphene micromotor and bubbles. However, for potential biomedical applications, rolled-up tubular micromotors have the ability of moving in H$_2$O$_2$ with low concentration.$^{[6a, 29]}$

Another advantage of graphene that has caught great attention is its antibacterial property. Experiments were carried out to characterize the antibacterial property of graphene/Ti/Cr/Pt tubular micromotors. Here, E. coli and S. aureus culture solution was dropped on the micromotors. After 24 h of culture, the sample was lyophilized to avoid deformation of micromotors and bacteria. Then SEM images were taken to characterize bacteria surviving situation. In Figure 4a-i, the bacteria in red circle have blurred edges and abnormal round shapes, compared with healthy rod-shape E. coli on the substrate, indicating that the bacteria are dead. Figure 4a-ii shows that bacteria can survive on the inner surface of the four-layered graphene/Ti/Cr/Pt nanomembrane, which is Pt and is not covered by graphene, and no E. coli can be observed on the outer graphene surface. This strongly proves the antibacterial property of graphene micromotor. Figure 4a-iii shows a micromotor with S. aureus growing on the inner surface (see red circle) but the graphene covered outer surface is smooth without bacteria. More experimental results demonstrating that bacteria can attach on the inner surfaces of graphene micromotors but not on the outer surfaces are presented in Figure S3. All these experimental results indicate that bacteria can hardly stick on the outer surface of graphene micromotors and multiply. In order to further prove the antibacterial property of the graphene micromotors, we applied fluorescent staining experiments on graphene micromotors, micromotors without graphene, and Si wafer.$^{[30]}$ and the results are shown in Figure 4b. In Figure 4b-i, an obvious blank area with tubular shape corresponding to graphene micromotor can be distinguished, and only a few bacteria can attach on the surface of the graphene micromotor. However, in Figure 4b-ii, considerably more bacteria attach on the surface of the micromotor without graphene, indicating that graphene has the ability of prohibiting E. coli from attaching on its surface. While in Figure 4b-iii, the bright stains indicating that the bacteria can attach and multiply on Si wafer. Here, for the mechanism of antibacterial behavior, we believe that neither sharp edge incising mechanism nor wrapping and trapping mechanism is suitable for graphene outer surface, and the death of bacteria co-cultured with graphene micromotors were caused mainly by oxidative stress generated by graphene.$^{[18a, 19]}$ The antibacterial property of graphene micromotors demonstrates great potential for in vivo applications.

Conclusions

In conclusion, we rolled up monolayer graphene with a metallic nanomembrane by strain engineering to fabricate a tubular micromotor with enhanced performance and antibacterial property. The hydrophobicity of graphene relieved the motion of the micromotor from being interfered by the bubbles in its trajectory, and a quick speed recovery was observed. Furthermore, the antibacterial property of the graphene micromotor was verified and culture experiments demonstrated that the bacteria were either killed by graphene or could not attach to the graphene surface. This kind of tubular catalytic micromotors is expected to be of importance for in vivo applications, such as drug delivery and minimally invasive surgery.

Experimental Section

Synthesis of monolayer graphene

Ge wafers (175 μm, ATX) were used as the substrates to carry out graphene synthesis in an ambient pressure CVD system. Firstly the Ge substrates were surrounded by the atmosphere of Ar and H$_2$ with flow rate ratio of 700:70 sccm to wait for the furnace heated to 916°C. Then CH$_4$ was filled in to start graphene growth with flow rate of 2.2 sccm at 916°C for 240 min, while H$_2$ and Ar were kept the same flow rate. At last, furnace was turned off and cooled to room temperature as CH$_4$ flow was cut to 0 sccm and H$_2$ and Ar were remain unchanged.

![Figure 4](image-url)

**Figure 4.** (a) SEM images of graphene micromotors on Ge substrate co-culture with (i) and (ii) E. coli and (iii) S. aureus. (i) Dead E. coli on the outer surface of the micromotor. (ii) A rolled four-layered graphene/Ti/Cr/Pt nanomembrane with E. coli on the inner surface. (iii) S. aureus on the inner surface of the micromotor and un-rolled nanomembrane on the substrate. Scale bar: 5 μm. (b) Fluorescent images of bacteria on (i) graphene micromotor, (ii) micromotor without graphene, and (iii) Si wafer. Scale bar: 25 μm.
Fabrication of rolled-up graphene micromotors

After monolayer graphene was grown on Ge substrate, Ti/Cr/Pt nanomembrane was deposited sequentially by e-beam evaporation with thicknesses of 10/2/0.2 nm and deposition rate of 2.0/1.0/0.1 Å s⁻¹. This procedure was carried out on electron beam evaporator (Tenstar TSV700, China). The change in deposition rates endowed the metal nanomembrane with built-in strain. Next, photoresist layer with patterns that had specific size and shape was obtained on the upmost Ti layer by conventional photolithography. Then, Ti, Cr, Pt, graphene, and part of the Ge substrate that were not covered by photoresist was removed by Ar ion beam etching (AdvancedMEMS IBE, China). To release the four-layer nanomembrane from the substrate, 30% H₂O₂, purchased from Sinopharm Chemical Reagen Co., Ltd was used to etch the Ge substrate at 90 °C. After Ge substrate was partially etched, tubular structure of the nanomembrane was formed. The whole sample with substrate was then transferred into pure ethanol and then drying was performed in a critical point dryer (CPD030, Leica, Germany).

Morphology and optical characterizations of rolled-up tubular micromotors

The morphologies of the fabricated tubular micromotors was characterized by scanning electron microscopy (Thermo Fisher Scientific Phenom proX desktop SEM, USA). Raman spectra of the synthesized monolayer graphene and the fabricated tubular micromotors were obtained on a Horiba Jobin Yvon HR-Evolution 2 model to confirm the existence of graphene on micromotors. The distribution of elements on the sample was observed by EDX spectroscopy (IXRF-SS01, IXRF systems, USA).

Characterizations of the motion of micromotors

The micromotors were transferred to H₂O₂ solution by scratching the substrate using a tapped micropipette. The motions of the micromotors were observed and recorded by an optical microscope (Olympus BX51TRF, Japan).

Antibacterial property characterization

E. coli (ATCC25922) and S. aureus (ATCC25923) were used in the experiments. A few drops of bacterial suspension (10⁻⁷ cfu mL⁻¹) was dropped on the Ge substrate with rolled-up tubular graphene micromotors and incubated for 24 h at 37 °C. SEM images of the samples after culture experiment were taken on a scanning electron microscope (HITACHI S3400, Japan). For fluorescent experiment, the bacteria were stained by the LIVE/DEAD BacLight Kit (L13152). The samples were rinsed twice by normal saline after being cultured for 24 h at 37 °C. Then the dye was dropped on each sample and stained for 15 min. At last, the samples were observed by a fluorescence microscope (GX71, Olympus, Japan).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: antibacterial property · catalytic motion · graphene · hydrophobic effect · micromotors
