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News & Views

Tubular micro/nanoengines: boost motility in a tiny world

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Since 20th century, the development of rocket science has put forward to the dream of humankind that one day we can reach other planets except for observing them through telescope. The rockets get rid of gravity by a powerful engine, consuming chemical fuel to generate a vast thrust. Inspired by rockets and motors in macroscale, researchers on nanoscience and nanotechnology are able to construct engines which can carry and transport cargos in micro and nanoscale. In 2016, the Nobel Prize in Chemistry was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa for their outstanding achievements in the design and synthesis of molecular machines. In 1977, Purcell [1] described the live objects with low Reynolds numbers in liquids, where micro and nanoscale motion in liquid is mainly influenced by viscous force and Brownian motion rather than gravity and air drag. To meet the demand, rocket-inspired engines in microscale were designed as a tubular structure and gained their fuels from surrounding media, called self-propelled tubular microengines (Fig. 1a) [2]. These microengines containing platinum (Pt) inside achieve thrust energy by chemical reaction with surrounding solution (normally hydrogen peroxide, H_2O_2) which produces gas bubbles for propulsion. Such strategy was able to generate a huge driving motion force for an entirely soft, pneumatic "octobot" with eight arms in macroscale as shown in Fig. 1b [3]. With the programmed control of syringe pump, hydrogen peroxide fuel was injected into the reaction chamber inside the arms, which was coated with Pt catalyst for the rapid decomposition of hydrogen peroxide with the product of oxygen gas. Hence, the expansion of soft reaction chambers led to bending and actuating behavior of arms, and thus realized the movements of designed soft robots. Similarly, rocket-like tubular microengines can be self-propelled by bubbles generated inside the tube. Under a proper treatment, the outer wall of tubular microengines can be modified with other materials and structures for various functions such as bio-compatible functionalization for biomedical application or guided wings for directional moving.

Such tubular microengines can be fabricated by two typical methods: rolled-up technology and template electrochemical deposition method. By using rolled-up nanotechnology, tubular microengines were fabricated by strain engineering of nanomembranes and lift-off process (Fig. 1c) [2]. Internal strain gradient originated from inherent built-in strain and different thermal expansion during materials deposition, and enabled the rolling of designed nanomembranes with the assistance of the undercut of sacrificial photoresist patterns. It was demonstrated that tubular microengines using rolled-up microtubes of Ti/Fe/Au/Ag nanomembranes were propelled by the decomposition reaction of hydrogen peroxide and controlled by external magnetic field due to the incorporation of Fe. In order to fabricate rolled-up tubular nanoengines, a combination of residual stress in nanomembranes and external surfaced tension was applied for overcoming the rolling limitation [5]. Structural layers with internal stress (e.g., SiO/SiO_2 or SiO/TiO_2) and ultra-thin Pt layer (several nanometers in thickness) were deposited on polymethyl methacrylate (PMMA) sacrificial layer subsequently. With the help of rapid thermal annealing, the dewetting of Pt layer provided surfaced tension force for rolling and thus achieved tubular nanoengines (several hundred nanometers in diameter). Another approach for tubular micro or nanoengines is using electrochemical deposition to grow tubular microengines within micro or nanopores of adopted templates as shown in Fig. 1d [4], where polyaniline (PANI)/Pt microtubes copied polycarbonate template with conically shapes. The PANI outer layer was grown first by electrodeposition due to solvophobic and electrostatic effects and subsequently, platinum layer was deposited using a galvanostatic method. The bilayer tubular microengines were released by the dissolution of template for the motion demonstration. Such template electrodeposition method provides a cost-saving production of large amounts of high-efficient tubular microengines.

With proper functionalization, tubular microengines can catch molecules or cargos in the solution, which enables tubular microengines for water remediation, molecular detection and biomedical application. With the presence of $NaBH_4$ in solution, the microengines used palladium at the inner wall to catalyze the decomposition reaction of 4-nitrophenol pollutant with hydrogen production [6], where generated bubbles propelled the microengines. Hence, the microengines swam in polluted water by taking the pollutant as fuel. Benefiting from motion, the degradation of pollutant was much faster with moving microengines than that by using still ones. Another application of bubble-propelled tubular microengines is for sensing and detection. With the help of microengines, the target molecules are gathered by microengines, where the molecular concentration reaches relatively high level around the microengines [7]. The outer wall of microengine was made of gold, serving as surface-enhanced Raman scattering substrate, and the inner wall was made of silver to decompose hydrogen

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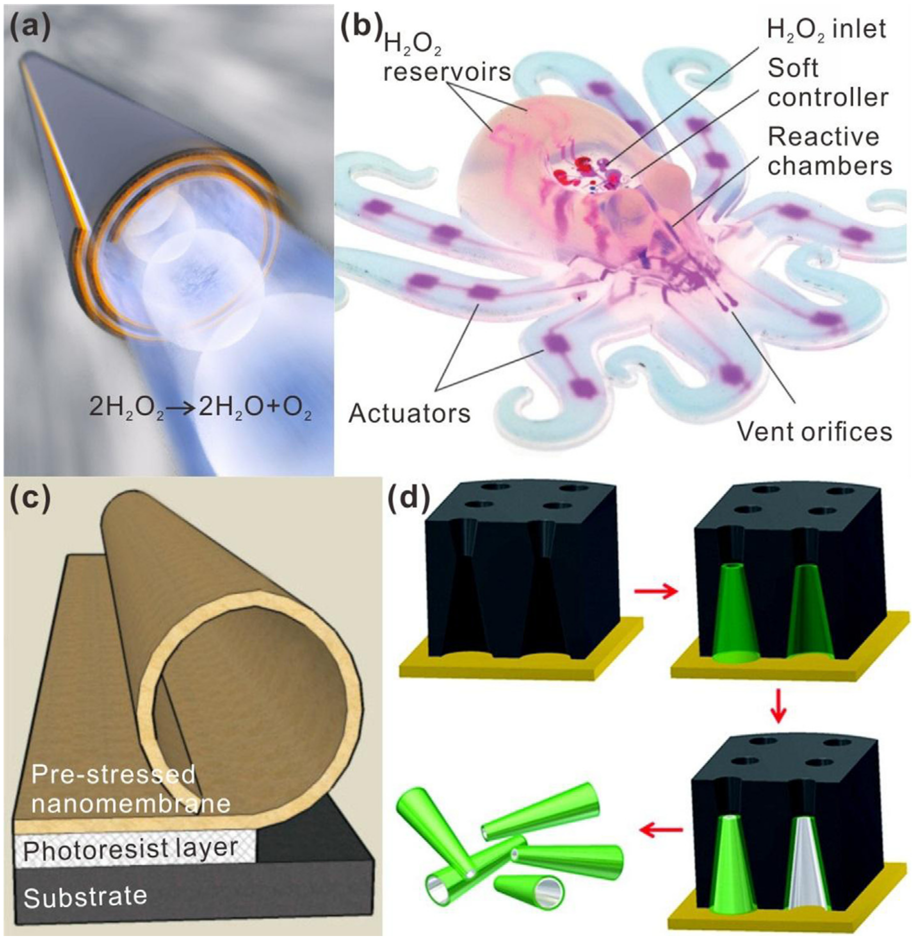

Fig. 1. (Color online) (a) Scheme depicting self-propelled tubular micro/nanoengines [2]. (b) Optical images of a fully soft, autonomous octobot powered by hydrogen peroxide decomposition [3]. (c) Scheme illustrating the rolled-up nanotechnology to fabricate tubular microengines [2]. (d) Scheme of bilayer tubular microengines using polycarbonate membranes [4].

peroxide. The microengine swimming in the solution collected molecular for Raman test. After the collection, the Raman signal of the microengine was five times higher than inactive microengines. Furthermore, another typical application of tubular micro/nanoengines is to transport drug or objects in organism for in vivo biomedical applications, which is realized by poly(3,4-ethylenedioxythiophene) (PEDOT) microengines coated with enteric polymer fabricated via template electrodeposition [8]. Instead of bubbles generated by decomposition of toxic hydrogen peroxide fuel, the power for propulsion was hydrogen bubbles created by magnesium inside the microengines, reacting with water in gastrointestinal tract. The enteric polymer coating prevents the microengines from the acidic gastric fluid environment. And with different thickness of coating, the microengines were released in a precise position of gastrointestinal tract. The motion of microengines enabled the drug delivery and enhanced the retention inside organism.

Recently, light-assisted propulsion of tubular microengines was applied as a trigger or energy source to control or power their motion. In bubble-propelled tubular microengines, temperature plays an important role that influences the speed of fuel decomposition, leading to different speed motion. There was a demonstration that used laser irradiation to heat the tubular microengine locally [9]. Such locally photo-thermal effects both accelerated and modulated moving speed of tubular microengines. Light can also power the motion by using photocatalyst such as titanium dioxide. Array of titanium dioxide nanotubes was fabricated using conventional electrochemical anodization of Ti sheets [10]. Such tubular nanoengines decomposed hydrogen peroxide with existence of the ultraviolet (UV) light irradiation, and generate oxygen bubbles for propulsion. Another demonstration was applying light-induced thermal gradient to propel tubular microengines [11]. In this work, polymer microtube with Au nanoparticles modified on the inner wall created a great deal of heat energy with near infrared light due to the strong plasma resonance absorption. The inner Au nanoparticles will heat surrounding water molecules into higher temperature compared with outside water, creating higher thermophoretic force. This propulsion force can achieve superfast movement and rapid control of tubular microengines.

In conclusion, we introduced the concept, design, fabrication and application of self-propelled tubular micro/nanoengines, which can be manipulated by external force, such as magnetic or light-induced driving force. Such tubular micro and nanoengines is mimetic to rockets and could offer more possibility for future applications, especially for the motion with a large propelling force at their ultra-small size [12]. Advanced functionalization and creative design with fine structures might enable such rocket-like micro/nanoengines as next generation small motors or robots with fast speed, precise control and complex function.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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