Tubular microjets: Fabrication, factors affecting the motion and mechanism of propulsion

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Abstract. Artificial micro- and nano-swimmers are interesting systems for both fundamental understandings of swimming at low Reynolds numbers and for their promising applications in many fields, such as environmental and biomedical fields. Different architectures of self-propelled systems present various propulsion mechanisms. Among them, tubular microjets are widely used for different applications. Here, we briefly describe the fabrication of microjets by rolling up thin film and electrodeposition techniques and the principles behind these processes. Different parameters affecting the motion of microjets and existing theoretical models about microjet propulsion are discussed.

1 Introduction

Catalytic motors are chemically powered micro- or nano-devices capable of autonomously swimming in fluid media and carrying out assigned tasks based on their functionalities. Sometimes, these tiny motors can be referred also as artificial microswimmers. Catalytic motors were first reported independently by the teams from Penn State \cite{1} and Toronto university \cite{2} after which, the field of catalytic motors has significantly grown in several areas \cite{3}. Catalytic motors are used to study the fundamentals of motion at the nanoscale where viscosity and Brownian motion makes swimming a challenging task \cite{4,5}. Moreover, a number of applications ranging from drug delivery to water treatment and different methods to control their motion are reported \cite{6}.

Among different geometries for micro- and nano-devices presented in the literature, here we describe the main two fabrication methods; i) the expensive but versatile photolithography and metal deposition based method and ii) the fast and cheap electrodeposition in porous templates \cite{7}. Tubular micro-motors are propelled by the ejection of a jet of bubbles, therefore, can be called as microjets, as it will be

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described in the following section. Microjets are a very attractive type of micro- and nanodevices due to their exhibited utility in several applications, from the drilling of soft matter [8], specific transport of cargo and cells on-chip [9,10], to the cleaning of polluted water [11,12]. They can act individually and collectively and be directed towards particular targets. There are a few examples in nature of jet-propelled swimmers as we will briefly summarize.

1.1 Motion at low Reynolds numbers

Reynolds number \((Re)\) is a dimensionless quantity defined as the ratio of inertial to viscous forces acting on an object in a fluid. \(Re\) is given by,

\[
Re = \frac{\rho V l}{\mu} = \frac{\text{Inertial Forces}}{\text{Viscous Forces}}
\]

where \(\rho\) is the density of the fluid, \(V\) and \(l\) are the velocities and the characteristic length of the object while \(\mu\) is the viscosity of the fluid [4]. Objects with very small size such as bacteria and artificial micro and nanomotors operate at the low Reynolds number where the viscous force dominates the inertial force. Swimming by conventional reciprocal motion works for the bigger objects such as humans or whales because at this scale inertial force can easily overcome the viscous force and a net momentum can be transferred to the fluid. At high Reynolds number, non-continuous work can also be enough to achieve continuous forward motion. However, at the size scale of microjets, continuous bubble generation and release is required for the continuous motion because the system quickly reaches the terminal velocity. Intermittent migration and ejection of the bubble from a microjet can only produce pulsatile motion.

Figure 1 depicts the maximum speeds of different swimmers from the blue whale, larger than 30 m, that swims at 0.4 body-length/second \((\text{bl} \cdot \text{s}^{-1})\) down to small 5 \(\mu\)m long bacteria, swimming at 200 \(\text{bl} \cdot \text{s}^{-1}\) [13]. In addition to absolute and relative speeds, Purcell described another important parameter to characterize types of swimmers and magnitudes, which is coasting distance \((d)\) for given characteristic size \((L)\), by the relation \(d = L \cdot Re\). For instance, for the bacteria plotted in Fig. 1, the coasting distance is about 50 nm while larger swimmers can make use of inertia to coast for long periods and trajectories. It is therefore necessary for swimmers at low Reynolds numbers to generate continuous propulsion to keep swimming.

Here, we describe two types of artificial tubular microjets: rolled-up and electrodeposited. Rolled-up microjets with a body length of 50 \(\mu\)m can swim at the speeds of more than 2 mm \cdot s\(^{-1}\) (55 bl \cdot s\(^{-1}\)) at room temperature [14] and at the physiological temperature they can reach up to 10 mm \cdot s\(^{-1}\) (200 bl \cdot s\(^{-1}\)) [15]. Electrodeposited microjets, of about 5 \(\mu\)m long, can swim above 375 bl \cdot s\(^{-1}\) [17,18] outswimming any type of swimmer in relative speed. These numbers demonstrate the high propulsion power exerted by the bubble-propelled microswimmers.

1.2 Bioinspired jet propelled microswimmers

Different architectures such as spherical colloidal micro- and nano-particles, metallic nanowires and hollow “conical” microtubes have presented several propulsion mechanisms over the last decade. The detailed mechanism of motion of micro- and nanomotors has been reported previously [19,20]. Here, we focus on jet propulsion, a mechanism of motion employed by some swimming creatures.

When talking about microswimmers, man-made engineered swimmers are usually compared with biological ones like bacteria or other flagellated microorganisms.
Fig. 1. Swimmers at different scales, their absolute and relative swimming speeds. Microjets swim at speeds as high as 2000 \( \mu \text{m s}^{-1} \) [14] at room temperature corresponding to 55 bl s\(^{-1}\) but increasing temperatures increases relative speed up to 200 bl s\(^{-1}\) [15]. Electrodeposited microjets (not plotted here) presented record in relative speeds up to 375 bl s\(^{-1}\) [16]. The Reynolds number is on the order of \(10^{-5}\) to \(10^{-2}\) for micrometer scale size of animals and objects. Reprinted from ref. [13]. (This figure is subject to copyright protection and is not covered by a Creative Commons license.)

However, flagellar locomotion is not the only means of locomotion at low Reynolds number, jet propulsion is another example of swimming behavior in nature. Many organisms, for example cephalopods, employ water jet propulsion to swim. This model seems to be more efficient than the rocket model, however, the efficiency decreases when the size of the swimmer increases. Squids swim by jet propulsion: they suck water into their cylindrical mantle cavity through openings on the head and expel it through a funnel at high pressure. Small squids such as the larvae *Loligo vulgaris* are capable of bursts as explosives that provide speeds of 25 bl s\(^{-1}\) [21].

At smaller scales, one can find myxobacteria and Cyanobacteria blue-green algae which thrust by slime extrusion and propel gliding along a substrate. These bacteria secrete mucilage through nozzle-like organelles. This so-called “slime extrusion” has been considered as the primary propulsion mechanism for adventurous motility in such organisms as *M. xanthus* [22]. As the slime exits the nozzle, it adheres to the substratum, and further slime extrusion produces a thrust. But this propulsion, unlike the jet propulsion at the high \( Re \) (e.g. jellyfish), is a non-inertial jet propulsion not involving any exchange of momentum into opposite direction of the thrust.

### 2 Fabrication of microswimmers based on jet engine

Chemically propelled microjets need catalytic materials in their interior to generate gas from the decomposition of the fuel solution that will be eventually ejected from
Fig. 2. The fabrication method of the rolled up microjets. (A) Deposition of the thin films containing tensile strain and compressive strain are grown on a sacrificial layer. (B) The scheme and the screenshots of the rolling up of the thin films by removing the sacrificial layer [26]. After etching the sacrificial layer selectively, the free multilayer thin films release the strain. The layer containing compressive strain starts to expand and the layer containing tensile strain starts to shrink with the force. The forces created by the expansion and the shrinkage are in the opposite directions and thus, the net force drives the bending and rolling process.

the tubes, propelling them. Up to now, the model system used is mainly composed by Pt (catalyst)/H$_2$O$_2$ (chemical fuel) although some exceptions are also reported [51].

2.1 Rolling up thin films

Self-assembly is one of the best approaches to fabricate advanced 3D micro- and nanostructures. Although it is known that strained membranes can bend, only in the last two decades it was demonstrated that a few nanometer thick strained heterostructures can spontaneously roll into tubes due to the relaxation process after a selective etching process [23,24]. In 2008, Mei et al. first reported the tubular catalytic microjets showing a great versatility in design and materials composition [25]. This technology can use any type of substrate on which photolithography can be performed. Thin films of variety of materials can be deposited on the patterned substrate by different deposition techniques such as sputtering, electron beam (e-beam) deposition or the molecular beam epitaxy (MBE). Figure 2(A) shows glancing angle deposition of two different materials on the patterned photoresist by e-beam and the Fig. 2(B) shows the rolling up of the deposited membranes after etching of the sacrificial photoresist layer.

In the deposition methods like Molecular Beam Epitaxy (MBE), the strain can be controlled very precisely based on the lattice constant of the material. The origin of stress in the thin film is mainly due to constraining imposed by the substrate on which the film is deposited. The internal force between the atoms is a function of the interatomic distance. When the thin film grows epitaxially on the substrate with smaller interatomic distance than equilibrium distance of the material, the film contains compressive strain and when the interatomic distance is larger than the equilibrium distance, the film contains tensile strain [23]. The diameter of the tubes fabricated from the lattice mismatched epitaxial layers can be predicted analytically with a good agreement between the experimental radius and the calculated theoretical radius [27]. Depending on the stress gradient across the thickness of the membranes, membranes bend or wrinkle, so several parameters must be carefully optimized. Larger
strain gradient leads to bending of the membranes and smaller gradient leads to wrinkling of the membranes. Strained heteroepitaxial nanomembranes grown by the MBE can be rolled up into very small tubular shapes enabling the fabrication of nanojets (Figs. 3(A), (B)) [8, 28]. The diameter of nanojets can be as small as 280 nm when rolled up from the nanomembranes of Pt (0.5 nm) deposited on InGaAs (3 nm)/GaAs (3 nm) layers (Fig. 3(B)). However, such method is very expensive and also not always suitable for metallic and dielectric or hybrid tube fabrication.

Thin films of metal and dielectric materials are mostly deposited by sputtering, e-beam or the thermal evaporation methods [29]. Although the growth of such thin film is non-epitaxial and amorphous or polycrystalline, there is always inherent strain present in the thin film deposited by the non-epitaxial method [30]. The rolling process consists of several steps. The sacrificial layers are patterned before the deposition; the thin films are deposited with a glancing angle to create shadowed window where the materials are not deposited on the sacrificial layer. Shadowed window allows the selective etching of the sacrificial layer from one side. Strained multilayers releases during the etching process of the sacrificial layer and let the lattice rearrangements to happen where the lower expands and the upper layer shrinks. Ideally, the multilayer membranes deposited with strain gradient across their thickness can be rolled up with many revolutions and by tuning the etching time and the layer thickness among other parameters, the diameter of microjet can be precisely controlled [25].

The strain gradient in the non-epitaxial film is not as predictable as the epitaxial film. That strain is produced due to the growth kinetic process itself and can originate from the various mechanisms such as stress at the grain boundary, thermal expansion coefficient between films, void regions and phase transformation. The deposition parameter such as deposition pressure, the temperature of the substrate and
deposition geometry can greatly influence the amount of strain generated due the wide range of mechanisms involved in the process [32]. It is very important to keep the parameters precisely constant in order to obtain highly reproducible results with non-epitaxial thin film.

The strain gradient in the deposited layer can be controlled by the evaporation rate of the material and the glancing angle. Thickness of the film is also important because the diameter of the tubes varies depending on this thickness. The pattern size can be easily tuned by designing different photomasks applicable for photolithography. In this way, microtubes from 25 μm up to 1 mm have been successfully reported in the literature, showing a large variability of lengths for various purposes. Figure 3(C) shows an optical microscope image of a 200 μm square pattern that led to the rolling of tubes from left to right using the shadow window for selective etching and Fig. 3(D) shows microjets ejecting bubbles while swimming.

2.2 Electrodeposition into porous templates

The synthesis of electrodeposited catalytic microjets has been recently demonstrated by Wang’s group [18,33]. Template assisted micro- and nano-motors are usually tubular motors consisting of a concentric polymer or organic compound/platinum (Pt) bilayer. Figure 4 shows the synthesis method and a scanning electron microscopy (SEM) image of the template assisted microjets. Firstly, a cyclopore polycarbonate membrane, containing 2 or 5 μm diameter conical-shaped micropores, is employed as template. The polycarbonate membrane is sputtered using a conductive material such as Au which acts as working electrode (WE). A Pt wire and Ag/AgCl (3 M KCl) are employed as the counter (CE) and reference electrodes (RE), respectively. Then, the membrane is assembled in a plating cell with an aluminum foil serving as the electric contact to fix the WE (Fig. 4). Tubular microjets are prepared using a common template directed electrodeposition protocol. After electrodeposition, the sputtered gold layer is completely removed by hand polishing with alumina slurry and the membrane is dissolved by immersing it in methylene chloride solution to release the microtubes. As an example, for polymer/Pt microtubes, the conductive polymer selected is PEDOT, being used in most of the experiments. PEDOT is prepared via electropolymerization at +0.80 V using a plating solution containing EDOT monomer with SDS and KNO₃. Subsequently, a Pt layer is deposited galvanostatically at −2 mA for a specific time by using a Pt plating commercial solution to provide the catalytic properties.

In addition, the basic bilayer presented in Fig. 4 can be tailored to include different functional materials like graphene [34] as outer layer and Ni and Au layers for their magnetic guidance and facile functionalization (i.e. with receptors), respectively [35], as inner layers. These microjets present intrinsically conical shape due to the shape of the templates used for the electrodeposition. The microjets fabricated by this technique display some significant advantages such as low-cost mass production synthesis method, fast production, very high relative speeds compared with other microjets, are commonly smaller than other typically found in the bibliography and can be made of polymers or graphene combined with metals rather easily.

3 Catalytic tubular microjets swimming in fluids

Microjets are microtubular structures which contain active materials as inner wall. These materials produce the decomposition of chemicals into gas molecules which trigger the motion of microjets. Those materials are catalytic or non-catalytic and
decompose diverse fuels, being the main common fuel so far H₂O₂. The motion of microjets is described in three stages. First, the fuel wets the catalytic layer of the microjet containing nucleation points where the decomposed O₂ accumulates and grows as bubbles (Fig. 5). In a second stage, the bubbles migrate towards the largest opening of the microtube and finally, the bubbles are released from the tube which induces another moving step. The stepping motion is described in Fig. 5 (bottom). Solovev et al. described that the velocity of microjets was linear to the product of bubble radius and frequency [14]. At high frequencies, collisions between bubbles may diminish the space travelled from the bubbles inside the tube limiting the releasing stage [36].

3.1 Factors affecting the motion of microjets

Once microjets swim in fluids, many factors such as their intrinsic geometry, viscosity of the medium, confinement where they swim, composition of the fluid and components, fuel concentration and additives affect significantly the physics of the motion and they should be carefully studied. Back in 2011, Solovev et al. reported a systematic study on different lengths of catalytic tubes fixed on substrates and studied the lowest concentration possible for inducing pumping of fluid. They found out that long tubes could be activated at H₂O₂ concentrations as low as 0.0009% v/v. Using polystyrene spheres as tracers, the flow of the pumped liquid which matched with the growth and migration of bubbles that displaces the fluid within the tube were demonstrated [37].

There are some differences in performance between rolled-up and electrodeposited microjets, which are due to their geometrical differences as well as their mechanical
Fig. 5. Bubble-propelled tubular microjets. (A) Sketch of multiple microjets self-propelled by bubble generation and releasing. Microjets are immersed in \( \text{H}_2\text{O}_2 \) solution which is decomposed into \( \text{O}_2 \) and \( \text{H}_2\text{O} \). (B) Step-wise mechanism of motion of microjets, including the pumping of fluid into the microtube, bubble nucleation in their interior, migration, and final bubble releasing from the tubes. Adapted from [6] and [36].

Microjets swim at low \( Re \) where inertia is negligible and viscous forces are dominant, small changes in viscosity may affect the dynamics of the microjets. Sanchez et al. observed superfast motion of microjets at physiological temperatures where viscosity is 50% reduced. In addition, it provokes changes in the dynamics of microjets from linear to circular trajectories [15]. Thus, to move microjets in reconstituted blood samples at physiological temperature [41], it is necessary to reduce the viscosity of the media since motion hampered at 25 °C [42]. It was observed that at higher
Re circular motions (or not linear) are preferable [43]. Furthermore, other factors, such as the components of the solution, can sometimes dramatically modify the swimming behavior of microjets. Blood metabolites, proteins, extracellular thiols, electrolytes and also source of water may affect the motion of microjets [44,45].

### 3.2 Proposed theoretical models for microjets

Due to the high interest that those microdevices have generated, some fundamental studies have been also carried out to understand their bubble propulsion mechanism. A theoretical model based on the bubble nucleation and ejection is described by Manjare et al. [46]. This model also investigates different parameters such as the effects of length and the diameters of the microjets on the hydrogen peroxide and oxygen transport across the microjet. As shown in Fig. 6(A), the model focuses on the flux of the oxygen to one end of the microjet. The bubble growth and its ejection from the one end of the microjet is described as the main parameter responsible for the movement. The growth force acting on the microjets is governed by the Rayleigh–Plesset equation, as previously described by the same group [47]. However, the group did not consider the migration of bubbles generated at any other point of the tube. Since bubbles have been observed to form at various points of inner walls of microjets, those steps could also be involved in the propulsion mechanism. Several other parameters are also described in this model such as the concentration of the hydrogen peroxide fuel, oxygen flux, rate of the bubble generation, frequency of the bubble ejection, radius of the microjet and average speed of the microjets during the bubble growth. Fick’s first law \( J = -D \frac{dC}{dx} \) is used to calculate the flux of oxygen going into the bubble growth.
According to the authors, after considering those parameters, the average speed of the microjets during the bubble growth can be expressed by an equation presented in their paper containing a bubble growth prefactor, an empirical constant, the mass density of the media and the mass of the micromotor. Surprisingly, even without considering the migration and nucleation steps, the speed of the microjets authors obtained during the bubble growth are comparable to the experimental data [46].

In the model together with the theory and experiments proposed by Li et al., the bubbles and the tubes are separately considered for the explanation of the mechanism [49]. In this model it is assumed that the microjet and the bubble stop at the same time when they are separated by the distance of the microjets diameter. Since after the separation both the microjet and the bubbles may have different dynamics and possibly are not associated anymore, this model is controversial. Because of the importance of the geometry in the performance of these microjets, a model which considers the non-uniform shape of the catalytic microjet (Fig. 6(B)) is described by Fomin et al. [48]. In this model authors have combined the time dependent hydrodynamics of the bubble growth and migration within the asymmetric shape of the microjet (Fig. 6(C)). The migration of the bubble in the microjet creates the net force which pushes forward the microjet. Authors have also compared their model with the other models proposed previously. They put forward the hypothesis that not the geometrical parameters but the asymmetries are important for the jet effect and the motion of a perfectly symmetric microjet as observed in the experimental results.

It can be assumed that with the time, the volume of a growing bubble increases in the asymmetric microjet. It can be denoted by the following equation,

\[ V(t) = kS_{\text{cat}} t. \]  

(2)

Here, \( k \) is the rate of the oxygen production from a unit surface area and \( S_{\text{cat}} \) is the catalytic area. The fluid pumping induced by the bubble migration, along with recoil propels the tube. Authors proposed a simplified preliminary model for the mechanism with an assumption that relaxation of the microjets momentum occurs at a finite rate in the surrounding fluid. The description of the fluid dynamics produced by the bubble motion in a microjet rigorously indicates that a time-dependent hydrodynamic analysis is required. A momentum transfer to the fluid occurs because of the motion of the bubble in an asymmetric microjet. The momentum transfer generates a motor force \( (F_{\text{motor}}) \) on the microtube,

\[ F_{\text{motor}} = M \frac{dV_t}{dt} \]  

(3)

where \( M \) is the mass of the tube and \( V_t \) is the velocity. On the other hand, swimming in the fluid creates the linear drag force that is acting on the microjet.

\[ F_{\text{drag}} = -2\eta\pi L \left[ \ln \left( \frac{L}{R_{\text{max}}} \right) - 0.72 \right]^{-1} v_{\text{tube}} \]  

(4)

and the balance of the forces \( (F_{\text{drag}} + F_{\text{motor}} = 0) \), the tube instantaneous speed can be described as

\[ v_{\text{tube}} = \frac{F_{\text{motor}}}{2\pi\eta L} \left[ \ln \left( \frac{L}{R_{\text{max}}} \right) - 0.72 \right] \]  

(5)

and the average speed as \( \langle v_{\text{tube}} \rangle (t) = \frac{1}{\tau} \int_0^\tau v_{\text{tube}}(\tau) d\tau \).

(6)

Microjets with the well-controlled velocities can be fabricated by considering different forces acting on it. For example, by controlling the shape and diameter of the
Fig. 7. Application of the microjets for the pollutant removal from the water. (A) Schematic of the graphene based microjets for the adsorption, removal and recovery of the heavy metal (B) Schematic of the reusability of the microjets for the degradation of organic waste in the water via Fenton like reaction. Reprint with the permission from [54] (A) and [26] (B). (This figure is subject to copyright protection and is not covered by a Creative Commons license.)

microjets, well-defined velocities can be achieved because of the strong dependent of the velocities on the microjets diameter. However, a separate analysis of the hydrodynamics of the fluid around the microjet is still required.

Another theoretical report by Sarkis et al. is related to the future medical application of those microdevices, aiming at the understanding of the bubble propulsion and the motion of microjets in a blood vessel [50].

4 Challenges and applications of microjets

Commonly used chemical fuels like H\(_2\)O\(_2\) and hydrazine are not biocompatible, therefore limiting possibilities for microjets in biomedical applications. Microjets driven just by water have been described but their lifetimes are short which inhibits their use. Electrodeposition of Zn as inner layer produced microjets able to self-propel by the production of H\(_2\) bubbles in acidic media [51]. Despite this new fuel, the same problem arises, as the microjets can only move for less than a minute. To address this limitation there has been an effort to develop more efficient propulsion methods and other biocompatible sources of motion. For instance, the use of enzymes [52] or motile cells [53] could give rise to biologically friendly micromotors. Therefore, the design of hybrid micromotors could be a very good strategy to develop the next micro- and nano-motors for biomedical applications. Even though biomedical applications of microjets face issues related to fuel toxicity and bubble productions, they are showing great promises for various environmental remediation and sensing applications [11,12].

Microjets enhance mass transfer and improve micromixing in the system which makes them very efficient for pollutant capture and degradation in aqueous media [55–58]. Recent reports showed application of the microjets for the removal of heavy metal [54,59] from the contaminated wastewater and long lasting reusable microjets [26] for the oxidation of organic pollutants in the water (Fig. 7).

5 Conclusions and outlook

There are several methods to fabricate microjet engines. We discussed two of them, rolled-up of thin films and electrodeposition in porous templates. Theoretical models have been proposed and briefly summarized here. Self-propelled motors are of little use for some practical applications, such as targeted drug delivery, if their motion cannot be accurately controlled and guided towards specific locations. The recently reported negligible toxicity of metallic tubular micromotors on the human lung cell viability [60] keeps the door open for in vivo applications. However, several issues and
challenges need to be solved before reaching real biomedical applications. For instance, preventing leaching of metallic ions into the surrounding solution due to corrosion of micro- nano- motors, and performing accurate studies of the effect of accumulation of bubbles inside of a living organism are crucial, for which the design of self-propulsion without bubbles will be a good strategy. While the quest for biocompatibility is a challenging and ongoing one, chemically propelled micro- nano- motors can still be used for a variety of other applications. Multifunctional microjets, composed of multiple materials are proposed for biosensing, micropumping, transport of cargo in microfluidics and environmental applications. Finding a real application is the big hope to continue moving the field of catalytic micromotors forward.

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