Nanoscale

PAPER

View Article Online
View Journal | View Issue

Cite this: *Nanoscale*, 2014, **6**, 11359

Tissue cell assisted fabrication of tubular catalytic platinum microengines†

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Received 3rd July 2014
Accepted 17th July 2014

DOI: 10.1039/c4nr03720k

www.rsc.org/nanoscale

We report a facile platform for mass production of robust self-propelled tubular microengines. Tissue cells extracted from fruits of banana and apple, *Musa acuminata* and *Malus domestica*, are used as the support on which a thin platinum film is deposited by means of physical vapor deposition. Upon sonication of the cells/Pt-coated substrate in water, microscrolls of highly uniform sizes are spontaneously formed. Tubular microengines fabricated with the fruit cell assisted method exhibit a fast motion of ~100 bodylengths per s (~1 mm s^{-1}). An extremely simple and affordable platform for mass production of the micromotors is crucial for the envisioned swarms of thousands and millions of autonomous micromotors performing biomedical and environmental remediation tasks.

Introduction

As a leading-edge nanotechnology, self-propelled micro-/nanoscale motors represent a fundamental step towards practical tiny machines.[1–5] These autonomous nano- and microsized devices are expected to perform a wide variety of tasks in the biomedical field,[6,7] environmental remediation[8–10] and natural resource discovery.[11] Self-propulsion at the nanoscale is achieved mainly by the mechanisms of self-electrophoresis,[12,13] self-diffusiophoresis[14,15] or bubble ejection.[16–18] The last mode of propulsion is of the greatest interest as it exhibits the strongest propulsion power and unprecedented velocity.[19,20] Bubble-propelled micromotors are typical of microtubes with a catalyst[17,21] on the inner surface. Hydrogen peroxide fuel is decomposed into oxygen and the resulting bubbles are expelled from one end of the microtube, thus propelling it in the opposite direction.

The fabrication of tubular micro/nanomotors is still a highly challenging task. The rolled-up nanotechnology[22] includes top-down photolithography, angled e-beam evaporation and stress-assisted rolling of nanomembranes upon etching away of the photoresist. The practical utility of this method is greatly hindered by the complicated fabrication process and high costs of related clean-room conditions. An alternative method of fabricating tubular micro/nanomotors is anodic aluminum oxide or polymer membrane-templated electrodeposition,[19,23] but this technique requires highly trained personnel and the cost of templates is not negligible. In addition, toxic electroplating solutions containing cyanide are usually needed in the electrodeposition process.

Recently, there has been intense interest in developing cheap and easy plant-derived approaches for fabrication of motors. Millimeter sized biocatalytic motors based on plant tissues[24] and magnetically driven helical micromotors harnessing spiral water-conducting vessels of different plants[25] have been reported. Here, we demonstrate an extremely simple and low-cost fabrication method of tubular microengines with the assistance of fruit cells. The use of cheap and widely accessible fruit cells instead of a lithographically defined material as the support of metal layers omits the etching step and significantly reduces the fabrication costs. The resulting microtubes display ultrafast motion in the presence of hydrogen peroxide. The new fruit cell assisted method allows for rapid and cost-effective fabrication of thousands of copies of tubular microengines using banana and apple fruit tissue cells.

Results and discussion

To prepare the tubular microengines, the aqueous dispersion of banana fruit cells was first prepared by homogenization of mashed banana tissue in water *via* ultrasonication. The homogenized dispersion of banana fruit cells was subsequently deposited on the glass cover slip. After complete evaporation of water, Pt was deposited on the glass cover slip coated with banana cells by sputtering. Upon ultrasonication of the modified cover slip in water, the multilayer film shattered and detached from the glass cover slip, rolling into scrolls. The whole fabrication process is illustrated in Scheme 1.

Fig. 1 shows optical images of aqueous dispersion of banana fruit cells and the fabricated tubular microengines. As can been seen from Fig. 1A, the banana fruit cells are several hundred micrometers in length and are flat in shape. After the

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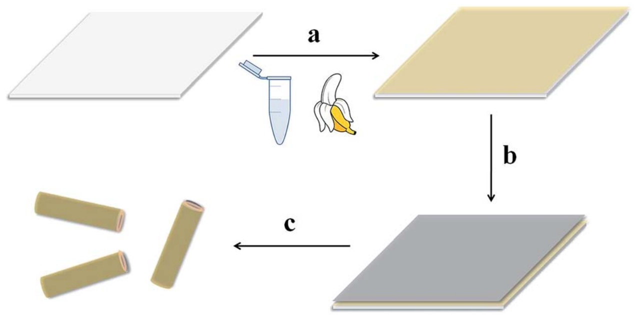
† Electronic supplementary information (ESI) available: Related video. See DOI: 10.1039/c4nr03720k



Scheme 1 Preparation of rolled-up tubular microengines using banana fruit cells: (a) deposition of banana fruit cells on the glass cover slip, (b) deposition of a Pt layer by sputtering, and (c) ultrasonication of the cells/Pt-coated cover slip.

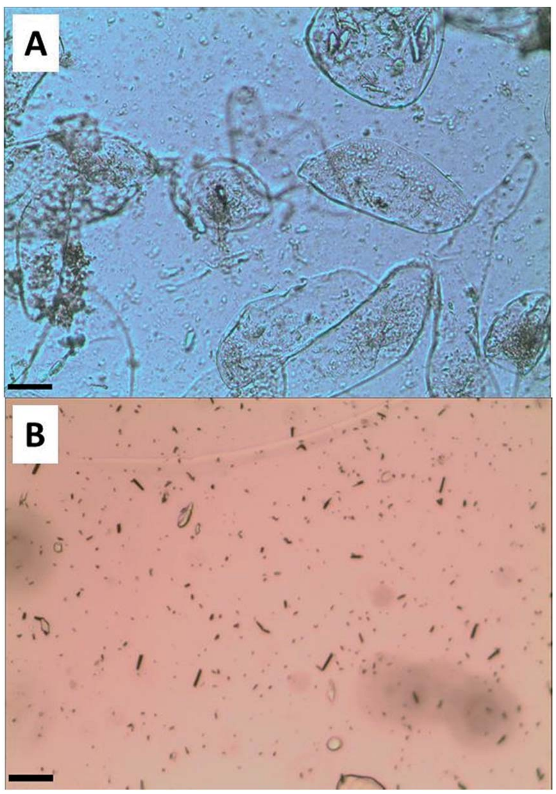


Fig. 1 Optical images of aqueous dispersion of (A) banana fruit cells and (B) tubular microengines obtained upon ultrasonication. Scale bar: 50 μm.

evaporation of water, the cells deposited on the cover slip became a layer of membrane that would detach from the surface upon coming into contact with water. There are no microtubes observed before and after deposition of the Pt layer, where only some cracks of the deposition layers emerged. However, microtubes were immediately obtained upon ultrasonication of the cells/Pt-coated glass cover slip in water, as shown in Fig. 1B.

The SEM images of the resulting microtubes are presented in Fig. 2A and B. The microtubes exhibit excellent size uniformity and the rolled-up structure is clearly visible. A size distribution analysis of the obtained microtubes was carried out, as shown in Fig. 2C. The majority of the fabricated tubular microengines are 10–15 μm long and the average opening diameters at opposite ends are around 2.5 μm and 3 μm, respectively. The uniformity of the tubular microengines fabricated by the new method is competitive with that of microtubes prepared by membrane-templated electrodeposition and rolled-up technology.[26]

The EDX mapping analysis of the fabricated tubular microengines (Fig. 3) clearly shows the presence of platinum, carbon and oxygen, demonstrating the existence of banana fruit tissue in the microtube structure. For the fabrication of rolled-up microstructures, the strain in the film creates the bending moment[27] and strain relaxation is the driving force of the rolling

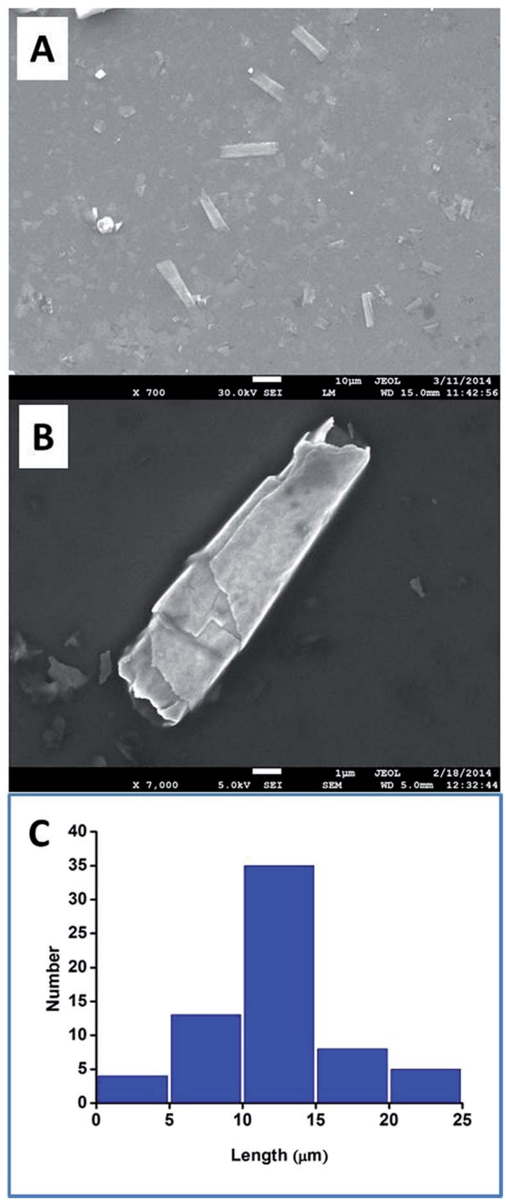


Fig. 2 (A and B) SEM images of the fabricated tubular microengines. Scale bars are 10 μm and 1 μm, respectively. (C) Length distribution of the tubular microengines, $n = 65$.

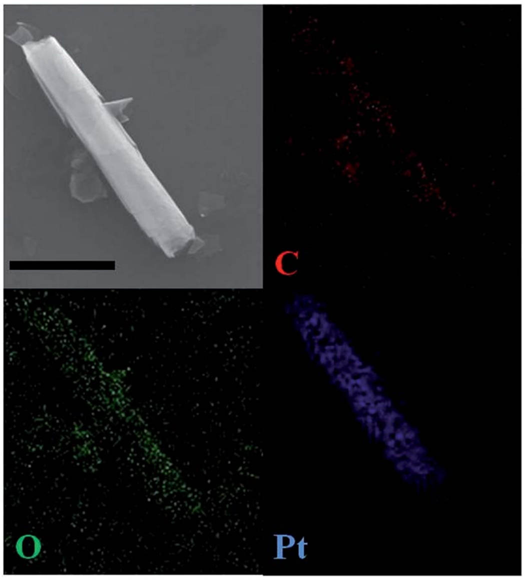


Fig. 3 SEM/EDX elemental characterization of the tubular micro-engine composition. Scale bar: 10 μm.

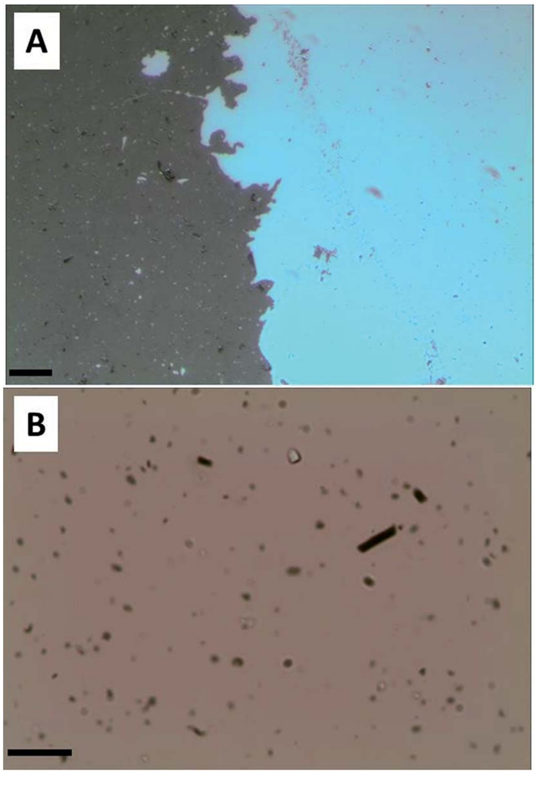


Fig. 4 (A) Optical image of the cover slip half coated with banana fruit cells (right side) after deposition of Pt and ultrasonication in water. Platinum is still on the uncoated cover slip after ultrasonication (left side). Scale bar: 50 μm. (B) Optical image of tubular microengines fabricated using apple fruit cells. Scale bar: 20 μm.

process.[28] The strain in the fruit cells/Pt bilayer mainly comes from two aspects. The Pt film deposited by sputtering is in a state of intrinsic stress, because of the accumulating effect of the crystallographic flaws that are built up during the deposition process.[29] The intrinsic stress is related to the deposition conditions and properties of the substrate surface.[29,30] In addition, the different swelling properties of banana fruit cells and a metal layer in water result in unequal changes in volume, thus generating swelling-induced strain.[27,28] The intrinsic stress of a platinum film and the swelling-induced strain together lead to the formation of the fruit tissue cells/Pt microscrolls.

Control experiment to prove the necessity of the banana fruit cells for successful formation of the microtubes was carried out. One half of the glass cover slip was covered with banana fruit cells while the other half of the glass was left bare. After deposition of the Pt layer and ultrasonication in water, the Pt layer still covered the bare glass surface while the Pt layer and banana tissue cells on the other side detached from the glass cover slip upon ultrasonication (Fig. 4A, the left and right side, respectively). The banana fruit cells provide an easily detachable interface between the metal layer and the glass substrate, which allows the instantaneous formation of microscrolls upon ultrasonication in water and eliminates the etching step using other chemical solutions. Additionally, we wish to show that banana fruit cells serve only as an example – other fruit cells can be employed to assist the preparation of tubular microengines as well. Fig. 4B shows the optical image of the microtube fabricated using apple fruit cells.

The tubular microengines fabricated with the fruit cell assisted method exhibit high propulsion power in the presence of hydrogen peroxide fuel. Fig. 5A shows a typical snapshot of the motion of the prepared microengines in 3% H_2O_2. The trajectory can be easily visualized from the oxygen bubble tail released from one end of the microtube. The speed of the tubular microengines can be modulated by varying the concentration of hydrogen peroxide. As shown in Fig. 5B, the average velocity of the fruit cells/Pt microtube engines increases from ~410 μm s^{-1} in 2% H_2O_2 to ~680 μm s^{-1} in 4% H_2O_2. Some microengines show ultrafast motion, up to 1 mm s^{-1} in 3% H_2O_2 (Video S1; ESI†). The mobility of the tubular microengines prepared with the introduced method is highly competitive with that of microengines fabricated by electrodeposition[19] and rolled-up technology.[20] In addition, the very low cost of the fabrication process using common fruits, such as bananas and apples, offers possibilities for mass production of micromotors. Thousands of microtube engines can be prepared with only milligrams of fruit tissue.

Conclusions

In summary, we demonstrated a very affordable and simple route for the fabrication of rolled-up tubular microengines, using fruit tissue cells as the support of the deposited metal layer. Given the cheap price of fruits and small amounts needed for the preparation process, the cost of fabrication is only cut down to the consumption of Pt used for sputtering. One can envision the use of the other soft tissues for assisted fabrication of microjets. Microtube engines fabricated by this method exhibited good uniformity in the dimensions and excellent mobility, up to ~100 bodylengths per s. The fruit tissue cell assisted fabrication process opens doors for mass fabrication of microscale devices at extremely low cost.

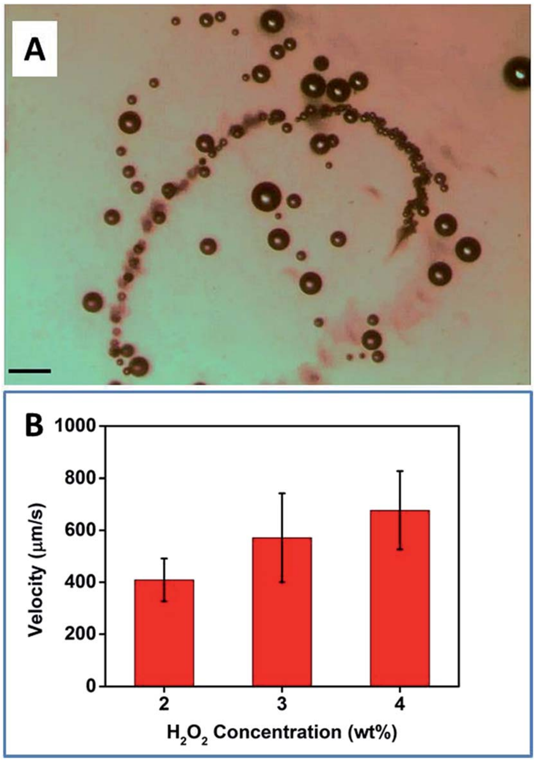


Fig. 5 (A) Snapshot of the motion of a microtube engine in 3% H_2O_2 and 0.5% SDS. Scale bar: 50 μm. (B) Dependence of the microjet speed on the H_2O_2 concentration in the presence of 0.5% SDS. Tracking data were obtained from 15 independent running experiments in order to obtain the average speed.

Experimental section

Materials

Hydrogen peroxide (35%, lot no. 10172592) was purchased from Alfa Aesar. Sodium dodecyl sulfate (SDS, lot no. 079K0335) was purchased from Sigma-Aldrich. VFM cover slips (22 × 22 mm, lot no. GP110220001) were purchased from Cellpath, UK. The platinum targets for sputtering were purchased from Quorum Technologies Ltd, UK. Bananas and apples were purchased from local markets. The chemicals were used as received and ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q purification system was used throughout the experiments.

Apparatus

The ultrasonication process was carried out with a Fisherbrand FB 11203 ultrasonicator. Sputtering was carried out with a JEOL JFC-1600 Auto Fine Coater. Scanning electron microscopy (SEM/EDX) analysis was obtained with a JEOL JSM 7600F instrument. Optical microscope images and videos were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-Elements software.

Methods

Preparation of microjets. The cover slips were cleaned with water and dried with nitrogen gas. Fruit tissue (banana or apple, 500 mg) was dispersed in water (2 mL) by ultrasonication and 50 μL of the aqueous suspension was applied on the cover slip to spread over the whole surface. The cover slip was left overnight to dry and platinum (15 nm) was sputtered on the cover slip. The cover slip was ultrasonicated subsequently in water and the aqueous suspension of tubular microengines can be obtained.

Propulsion of microjets. The experiments for the motion study of the fabricated tubular microengines were carried out in an aqueous solution containing different concentrations of hydrogen peroxide at a constant surfactant concentration (0.5 wt% of SDS). A mixture of microjets, SDS, H_2O_2 and water was applied on a glass slide freshly cleaned with a nitrogen gas. Optical microscope videos and images were obtained with a Nikon Eclipse 50i microscope. Video sequences were processed with Nikon NIS-ElementsTM software.

Acknowledgements

M. P. acknowledges Nanyang Technological University and Singapore Ministry of Education Academic Research Fund AcRF Tier 1 (2013-T1-002-064, RG99/13) for the funding support.

Notes and references

1 S. Sengupta, M. E. Ibele and A. Sen, *Angew. Chem., Int. Ed.*, 2012, **51**, 8434–8445.
2 G. Zhao and M. Pumera, *Chem.–Asian J.*, 2012, **7**, 1994–2002.
3 J. Wang, *ACS Nano*, 2009, **3**, 4–9.
4 S. Campuzano, D. Kagan, J. Orozco and J. Wang, *Analyst*, 2011, **136**, 4621–4630.
5 S. Sanchez and M. Pumera, *Chem.–Asian J.*, 2009, **4**, 1402–1410.
6 J. Wang and W. Gao, *ACS Nano*, 2012, **6**, 5745–5751.
7 J. Wang, *Lab Chip*, 2012, **12**, 1944–1950.
8 W. Gao and J. Wang, *ACS Nano*, 2014, **8**, 3170–3180.
9 L. Soler and S. Sanchez, *Nanoscale*, 2014, **6**, 7175–7182.
10 (*a*) G. Zhao, T. H. Seah and M. Pumera, *Chem.–Eur. J.*, 2011, **17**, 12020–12026; (*b*) T. H. Seah, G. Zhao and M. Pumera, *ChemPlusChem*, 2013, **78**, 395–397.
11 A. Sen, M. Ibele, Y. Hong and D. Velegol, *Faraday Discuss.*, 2009, **143**, 15–27.
12 Y. Wang, R. M. Hernandez, D. J. Bartlett, J. M. Bingham, T. R. Kline, A. Sen and T. E. Mallouk, *Langmuir*, 2006, **22**, 10451–10456.
13 M. Pumera, *Nanoscale*, 2010, **2**, 1643–1649.
14 L. Baraban, D. Makarov, R. Streubel, I. Mönch, S. Sanchez and O. G. Schmidt, *ACS Nano*, 2012, **6**, 3383–3389.
15 W. Gao, A. Pei, R. Dong and J. Wang, *J. Am. Chem. Soc.*, 2014, **136**, 2276–2279.
16 A. A. Solovev, Y. F. Mei, E. B. Ureña, G. Huang and O. G. Schmidt, *Small*, 2009, **5**, 1688–1692.
17 A. A. Solovev, S. Sanchez, M. Pumera, Y. F. Mei and O. G. Schmidt, *Adv. Funct. Mater.*, 2010, **20**, 2430–2435.
18 H. Wang, G. Zhao and M. Pumera, *J. Am. Chem. Soc.*, 2014, **136**, 2719–2722.
19 W. Gao, S. Sattayasamitsathit, J. Orozco and J. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 11862–11864.

20 S. Sanchez, A. N. Ananth, V. M. Fomin, M. Viehrig and O. G. Schmidt, *J. Am. Chem. Soc.*, 2011, **133**, 14860–14863.
21 S. Sanchez, A. A. Solovev, Y. F. Mei and O. G. Schmidt, *J. Am. Chem. Soc.*, 2010, **132**, 13144–13145.
22 Y. Mei, G. Huang, A. A. Solovev, E. B. Ureña, I. Mönch, F. Ding, T. Reindl, R. K. Y. Fu, P. K. Chu and O. G. Schmidt, *Adv. Mater.*, 2008, **20**, 4085–4090.
23 G. Zhao and M. Pumera, *RSC Adv.*, 2013, **3**, 3963–3966.
24 Y. Gu, S. Sattayasamitsathit, K. Kaufmann, R. Vazquez-Duhalt, W. Gao, C. Wang and J. Wang, *Chem. Commun.*, 2013, **49**, 7307–7309.
25 W. Gao, X. Feng, A. Pei, C. R. Kane, R. Tam, C. Hennessy and J. Wang, *Nano Lett.*, 2014, **14**, 305–310.
26 G. Zhao, A. Ambrosi and M. Pumera, *J. Mater. Chem. A*, 2014, **2**, 1219–1223.
27 V. Luchnikov, O. Sydorenko and M. Stamm, *Adv. Mater.*, 2005, **17**, 1177–1182.
28 M. Huang, F. Cavallo, F. Liu and M. G. Lagally, *Nanoscale*, 2011, **3**, 96–120.
29 J. A. Thornton, *Thin Solid Films*, 1989, **171**, 5–31.
30 S. V. Golod and V. Y. Prinz, *Appl. Phys. Lett.*, 2004, **84**, 3391–3393.