Large-scale and uniform fabrication of anodic TiO_2 nanotubes at the inner surface of high-aspect-ratio Ti tubes

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Because of their high specific strength and superior corrosion resistance, titanium and its alloys have been widely used in aerospace, navigation, desalination, automotive and petroleum industries. Titanium tubes and pipes are of particular interest for heat and mass transfer in heat exchangers in these fields. However, a few critical problems are currently concerned: the frictional drag at the solid/liquid interface and the fouling that lowers the heat transfer coefficient.[1] A superhydrophobic coating developed at the inner and/or outer surface of a tube is capable of providing drag reduction, suppressing fouling formation, and producing condensation heat transfer, therefore enhances the performance of heat exchangers.[2-6] Nevertheless, it remains a great challenge to fabricate such superhydrophobic coatings on tubular substrates, especially at their inner surfaces considering the partially opened geometrical feature.

Anodic oxidation of titanium and its alloys enables the formation of highly ordered TiO_2 nanotubes, which have attracted growing interest in the fields of solar cells,[7-10] photocatalysis,[11] drug delivery,[12] lithium-ion batteries,[13] and so on. Wetting property of the TiO_2 nanotubes can be well tailored by controlling their structures and employing organic molecules of low surface energy. They are thus competent as the superhydrophobic coatings mentioned above. Nonetheless, the existing methods are unsuitable for large-scale and mass production of uniform TiO_2 nanotubes on tubular substrates.

Sun and co-workers[14] systematically studied the effect of electrode deployment on the formation of TiO_2 nanotubes, as shown in ***Figure 1***. A conventional planar cathode was used. The results reveal that nanotubes are formed at both surfaces of a titanium tubular electrode, regardless of the deployment. When the anode is dipped into electrolyte solution (about 17 mm immerged) and set perpendicular to the liquid surface (see ***Figure 1a***), the nanotube length exhibits an almost linear decrease from the tube bottom to top at the inner surface (see ***Figure 1d***). This is attributed to the limited diffusion pathway available only from tube bottom for F^{-} ions. When the anode is completely immerged into the electrolyte solution while kept parallel to the liquid surface and the cathode (see Figure 1b), the nanotube length decreases gradually from tube mouth at both ends to the middle part, as exhibited in ***Figure 1e***. This is due to the situation that the F^{-} ions can diffuse into the tube from either side. In a similar case where the anode is set perpendicular to the cathode (Figure 1c), the nanotube length decreases progressively from the end near the cathode to the other end, as shown in ***Figure 1f***. In all of the experimental setups, at the outer substrate surface the nanotube length decreases gradually from the part close to the cathode to that far away, because of the potential drop in the organic electrolyte solution.[15,16] This study indicates that it is difficult to coat either inner or outer surface of a Ti tube with uniform TiO_2 nanotube arrays using conventional anodization scheme.

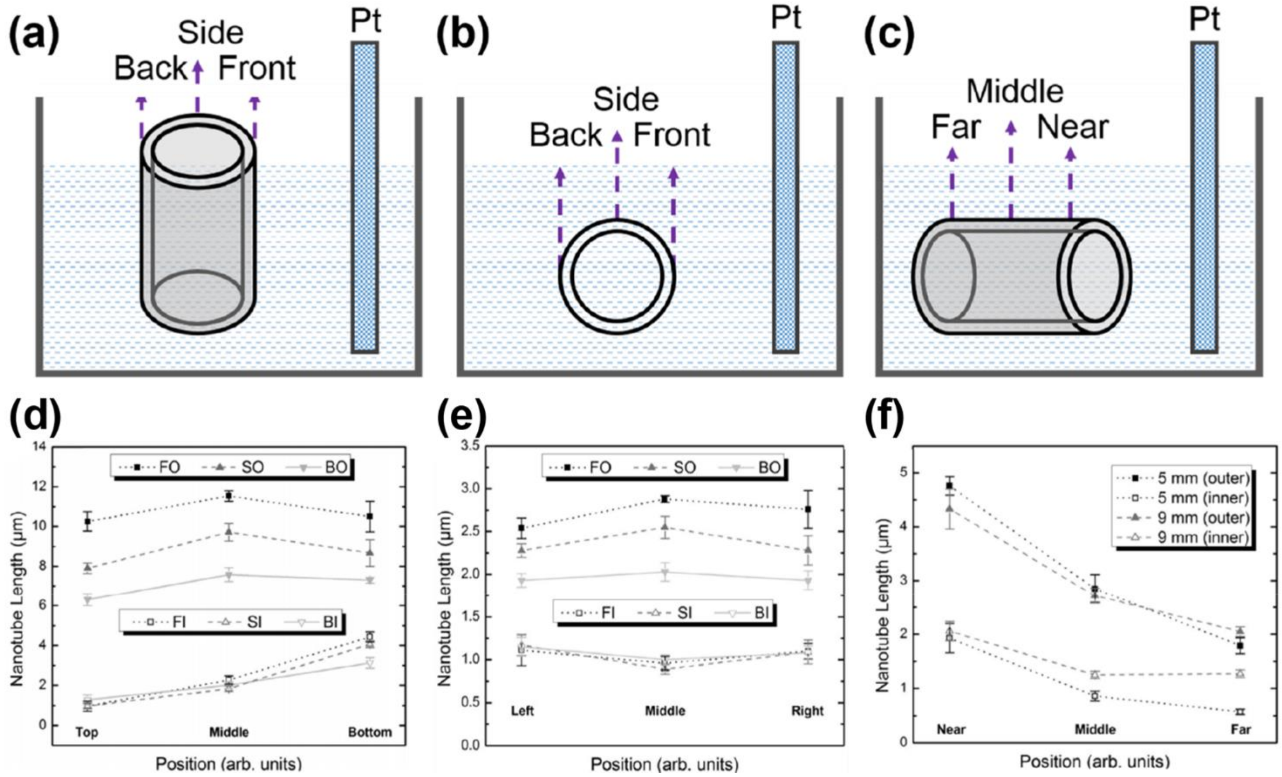

Figure 1. Schematic illustration of different electrode deployments, where a planar cathode is used with the tubular anode being: (a) perpendicular to the liquid surface and parallel to the cathode, (b) immersed in the solution and parallel to the cathode, and (c) immersed in the solution and perpendicular to the cathode. Corresponding length of TiO_2 nanotubes at both inner and outer surfaces is given below each illustration in (d), (e) and (f), respectively. Reprinted with permission from L. Sun, *et al.*, *Langmuir* 30 (10), 2835-2841. Copyright © 2014 American Chemical Society.

The key to control the nanotube uniformity is to ensure a uniform distribution of electric field along the radial and axial directions. To this end, Xiang and co-workers[5] designed a coaxial electrochemical anodization, as illustrated in ***Figure 2a***. In this setup, a titanium tube is employed as the anode while a stainless steel wire is used as the cathode, where the substrate itself also performs as a container to accommodate electrolyte solution. With this method, uniform TiO_2 nanotube arrays are produced at the inner surface of Ti tubes with a dimension of 1000 mm in length and 10 mm in diameter (aspect ratio: 100), as displayed in ***Figure 2b***. This is in good contrast to the non-uniform nanotubes yielded with conventional deployments in ***Figure 1***, though with much smaller substrates (aspect ratio: <6). A length limit of about 1 μm exists for the nanotubes, as a result of limited electrolyte volume confined inside the tubular compartment. The coaxial electrochemical anodization can be applied to longer substrates and also other valve metals suitable for anodic oxidation. However, it is further found that once the substrate diameter drops to a very low regime, e.g., 3 mm, the nanotubes become non-uniform again and even are absent at certain regions. This is ascribed to the limited volume rendered by the small tubes. Bubbles that are released in the process of anodization are adsorbed to the inner surface, accumulate and eventually expel the electrolyte solution out of the tubular compartment.

In application of microfluids and microelectronics, slim tubes of small diameters have been frequently used. In this regard, Wang and co-workers[6] further developed a coaxial anodic oxidation under dynamic electrolyte conditions, as sketched in ***Figure 3a***. In this setup, the flowing electrolyte is adopted to make up the solution, drive out the bubbles, and also cool down the system. The growth of TiO_2 nanotubes is closely related to the electrolyte flow rate. When the flow rate is too low, the nanotube growth rate is limited. The problem still remains. When the flow rate is too high, the nanotubes are able to fully cover the inner surface, whereas the length increases from substrate bottom to the top. This is because fresh electrolyte flows into the tubular compartment at the bottom part, where the fluoride concentration is high. This leads to an enhanced etching rate to the already-formed TiO_2 nanotubes by chemical dissolution and hence shorter nanotubes close to the inletting end.[17] Consequently, the length at the inner surface is tailorable by controlling the electrolyte flow rate. Accordingly, uniform coatings of TiO_2 nanotubes are attained using Ti tubes of 930 mm in length and 3 mm in diameter (aspect ratio: 310), as shown in ***Figure 3b***.

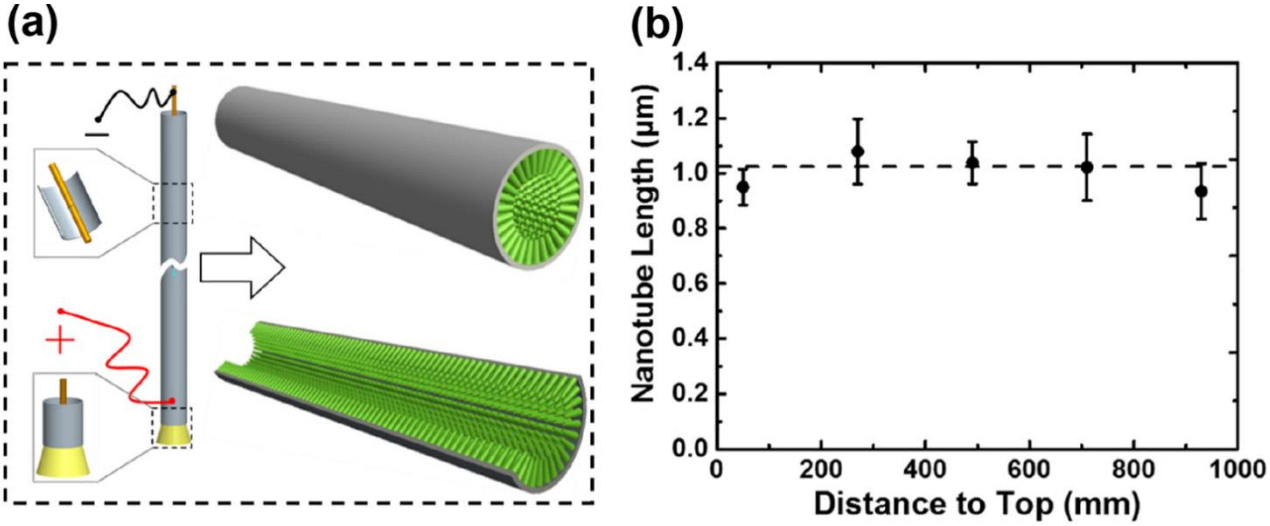

Figure 2. (***a***) Schematic illustration of coaxial electrochemical anodization; (***b***) Length of TiO_2 nanotubes at the inner surface of Ti tubes examined along the axial direction. Adapted with permission from C. Xiang, *et al.*, *J. Phys. Chem. C* 121 (28), 15448-15455. Copyright © 2017 American Chemical Society.

The above coatings of TiO_2 nanotubes are intrinsically hydrophilic, and can be further tailored to be superhydrophobic with a water contact angle of over 160° and sliding angle of below 3°, with judiciously designed structure. It is thus promising for applications in drag reduction, condensation heat transfer, antifouling, and so on.

The coaxial electrochemical anodization can also be extended to the outer tube surface, and even to both surfaces anodized simultaneously. In the latter case, the uniformity control becomes more difficult. The asymmetric deployment between the anode and cathode results in different oxidation and dissolution processes, which should be taken into account to ensure uniform nanotubes.

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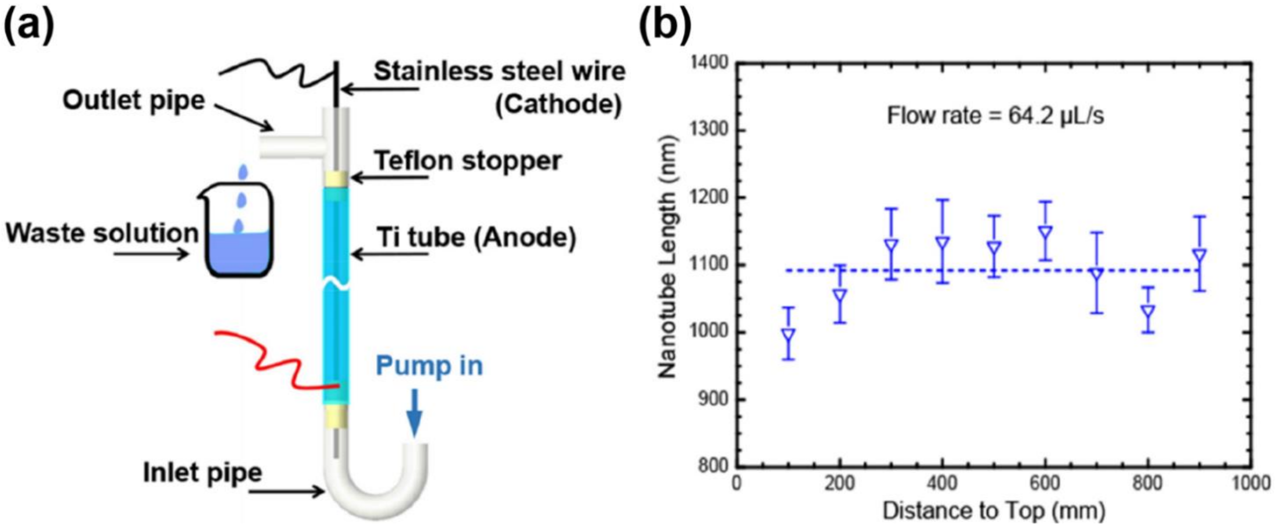

Figure 3. (***a***) Schematic illustration of coaxial electrochemical anodization with flowing electrolyte; (***b***) Length of TiO_2 nanotubes at the inner surface of Ti tubes examined along the axial direction. Reprinted from *Corros. Sci.*, Volume 124, Y. Wang, *et al.*, Coaxial anodic oxidation under dynamic electrolyte conditions for inner surface patterning of high-aspect-ratio and slim Ti tubes, 193-197. Copyright ©2017, with permission from Elsevier.

References

[1] Y. C. Jung and B. Bhushan, *J. Phys.: Condens. Matter*, **2010**, 22, 035104.
[2] N. Miljkovic, *et al.*, *Nat. Commun.*, **2013**, 4, 2517.
[3] N. Miljkovic, *et al.*, *Nano Lett.*, **2013**, 13(1), 179-187.
[4] F. Y. Lv, and P. Zhang, *Energy Convers. Manage*, **2016**, 113, 165-176.
[5] C. Xiang, *et al.*, *J. Phys. Chem. C*, **2017**, 121(28), 15448-15455.
[6] Y. Wang, *et al.*, *Corros. Sci.*, **2017** 124, 193-197. https://doi.org/10.1016/j.corsci.2017.04.029
[7] L. Sun, *et al.*, *Energy Environ. Sci.*, **2011**, 4(6), 2240-2248. http://dx.doi.org/10.1016/j.electacta.2016.03.099
[8] X. Zhao, *et al.*, *Electrochim. Acta*, **2016**, 199, 180-186.
[9] L. Sun, *et al.*, *J. Nanosci. Nanotechnol.*, **2014**, 14(2), 2050-2064.
[10] L. Sun, *et al.*, *Nanosci. Nanotechnol. Lett.*, **2012**, 4(5), 471-482.
[11] A. Ghicov, *et al.*, *Nano Lett.*, **2006**, 6(5), 1080-1082.
[12] Y.-Y. Song, *et al.*, *J. Am. Chem. Soc.*, **2009**, 131(12), 4230-4232.
[13] Y. Tang, *et al.*, *Adv. Mater.*, **2014**, 26(35), 6111-6118.
[14] L. Sun, *et al.*, *Langmuir*, **2014**, 30(10), 2835-2841.
[15] L. Sun, *et al.*, *J. Electroanal. Chem.*, **2009**, 637(1-2), 6-12.
[16] L. Sun, *et al.*, *Langmuir*, **2010**, 26(23),18424-18429.
[17] L. Sun, *et al.*, *ChemPhysChem*, **2011**, 12(18), 3634-3641.