Electronic Supplementary Information (ESI)

TiO_2 Nanotubes with Ultrathin Walls for Enhanced Water Splitting

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Synthesis of thin and thick walled nanotubes:

TiO_2 nanotube arrays were synthesized via the anodization of Ti foil at room temperature (approximately 22 °C). Prior to anodization, pure titanium foil samples (1.5 cm × 1.0 cm × 0.25 mm) were ultrasonically cleaned with acetone, ethanol and finally rinsed with distilled water. The anodization was carried out in an electrochemical cell with platinum foil as the counter electrode and titanium foil as the working electrode for 5h at 20V. After anodization, the samples were rinsed thoroughly with acetone and distilled water. TiO_2 nanotubes samples were annealed in air for 4 h at 450 °C with heating and cooling rates of 1 °C/min.

The thick- walled titania nanotubes were obtained by anodizing Ti foil in formamide-based electrolytes containing 0.2M ammonium fluoride, 1 ml water and 1.5 ml phosphoric acid. However, the thin-walled titania nanotubes were prepared using glycerol-based electrolytes containing 0.1M ammonium fluoride, 3 ml water and 7 ml formamide.

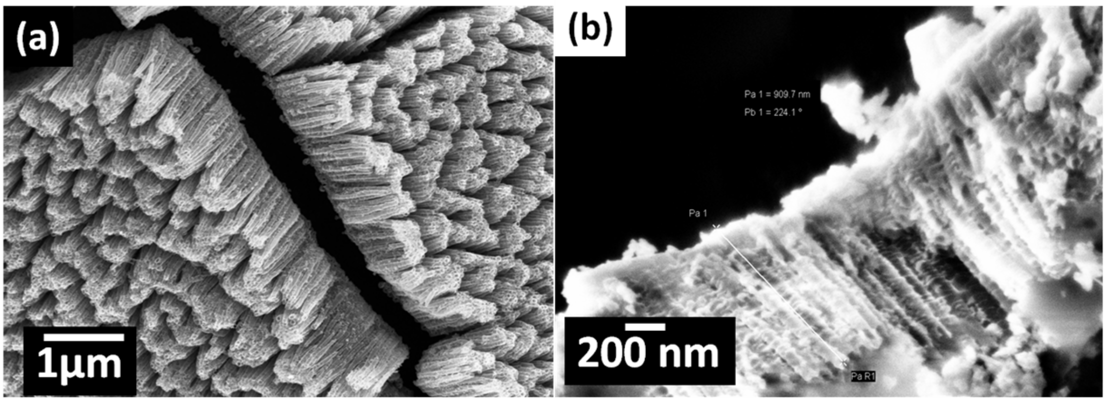

Figure S1: FESEM cross-sectional images of the fabricated (a) thick-walled and (b) thin-walled nanotubes

Note that we have used a mixture of glycerol and formamide and not pure glycerol-based electrolyte. The used mixture helped us to tune the viscosity and conductivity of the electrolyte to enable the formation of thin-walled titania nanotubes. In fact, it seems that this electrolyte mixture can be used, after minor modification, to fabricate thin-walled nanotubes from other metal oxide systems. For example, see our recent paper on ZrO2 nanotubes[1]. As of why thin-walled nanotubes are formed, we believe that this is a combination of factors such as applied voltage (affect the wall thickness), formamide (affect the tube length), glycerol (affect the homogeneity) and water content (affect the etching rate and consequently the tube diameter).

Surface area of the nanotubes:

As the nanotubes are attached to the metal substrate, it was very hard to do BET measurements for the surface area. However, the real surface area can be parameterized by the geometric roughness factor (G), which stands for the ratio of the cylindrical (inner and outer) and flat (top and bottom) surfaces of the tube arrays relative to the corresponding projected area, which is a function of the nanotubes' length, wall thickness (W) and inner diameter (D). G factors can be estimated using the following Eq.1[2]

$$G = \frac{4\pi L(W + \mathrm{D})}{\sqrt{3}(2W + \mathrm{D})^2} + 1 \tag{1}$$

The calculations show the superiority of our fabricated thin-walled nanotubes over the thick-walled counterparts. The thin walled titania nanotubes have a G factor of of 185 compared to 60 for the thick-walled counterparts. We have added this info to the revised manuscript.

EIS parameters:

Table S1: EIS parameters extracted from Nyquist plot

	Thick-walled nanotubes	Thin-walled nanotubes
Equivalent Circuit	R1+C2/R2+C3/(R3+W3)	R1+C2/R2+C3/(R3+W3)
R1	15 Ohm	15 Ohm
C2	7.72e-6 F	3.826e-6 F
R2	359.5 Ohm	439.2 Ohm
C3	3.212e-6 F	1.798e-6 F
R3	1 577 Ohm	12 627 Ohm
W3	92 972 Ohm.s^-1/2	2 308 Ohm.s^-1/2

References

1. Amer, A. W. et al., *RSC Advances* **2014**, *4*, 36336-36343
2. Kontos, A.G. et al., *Chem. Phys. Lett.* **2010**, *490*, 58–62