

Supporting information

Ordered “superlattice” TiO₂/Nb₂O₅ nanotube arrays with improved ion insertion stability

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Experimental

Metallic Ti/Nb multilayer substrates were obtained from PT&B Plasma technologies, Magdeburg (Germany). The multilayers were deposited on Si substrates by a STARON 60–80 sputtering apparatus equipped with four 6 inch magnetron sources. Titanium and Niobium of 99.95% purity were used as targets. The total multilayer stack is approx. 1 μm thick with alternating Ti/Nb layers (normally 2 nm thick Ti and 2 nm thick Nb). For fabrication of TiO₂/Nb₂O₅ nanotube arrays, Ti/Nb multilayer substrates were degreased by sonicating in acetone, isopropanol, and methanol, rinsed with deionized (DI) water, and dried in a nitrogen stream. Ohmic contact on the back side was achieved using Ga–In alloy. Anodization was carried out in a two electrode system using a high voltage potentiostat Jaisle IMP 88 PC. For the best condition anodization, the substrates were polarized in ethylene glycol electrolyte containing 0.1 M NH₄F and 1 M H₂O at 40 V for 10 min to achieve approx. 1 μm thick nanotube film. For comparison, a pure Ti film sputtered on Si substrate was used to grow 1 μm TiO₂ nanotube layer by using the same

electrolyte (See Fig.S4a). After rinsing with DI water and drying in a nitrogen stream, the layers were annealed at 150 °C, 300°C and 450°C in air, respectively, using a furnace.

For the morphological characterization of TiO₂/Nb₂O₅ nanotube arrays, a field emission scanning electron microscope (Hitachi FE-SEM S4800) was used. The length of the nanotubes was directly obtained from SEM cross-sections. For all TEM based measurements, a FEI Titan³ 80-300 microscope equipped with an image aberration corrector was used at an acceleration voltage of 300 kV. The TEM specimens were prepared by scratching the tube layers onto a carbon film covered Cu grid. All shown HAADF images were acquired in STEM mode with large inner collection angle (> 50 mrad) to fulfill Z-contrast conditions. XRD patterns were collected on a powder diffractometer (X'pert Philips MPD with a Panalytical X'celerator detector) using graphite-monochromatized CuK α radiation ($\lambda=1.54056 \text{ \AA}$). The chemical composition of the layer was characterized with X-ray photoelectron spectroscopy (XPS, PHI 5600 XPS spectrometer, US).

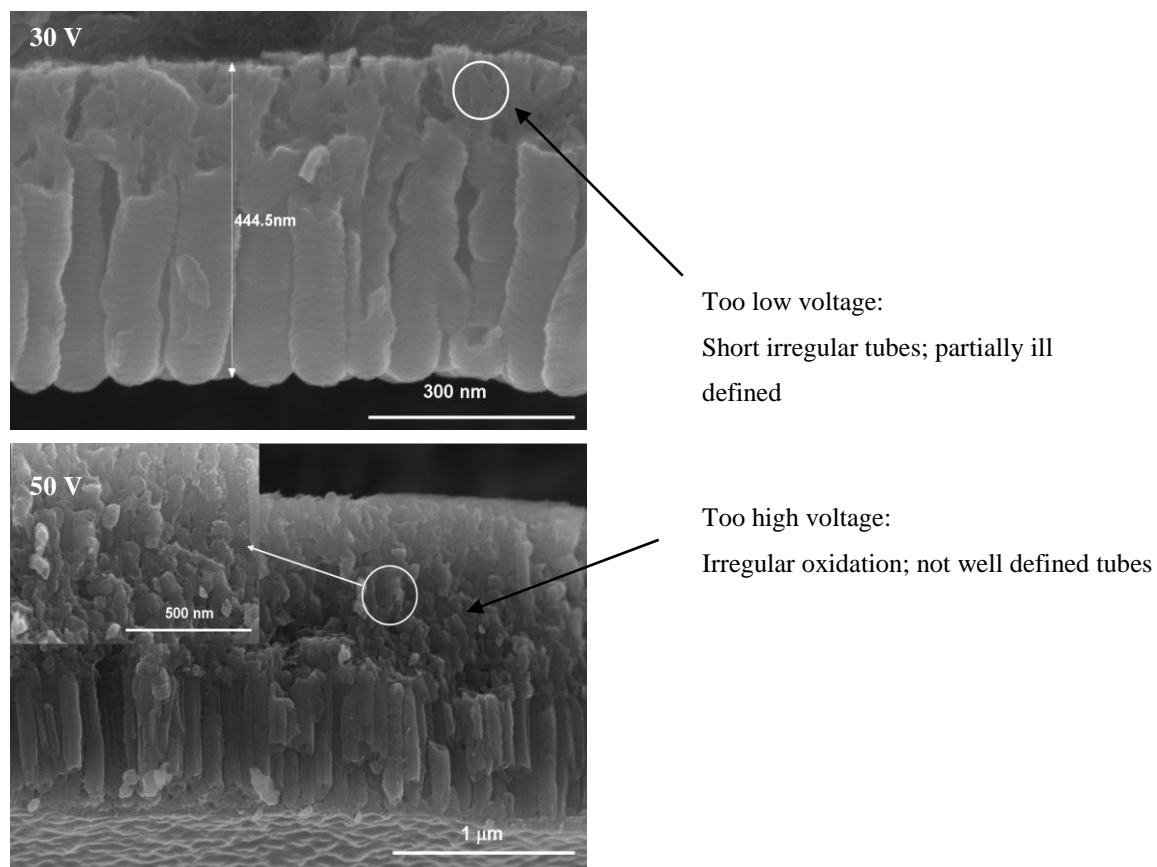
For insertion of Li⁺ and electrochromic measurements of “superlattice” TiO₂/Nb₂O₅ nanotube arrays, a conventional three electrode system was used. It should be noted that both “superlattice” tubes and reference tubes were grown on the Si only to a length of 1 μm , i.e. leaving approx. 500 nm of substrate metal at the base. This step was taken to avoid any contribution of the Si substrate to the intercalation reaction.

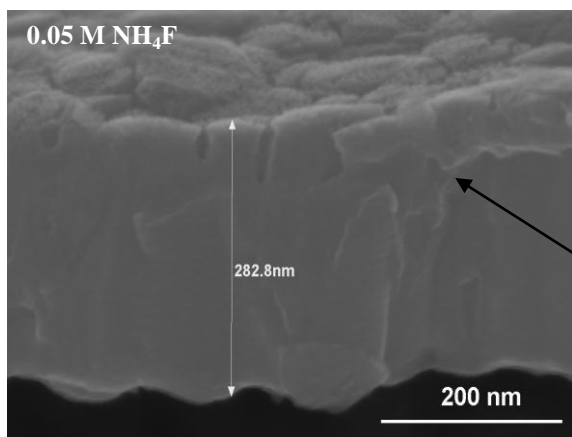
Samples were contacted with a Cu back-plate and then pressed against an O-ring sealed opening in the wall of the electrochemical cell. A platinum plate served as a counter electrode and an Ag/AgCl (3 M) electrode as a reference electrode. The cyclic voltammetry measurements were performed in propylene carbonate solution containing 1 M LiClO₄ using an Autolab/PGSTAT30 setup at a sweep rate of 0.1 V/s. For electrochromic characterization, reflectance intensities were measured as a function of time at $\lambda=620 \text{ nm}$ by fiber optic illuminator (tungsten halogen lamp, Ocean Optics).

Table S1 Absolute charges of “superlattice” TiO₂/Nb₂O₅ NTs and TiO₂ NTs calculated from CV curves.

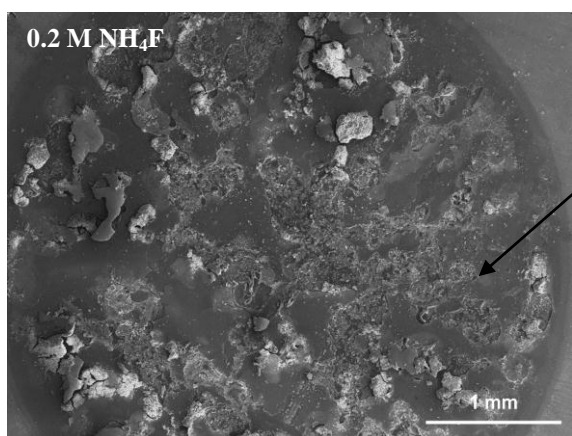
	TiO ₂ /Nb ₂ O ₅ nanotubes annealed at 300°C		TiO ₂ nanotubes annealed at 300°C		TiO ₂ nanotubes annealed at 150°C	
	Q ⁺ (mC)	Q ⁻ (mC)	Q ⁺ (mC)	Q ⁻ (mC)	Q ⁺ (mC)	Q ⁻ (mC)
1 st cycle	6.674	-7.308	5.827	-7.372	4.211	-4.547
1200 th cycle	6.249	-6.313	1.901	-2.102	4.640	-4.702

Fig. S1 SEM images under other anodization conditions (various anodization voltages, F⁻ concentrations and H₂O contents)

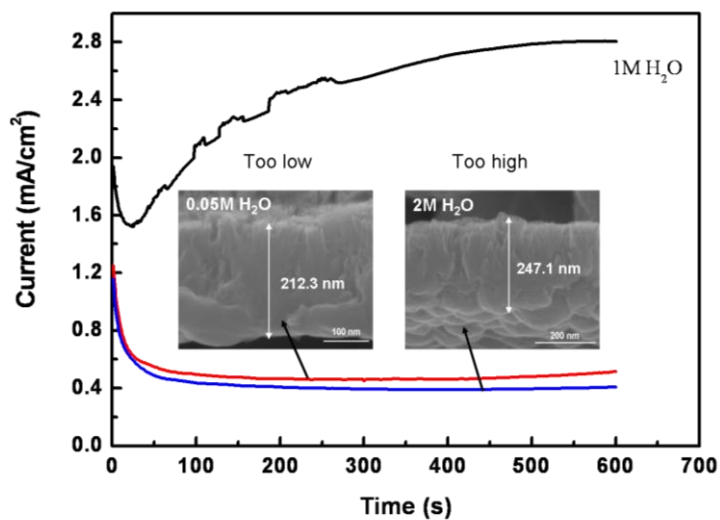




Too low F⁻ concentration:
Short oxide layers; no clear definition
of tubes



Too high F⁻ concentration:
No uniform layer formation
(lift-off, detachment)



Too low and too high H₂O content: Only thin,
irregular oxides (passivation)

Fig. S1 (continuation) SEM images under other anodization conditions (various anodization voltages, F⁻ concentrations and H₂O contents)

The current oscillations appear somewhat damped over time as the precision of simultaneous (over the entire surface) element oxidation in the stack gets somewhat smeared out. This to some extent is merely a consequence of the experimented set-up used (an O-ring cell) that leads to a non entirely homogeneous current distribution.

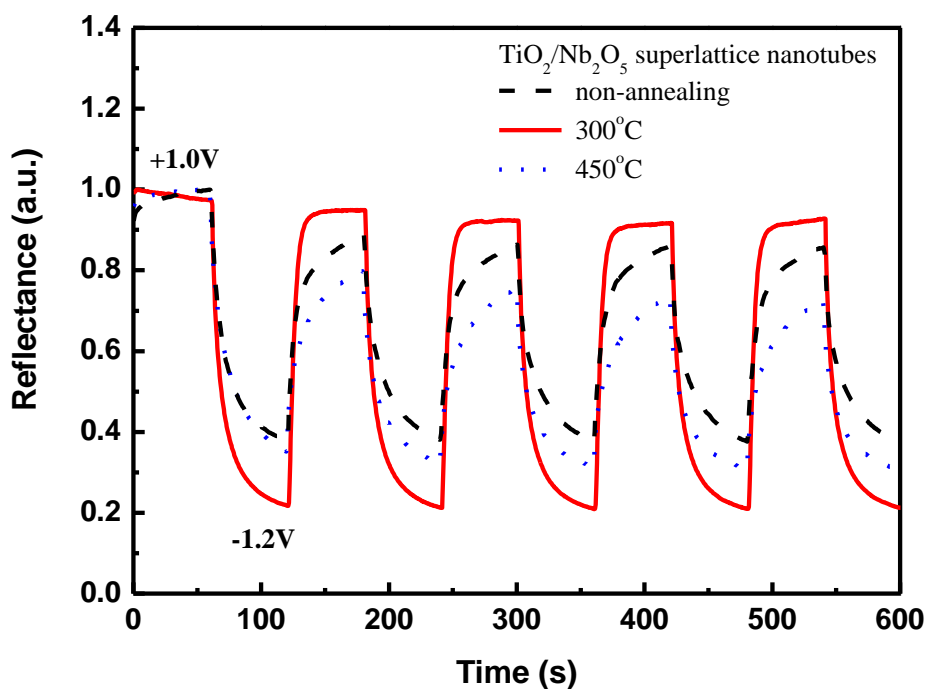


Fig. S2 *In situ* reflectance measurements obtained from “superlattice” TiO₂/Nb₂O₅ nanotube arrays in different heat-treatment conditions.

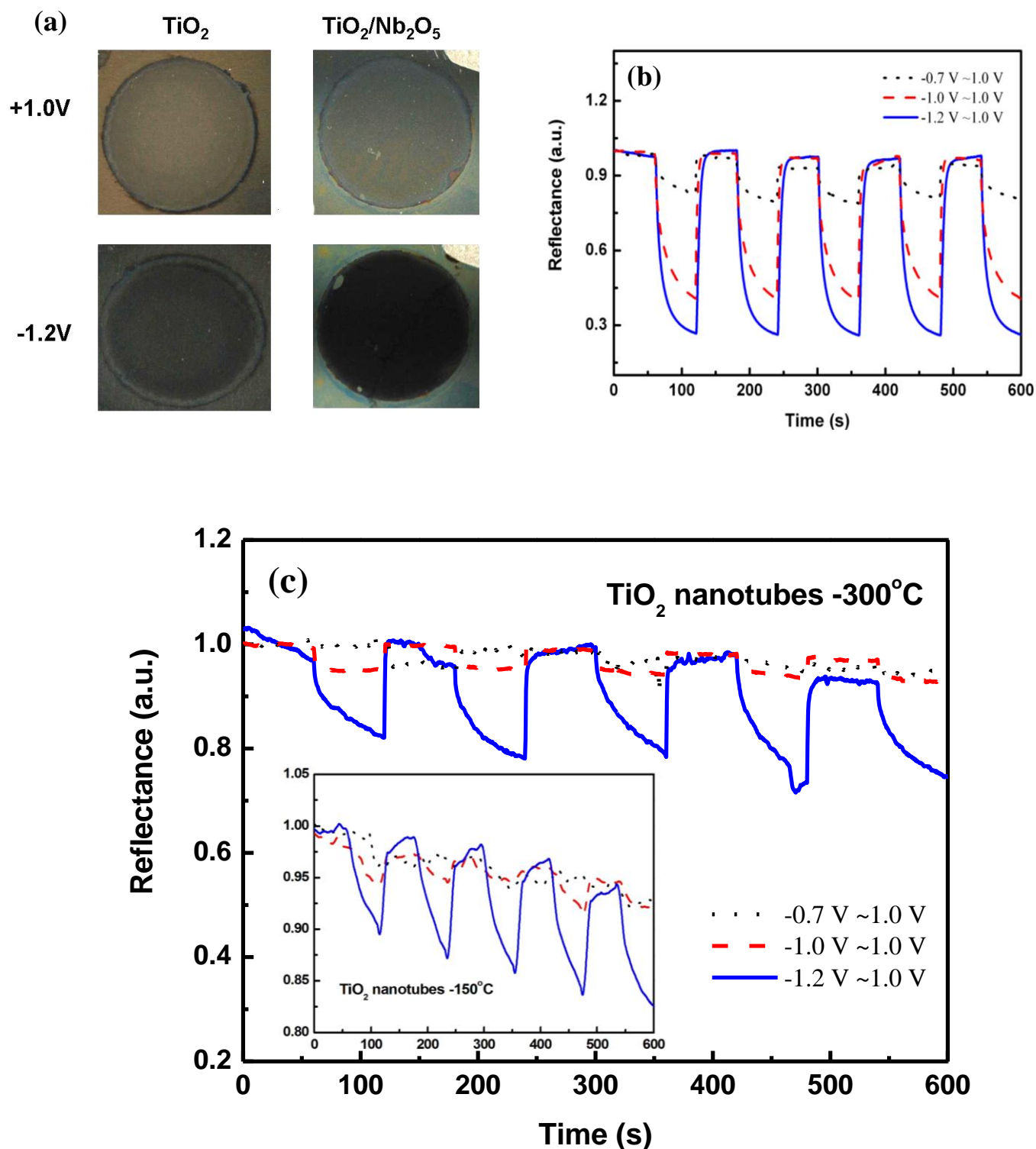


Fig.S3 (a) Surface optical images of pure TiO₂ and “superlattice” TiO₂/Nb₂O₅ nanotube layers during polarization between -1.2 V and +1.0 V in propylene carbonate electrolyte contained 1M LiClO₄. *In situ* reflectance curves obtained from (b) “superlattice” TiO₂/Nb₂O₅ and (c) pure TiO₂ nanotube layers at different voltages.

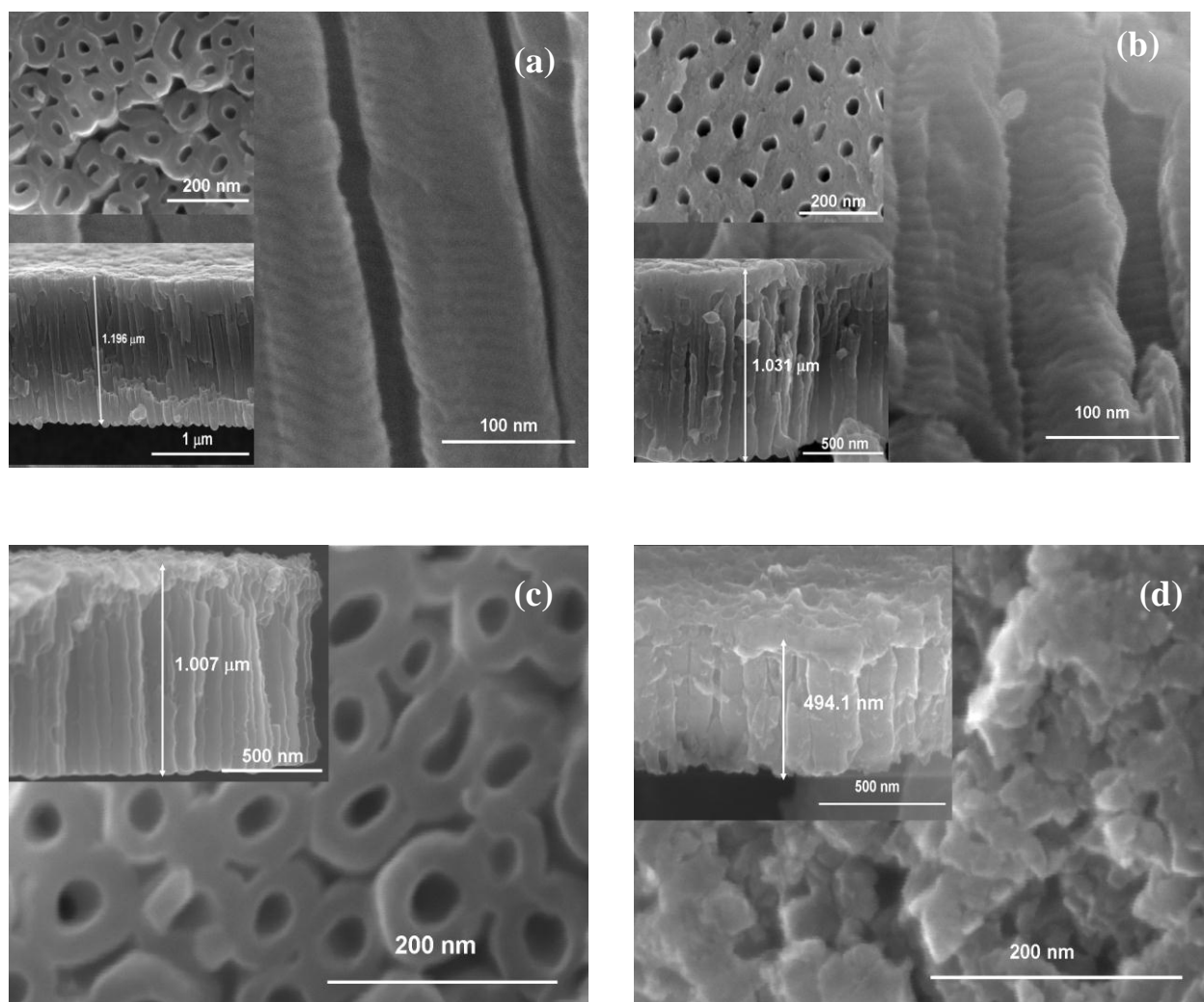


Fig.S4 Cycling stability: surface and cross-section morphologies of “superlattice” TiO₂/Nb₂O₅ (a,b) and pure TiO₂ nanotube arrays (c, d) before (a, c) /after (b, d)1200 CV cycles between -1.5 V and 1.0 V in 1 M LiClO₄ / propylene carbonate electrolyte. The superlattice nanotubes remain stable the TiO₂ nanotubes “crumble away”.

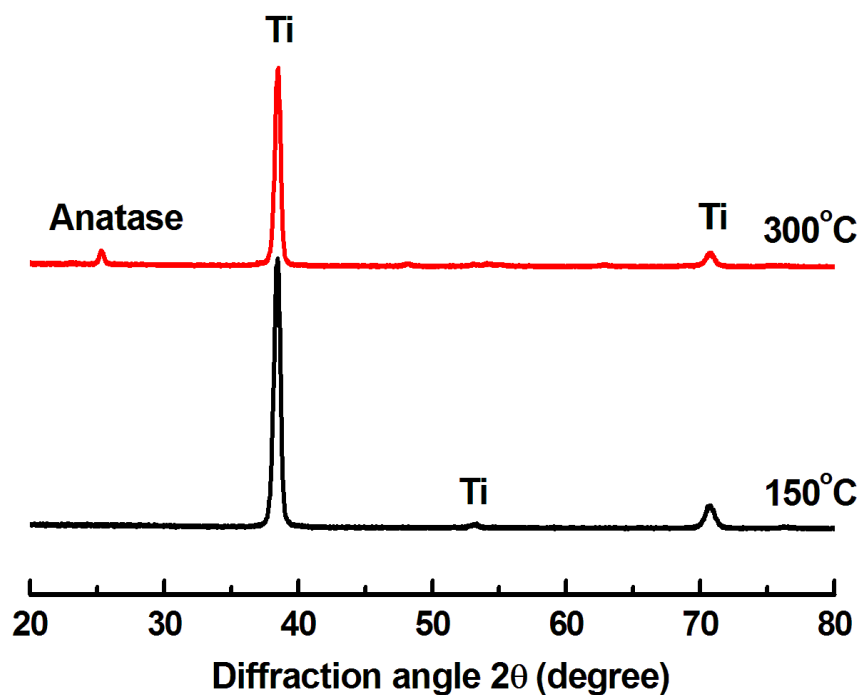


Fig. S5. XRD patterns of TiO₂ nanotubes annealed at 150°C and 300°C

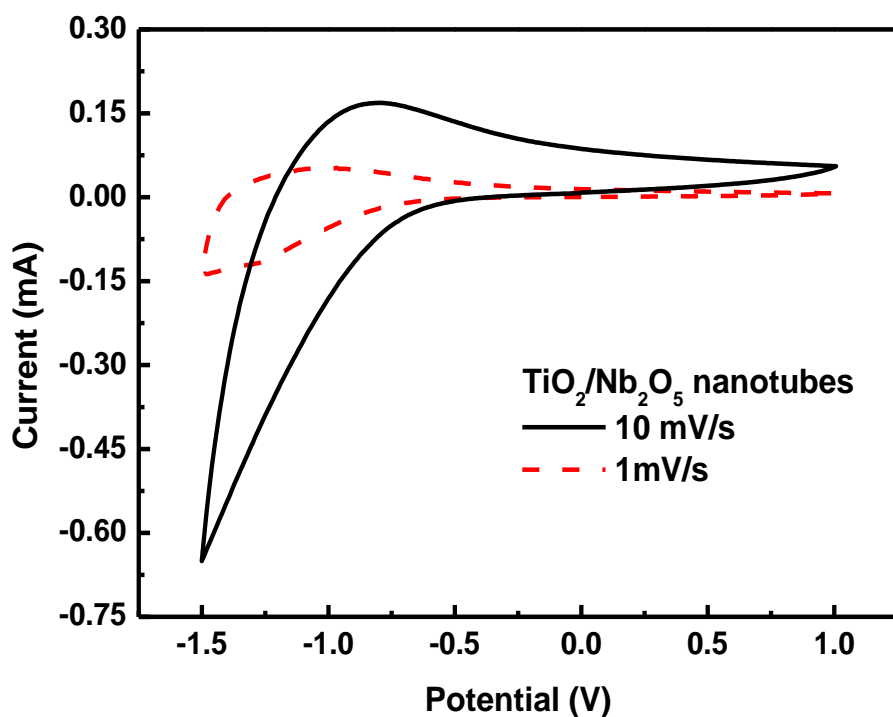


Fig.S6 CV curves of TiO₂/Nb₂O₅ with different scan rate in a propylene carbonate electrolyte containing 0.1 M LiClO₄ between -1.5 V and +1.0 V with a sweep rate of 10 mV/s and 1mV/s.