Current dependent formation of PEDOT inverse nanotube arrays

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ESI1. Titania nanotubes template

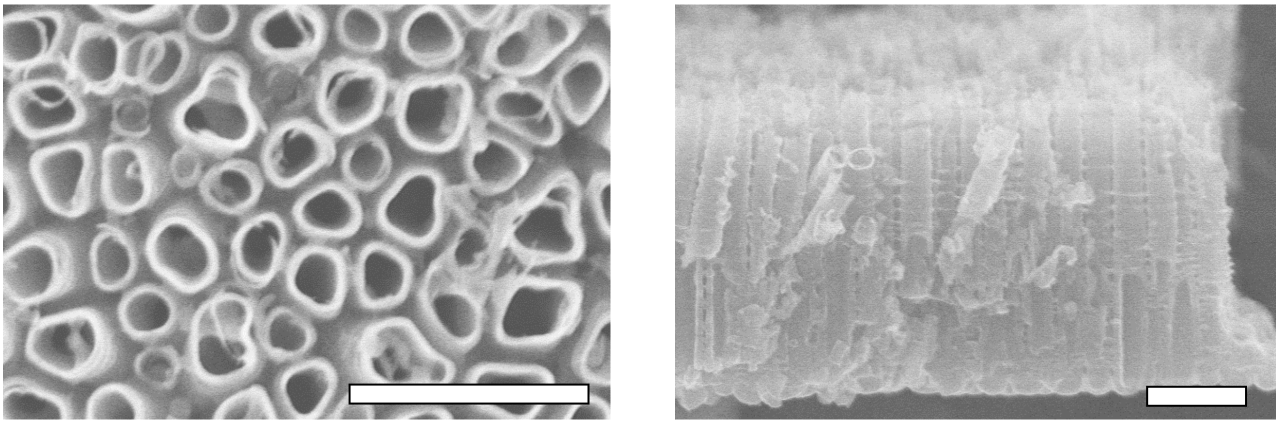

Fig. ESI1 SEM images of titania nanotubes formed in glycerol-water electrolyte (55:45 v/v) containing ammonium fluoride (0.27 M) at 30V for 3h. The tubes were annealed for 3h in Ar atmosphere at 450°C. The scale bares at the bottom represent 500nm.

ESI2. PEDOT nanostructures

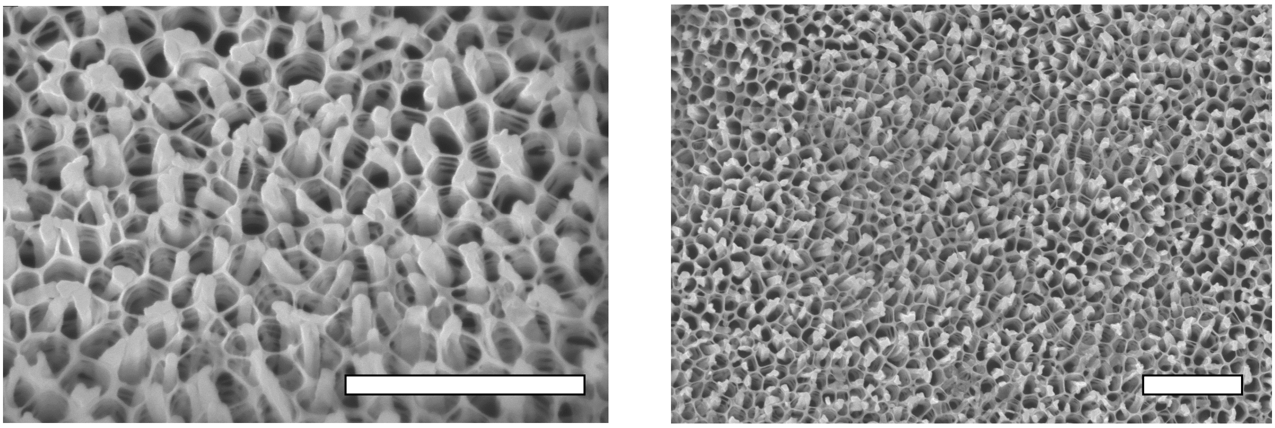

Fig. ESI2 SEM images of PEDOT inverse-nanotube array formed in titania nanotubes (Fig. ESI1) with pulse current protocol at 1.0 mA anodic pulse (10ms) followed by cathodic pulse at -1.0 mA (4ms) and rest current at 0 mA (500ms). Titania nanotubes were dissolved for polymer structure observation. The scale bares at the bottom represent 1μm.

ESI3. PEDOT/Titania composite

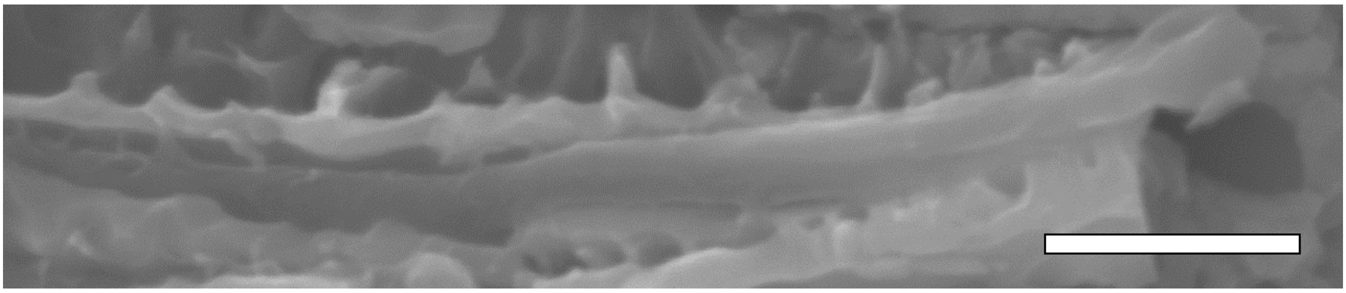

Fig. ESI3 The image shows single PEDOT nanowire which was filled inside titania nanotube. The brighest parts on the picture reprent broken titania nanotube. The polymer was deposited with protocol at 0.85 mA anodic pulse (10ms) followed by cathodic pulse at -0.85 mA (4ms) and rest current at 0 mA (500ms). The scale bare at the bottom represnts 200 nm.

Experimental Section

Titania nanotubes were formed by anodization of 0.1 mm thick titanium foils of purity 99.6 % purchased from Advent Materials. Before use, titanium specimens were degreased by sonication in acetone, isopropanol and methanol, rinsed in deionized Milli-Q water and dried in a nitrogen stream. The foils were anodized in glycerol-water (55:45 v/v) electrolyte containing ammonium fluoride (0.27 M) at 30 V.[18] Anodization was carried out in a two-electrode cell (10 cm^3) with platinum counter electrode. The geometrical surface of the titanium working electrode was 1 cm^2. After that the tubes were annealed for 3h at 450°C in Ar atmosphere.

A three-electrode cell with 5 cm^3 volume was used for electropolymerization of 3,4-ethylenedioxythiophene in titania nanotubes. A Ag/AgCl/3M KCl electrode with a Luggin capillary and a platinum foil were used as reference and counter electrodes, respectively. The geometrical area of working electrode (titania nanotubes) was 0.2826 cm^2. The cell was under nitrogen atmosphere during all electrochemical experiments. The electropolymerization was carried out at room temperature in aqueous solution containing 3,4-ethylenedioxythiophene monomer (50 mM) and sodium dodecyl sulfate (0.1 M). 3,4-ethylenedioxythiophene monomer purchased from Sigma-Aldrich was used without any pre-treatment. Before polymerization, all solutions were deoxygenated by nitrogen bubbling for 20 min before use. The polymerization was carried out using pulse current protocol containing 10ms of anodic pulse, 4 ms cathodic pulse, and 500ms rest current. The anodic pulse was adjusted with the current in the range from 0.6 to 1 mA (A=0.2826 cm^2) to control deposition in titania nanotubes. The current ratio of andodic to cathodic pulse was kept constant at 1/1. After deposition step the composite was investigated as received or titania nanotubes were selectively dissolved in diluted hydrofluoric acid. The anodization of titanium was carried out using a JAISSLE IMP88PC-200V potentiostat/galvanostat coupled with a PRODIS 1/16I and a KEITHLEY 2000 digital multimeter. The electropolymerization was done using a JAISSLE 1002 T-NC potentiostat/galvanostat coupled with a PRODIS 1/16I and a KEITHLEY 2000 digital multimeter. A field emission scanning electron microscope (FE-SEM, Hitachi S4800) was used for structural and morphological characterization of titania nanotubes and nanostructured polymers. Surface analysis of the polymer was carried out by X-ray photoelectron spectroscopy (XPS) PHI 5600 (monochrom.Al Ka X-ray source). The energy calibration was performed by using C1s line for aliphatic carbon. The surface composition was calculated comparing the ratio of S2p peaks. The analysis of the peaks included Shirley background subtraction and asymmetric line shape decomposition by using Multipack 9.3.0.3 software.

The AC impedance spectroscopy studies were performed by using Autolab PGSTAT302N. Circular gold electrodes were evaporated (LEICA EMSCD500) on titania nanotubes and titania/polymer composites. The devices were constructed in the following order: Au/titania/Ti and Au/PEDOT-titania/Ti. The measurements were performed in the frequency range 500kHz - 1Hz with the amplitude of perturbation signal of 10 mV at open circuit conditions and under constant potential 25-150 mV applied in the forward bias.