

Supporting information

Experimental details

3,4-ethylenedioxythiophene (EDOT), acetonitrile, propylene carbonate and poly(styrenesulfonic acid), 1-butyl-3-methylimidazolium hexafluorophosphates (BMIPF₆), NaCl, LiClO₄ and NaPF₆ were purchased from Sigma Aldrich. All reagents were used as supplied without further purification. The detail experimental procedure to grow nanowires is given in SI.

The conductance of the wires was measured *ex-situ* using a Keithly 2400 SMU probe unit to measure the current-voltage (*I*-*V*) profile. The length and diameter of the wires were obtained from SEM images. Since the wires were not straight, nor of a very uniform diameter, the measurement from the image was not precise. The conductivity σ , was then estimated assuming that the wires were circular in cross-section: $\sigma = l/RA$, where R is the resistance of the wire, A is the cross-sectional area and l is the length of the wire.

Raman spectra of PEDOT samples were recorded using a Renishaw Raman spectrometer (system 1000) with 785 nm laser excitation. The samples were examined under ambient conditions without any prior treatment. The curve-fitting of the Raman spectra was carried out using Grams/32 processing program with assumption of 80% Gaussian and 20% Lorentzian component peaks. The Raman peak positions were obtained from the fitting values. Peak assignment was from literature that used 1064 nm Raman excitation^{28, 33}.

The cyclic voltammograms were measured using SICM. The details of SICM setup was previously reported³⁴.

The morphology of the PEDOT nanowires were scanned using ESEM under the gun pressure of 1.5 e⁻⁹ torr at high voltage of 20.0 kV.

Experimental procedure to grow nanowires

The electrodes, in the form of opposing wedges, were patterned via photolithography and consist of a ~ 50 nm thick Au top layer and a 50 nm thick Cr adhesion layer, on a glass substrate. The gap between the electrodes varied between 10 and 20 μ m because of variability in the etching process. The slide was mounted on an inverted microscope using which the progress of the experiment was closely visually monitored. A small droplet (typical radius 150 μ m, contact angle 41 $^\circ$, height 70 μ m) of electrolyte solution containing EDOT monomer and dopant anion was placed across the electrodes, and a waveform function generator was used to apply across the gap a symmetrical square wave with 0 V mean signal. Frequency and peak-to-peak amplitude were variables. Obtaining single wires necessitated careful manual adjustment of the excitation amplitude and close microscopic observation during the procedure. We observed that to grow single wires the amplitude had to be just high enough to induce convection, indicated by movement of specks of dust in the solution. To grow a single nanowire at an excitation frequency where this proved feasible, the amplitude was first set at a value ('safe' value, table 1.S1) where no convection and no observable electrochemical phenomena occurred. Then the amplitude was increased slowly until the first signs of convection were observed in the solution. Then the amplitude was increased carefully a little further (0.2-0.5 V) until a black dot (most likely the initiation of etching of the gold electrode) was observable on the live electrode. Then, after a short pause, ~2 sec, the amplitude was reduced to zero. The wire was sometimes visible as a faint shadow in the optical microscope; its presence was subsequently confirmed by an electrical connection established between the electrodes in the absence of the solution, and by electron microscopy. Excitation amplitude was quickly read from an oscilloscope, to the nearest 1 V grid mark. The amplitude and frequency required depended on the nature of the solvent used (See Table 1.SI). We used three different solvents: water, propylene carbonate (PC) and acetonitrile (ACN) and varied the concentration of EDOT monomer (0.1, 0.05 and 0.01 M) while fixing the concentration of the anionic dopants (PSSA and BMIPF₆). Addition of the PSSA solution evidently also introduced a small amount of water to the organic solvents. We verified that evaporation of the electrolyte was not an issue by tracking the drop size under the microscope. The only case where evaporation was an issue was with acetonitrile as solvent, where a visible change in drop size was noted ~ 10-20 sec after the drop was applied between the electrodes. However, with experience, the whole experiment could be completed in less than 6 sec, so evaporation of the electrolyte was not a limiting factor.

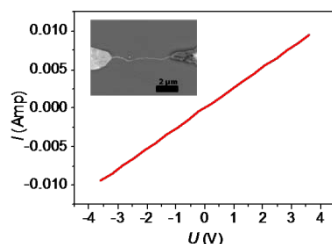


Figure 1.SI *I*-*V* graph of PEDOT: BMIPF₆ (1:1 ratio) obtained from ACN solution. Inset is the ESEM image of the wire.

Frequency / kHz	Concentration of Monomer / mol.dm ⁻³	'Safe' potential/± 0.5 V	Initiation potential /± 0.5 V	Gap between the electrodes / μm	Wire format
220-40	0.01 to 0.1	± 8 to ± 5	± 9 to ± 6	15-22	no wire
35.7	0.1	± 7	± 8	19.9	no wire
33.3	0.1	± 6	± 7	16.5	nodule
31.7	0.1	± 5	± 6	15.9	nodule
22.6	0.1	± 5	± 6	15.0	nodule
11.9	0.1	± 5	± 6	12.7	nodule
1.43	0.01	± 4	± 5	18.2	no wire
45.0	0.01	± 6	± 7	14.2	multiple
40.1	0.01	± 6	± 7	13.3	multiple
33.4	0.01	± 6	± 7	13.3	multiple
30.1	0.01	± 6	± 7	15.1	multiple
24.6	0.01	± 5	± 6	16.2	single
22.1	0.01	± 5	± 6	11.1	single
18.7	0.01	± 5	± 6	14.1	single
14.1	0.01	± 5	± 6	13.4	single
42.1	0.05	± 6	± 7	10.1	no wire
26.7	0.05	± 6	± 7	15.8	multiple
10.9	0.05	± 5	± 6	11.0	multiple
0.23	0.05	± 4	± 5	15.1	no wire

Table 1.SI. Formation condition for PEDOT: