Highly Conductive Poly(3,4-ethylenedioxypyrrole) and Poly(3,4-ethylenedioxythiophene) Enwrapped Sb_2S_3 Nanorods for Flexible Supercapacitors

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Electronic Supplementary Information

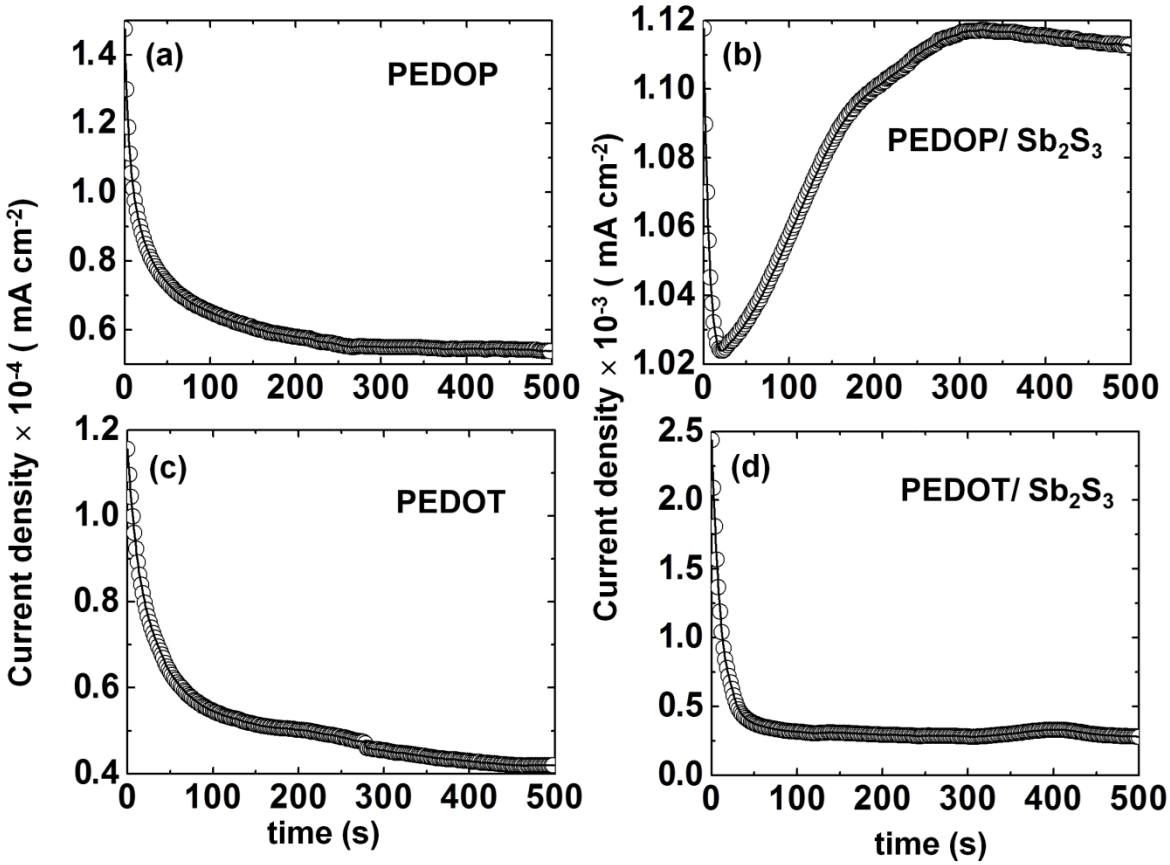

Figure S1 Current density *versus* time transients recorded for the oxidative electro-synthesis of PEDOP, PEDOT films and their composites PEDOP/Sb_2S_3, PEDOT/ Sb_2S_3 from solutions of (a) 0.1 M 3,4-EDOP (b) 0.1 M 3,4-EDOP/ 1 mg Sb_2S_3 and (c) 0.1 M 3,4-EDOT (d) 0.1 M 3,4-EDOT/ 1 mg Sb_2S_3 both in AN and each containing the ionic liquid: 0.1 M 1-butyl-3-methyl-imidazolium tris(pentafluoroethyl)trifluorophosphate.

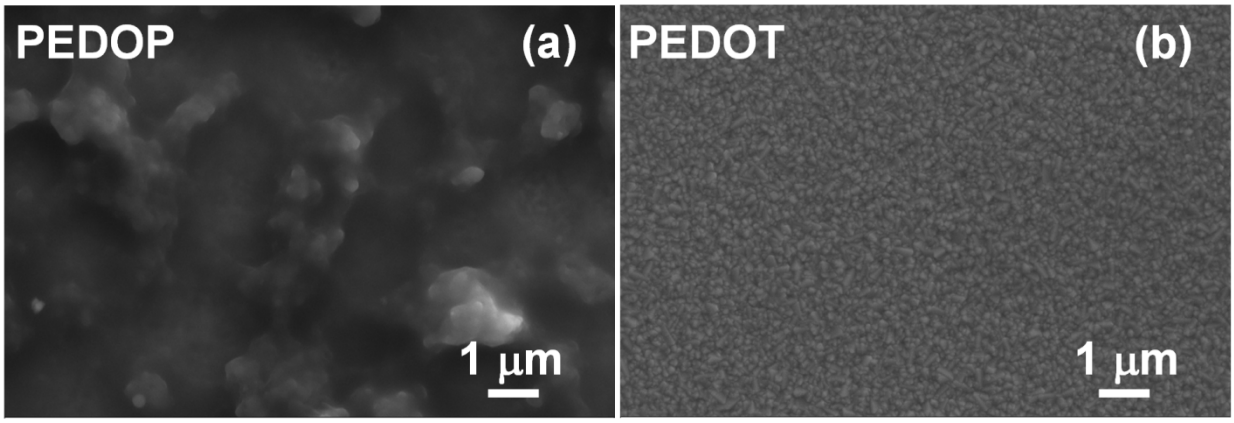

Figure S2 SEM images of (a) PEDOP and (b) PEDOT films.

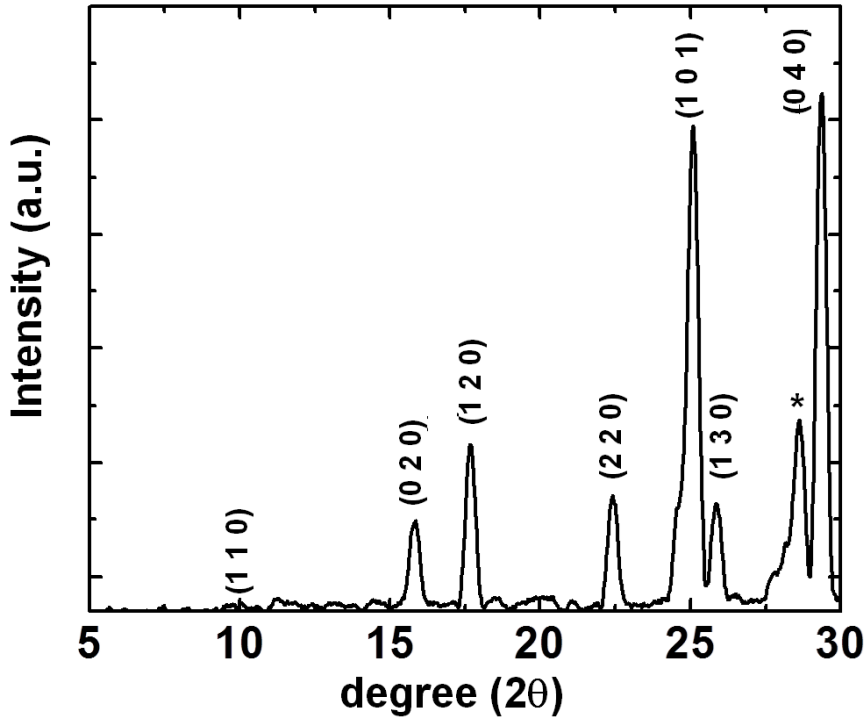

Figure S3 X-ray diffraction pattern of Sb_2S_3 nanorods; the asterisk marked peak arises from the substrate.

The XRD pattern of Sb_2S_3 nanorods shows main peaks at d = 7.86, 5.70, 4.97, 3.95 and 3.5 nm corresponding to the (020), (120), (220), (101) and (040) planes of orthorhombic Sb_2S_3, as per the JCPDS file number 42-1393. No peaks of any other phases were detected, indicating that the nanorods sample is a high-purity, single-phase sample.

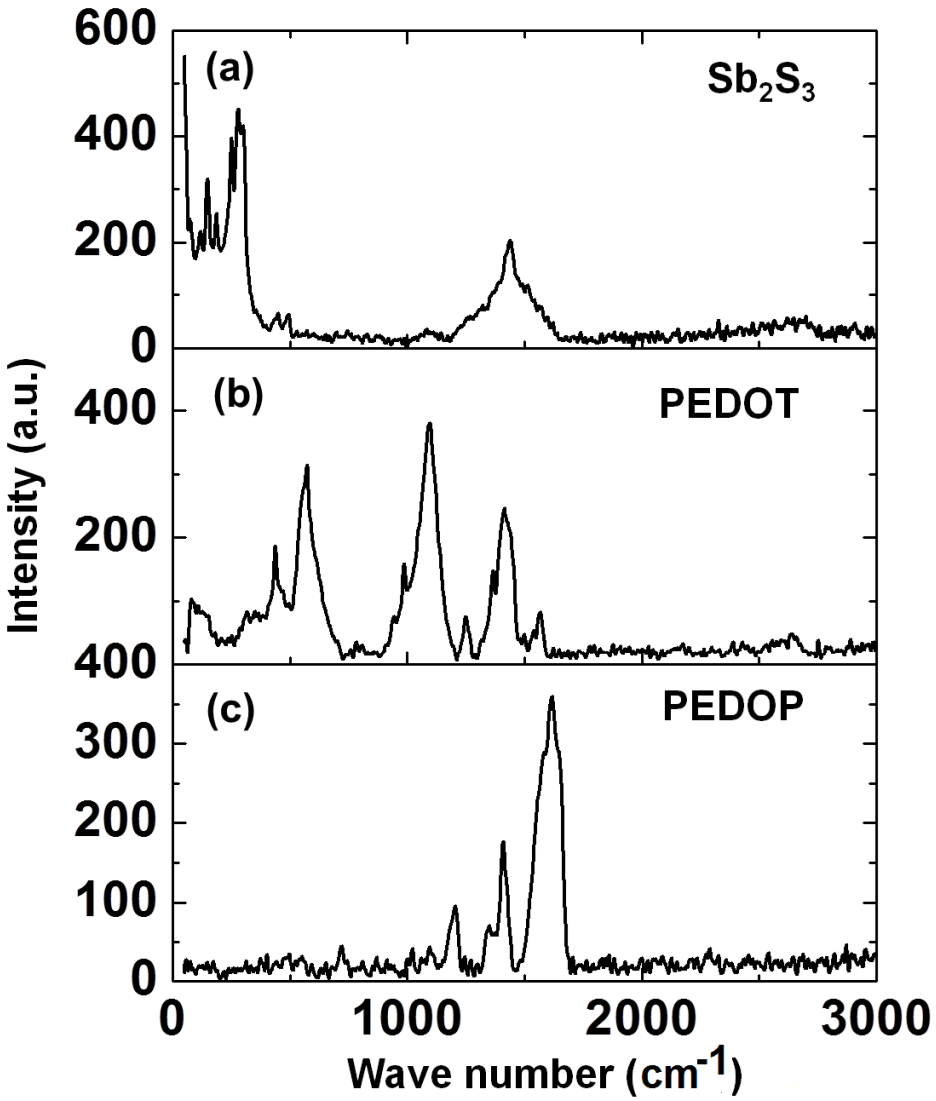

Figure S4 Raman spectra of (a) Sb_2S_3 nanorods, (b) neat PEDOT and (c) neat PEDOP films.

Table S1 Band positions and assignments for neat PEDOP and neat PEDOT films (ν: stretching, ν_{asy}: asymmetric stretching and δ: bending modes).

PEDOT (cm^{-1})	PEDOP (cm^{-1})	Assignment
2627	–	ν(C=C–H)
–	2095	ν(-C–H)
1650	1641	ν(C=C)
1562		ν_{asy}(C=C)
1422		ν(C_α=C_β)
1355	1405	ν(C_β-C_β)
1249		ν(C_α-C_α)
1230	1290	ν(C-S), ν(C-N)
1077	–	δ(C-O-C)
845	820	ν(P-F) (from ionic liquid dopant)
	733	ν(N-H)
519		δ(C-S-C)

Sb_2S_3 nanorods show peaks at 269 cm^{-1} and 295 cm^{-1}, corresponding to the stretching vibrations of the Sb-S bond.[1]

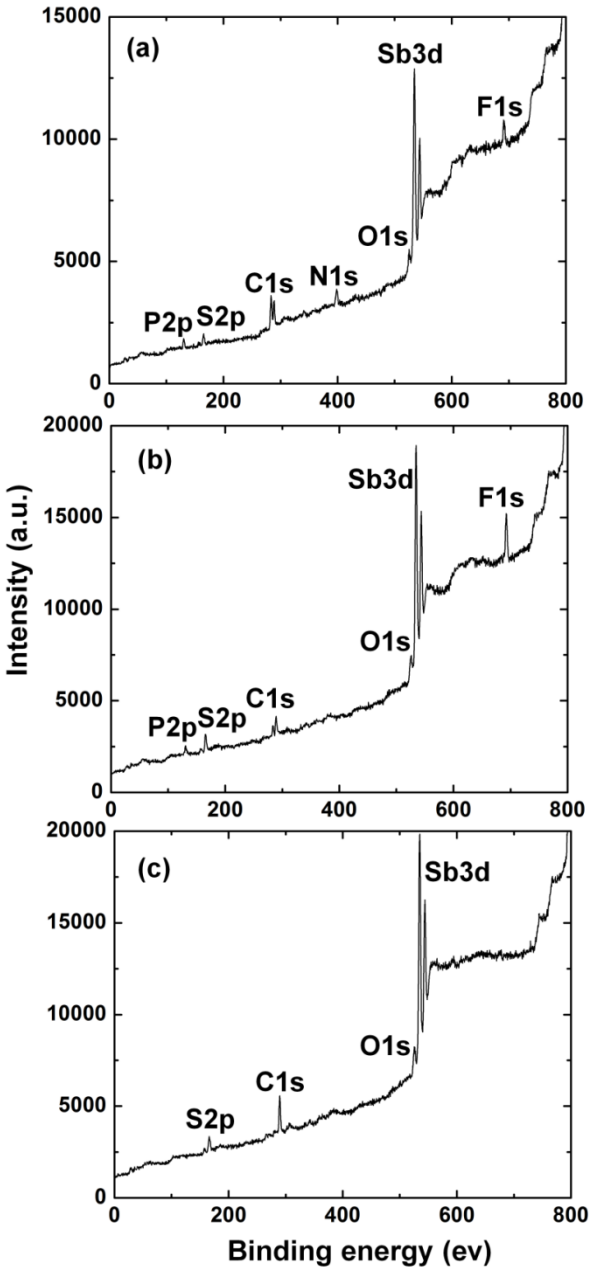

Figure S5 Survey spectra of (a) PEDOP-Sb_2S_3, (b) PEDOT-Sb_2S_3 and (c) Sb_2S_3 illustrating the different elemental contributions in each sample.

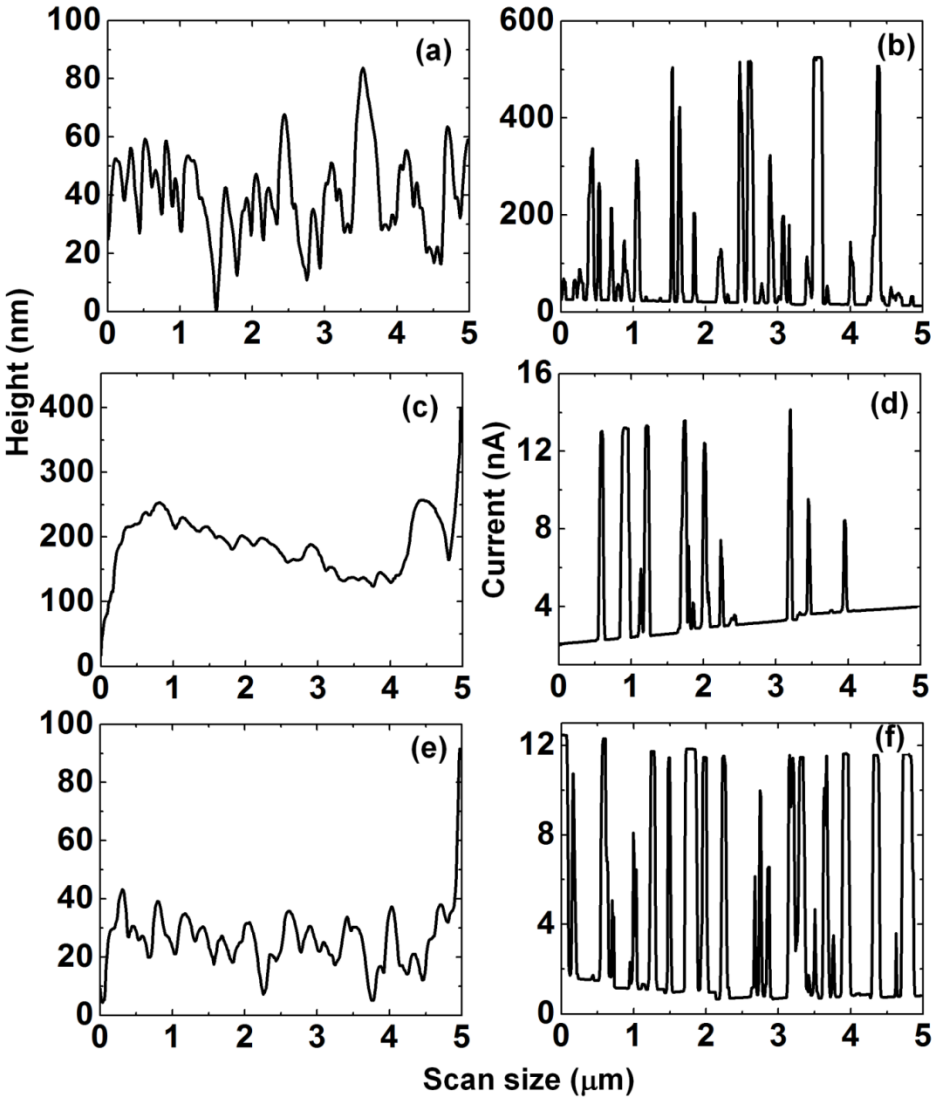

Figure S6 Cross section profiles of topography and current images of (a, b) Sb_2S_3 nanorods, (d,e) PEDOP/Sb_2S_3 and (g,h) PEDOT/Sb_2S_3 films recorded over scanned areas of 5 μm × 5 μm (corresponding to the images in Figure 5).

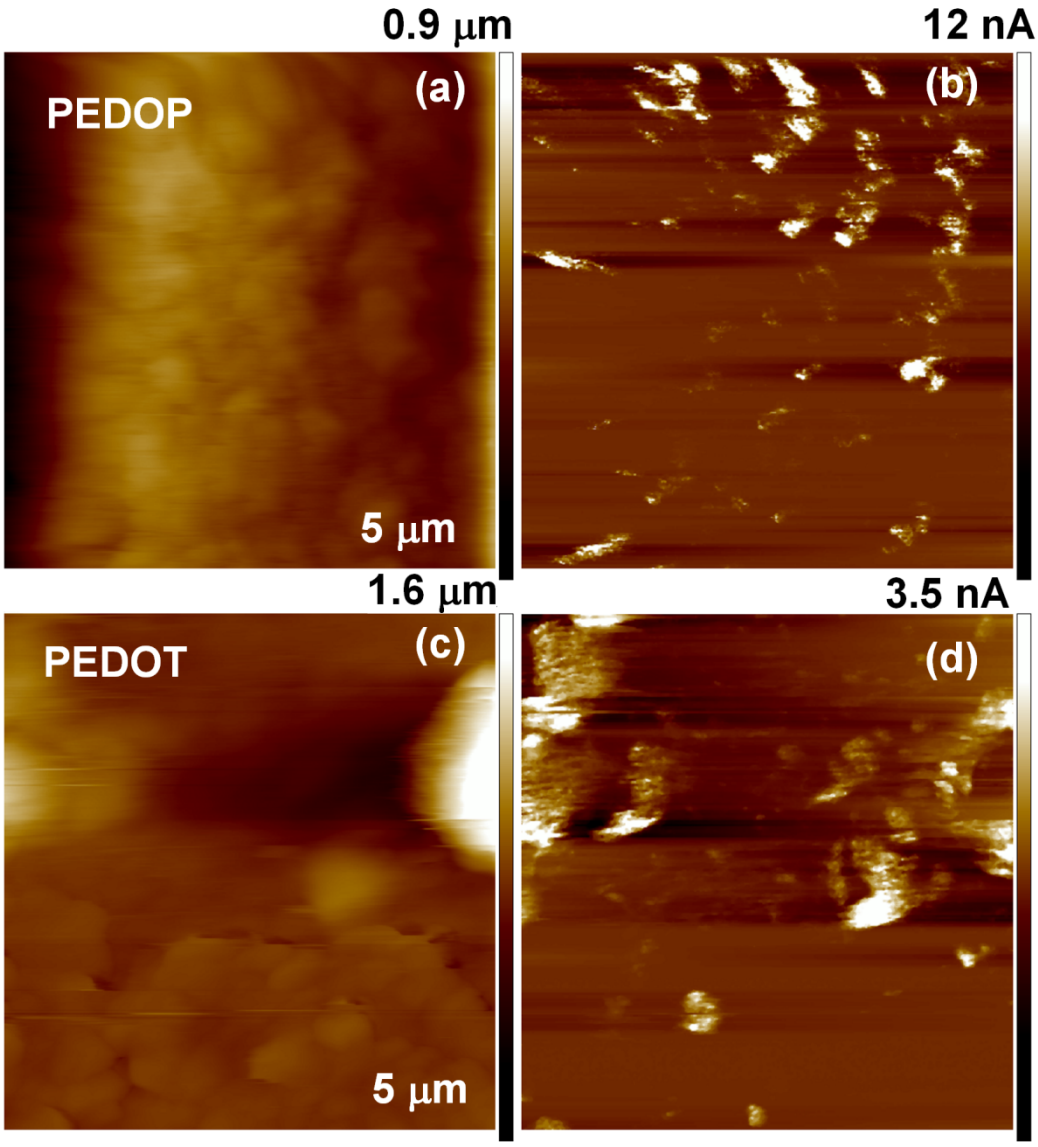

Figure S7 Simultaneous topography and current images of (a, b) neat PEDOP and (c, d) neat PEDOT films recorded over scanned areas of 5 μm × 5 μm.

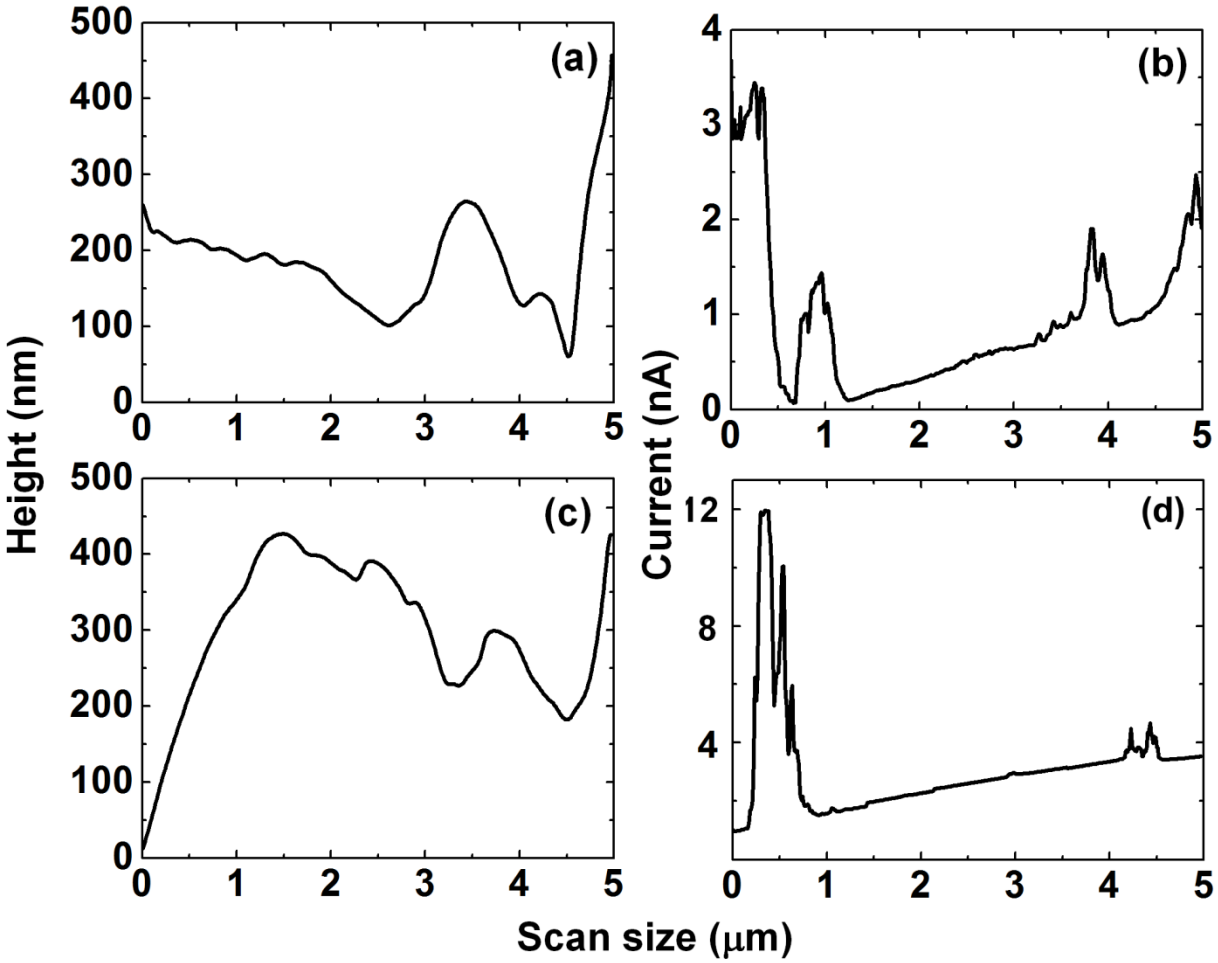

Figure S8 Cross section profiles of topography and current images of (a, b) neat PEDOP and (c, d) neat PEDOT films recorded over scanned areas of 5 μm × 5 μm (corresponding to the images a-d in Figure S7).

C-AFM details

The difference in the topography ongoing from Figure 5a and d to Figure 1 for the same samples (Sb_2S_3, PEDOP/Sb_2S_3 and PEDOT/Sb_2S_3 films) arises from the different modes used for making the measurement; and the method of measurement: contact mode in C-AFM and tapping mode in conventional topography, cannot be changed. Since the samples are soft (relative to a hard surface like that of a metal) better quality images are obtained in tapping mode compared to contact mode (C-AFM). In contact mode, the tip touches the samples and if sample

is soft, the image quality is affected. In tapping-mode, the instrument measures topography by tapping the surface with an oscillating probe tip so that the tip makes contact with the sample only for short duration in each oscillation cycle. The method of operation results in lower lateral forces compared to conventional contact mode in which the probe slides across the surface, so the irreversible destruction on soft surface can be eliminated. For this reason, TM-AFM (Tapping mode-AFM) has been established as a standard tool to investigate surfaces of soft materials.[2] And therefore the topography image obtained in Figure 1 is truly representative of the samples, as it is non-destructive.

Table S2 Impedance parameters for different working electrodes, with graphite as the counter electrode, determined from Figure 8.

Sample	R_{CT} (Ω)	R_{Σ} (Ω)	C_{dl} (μF)
PEDOP	296	240	51
PEDOP/Sb_2S_3	55	9	48
PEDOP/Sb_2S_3 (after 1000 cycles)	67	3	61
PEDOT	80	18	47
PEDOT/Sb_2S_3	50	3	45
PEDOT/Sb_2S_3 (after 1000 cycles)	63	6	60

Capacitance calculation:

The capacitances of conducting polymer films and composite films were calculated as follows. First, taken the weight of a well-cleaned FTO glass substrate (of area 2 cm × 2 cm) by using Sartorius electrical weighing balance (resolution of the balance = 0.1mg). Then the conducting polymer or composite was electrodeposited on substrate and dried for few hours. Then the weight of the (film+substrate) was measured. Subtraction of the former from the latter gave the actual weight of conducting polymer or composite film.

Final weights of PEDOT = weight of PEDOP = 0.8 mg.

Final weight of PEDOT/Sb_2S_3 = weight of PEDOP/Sb_2S_3 film = 1.2 mg

The specific capacitance of the polymer or composite based cells were calculated from slopes of the discharge curves and by using the following equation.

$$C = i \times \Delta t / \Delta V \times m$$

C is the specific capacitance, i is the current applied for discharge, Δt is the time in seconds for discharge, ΔV is voltage window and m is mass of active material of the working electrode.

For example, specific capacitance calculation for PEDOP/Sb_2S_3 film is,

$$C = 1.2 \text{ mA} \times 1209 \text{ s} / 1 \text{ V} \times 1.2 \text{ mg}$$

$$= \sim 1007 \text{ F g}^{-1}$$

Specific capacitance calculation for PEDOP film:

$$C = 0.8 \text{ mA} \times 574 \text{ s} / 1 \text{ V} \times 0.8 \text{ mg}$$

$$= \sim 717 \text{ F g}^{-1}$$

Specific capacitance calculation for PEDOT/Sb_2S_3 film:

$$C = 1.2 \text{ mA} \times 996 \text{ s} / 1 \text{ V} \times 1.2 \text{ mg}$$

$$= \sim 830 \text{ F g}^{-1}$$

Specific capacitance calculation for PEDOT film:

$$C = 0.8 \text{ mA} \times 504 \text{ s} / 1 \text{ V} \times 0.8 \text{ mg}$$

$$= \sim 630 \text{ F g}^{-1}$$

References

1. C. An, K. Tang, Q. Yang and Y.Qian, *Inorg. Chem*. 2003, **42**, 8081–8086.

2. Y. Wang, Song, R. Y. Li and J. Shen, *Surf. Sci*. 2003, **530**, 136–148.