surfaces

MDPI

Supplementary Materials: Electrodeposition of Cu on PEDOT for a hybrid solid-state electronic device

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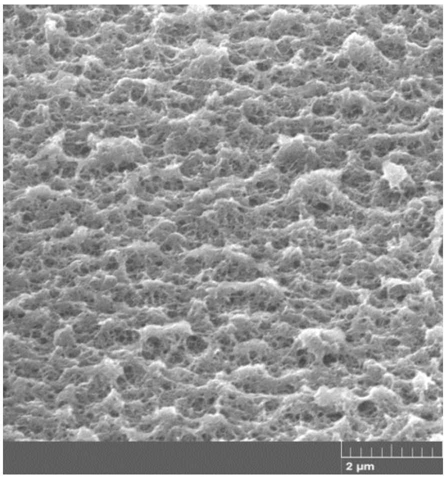
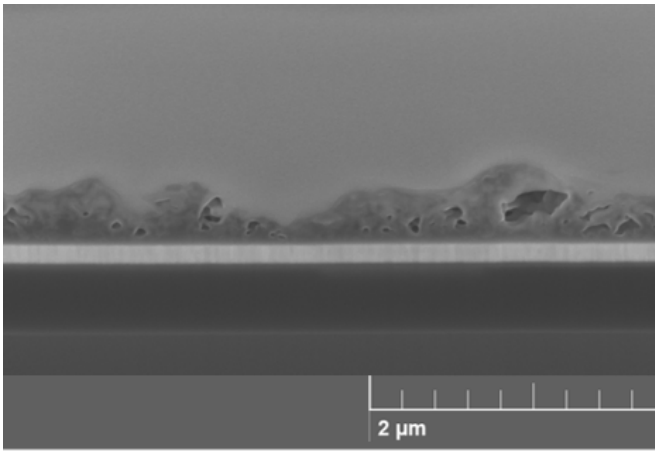
1. Thickness analysis

The thickness of PEDOT deposit on Au was estimated by both FIB-SEM analysis and using a differential weighting method. The latter consisted in evaluating the polymeric film mass by considering the weight of the electrode before and after the deposition process. Then, taking in account the surface area and the density of the polymer, the thickness was calculated to be approximately 500 ± 50 nm. Moreover, FIB-SEM analysis was used to obtain an image of the cross section of PEDOT film on Au (Figure S1b). Figure S1a shows that the morphology of PEDOT on Au is rough and dense, with clearly defined cluster sites. Due to the irregularity of the surface of the polymeric deposit, the height of the cross section of PEDOT (Figure S1b) was measured at different points along the surface of the electrode. Then, an average estimation of the thickness of the polymer was calculated. The FIB-SEM analysis confirmed the value of 500 ± 50 nm, previously obtained by means of the differential weighting method.



(a)

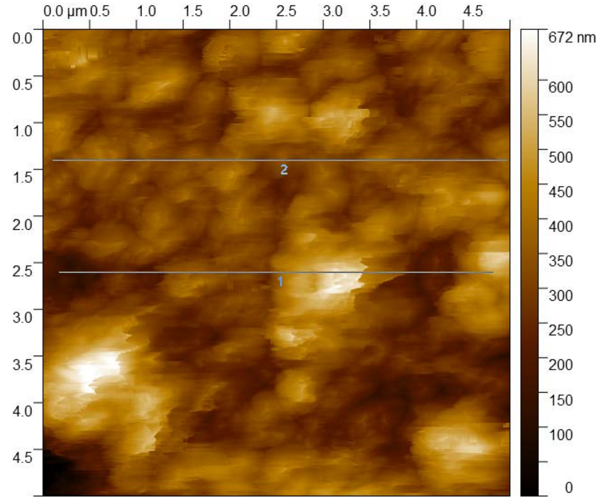


(b)

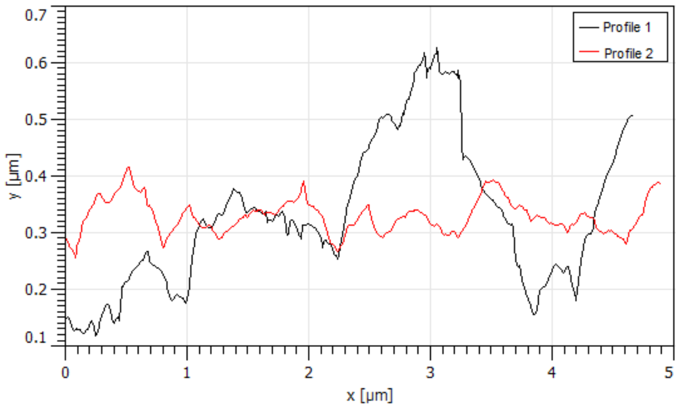
Figure S1. SEM images of **(a)** the PEDOT film on Au and **(b)** the cross section of the polymeric deposit on Au.

2. AFM analysis

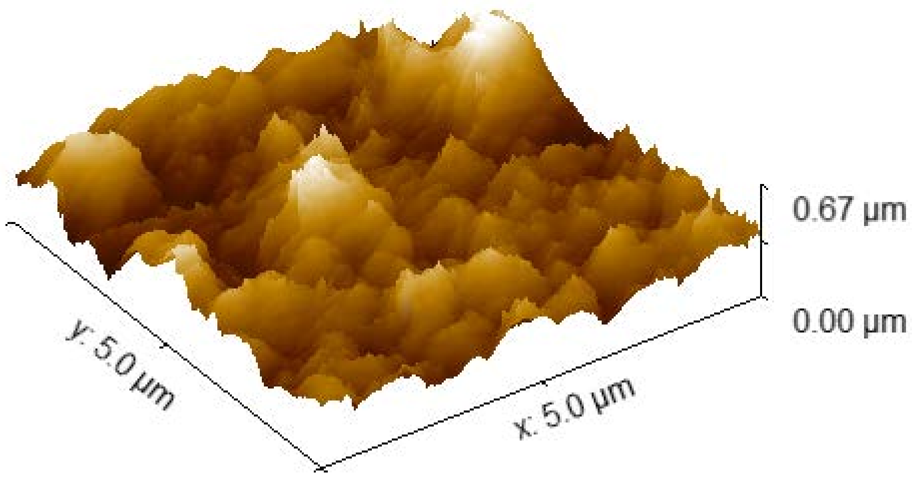
The AFM analysis of PEDOT deposit on Au is reported for illustrative purposes only (Figure S2). The measurements were performed considering a 5 µm x 5 µm area and showed that the film is continuous but irregular, with a root mean square roughness (Rq) of 92 nm. Nuclei with an average height of 100 nm are present, but also some bigger agglomerates with heights ranging from 300 nm to 400 nm are visible. This rough and dense morphology of the PEDOT deposit on Au was confirmed by the SEM analysis (Figure S1).



(a)



(b)

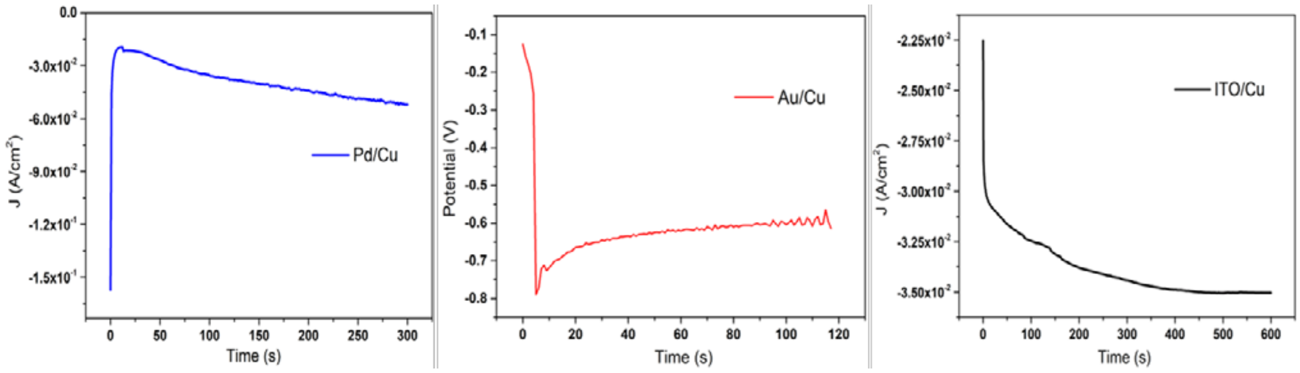


(c)

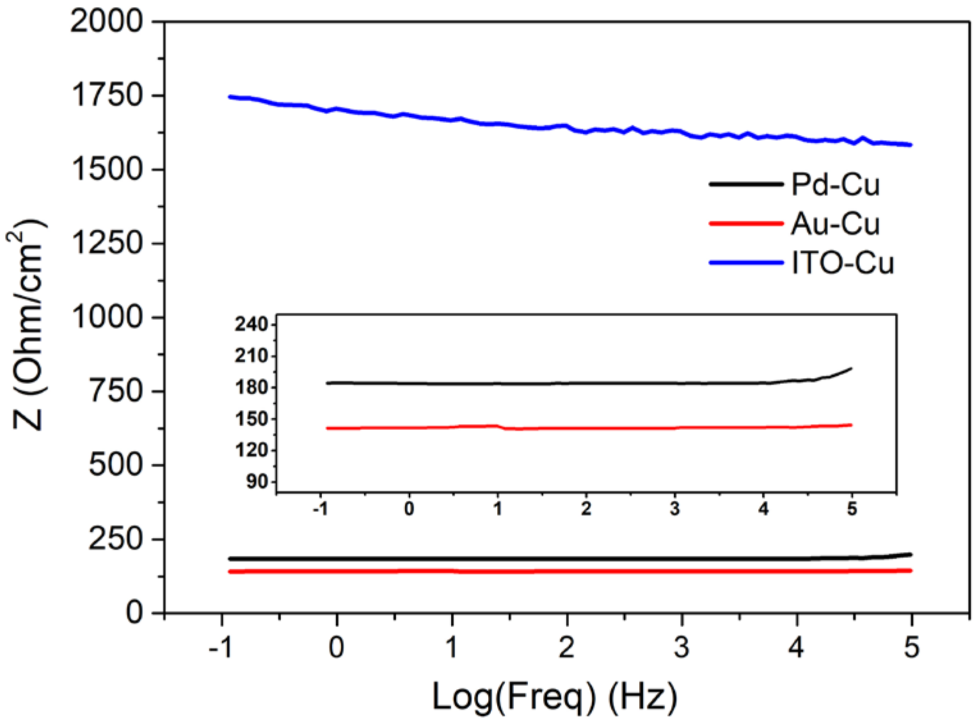
Figure S2. (a) AFM analysis of PEDOT film on Au (the horizontal lines 1-2 are to be intended as references for the plot profile (Figure S2b). **(b)** Plot profile of PEDOT film on Au observed from the two different horizontal lines present in Figure S2a. **(c)** 3D view of the AFM analysis.

3. Substrates Cu metallization and EIS

Electrical Impedance Spectroscopy was performed on Substrate/Cu systems, in order to cross-reference the resistance data. Cu was deposited directly on the three analyzed substrates (Pd, Au, ITO), without the polymer mid-layer. Potentiostatic and galvanostatic Cu depositions were performed in a 3-electrodes electrochemical cell, from an aqueous solution of 1.5 M H2SO4 and 0.5 M CuSO4, with the same procedure described for the hybrid Substrate/PEDOT/Cu samples. The results emerging from the EIS Bode plot (Figure S3b) evidence appreciably lower resistance values for all the three Substrate/Cu systems, with respect to the correspondent sandwich-like hybrid device.



(a)



(b)

Figure S3. (a) Curves of the Copper deposition on three different working electrodes: Pd, Au and ITO. **(b)** Electrical Impedance Spectroscopy of the Substrate/Cu devices, (Pd in black, Au in red, ITO in blue).