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Electronic Supplementary Information

Multiple resistive switching in core-shell ZnO nanowires exhibiting tunable surface states

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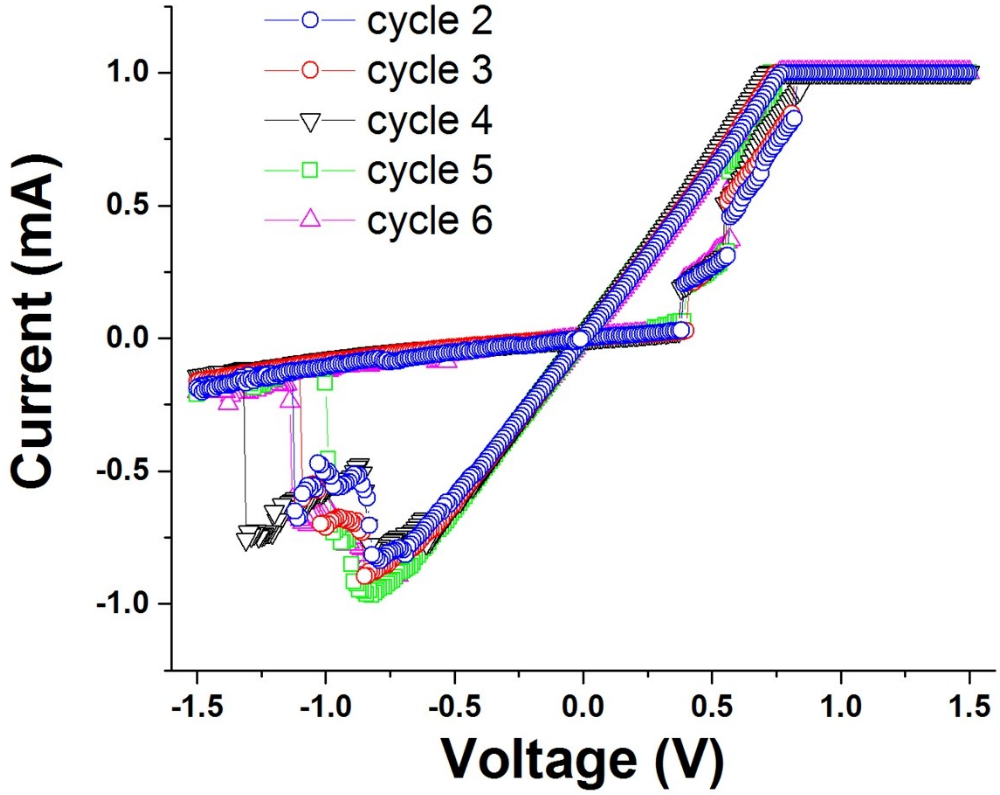

Figure S1. Additional (consecutive) I-V curves of the device reported in Figure 4c.

Variation of multistates:

Table S1. Average values of the multistate resistances in devices based on polymer-coated ZnO NWs. Standard deviation values indicate very low variability over cycling, demonstrating excellent stability.

	HRS	IRS1	IRS2	LRS
Av. Res. [kΩ]	13.83	3.22	0.946	0.773
St. Dev. [kΩ]	0.38	0.04	0.004	0.009
Variation %	2.77	1.10	0.41	1.15

FTIR measurements:

Fourier transform infrared spectroscopy (FTIR) measurements were performed on ZnO NWs before polymer deposition, just after polymer deposition and after electrically switching the device into LRS. These measurements were performed to get experimental evidence of the simulated redox reactions. The spectra were collected in reflectance mode, in the spectral range between 4000 and 500 cm^{-1}, using a Tensor 37 FTIR spectrophotometer (Bruker Optics-DE) coupled to a Hyperion 2000 FTIR Microscope equipped with a MCT cryodetector and a X15 objective (numerical aperture 0.58, light spot diameter 50 μm). The spectra were acquired with a resolution of 2 cm^{-1} using a gold substrate for the background acquisition, and 32 interferograms were collected for each spectrum.

The blue curve of Figure S2 shows the full range spectrum of ZnO NWs. Only a broad absorption is observable in the range 3600-3000 cm^{-1} due to O-H stretching species. The spectrum of freshly deposited polymer (red curve) shows in the range 3600-3100 cm^{-1} shows the signals related to O-H stretching due to hydroxyls belonging to carboxylic groups, centered at ~3400 cm^{-1}, and the vibrational mode of inter-molecule interacting O-H species, through hydrogen bonds, centered at ~3250 cm^{-1}. The signals at 2980-2870 cm^{-1} are related to

aliphatic C-H stretching mode, while in the 1760-1700 cm^{-1} range the absorptions are related to C=O stretching corresponding to different carbonyl functionalities, mainly related to carboxylic groups. Finally, the C-H bending mode at 1460-1370 cm^{-1} and the C-O stretching mode at 1200 cm^{-1} are also observable.[S1] After electrically switching the device into LRS (purple curve), the polymer bands increase due to isolated O-H stretching, suggesting that some carboxylic species are lost and probably consumed by the polymer-ZnO interface reactions (carboxylic ➔ carboxylate ➔ aldehyde). Moreover, the band due to C=O stretching decreases and changes its components ratio. A more intense component at 1730 cm^{-1} can be observed and attributed to the C=O stretching of aldehyde species. A new band appearing at ~1560 cm^{-1} can be attributed to the C=O stretching in dihydrate $Zn(OOCCH_3)_2$ species.[S2]
The dashed purple curve corresponds to the spectrum acquired on the Cu-coated polymer-ZnO NWs. Despite the loss of reflection due to metal charge carriers absorption, the features centered at ~1710 cm^{-1} and at ~1560 cm^{-1} produced by the underlying polymer are still visible (circled). Figure S3 shows the magnification of 4000-2000 and 2000-500 cm^{-1} range bands previously discussed. The evolving bands before and after electrical switch are highlighted. The pristine spectroscopical features of the polymer, mainly related to carboxylic functionalities, are nearly restored after cycling (Figure S2 and S3, green curve), as the isolated O-H stretching mode at about 3400 cm^{-1} decreased again and the band at ~1560 cm^{-1} asssigned to carboxylate species nearly disappeared, confirming the reversibility of the redox reaction.

[S1] S. Ricciardi, R. Castagna, S. M. Severino, I. Ferrante, F. Frascella, E. Celasco, P. Mandracci, I. Vallini, G. Mantero, C. F. Pirri, P. Rivolo, *Surf. Coat. Tech.* **2012**, *207*, 389.

[S2] M. K. Johnson, D. B. Powell, R. D Cannon, *Spectrochim. Acta A* **1981**, *37*, 899.

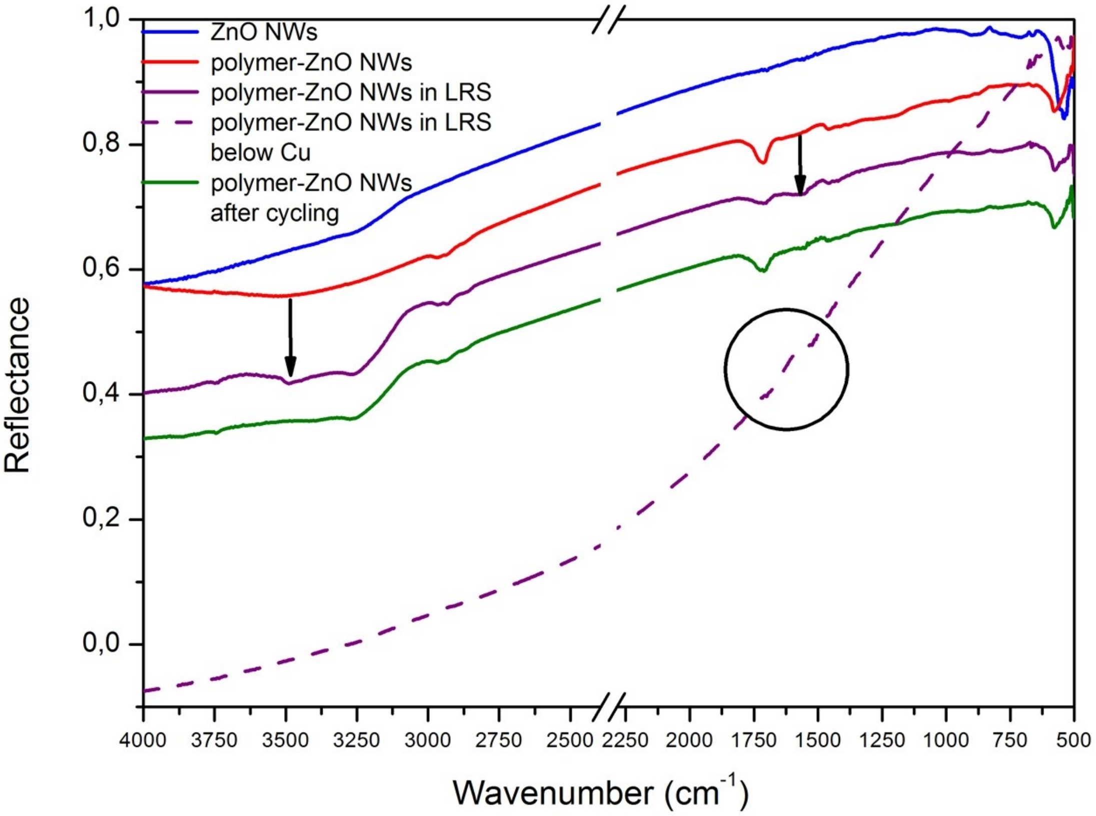

Figure S2. Reflectance IR spectra of ZnO NWs (blue curve), polymer-ZnO NWs before electroforming (red curve), after electrical switch to LRS (purple curve), after cycling (green curve), and spectrum of Cu-coated polymer-ZnO NWs (dashed purple curve).

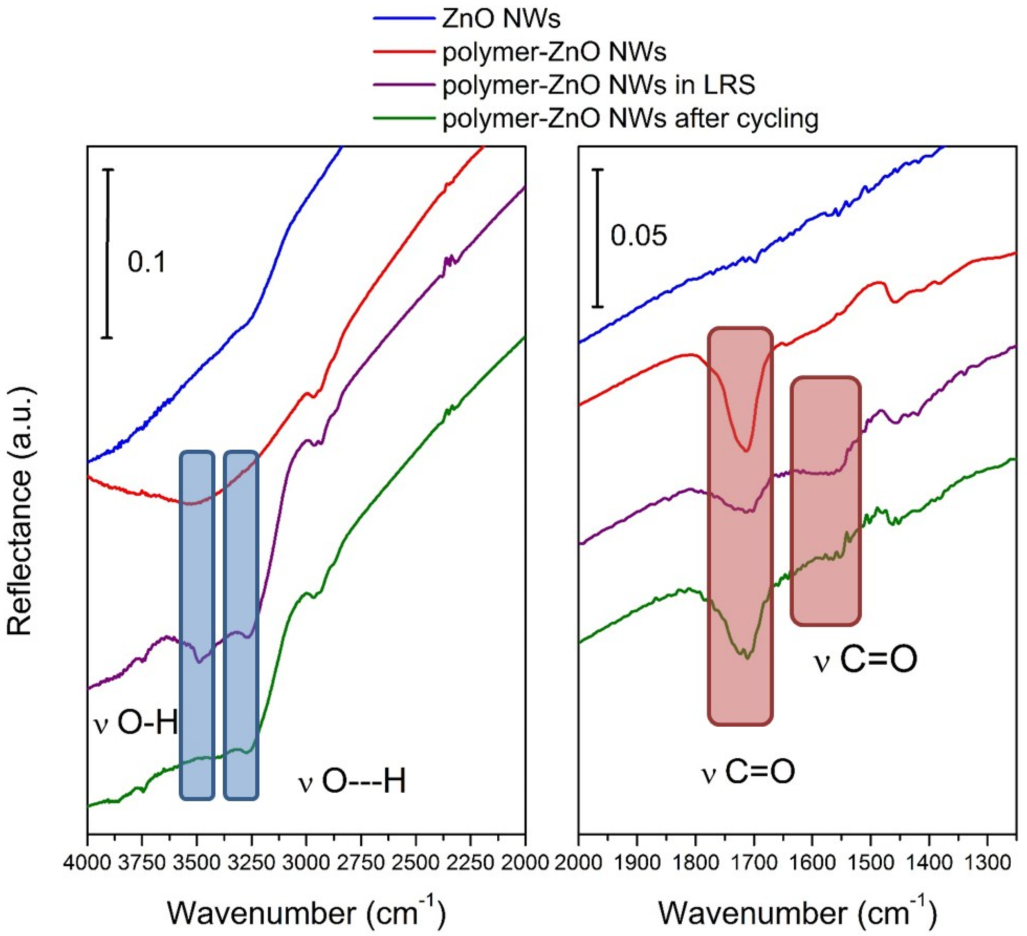

Figure S3. Magnification of 4000-2000 cm^{-1} and 2000-1200 cm^{-1} range bands: reflectance IR spectra of ZnO NWs (blue), polymer-ZnO NWs before electroforming (red), after electrical switch to LRS (purple), and after cycling (green curve). The main absorption features discussed in the text are highlighted.

Electroforming of polymer coated NWs device:

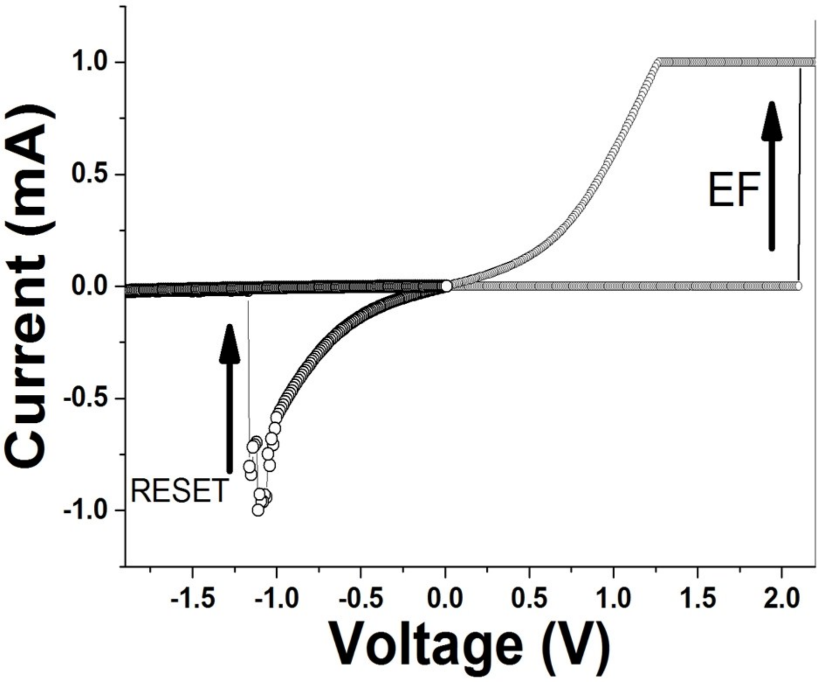

Figure S4. Electroforming cycle of the device reported in Figure 4c and Figure S1. After the electroforming (EF, 2.1 V), the device undergoes a "transient" intermediate state before consolidating in the following cycles the states described in the Results and discussion paragraph.