materials

MDPI

*Supplementary Materials*

# Capacitance Enhancement by Incorporation of Functionalised Carbon Nanotubes into Poly(3,4-Ethylenedioxythiophene)/Graphene Oxide Composites

**Anita Cymann [1], Mirosław Sawczak [2], Jacek Ryl [3], Ewa Klugmann-Radziemska [1] and Monika Wilamowska-Zawłocka [1,*]**

[1] Department of Energy Conversion and Storage, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland; anita.cymann@pg.edu.pl (A.C.); ewa.klugmann-radziemska@pg.edu.pl (E.K.-R.)

[2] Institute of Fluid Flow Machinery, Polish Academy of Sciences, Fiszera 14, 80-231 Gdańsk, Poland; mireks@imp.gda.pl

[3] Department of Electrochemistry, Corrosion and Materials Engineering, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland; jacek.ryl@pg.edu.pl

* Correspondence: monika.wilamowska@pg.edu.pl; Tel.: +48-58-347-24-74

Received: 30 April 2020; Accepted: 22 May 2020; Published: 25 May 2020

**Preparation of PEDOT/GOx Composite Layer.**

PEDOT/GOx layers were deposited from the solution containing monomer EDOT (0.015 mol $dm^{-3}$) and graphene oxide (1 mg per 1 ml of the solution). The composite films were deposited in the three-electrode system at a constant potential of 1 V vs Ag|AgCl|0.1 M KCl on the working glassy carbon electrode (GC, 2 mm in diameter), with a deposition charge of 0.8 C $cm^{-2}$; Pt mesh served as a counter electrode.

**Preparation of PEDOT/PSS Layer.**

PEDOT/PSS layers were deposited from the solution containing monomer EDOT (0.015 mol $dm^{-3}$) and sodium polystyrenesulphonate (0.1 mol $dm^{-3}$). The polymer layers were deposited in the three-electrode system at a constant potential of 1 V vs Ag|AgCl|0.1 M KCl on the working glassy carbon electrode (GC, 2 mm in diameter), with a deposition charge of 0.8 C $cm^{-2}$; Pt mesh served as a counter electrode.

**Table S1.** Elemental analysis results obtained for the composites.

| | N [wt%] | C [wt%] | H [wt%] | S [wt%] | C/S |
|---|---|---|---|---|---|
| pEDOT/GOx/(0.1)ox-MWCNTs | 0 | 47.24 | 3.07 | 17.36 | 2.72 |
| pEDOT/GOx/(0.5)ox-MWCNTs | 0 | 49.52 | 2.52 | 15.10 | 3.28 |

**Table S2.** Results of XPS spectra analysis performer for GOx and the composites in their oxidised (after electrodeposition) and reduced (electrochemically at -1V vs. Ag/AgCl) state.

| | **GOx oxidised** | | | | **GOx reduced** | | |
|---|---|---|---|---|---|---|---|
| | **BE/eV** | **atomic %** | **assignment** | | **BE/eV** | **atomic %** | **assignment** |
| **O 1s** | | | | **O 1s** | 530.45 | 6.72 | O–C=O |
| | 531.81 | 5.48 | O=C/C-O-C | | 531.7 | 36.12 | O=C / C-O-C |
| | 533.04 | 25.56 | O-C | | 533.17 | 3.92 | O-C |
| **C 1s** | 284.4 | 5.95 | C=C | **C 1s** | 284.27 | 27.48 | C=C |
| | 285.23 | 21.68 | C-C/C-H | | 285.08 | 8.57 | C-C/C-H |
| | 287.23 | 32.73 | C=O | | 287.01 | 12.66 | C=O |
| | 288.52 | 7.08 | O-C=O / COOH | | 288.47 | 3.07 | O-C=O / COOH |
| | **PEDOT/GOx/(0.1)oxMWCNTs oxidised** | | | | **PEDOT/GOx/(0.1)oxMWCNTs reduced** | | |
| | **BE/eV** | **atomic %** | **assignment** | | **BE/eV** | **atomic %** | **assignment** |
| **O 1s** | 531.5 | 5.45 | O=C / O-S | **O 1s** | 531.6 | 9.8 | O=C / O-S |
| | 532.7 | 24.1 | O-C / C-OH | | 533.4 | 13.09 | O-C / C-OH |
| **C 1s** | 283.9 | 3.92 | C=C | **C 1s** | 284.1 | 0.29 | C=C |
| | 284.8 | 17.79 | C-C/C-H | | 285.4 | 43.63 | C-C/C-H |
| | 285.7 | 7.65 | C-O/C-S* | | | | |
| | 286.8 | 28.32 | C=O/C-S | | 287.0 | 26.34 | C=O/C-S |
| | 288.3 | 8.68 | O-C=O / COOH | | 288.7 | 4.59 | O-C=O / COOH |
| **S 2p3/2** | 163.7 | 1.93 | S* -C | **S 2p3/2** | 164.4 | 1.94 | S-C |
| | 164.7 | 0.74 | S-C | | | | |
| | 168.0 | 0.91 | S···O | | 168.3 | 0.31 | S···O |
| | **PEDOT/GOx/(0.5)oxMWCNTs oxidised** | | | | **PEDOT/GOx/(0.5)oxMWCNTs reduced** | | |
| | **BE/eV** | **atomic %** | **assignment** | | **BE/eV** | **atomic %** | **assignment** |
| **O 1s** | 531.48 | 5.19 | O=C / O-S | **O 1s** | 531.3 | 13.9 | O=C / O-S |
| | 532.89 | 22.78 | O- C / C- OH | | 533.6 | 5.37 | O-C / C-OH |
| **C 1s** | 284 | 4.16 | C=C | **C 1s** | 284.2 | 5.1 | C=C |
| | 284.78 | 13.08 | C-C/C-H | | 285.3 | 57.32 | C-C/C-H |
| | 285.8 | 16.53 | C-O/C-S* | | | | |
| | 286.76 | 25.26 | C=O/C-S | | 286.9 | 11.18 | C=O/C-S |
| | 288.61 | 6.98 | O-C=O / COOH | | 288.5 | 5.43 | O-C=O / COOH |
| **S 2p3/2** | 163.7 | 4.23 | S*-C | **S 2p3/2** | 164.5 | 1.52 | S-C |
| | 164.8 | 1.26 | S-C | | | | |
| | 167.7 | 0.53 | S···O | | 168.5 | 0.19 | S···O |

**Table S3.** Data obtained from curve fitting of the Raman spectra of the investigated materials.

| | **Peak position/cm$^{-1}$** | **% of the total integrated area** | **FWHM** |
|---|---|---|---|
| **oxMWCNTs** | 1358.4 | 66.94 | 79.14 |
| | 1591.4 | 24.48 | 43.96 |
| | 1622.4 | 8.58 | 19.98 |
| **GOx** | 1361.1 | 59.17 | 138.31 |
| | 1588.7 | 40.83 | 89.28 |
| **PEDOT/PSS** | 1106.9 | 2.42 | 55.59 |
| | 1257.2 | 9.84 | 78.57 |
| | 1366.5 | 8.88 | 43.51 |
| | 1437.3 | 46.18 | 39.37 |
| | 1500.7 | 16.83 | 28.17 |
| | 1562.2 | 15.38 | 72.09 |
| | 1621.0 | 0.47 | 24.61 |
| **PEDOT/GOx/(0.1)oxMWCNTs** | 1106.0 | 1.46 | 62.63 |
| | 1264.6 | 8.53 | 119.75 |
| | 1360.7 | 29.16 | 94.30 |
| | 1436.6 | 25.16 | 40.65 |
| | 1510.3 | 9.19 | 36.47 |
| | 1569.2 | 19.72 | 65.86 |
| | 1609.6 | 6.78 | 42.57 |
| **PEDOT/GOx/(0.5)oxMWCNTs** | 1103.0 | 2.14 | 86.10 |
| | 1271.6 | 9.90 | 125.42 |
| | 1360.2 | 26.78 | 86.86 |
| | 1437.3 | 23.56 | 40.33 |
| | 1506.5 | 10.62 | 39.25 |
| | 1571.6 | 21.24 | 68.82 |
| | 1611.6 | 5.77 | 39.02 |

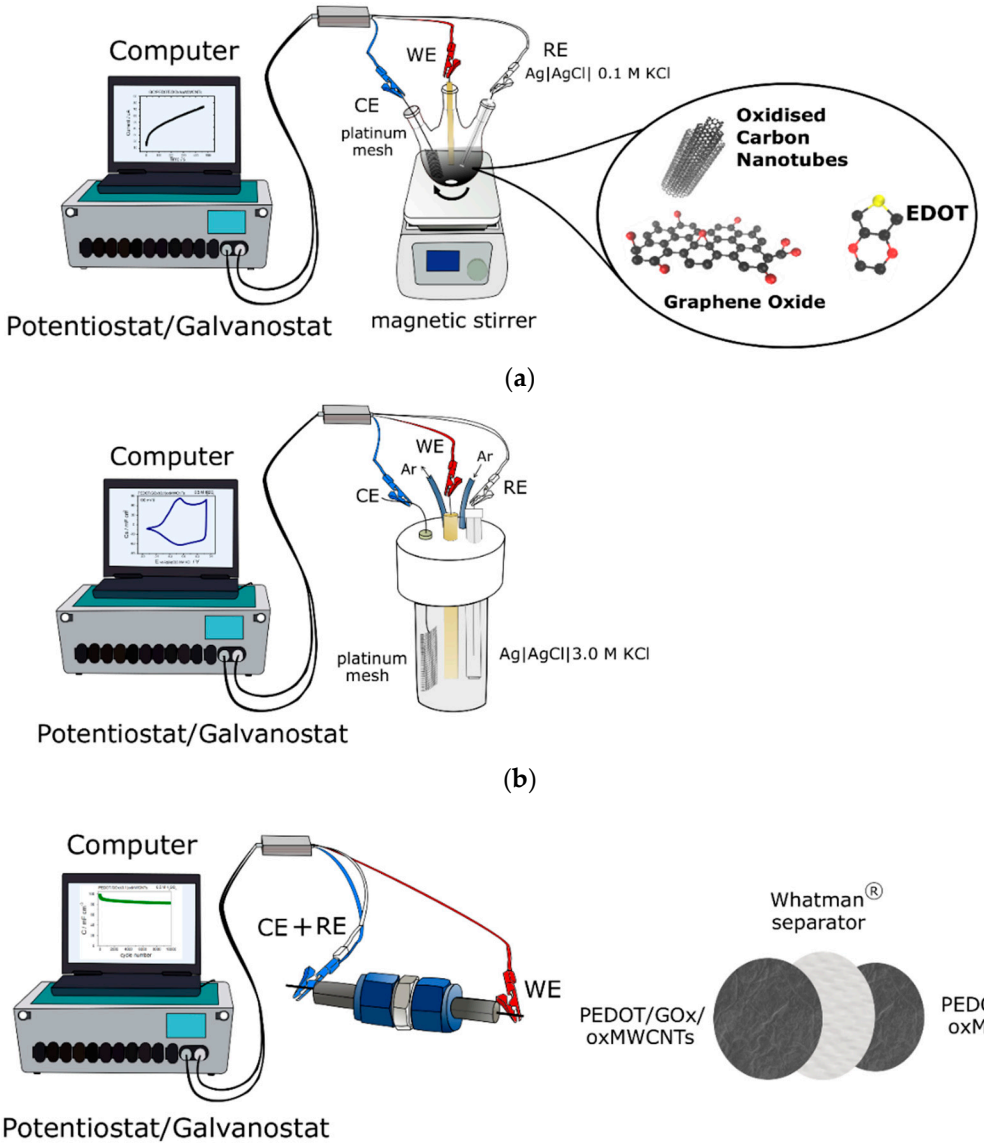
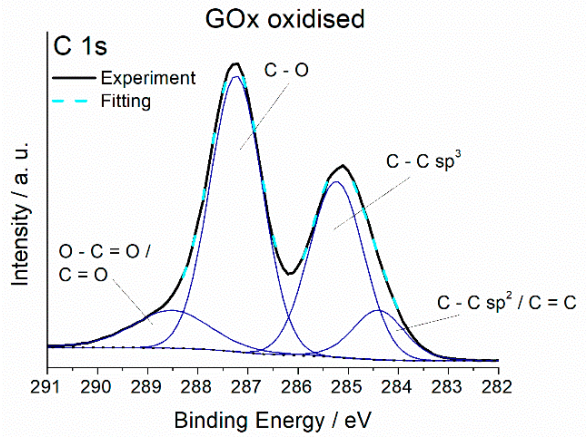
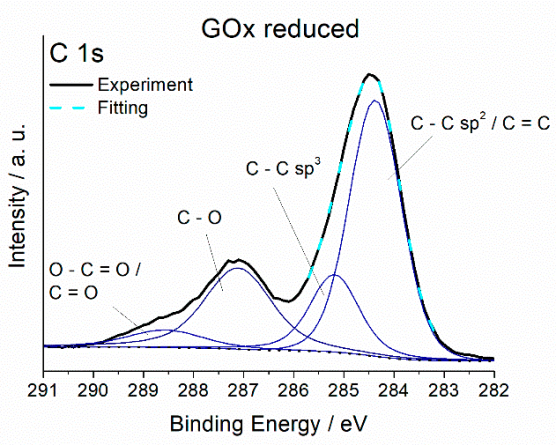



**Figure S1.** Experimental set-up for: (**a**) electrodeposition process; (**b**) electrochemical measurements in the three-electrode configuration, (**c**) electrochemical tests of symmetric capacitor.






(**b**)

**Figure S2.** XPS spectra of C1s orbital recorded for (**a**) graphene oxide layer, (**b**) electrochemically reduced graphene oxide layer.

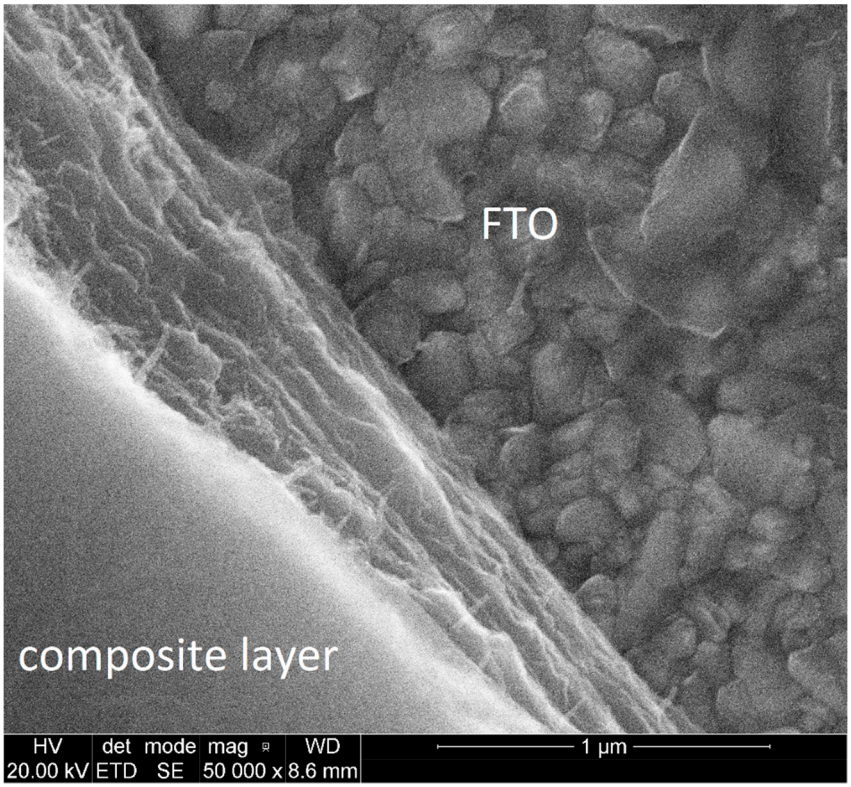
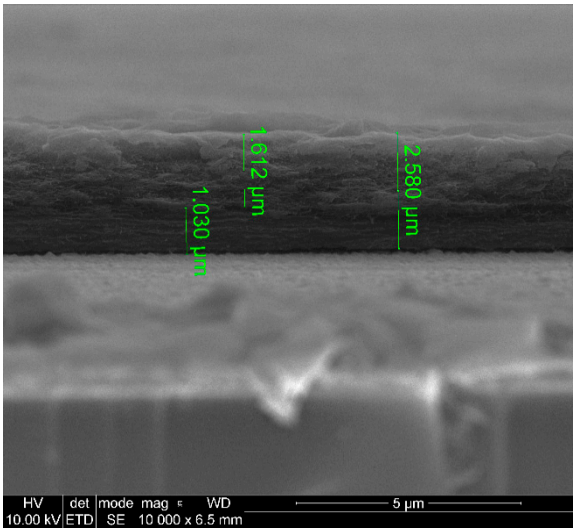
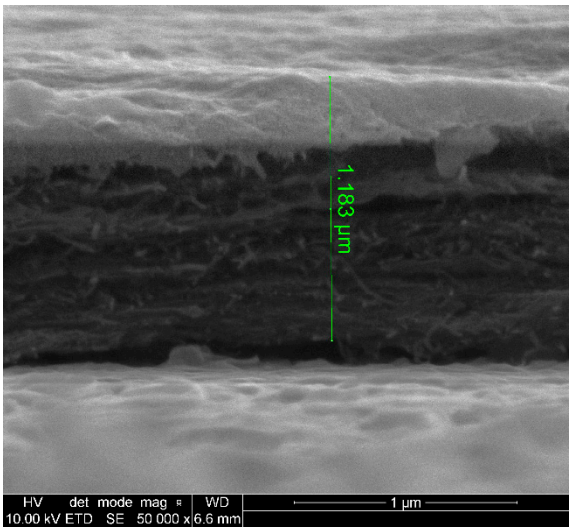



**Figure S3.** SEM image of broken PEDOT/GOx/(0.5)oxMWCNTs composite layer electrodeposited on FTO-coated glass.

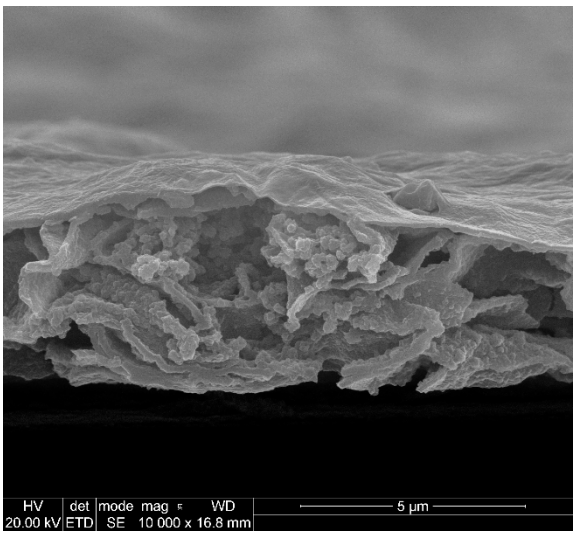



**(a)**

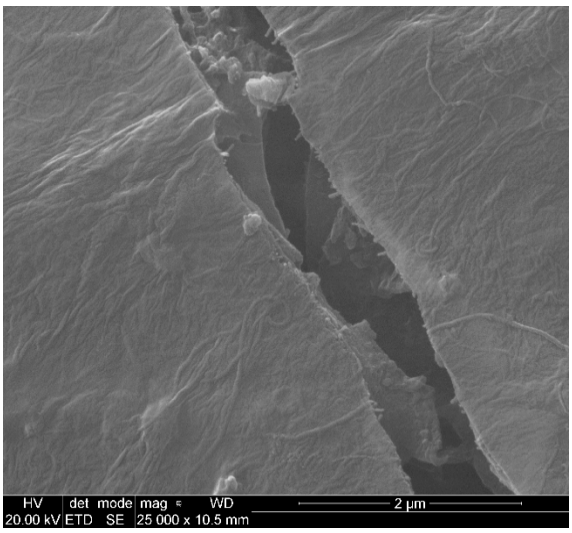



**(b)**

**Figure S4.** SEM image of PEDOT/GOx/(1)oxMWCNTs composite layer electrodeposited on FTO-coated glass, deposition charge 200 mC $cm^{-2}$; (**a**) magnification 10,000, (**b**) magnification 50,000.

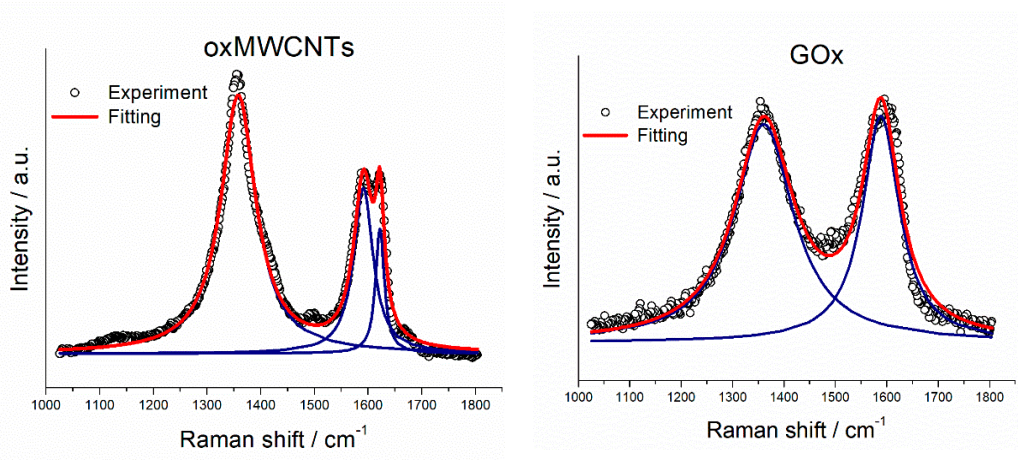



**(a)**




**(b)**

**Figure S5.** SEM pictures of (**a**) cross-section, (**b**) surface of PEDOT/GOx/(0.5)oxMWCNTs electrodeposited from the solution containing agglomerated graphene oxide flakes (3 weeks after preparation of the synthesis suspension), deposition charge 800 mC $cm^{-2}$.




(**a**) (**b**)

**Figure S6.** Deconvoluted Raman spectra of (**a**) oxMWCNTs, (**b**) GOx.